



Investigating Erosion-Corrosion and Flow-Assisted Galvanic Corrosion Behaviour of Tantalum/Tungsten.

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Investigating Erosion-Corrosion and Flow-Assisted Galvanic Corrosion Behaviour of Tantalum/Tungsten

Jitendra Singh Chouhan

A thesis submitted in partial fulfilment of the requirements of
Sheffield Hallam University
for the degree of Doctor of Philosophy

In collaboration with UKRI Rutherford Appleton Laboratory,
Materials and Engineering Research Institute at
Sheffield Hallam University (UK)

February 2024

“This thesis is dedicated to my mentors; Late Prof. Mahendra Singh Hada (Vice Chancellor, Vikram University, Ujjain, India) and Late Prof. Papken Eh. Hovsepian (Head of Thin Films Research Centre, Sheffield Hallam University, UK), who forever inspired me with their words of wisdom and educational legacy”

Declaration

I hereby declare that:

1. I have not been enrolled for another award from the University, or other academic or professional organisation, whilst undertaking my research degree.
2. None of the material contained in the thesis has been used in any other submission for an academic award.
3. I am aware of and understand the University's policy on plagiarism and certify that this thesis is my own work. The use of all published or other sources of material consulted has been properly and fully acknowledged.
4. The work undertaken towards the thesis has been conducted in accordance with the SHU Principles of Integrity in Research and the SHU Research Ethics Policy.
5. The word count of the thesis is 35831 (excluding References and Appendix).

Name	<i>Jitendra Singh Chouhan</i>
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Abstract

Tantalum (Ta) and Tungsten (W) are currently used as a neutron spallation target at UKRI Rutherford Appleton Laboratory (RAL). This target suffers from frequent failures susceptible due to erosion-corrosion phenomenon, reducing its operational life significantly. These failures prompted investigation of pure Ta and W with an overarching aim to improve the service life of RAL's target. This study investigated erosion, corrosion, and erosion-corrosion behaviour of Ta and flow-assisted galvanic corrosion behaviour between Ta and W, using an impinging jet erosion-corrosion apparatus and potentiostat.

The pure erosion experiments were performed using deionised aqueous slurry of SiC particles at a range of impact angle, concentration, and impact velocity. The pure corrosion, erosion-corrosion, and flow-assisted galvanic corrosion experiments were performed using solutions of different pH (4, 7, and 10). The potentiodynamic and potentiostatic polarisation techniques were performed in these solutions, at fixed impact velocity (5 ms^{-1}) and variable impact angles (30° and 90°), to assess pure corrosion and erosion-corrosion rate of Ta, respectively. Zero resistance ammeter technique was performed at 90° and different flow velocities (5 ms^{-1} and 9 ms^{-1}) to assess flow-assisted galvanic corrosion between Ta and W.

Findings on pure erosion of Ta revealed its distinct material removal mechanism which was discussed underpinning theories of solid particle erosion and grain boundary sliding under localised indentation loading. Erosion-corrosion of Ta showed a positive synergy under all pH levels at 30° impact angle, and a negative synergy in neutral and alkaline solutions at 90° impact angle. Galvanic coupling between Ta and W increased corrosion rate of W in alkaline solutions, while Ta suffered minimum damage due to the presence of stable oxide layer on its surface. The findings of this study provide insights into erosion-corrosion and flow-assisted galvanic corrosion response of Ta and W and suggest ways to improve performance of RAL's target.

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Conferences Attended

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**High Impact Factor Top Quartile (Q1)*

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Chapter-1

General Introduction

1.1 Research background

Spallation

The ISIS Neutron and Muon Source is a world-leading centre for research based at Rutherford Appleton Laboratory (RAL) UK. This facility is an accelerator-based neutron source comprising of proton accelerator that produces high-velocity pulses of protons which strike a metallic target (made of tantalum clad tungsten materials). This collision of the proton beam with the nucleus of the core target (tungsten) atom results in the production of neutron pulses and this neutron generation process is also known as 'spallation'. These neutrons from the spallation process are used in neutron scattering experiments, performed by world scientists, to study the properties of materials on the atomic scale [1] .

Target material

In the spallation process, the core target is made of tungsten clad with tantalum, herein referred as target material as shown in Fig. 1.1. This cladding of tantalum on tungsten is done through electron beam welding followed by a diffusion bonding process known as hot isostatic pressure or HIP bonding. During HIP bonding, the materials are heated to a high temperature and pressure under an inert gas atmosphere to create a strong diffusion bonded interface between tantalum and tungsten [2,3]. The HIP bonding technique was first successfully utilised by scientists at RAL and was also replicated at Los Alamos Neutron Science Center (LANSCE) USA and KEK Neutron Source Facility (KENS) Japan [2,4,5]. Moreover, this tantalum-clad tungsten was also chosen as the target material for the next generation of spallation research facilities [6,7].

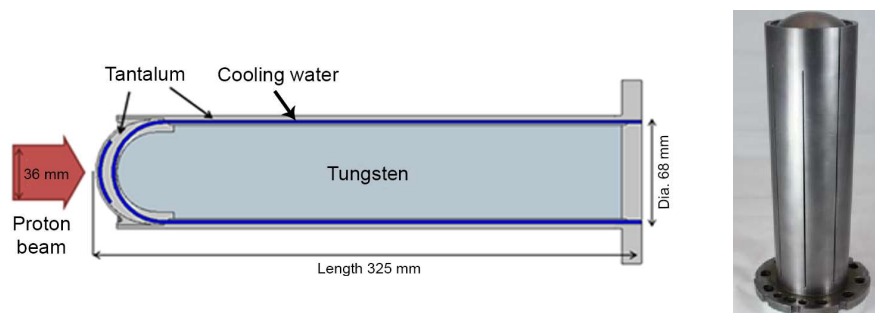


Figure 1.1 Cross-section of RAL Ta-W target and HIP bonded target assembly [8]

In the spallation process, as protons strike target material at very high speeds, it causes partial transformation of proton kinetic energy into heat energy which makes the target material very hot and radioactive. This high-temperature target,

as such, needs to be cooled and therefore cooling water (shown in blue in Fig. 1.1.) is circulated to ensure material and operational safety. Preliminary investigation has found radioactive isotopes of tungsten in the cooling water loop which is speculated to have happened due to the erosion-corrosion of target material [8]. This phenomenon of erosion-corrosion, susceptible, led to premature failure of target material within a year of operation which was against the expected design lifetime of around five years [9]. Moreover, for RAL, this radioactive target material disposal and its remanufacturing led to a very high annual cost.

Erosion-corrosion and flow-assisted galvanic corrosion

This study investigates erosion-corrosion of tantalum and flow-assisted galvanic corrosion between tantalum and tungsten to explore the target material's response to cooling water and aid RAL in formulating a strategy to improve their ISIS target life. Erosion-corrosion refers to the degradation of metal surfaces caused by the flow of corrosive slurry [10]. This process involves a complex interplay between erosion and corrosion which results in an additive effect when erosion enhances corrosion or a synergistic effect when corrosion enhances erosion [11,12]. Galvanic corrosion occurs when two dissimilar metals are in physical or electrical contact with each other and are immersed in the same electrolyte [13,14]. Additionally, in a corrosive environment, one of the metal acts as anode and undergoes corrosion, while the other metal acts as a cathode and remains protected by the anode corrosion [15]. There is a lack of research on the erosion-corrosion and flow-assisted galvanic corrosion of tantalum and tungsten. As a result, there is a very limited understanding of erosion-corrosion and galvanic corrosion performance of tantalum and tungsten.

1.2 Aim and objectives

The aim of this research is to understand slurry erosion and erosion-corrosion performance of tantalum, and flow-assisted galvanic corrosion performance of tantalum and tungsten. This aim is met through the following research objectives:

- (1) To investigate **pure erosion** response of pure tantalum specimens under silicon carbide (SiC) slurry conditions using an impinging jet aqueous erosion test apparatus. This objective involves the following two sub-objectives:

- a. To estimate pure erosion rate as a function of various process parameters, i.e. impact angle, slurry concentration, and impact velocity.
 - b. To identify material removal mechanisms for oblique and normal impact erosion with the help of SEM analysis of wear scars.
- (2) To investigate **pure corrosion and erosion-corrosion** response of pure tantalum specimens under SiC slurry with different pH solutions using an impinging jet aqueous erosion-corrosion test apparatus. This objective involves the following two sub-objectives:
- a. To estimate the rates of pure corrosion, erosion-corrosion, and synergy as a function of process parameters, i.e. impact angle and solution pH.
 - b. To identify material removal mechanisms under oblique and normal impact erosion-corrosion with the help of SEM analysis of wear scars.
- (3) To investigate **flow-assisted galvanic corrosion** performance of pure tantalum and pure tungsten specimens under different pH solutions and impact velocities using impinging jet aqueous erosion-corrosion apparatus. This involves the following sub-objective:
- a. To estimate various galvanic parameters as a function of process parameters, i.e. impact velocity and solution pH, for tantalum and tungsten in both coupled and uncoupled state.

Chapter-2

Literature Review

2.1 Introduction

2.1.1 Overview of erosion-corrosion

Erosion-corrosion is a type of wear process that involves progressive loss of material due to the combined processes of mechanical erosion and chemical corrosion. The combined erosion and corrosion processes can result in accelerated material wastage due to their well-known interaction effect, namely the synergistic effect (corrosion enhanced erosion rate) and additive effect (erosion enhanced corrosion rate) [12]. The wastage rate can also slow down when corrosion obstructs erosion process, known as negative synergy or antagonistic effect [16,17]. In erosion, the governing process is the action of wear caused by abrasive particles while corrosion is the result of chemical action facilitated by the presence of an aqueous medium.

In most engineering applications, surface erosion of material is not desirable. For example, in the case of fluid flows in piping systems, the pipes can suffer from premature failure due to erosion at bends [18,19]. Similarly, erosion can also take place in turbine blades or pump blades, and the subsequent material loss can lead to poor structural integrity [20]. Similarly, corrosion is also undesirable for many engineering applications involving metals which are more susceptible to corrosion and subsequent failure due to fatigue and fracture over time [21]. For example, in the oil and petrochemical industries, corrosion has been identified as the predominant cause of heat exchanger failures [22].

There are some beneficial aspects of erosion and corrosion as well. The process of erosion can be useful for example in blast cleaning of industrial gas turbine components [23] and in abrasive water-jet cutting of composite materials which are extensively used in aerospace and automotive applications [24]. On the other hand, corrosion can impart passive rust layers on low alloy steels (weathering steels) and blue-green patinas (oxide film) on copper surfaces, all of which are useful for applications, such as construction of buildings, utility towers, bridges, and rooftops [25,26]. Some other benefits of corrosion include etching, pickling (metal cleaning), electrochemical machining, and cathodic protection [26].

2.1.2 Chapter outline

This chapter is organised into four different sections. The first three sections describe the basics supported by previous studies relevant to particulate erosion, aqueous corrosion, erosion-corrosion, and their measurement. The fourth section reviews the available literature on the erosion-corrosion of tantalum and tungsten. The elements of each section are as follows:

- i. Erosion: The fundamentals of particulate erosion and various factors that can affect erosion are discussed in this section. This is followed by a literature review on the various erosion mechanisms for ductile and brittle materials.
- ii. Aqueous corrosion: This section presents the fundamentals of aqueous corrosion, focussing mainly on the thermodynamics and kinetics of corrosion. In addition, the section also includes literature on corrosion measurement techniques and flow-assisted galvanic corrosion.
- iii. Aqueous erosion-corrosion: This section reviews aqueous erosion-corrosion and its associated processes covering mainly its mechanisms, followed by testing methods.
- iv. Erosion-corrosion of tantalum and tungsten: This section presents a literature review on erosion-corrosion of tantalum, tungsten, and tantalum clad tungsten material which is used as a target material in the neutron scattering facility of Rutherford Appleton Laboratory - RAL, UK.

2.2 Fundamentals of particulate erosion

Erosion is a material surface degradation process in which material is removed due to a mechanical interaction between hard erodent particles and the target material surface, as schematically shown in Fig. 2.1.



Figure 2.1 Erosive particles of various shapes/sizes striking the material block at a specific angle/velocity.

According to the American Society for Testing and Materials (ASTM) standard G76-95 [27], erosion is defined as “the progressive loss of original material from

a solid surface due to mechanical interaction between that surface and a fluid, a multi-component fluid, or an impinging liquid or solid particles”. Erosion can be operative under both dry and wet conditions. In the case of dry erosion, erodent particles are driven by a flowing gas or air, and in the case of wet erosion, those are driven by a flowing liquid (aqueous or non-aqueous) [28]. The resistance to solid particle erosion is widely understood to be a non-intrinsic property of a material, but rather one that is heavily influenced by the conditions under which it operates. Factors such as the shape and size of the eroding particles, impact velocity, particle concentration, and impact angle are well known to significantly affect the erosion rate [29,30]. Further details on these factors are presented in the following section.

2.2.1 Factors affecting erosion

Many researchers have previously proposed various factors that can affect the erosion process [31–35]. These factors are mainly in relation to erodent particles, target materials, and fluid flow. Table 2.1 details the parameters constituting these factors.

Table 2.1 Three primary categories of erosion influencing factors.

Erodent particles	Target material	Fluid flow
Concentration	Hardness	Impact velocity
Shape	Toughness	Impact angle
Size	Ductility	Viscosity
Hardness	Microstructure	Density

The subsequent sections delve into an analysis of some of the key elements outlined in Table 2.1.

1. Impact angle

The effect of impact angle on erosion rate was investigated by various researchers [36–41]. The relationship between erosion and impact angle was reported to follow a specific pattern for ductile and brittle materials, as shown in Fig. 2.2 [41].

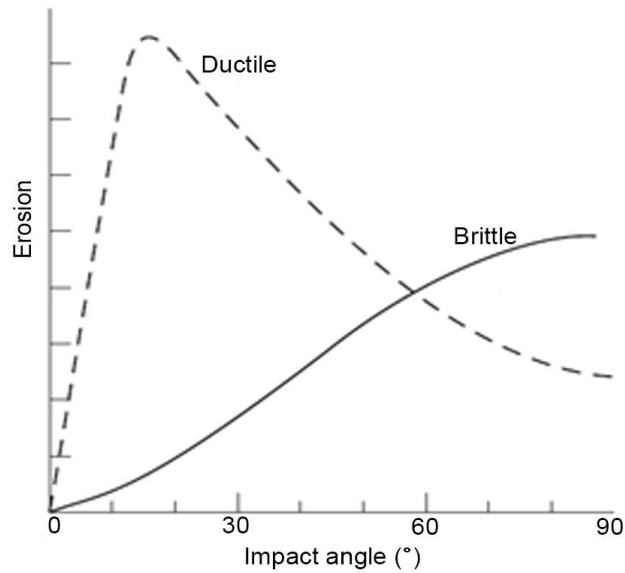


Figure 2.2 Erosion variation with particle impact angle. [41]

As depicted in Fig. 2.2, a ductile material demonstrates a peak erosion rate at a shallow angle, typically around 15°-20°. On the other hand, a brittle material exhibits a maximum erosion rate at 90°; this rate consistently decreases as the impact angle reduces [34,41,42].

Please note, the Y-axis title (in Fig. 2.2) is erosion (dimensionless), which is a ratio of the rate of material loss to the rate of mass flow of the impacting erodent particles [41], herein referred to as erosion rate.

2. Impact velocity

One of the most important factors that affect erosion rate is particle impact velocity. Various studies have demonstrated that the erosion rate follows an empirical power law correlation with velocity, as follows [43–47],

$$E = KV^n \quad \text{Eq. (2.1)}$$

where 'E' is erosion rate, 'V' is impact velocity, 'K' is a constant, and 'n' is velocity exponent, which typically ranges between 2 and 3.5 for metallic materials [41,48,49]. Figure 2.3 shows the dependence of erosion rate on the impact velocity, for the erosion of copper under 20° and 90° impact angles [50]. It can be seen that the erosion rate increased with impact velocity, a trend which was similar under both impact angles.

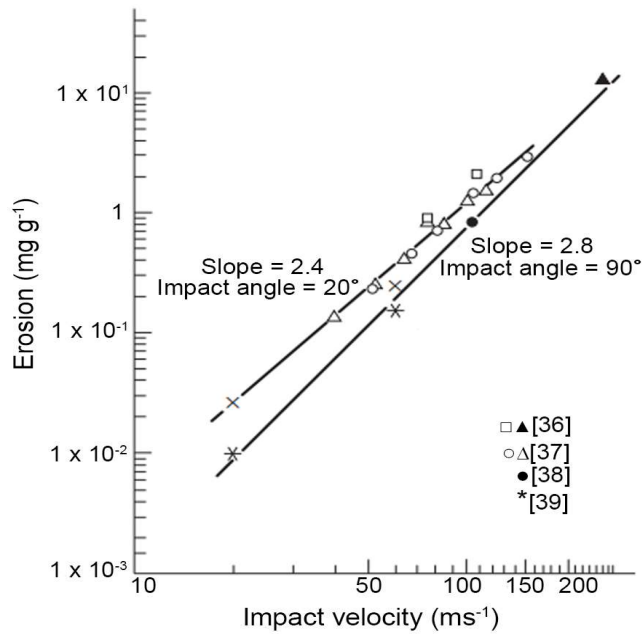


Figure 2.3 Copper erosion rate variation with impact velocity. [50–53]

The escalation in the erosion rate with velocity was linked to the rise in the erodent's kinetic energy, which results in more effective damage to the metal surface. Additionally, the frictional force exerted on the surface during particle impact and its effective path of action are crucial factors in the erosion process.

3. Particle concentration

In both dry and slurry erosion conditions, various investigations were conducted to assess the effect of particle concentration on erosion rate [54–60]. It was generally found that the erosion rate decreases with the increase in particle concentration. Figure 2.4 illustrates the influence of sand concentration on the slurry erosion rate of stainless steel [59]; it indicates that the erosion rate decreases with the increase in sand concentration.

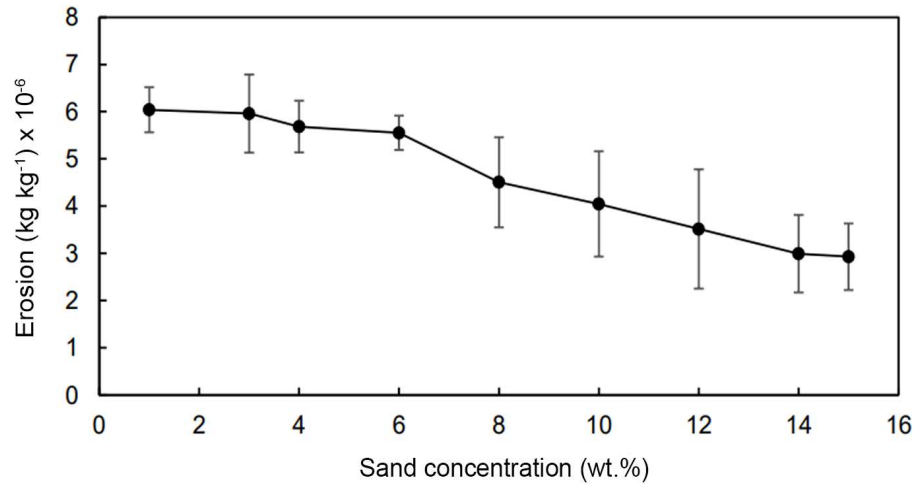


Figure 2.4 Erosion variation with sand concentration (300 μm particle size) for Stainless steel (SS 316) under aqueous slurry flow at 14 ms^{-1} . [59]

The fall in erosion rate with the rise of sand concentration was explained based on the ‘blanketing effect’ [54]. According to this effect, a surge in particle concentration leads to a high number of interparticle collisions which decreases the effective number of particle impacts (on the target material) and consequently reduces the rate of erosion.

4. Particle shape

The erosion rate is also affected by the shape of the particles. As a general trend, particles with an angular shape are more efficient at removing material compared to their spherical counterparts [32,33]. This observation was further corroborated by an experimental study, which revealed that the angularity of particles leads to increased erosion rates [61]. In that study, the ‘spike parameter’ was used to quantify the angularity, representing the boundary of the particles with a triangular depiction (shown in Fig. 2.5). The size and sharpness of these triangles are indicative of the particle’s effectiveness in erosion – larger and sharper triangles suggest a higher erosive ability of the particle.

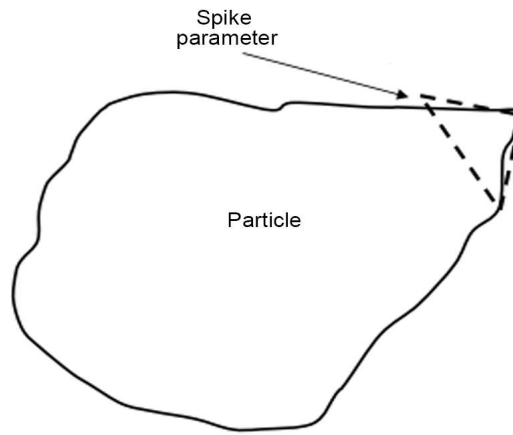


Figure 2.5 Diagram showing Spike parameter to characterise particle angularity. [61]

Another study compared the effectiveness of angular and spherical-shaped particles in removing the surface oxide layer from the target material, which generally protects the material during an erosion event. It was reported that angular particles led to a quicker removal of the oxide surface layer, leading to a higher erosion rate of the substrate [62]. In contrast, spherical particles were less effective in removing the oxide layer leading to a relatively lower erosion rate.

5. Particle size

Erodent particle size is also known to influence erosion rate. Previous experimental studies on erosion reported a lower erosion rate for materials with smaller particle sizes [63,64].

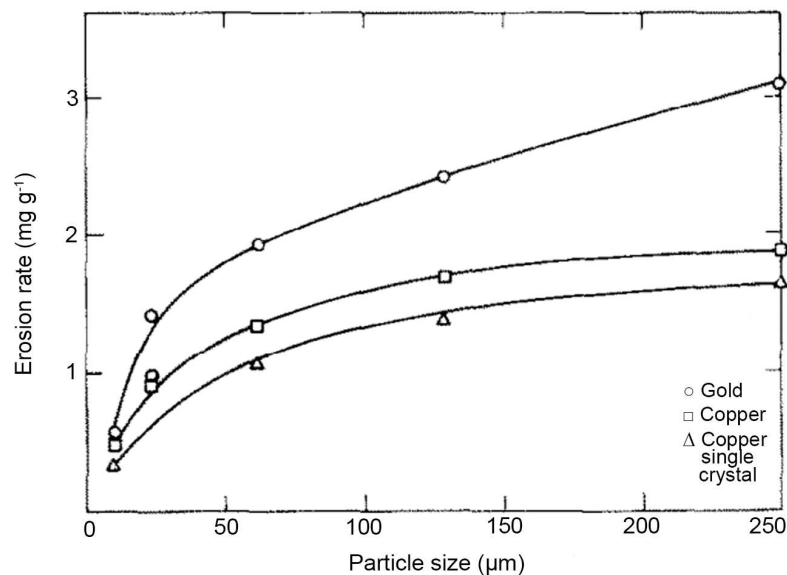


Figure 2.6 Erosion rate variation with SiC particle size for metallic impact. [65]

Figure 2.6 shows erosion versus particle size plot for a number of metals (Gold, Copper, and Copper single crystal), tested under SiC particle impact at an impact velocity of 120 ms^{-1} and an impact angle of 20° . It reveals that the erosion rate increased with particle size, but only up to a certain threshold size. Beyond this point, the particle size did not significantly impact the erosion rate. This erosion behaviour was attributed to the wear process efficiency (material removal based on particle impact), which was higher for larger particles compared to smaller ones. Another study observed a similar pattern of erosion with spherical and angular particle impacts, where increased particle size led to higher erosion [33]. In that study, it was also observed that the erosion rate decreased beyond a critical particle size.

6. Hardness (particle and target material)

The hardness of both the particle and target material is known to significantly influence the erosion rate. For ductile metals, it is generally found that the erosion rate was inversely proportional to the hardness of the target material [41,66,67]. A study examined the impact of the hardness ratio (the ratio of particle hardness to target material hardness) on the erosion rate [41]. This study found that if this ratio was less than 1.2, then it resulted in plastic flow within the particle, regardless of its shape. Conversely, for a ratio greater than 1.2, it induced indentation or plastic flow within the target material surface. This is shown in Fig. 2.7.

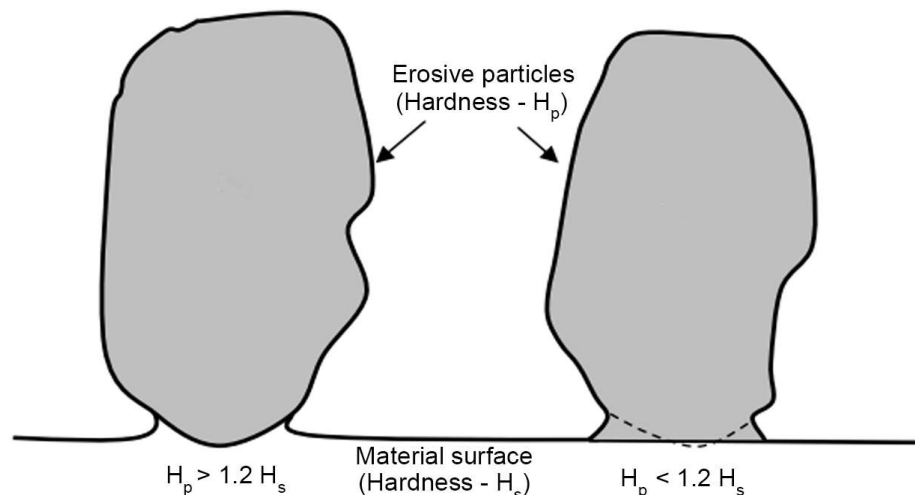


Figure 2.7 Illustration of a particle interacting with a plane surface under normal load. (a) The particle indents the surface when H_p exceeds $1.2 H_s$ (b) The particle undergoes plastic flow when H_p is less than $1.2 H_s$. [41]

A similar experimental study also observed lower erosion rates, based on a decreasing ratio of particle hardness to target material hardness [68]. Other research identified fracture toughness as a key parameter influencing material resistance to erosion, rather than hardness alone [61]. Materials with lower strain hardening exhibited higher rates of erosion [67]. However, it was argued that bulk hardness as a material property does not accurately reflect true erosion behaviour [41,66]. This is because, upon particle impact, the target material surface undergoes work hardening, resulting in surface hardness values that differ from those of the bulk material.

7. Microstructure (target material)

The influence of the target material microstructure and its grain size on erosion resistance was examined and correlated in several studies [69–74]. These investigations revealed that a finer grain size results in enhanced erosion resistance due to material strengthening, compared to a coarse grain size which produces a softer material with diminished erosion resistance. Additional experimental studies reported analogous findings, noting an elevated erosion rate with an increase in material grain size [75,76]. The type of microstructure also affects the rate of erosion. This was reported in one of the studies in which a high erosion rate was attributed to the emergence of cracks on and beneath the surface of the pearlitic microstructure [77]. Conversely, the spheroid microstructure displayed fewer surface cracks, resulting in a lower erosion rate as compared to that of the pearlitic microstructure.

8. Fluid viscosity

The rate of erosion is also affected by fluid viscosity. It was generally found that the erosion rate decreases with the increase in fluid viscosity [54,78,79]. One of the comprehensive studies demonstrated a correlation between particle velocity and fluid viscosity [78]. In that study, the researchers observed a decrease in impact velocity for all tested particle sizes when the viscosity of the water-glycerine solution was increased. Similar observations were found in another study in which mild steel was eroded using water and highly viscous solvent-based SiC slurries [54]. As mentioned in the earlier section, impact velocity is a crucial determinant of erosion rate. Consequently, a decrease in velocity implies a reduction in kinetic energy, which was transferred to the target material during impact, resulting in lower erosion rates.

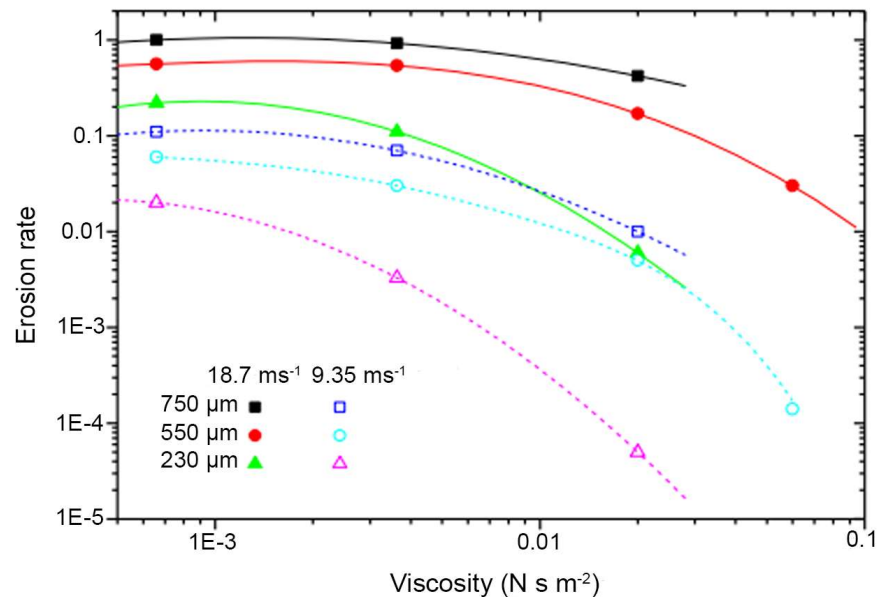


Figure 2.8 Influence of fluid viscosity on the erosion rate of copper under various impact velocities and particle sizes. [79]

Figure 2.8 illustrates the influence of fluid viscosity on the relative erosion rate of copper at varying velocities and particle (glass bead) sizes [79]. It can be seen that at a given velocity and particle size, the erosion rate decreases with the increase in fluid viscosity, a trend that was similar for all the particle sizes and flow velocities studied. In addition, the figure also shows that at a given fluid viscosity, the erosion rate increases with velocity and decreases with particle size. This is due to the smaller particles experiencing a significant reduction in velocity under high fluid viscosity. As a result, particles do not have sufficient kinetic energy and momentum, to reach and impact the sample; hence reducing the rate of erosion.

2.2.2 Erosion mechanism of ductile materials

The process of material removal in solid particle erosion has been thoroughly researched for both ductile and brittle materials under a variety of conditions, including different angles of impingement [80–82]. It is widely reported that the main mechanism of material removal at oblique impact angles is cutting or micromachining [83]. Based on particle shapes, three different types of material removal mechanisms have been reported [41]: these are Ploughing, Type I cutting, and Type II cutting; these mechanisms are shown in Fig. 2.9. Ploughing is caused by the impact of spherical erodent at oblique impact angles (Fig. 2.9a). When a spherical-shaped particle strikes the target material, a crater is formed

over the material surface as it moves from one end to the other, and in the process, it accumulates the material at the edge of the crater in the form of a 'lip' or 'rim'. With successive particle impacts, this rim is further strained and eventually detached. The Type I and Type II cutting mechanisms are caused by the angular-shaped particles striking at oblique impact angles. In Type I cutting, the angular-shaped particle strikes the target material and rolls forward which leads to indentation and a large accumulation of material in the form of a lip or rim (Fig. 2.9b). This rim material is then further strained and removed upon successive particle impacts. In Type II cutting, when an angular-shaped erodent particle hits the target material, the particle rolls forward and then backwards, and in the process, it causes target material surface machining with no lip or rim formation (Fig. 2.9c).

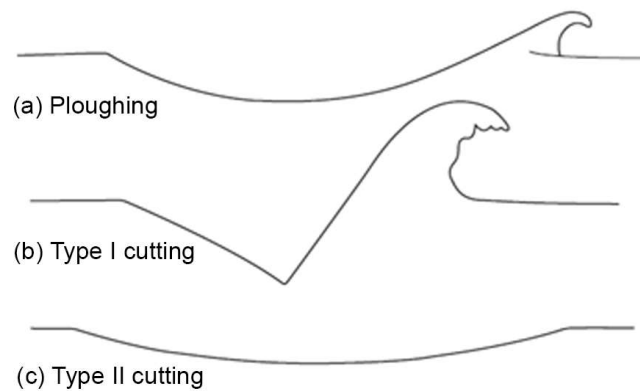


Figure 2.9 Formation of the material crater (lip or rim) after being struck by an erosive particle at 30° (from horizontal) with shape (a) spherical, (b and c) angular. [41]

The mechanism of ductile material erosion at normal impact angles is due to localised plastic deformation of the substrate, which is eventually removed due to repeated erodent impacts [51,84,85]. A widely accepted theory for the ductile material erosion mechanism at normal impact angles is based on the formation and removal of extruded lips. This mechanism generally creates wear debris in the form of platelets [84–86]. Each erodent impact creates a localised zone of plastic deformation, which can result in the formation of a crater with extruded lips around its edge, depending on the contact conditions. These lips are then removed by subsequent erodent impacts, provided they meet the necessary strain-induced material failure requirement [85].

Various other mechanisms for ductile material erosion can also be found in the literature [43,87–91]. An experimental study reported that when an erosive particle hits a ductile surface, either at a shallow or normal impact angle, the material is displaced and moved toward the sides of the crater or cavity [87]. This material is further strained by the particle advancement until the material is dislodged from the metal surface. This material removal process was found to be akin to single point cutting mechanism and this study also assumed that particle penetration depth is related to the volume of the material removed. In another study, erosion was termed as a dual-stage process [43]. The first stage is when a particle impacts the target material causing an indentation thereby removing a slice of material for the primary damage. The second stage is when the impacting particle itself disintegrates and sub-particles radiate out of the primary impact site leading to secondary damage of the material in the nearby region. The erosion mechanism, based on target material melting (due to the conversion and transfer of particle kinetic energy into heat) was reported for different ductile materials [88]. In the erosion of ductile alloys, especially for slurry erosion conditions, it was found that the kinetic energy of the impacting particle, responsible for the plastic deformation of the target material, was a function of the coefficient of restitution (i.e. the ratio of the erodent rebound velocity to the impacting velocity) [90]. Another study reported an impacting particle striking the target material imposes both normal and tangential forces due to which both deformation and cutting action took place during the removal of material [91].

2.2.3 Erosion mechanism of brittle materials

In brittle materials, the main mechanism of material removal is the propagation and intersection of cracks [92]. The type of crack formed in brittle material depends on both the shape and size of erosive particles hitting the target material. The erosion of brittle materials due to hard and angular particles of less than 2 mm in size generally involves the material removal mechanism through the formation of indentation zones, median vent cracks, and lateral cracks [92,93], as shown in Fig. 2.10.

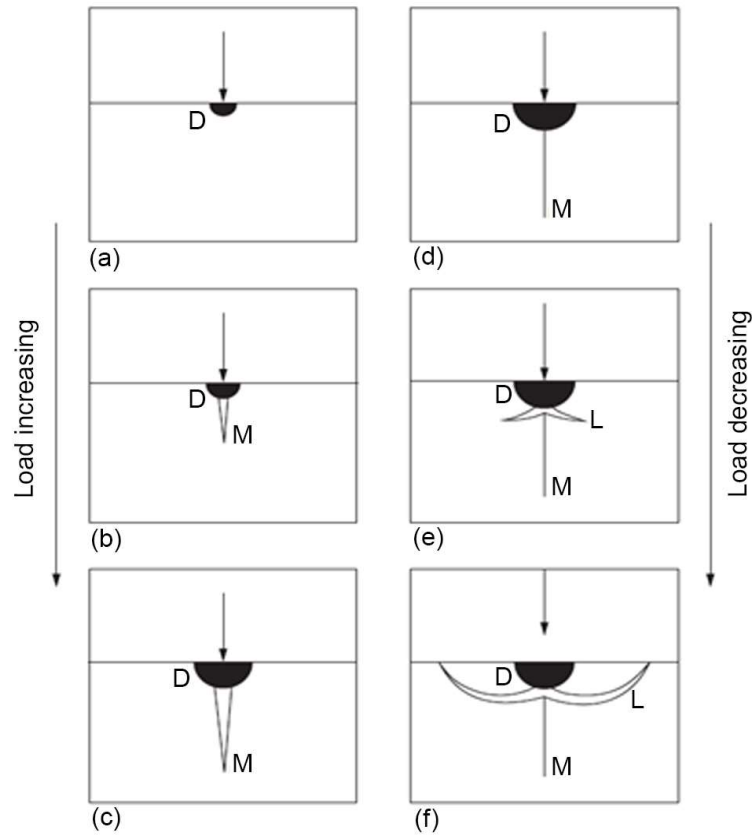


Figure 2.10 Zone of indentation (D), formation of median vent crack (M) with increasing load (a) to (c), and formation of lateral vent crack (L) with reducing load (d) to (f). [41]

The indentation of hard particles on the material surface is represented through zone D (Fig. 2.10a). During particle impact, as load is increased beyond a critical value, a median vent crack nucleates and grows along the indentation zone; this is due to the tensile stresses acting on either side of the crack. As the particle indentation load is further increased, the size of the crack also increases, as shown in Fig. 2.10(b-c).

Following particle impact, as the load is reduced, the vent crack opening closes, and with further load reduction, the lateral crack nucleates and grows. With further reduction of indentation load, the lateral vent crack grows further on either side of the crack until it touches the top surface of the material thereby removing the entire material volume which is covered by the lateral vent crack length.

For softer and more rounded angular particle (more than 2 mm size) impact, the material is removed through the formation of conical Hertzian fractures [92,93], as shown in Fig. 2.11.

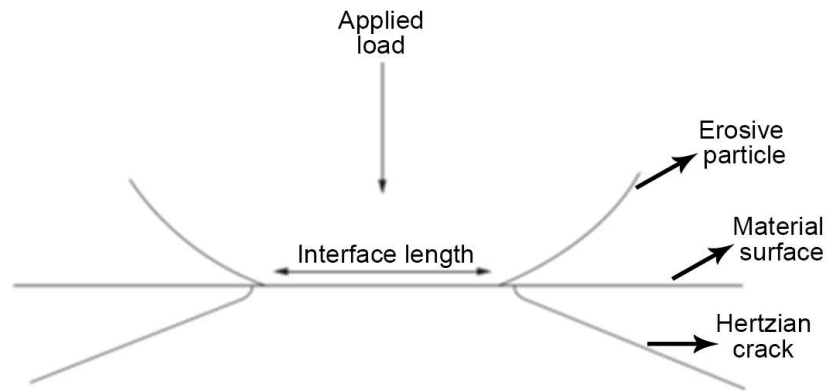


Figure 2.11 Hertzian crack formation on the material surface as the particle load reaches beyond a critical value. [41]

2.3 Corrosion in aqueous environment

This section presents relevant theories of metallic corrosion in aqueous media covering mainly the thermodynamics and kinetics aspects of electrochemical processes. In addition, the section also includes a literature review on galvanic corrosion in flow conditions (also known as flow-assisted corrosion). Finally, the chapter also describes some relevant laboratory-based test methods for aqueous corrosion.

2.3.1 Theoretical background

Many authors have defined corrosion in different ways. The National Association of Corrosion Engineers (NACE), one of the premier global organisations for corrosion control has defined corrosion as “the deterioration of a material (usually a metal) due to an electrochemical reaction with its environment” [94]. As per Fontana and Staehle [95], corrosion can be defined as “the reaction of metals, glasses, ionic solids, polymeric solids and composites with environments that embrace liquid metals, gases, non-aqueous electrolytes, and other non-aqueous solutions”. According to Evans [96], corrosion may be considered as a branch of chemical thermodynamics or kinetics, as the outcome of electron affinities of metals and non-metals, as short-circuited electrochemical cells, or the destruction of the metallic crystal structure. Trethewey and Chamberlain [97] explained the corrosion phenomenon based on thermodynamic laws in which the greater tendency for the transformation of high energy states to lower energy states is analogous to the greater tendency for metals to recombine with elements of the environment (corrosion).

Collectively, corrosion is the degradation of a material due to its reaction with the surrounding environment. When this corrosion takes place in an aqueous solution, it is termed aqueous corrosion [97,98]. In the electrochemical process of aqueous corrosion, metal degradation takes place through the liberation of metal ions and electrons from atomic lattice at the anodic site through an electrochemical reaction as follows [99]:-

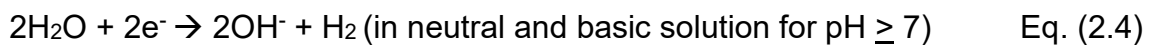
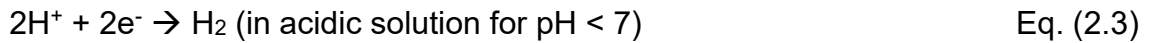


where, M is the metal atom, M^{n+} refers to metal ions, n is the valency of the metallic element, and e^{-} is electron.

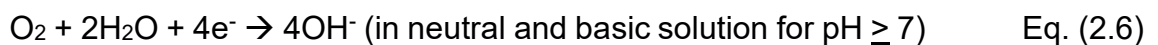
This electrochemical reaction is called oxidation and the region where this happens is termed as an anode or anodic half-cell.

The region where an ionic specie of an aqueous solution (or electrolyte) gain the electrons (liberated by the anode) and reduces to its atomic element is termed as cathode; this is known as a reduction reaction or cathodic half-cell reaction. In aqueous corrosion, the cathodic reaction can take place in the following ways:-

In a solution with a lack of oxygen, the following reactions take place [97–100],



The following reaction takes place in an oxygen-dominated solution [97–100],



The anodic and cathodic half-cell reactions, as mentioned earlier, need to happen in the presence of an electrolyte to complete the circuit (for the flow of electrons from the anode to the cathode and ions to the cathode). The occurrence of both of these half-cell reactions, commonly termed ‘redox’ reactions, is a prerequisite to initiating the process of corrosion [97,98].

An exemplary aqueous corrosion schematic is shown in Fig. 2.12.

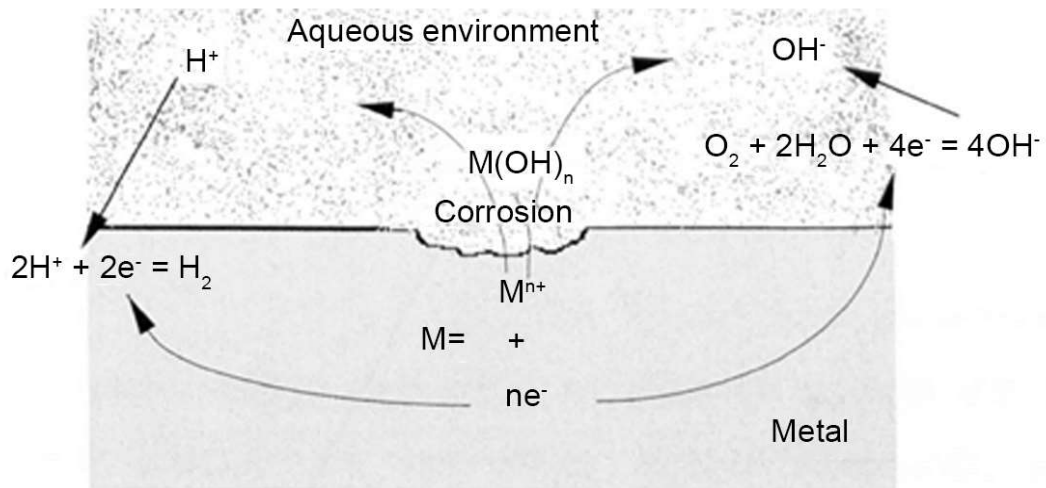
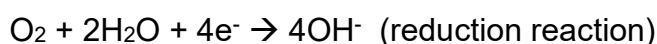
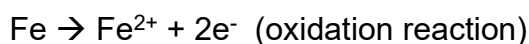


Figure 2.12 Corrosion in aqueous environment. [99]

Figure 2.12 depicts both metallic oxidation (Eq. 2.2) and hydrogen/oxygen reduction reactions (Eq. 2.3 and Eq. 2.6), in an aqueous environment. In metallic oxidation, at an anodic site, the metallic ions (Mⁿ⁺) are liberated from the metal atom (M) to the aqueous electrolyte. Also, the valence electrons (ne⁻) move to the nearby cathodic site within the metallic surface. Assuming a lack of oxygen in an acidic aqueous environment, it will lead to a hydrogen reduction reaction in which hydrogen ions (H⁺) in the electrolyte move to the cathode and combine with electrons to produce hydrogen gas. In another case, assuming an oxygen-dominated neutral or basic aqueous environment, it will lead to a reduction reaction in which dissolved oxygen (O₂) in the electrolyte reacts with water molecules and electrons and is reduced to hydroxyl ions (OH⁻) at the cathode. These hydroxyl ions then react with liberated metallic ions and form a metallic hydroxide – M(OH)_n, as shown in the figure. This way both oxidation and reduction reactions or redox reactions lead to metallic deterioration in the form of corrosion.

The corrosion schematic, as shown in Fig. 2.12, when applied to the corrosion of iron in an alkaline solution with dissolved oxygen, leads to the following reactions:-

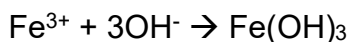


Further oxidation of ferrous ions (Fe²⁺) to ferric ions (Fe³⁺) takes place as,



The ferric ions then react with hydroxyl ions to form ferric hydroxide - Fe(OH)₃,

according to the following reaction,



$\text{Fe}(\text{OH})_3$ is also known as rust which is a reddish brown insoluble scale often found on iron surfaces due to its corrosion in an aqueous environment [99].

2.3.2 Aqueous corrosion thermodynamics

It is important to understand the feasibility and direction of an electrochemical reaction (involving both anodic and cathodic half-cells) during a corrosion process. This can be understood with the help of corrosion thermodynamics which states that any reaction will proceed in the direction that minimises the change in Gibb's free energy [100].

The Gibb's free energy change for an electrochemical process when all the reactants and products are in their standard states (1 atmospheric pressure and 298 K) is given by the following equation [101],

$$\Delta G^\circ = -nFE^\circ \quad \text{Eq. (2.7)}$$

where,

ΔG° is the change in Gibb's-free energy (J mol^{-1}),

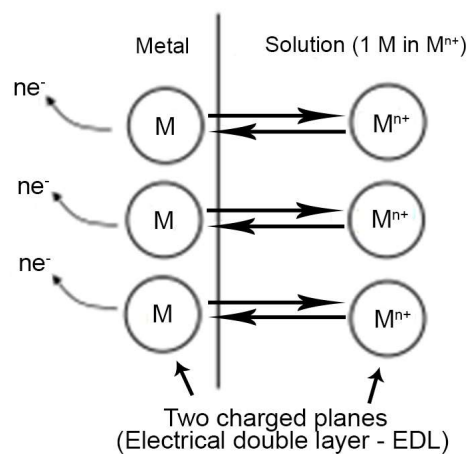
n is the number of electrons in an anodic corrosion reaction (e.g. $n = 2$ for the corrosion of metal, $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^-$).

F is faraday's constant ($96485 \text{ coulombs mole}^{-1}$).

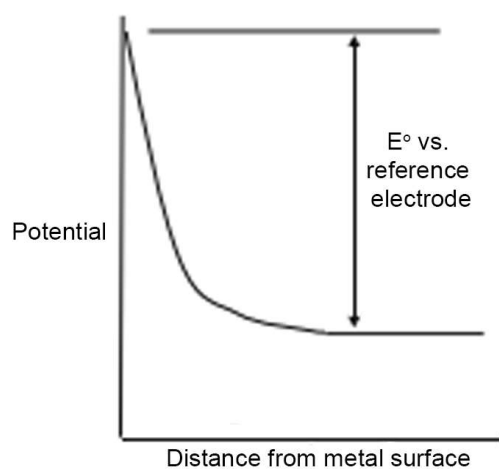
E° is the standard electrode potential (volts).

The electrode potential (E°) is attained when equilibrium is established. This happens according to the law of charge conservation [102], when the rate of anodic oxidation reaction is the same as the rate of cathodic reaction, also shown in Fig. 2.13(a).

Figure 2.13 shows the standard electrode potential (E°), which is achieved for a metal (M) immersed in a solution of its ions (M^{n+}) at 1 M concentration.



(a)



(b)

Figure 2.13 Electrochemical process for standard state metallic reaction (a) metallic dissolution and ionic redeposition at equilibrium, (b) potential variation across EDL. [103]

Figure 2.13 can be explained by taking an example of the corrosion of iron in water.

The dissolution of iron atoms into the water as ferrous ions (Fe^{2+}) is the predominant reaction which can also be represented as,

Iron atoms in the metal $\rightleftharpoons$ Iron ions in the solution



The above reaction represents the condition of equilibrium or lowest free energy state in which ferrous ions dissolved in the solution are at equilibrium with iron atoms on the metal surface. Moreover, at equilibrium, the metal ions remain close

to the metal surface creating a situation where metal ions theoretically re-enter and transform back to metal atoms when other atoms leave the surface and transform into metal ions. This proximity of positively charged metal ions with the metallic surface valence electrons creates two charge planes which are collectively known as the electrical double layer (EDL) [103–105], as shown in Fig. 2.13(a).

An electrical potential is produced (due to the charge separation in EDL) that can be measured as the difference between the test electrode (known as a working electrode) and a reference electrode. This potential varies across the EDL that extends from the metal surface to the solution, as shown in Fig. 2.13(b). In the absence of externally applied potential, the measured electrode potential (E^0) is referred to as open-circuit potential (OCP). The applied potential will change the composition of EDL and will result in changes in electrode potential (E^0). The Nernst equation [106] mathematically relates EDL composition to an applied electrode potential (E) as,

$$E = E^0 - \left(\frac{RT}{nF} \right) \ln K_c \quad \text{Eq. (2.8)}$$

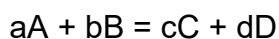
where,

R is Universal gas constant ($8.314 \text{ J mole}^{-1} \text{ K}^{-1}$).

T is the absolute temperature (in degrees Kelvin).

K_c is the concentration constant

For a given reaction as follows,



where, A and B are the concentrations of the reactants, C and D are the concentration of the products; a , b , c , d are the number of moles,

then K_c for the reaction can be given as,

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

2.3.3 Aqueous corrosion kinetics

As stated earlier, the field of thermodynamics provides insights into the feasibility, direction, and equilibrium of electrochemical reactions. However, while thermodynamics can predict the occurrence of corrosion, it does not provide information on the rate of electrochemical reactions, a crucial factor in determining

the lifespan of structural materials [107]. This gap is addressed by the kinetics of aqueous corrosion, specifically polarisation and mixed potential theory, which provide valuable insights into the rate of electrochemical reactions.

Polarisation refers to the changes in electrode potential due to the flow of current. The degree of polarisation (also known as overvoltage or overpotential), denoted by the symbol ' η ', can be calculated based on the following equation.

$$\eta = E - E_o \quad \text{Eq. (2.9)}$$

where,

E is the electrode potential.

E_o is the electrode potential for zero current flow (also called the open-circuit potential (OCP), corrosion potential, or rest potential).

The Butler-Volmer equation establishes a relation between η and the current density (due to polarisation) [107–109] as follows:

$$i_{\text{net}}^{\leftarrow} = i_o \left[\exp \left(\frac{\alpha n F \eta}{RT} \right) - \exp \left(\frac{-(1-\alpha) n F \eta}{RT} \right) \right] \quad \text{Eq. (2.10)}$$

$$| i_{\text{net}}^{\rightarrow} | = i_o \left[\exp \left(\frac{-(1-\alpha) n F \eta}{RT} \right) - \exp \left(\frac{\alpha n F \eta}{RT} \right) \right] \quad \text{Eq. (2.11)}$$

where,

$i_{\text{net}}^{\leftarrow}$ and $| i_{\text{net}}^{\rightarrow} |$ are the net anodic and cathodic reaction rates, respectively.

i_o is the exchange current density (A cm^{-2}) at E_o .

α is the dimensionless parameter with values ranging from 0 to 1.

Eq. (2.10) and Eq. (2.11) apply to reversible electrode potentials in which metal exists in solutions of its ions at equilibrium conditions.

However, in practical applications, the solution does not originally contain ions of the metal and it may contain ions of other elements as well e.g. Cl^- , H^+ , OH^- , CO_3^{2-} etc. Also, the metal atoms may pass into the solution continuously and irreversibly. In these cases, the electrode potential is said to be an irreversible potential and is not given by the Nernst equation [107].

For example, the dissolution of iron in acid solution proceeds under an irreversible potential which involves two separate oxidation-reduction reactions (Eq. 2.13 and Eq. 2.14).



The half-cell reaction (Eq. 2.13 or Eq. 2.14) does not operate reversibly and the electrode potential under which Eq. (2.12) proceeds is an irreversible one which is determined by mixed potential kinetics.

The mixed potential theory of corrosion states that any electrochemical reaction can be bifurcated into a couple of partial oxidation and reduction reactions [110]. At equilibrium, the net rate of anodic oxidation reactions is equal to the net rate of cathodic reduction reactions, and this equates to the corrosion rate of the freely corroding metal or i_{corr} . The electrode potential for the steady-state, free corroding condition given by Eq. (2.12) is called the corrosion potential (E_{corr}) which is not related to E° values of either half-cell reaction through the Nernst equation [107].

Figure 2.14 shows the Tafel plot [111], which represents the application of mixed potential theory for iron dissolution, as shown by Eq. (2.13) and Eq. (2.14). In this case, the corrosion potential is established when the rate of iron dissolution into ions is equal to the rate of hydrogen ion reduction into hydrogen gas. As shown in Fig. 2.14, it happens at corrosion potential E_{corr} (with current density i_{corr}) at which the sum of anodic currents in both half-cells is equal to the sum of cathodic currents and the system will be in a steady state.

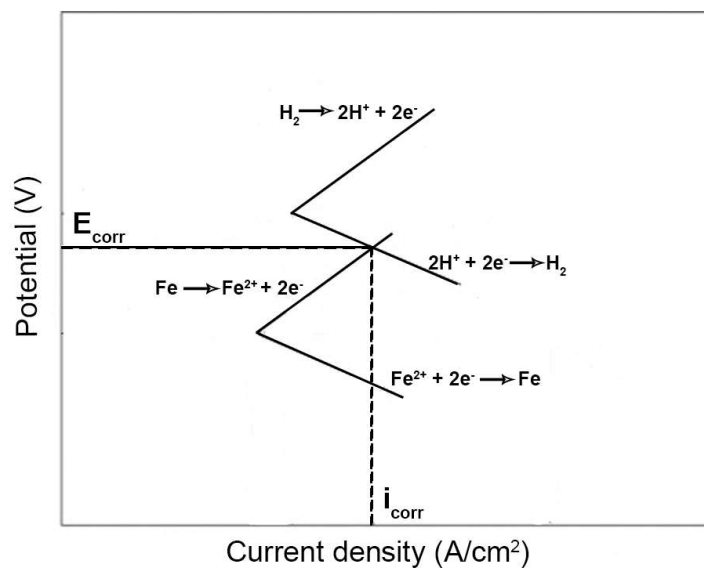


Figure 2.14 Tafel plot representing mixed electrode potential (E_{corr}). [111]

2.3.4 Aqueous corrosion measurement

In the literature, the aqueous corrosion measurements were established through various electrochemical techniques. Among those, the techniques which were found to be most widely used are as follows [112]:

1. Potentiodynamic and potentiostatic polarisation measurements.
2. Linear polarisation resistance.
3. Electrochemical impedance spectroscopy.

The first two techniques are based on the application of direct current (DC) while impedance spectroscopy is based on the use of alternating current (AC).

1. Potentiodynamic and potentiostatic polarisation measurements

Potentiodynamic measurement

The schematic diagram of potentiodynamic polarisation equipment is shown in Fig. 2.15.

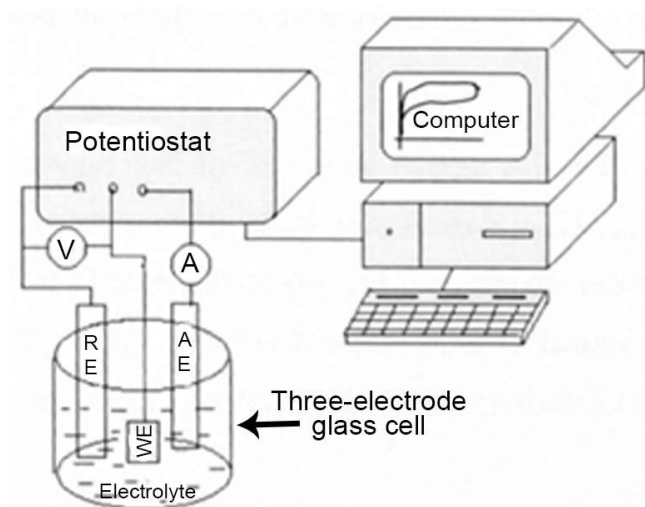


Figure 2.15 Schematic of potentiodynamic polarisation measurement. [113]
(RE – Reference Electrode, WE – Working Electrode, AE – Auxiliary Electrode,
'V' and 'A' signify voltage and ampere current measurements across electrodes).

As shown in Fig. 2.15, the three electrodes (reference electrode, working electrode, and auxiliary electrode) are housed in an enclosure called a three-electrode cell which is normally made of glass and is based on ASTM approved design specifications [114]. This three-electrode glass cell is filled with an electrolyte in which all three electrodes are submerged. The sample under

investigation also referred to as the working electrode (WE), is prepared (through grinding/polishing) and cleaned before its immersion into the electrolyte. The reference electrode (RE) is used to measure the potential of the working electrode. It is available in various types and the most commonly used are either saturated calomel electrode (SCE) or silver-silver chloride (Ag/AgCl) reference electrode [115,116]. The auxiliary electrode (AE) allows the current to flow through itself and the working electrode when there is a shift in the working electrode potential. It is commonly made of inert materials such as platinum or graphite [117]. The three-electrode cell is connected to a potentiostat with which the sample can be polarised and the resulting polarisation curves can be displayed on a computer system which is also connected to the potentiostat.

The polarisation curves are obtained through the potential sweep technique [118]. In this technique, the potentiostat sweeps the working electrode potential, from a more negative cathodic potential (than E_{corr}) to a more positive anodic potential (than E_{corr}). This sweeping potential can range from -1 V to + 1 V, from E_{corr} [118,119]. The resulting current is then recorded, at each potential, and the entire polarisation curve is obtained. An exemplary polarisation curve (E vs log i) is shown in Fig. 2.16.

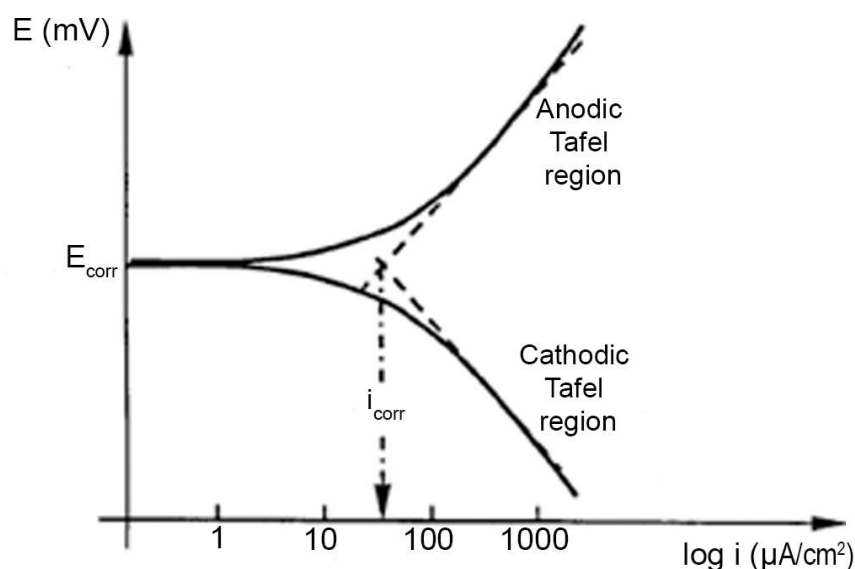


Figure 2.16 Tafel extrapolation to determine corrosion current density (i_{corr}). [113]

The potential sweep (also known as potentiodynamic) scan makes use of a broader spectrum of potentials to obtain curves in both anodic and cathodic regions (also known as Tafel regions) [113]. The extrapolation of linear parts of

the anodic and cathodic curve back to the E_{corr} gives a point of intersection at which the corresponding current represents the corrosion current density (i_{corr}) [110,120,121].

Potentiostatic measurement

The potentiostatic polarisation measurement follows a similar schematic of potentiodynamic measurement, as shown in Fig. 2.15. The measurement plots are obtained through the application of potentiostatic technique [122]. In this technique, the potentiostat applies a constant potential to the working electrode for a fixed time duration. The resulting current is measured in each time step for the entire duration and is obtained as current density versus time plot.

2. Linear polarisation resistance

In the linear polarisation resistance (LPR) measurement technique, the working electrode potential is scanned within a narrow potential range, usually ± 20 mV from corrosion potential (E_{corr}), and the current potential plot is obtained [123].

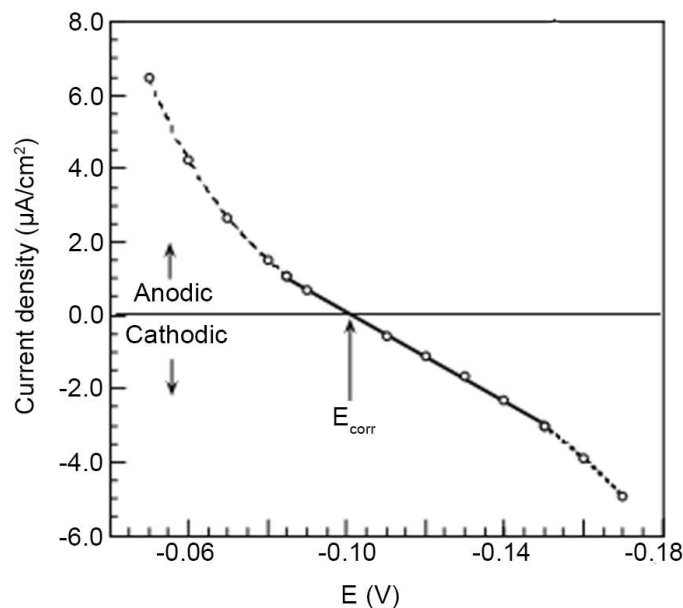


Figure 2.17 Polarisation curve showing a linear region near corrosion potential (E_{corr}). [123]

Figure 2.17 shows the current potential plot, the slope of which gives the polarisation resistance (R_p). From this polarisation resistance (R_p), the corrosion current density (i_{corr}) can be determined mathematically using the Stern-Geary equation [121,124,125] as,

$$i_{\text{corr}} = \left[\frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)(R_p)} \right] \quad \text{Eq. (2.15)}$$

where, β_a , β_c = anodic and cathodic Tafel constants (V Decade⁻¹), respectively, R_p = polarisation resistance (ohm.cm²).

In the potential range of ± 20 mV, the measured current is linear, as shown in Fig. 2.17, and therefore this technique is known as a linear polarisation technique [126]. This technique gives a reasonable approximation of changes in the rate of corrosion without affecting specimen surface conditions. However, the accuracy of the corrosion rate mainly depends on reliable β_a and β_c values, obtained through the curve fitting method [121,127].

3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a very useful technique for investigating passivation mechanisms, assessing corrosion rates, and evaluating reaction mechanisms [128–131]. All those materials, such as anodised aluminium and polymer-coated metals, which cannot be studied with direct current (DC) based methods can be rapidly and reliably investigated with the EIS technique, which is an alternating current (AC) based technique [132].

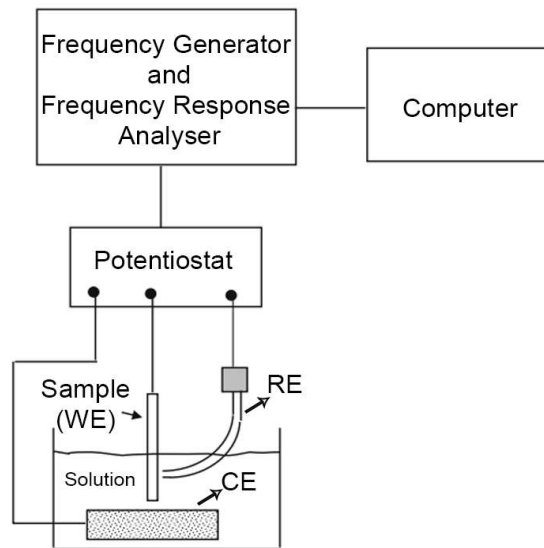


Figure 2.18 Schematic of impedance measurement by EIS. [133]
(WE – Working Electrode, RE – Reference Electrode, CE – Counter Electrode).

EIS setup, as shown in Fig. 2.18, comprises a 3-electrode electrochemical cell, a potentiostat for electrode potential control, a frequency generator, a frequency response analyser (FRA), and a computer for control of experiment and data

storage. The EIS measurement involves applying a small amplitude alternating current (AC) signal, typically a voltage between 5 and 50 mV, to a sample across a frequency range from 1 mHz to 100 kHz [134,135]. The FRA quantifies various components of the complex impedance, which represents the resistance to the AC current flow. The analysis determines the sample-solution system's impedance and the phase angle (between the impedance and the applied potential) as functions of the applied frequency. These values are then interpreted in terms of the electrochemical, chemical, and physical processes related to the cell. Further information on the experimental aspects of AC impedance techniques can be found in other sources [97,136,137].

In this research work, the corrosion measurements were performed using the potentiodynamic polarisation technique. Despite being a destructive technique, it is one of the most widely used direct current (DC) techniques for corrosion measurement [123,138–140]. Some of the main advantages of using this method include: (i) simple, fast, and accurate determination of corrosion rates, (ii) provide useful information regarding mechanisms of corrosion and susceptibility of material corrosion in specified environments [139,140]. The other measurement techniques (Linear polarisation and electrochemical impedance spectroscopy) are useful in terms of non-destructive repetitive sample usage however suffer from disadvantages such as limited sweeping potential range, measurement errors, and high instrumentation costs [123,138].

2.3.5 Flow-assisted galvanic corrosion and its measurement

Galvanic corrosion takes place when two dissimilar metals are in contact (physical or electrical) with each other in the presence of an aqueous electrolyte solution, as shown in Fig. 2.19.

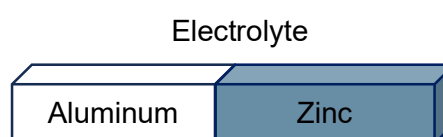


Figure 2.19 Galvanic couple between two different metals.

The corrosion potential (E_{corr}) of each metal forms the basis of its corrosion tendency. The metal with more negative corrosion potential acts as an anode and the other metal becomes a cathode [15]. The anodic member, which is more

active and electronegative, has excess electrons that move to the cathodic member which is more noble and it results in the flow of galvanic current from anode to cathode [141]. The presence of electrolyte facilitates the migration of metallic ions from anode into the solution. This results in an accelerated rate or preferential corrosion for the less noble metal in the coupled state as compared to its corrosion rate in the uncoupled state in a similar electrolytic environment [13,14].

In the literature, a galvanic series of different metals is available [141,142]. However, this series is constructed using seawater only. A galvanic series lists the measured corrosion potentials of different metals. The more electronegative metal in the galvanic series will have a higher corrosion tendency as compared to the more positive metal in that series. However, this behaviour can be expected for metallic behaviour only in seawater or in similar aqueous conditions and therefore restricts the applicability of galvanic series to acidic or alkaline conditions [14].

Measurement of galvanic corrosion

The method for determining galvanic currents between coupled metals or alloys relies on the application of a zero resistance ammeter (ZRA) technique [143–145]. In this technique, the metallic pair or a galvanic couple is connected to a potentiostat, which is commonly used in ZRA experiments [146]. One of the metals of this galvanic couple is connected as a working electrode and the other one is connected as an auxiliary electrode. The potentiostat ensures electrical continuity with zero resistance between the elements of the galvanic couple. The galvanic current flowing between a working electrode and an auxiliary electrode, as well as their galvanic potential, is measured with respect to a reference electrode: saturated calomel electrode (SCE) or silver-silver chloride (Ag/AgCl) reference electrode [115,116].

It is a common practice to perform ZRA in conjunction with other methods such as polarisation and mass loss measurements since each of these techniques can be subjected to experimental errors [143,147–150].

Flow effect on galvanic corrosion

Some of the past research efforts have delved into the impact of fluid flow on galvanic corrosion [148,151–153]. In general, the flow velocity enhances the

galvanic corrosion rate of a galvanic system that is predominantly under mass transfer control. One of the studies investigated the influence of flow velocity on the galvanic corrosion of a carbon steel/stainless steel pair in an alkaline chloride solution [151]. The study concluded that the flow velocity of the solution amplified the carbon steel galvanic corrosion, operated under increased oxygen transfer in diffusion control reactions. On the contrary, the same study found solution pH increase led to galvanic corrosion rate reduction, which was due to the formation of a stable oxide layer (passivation) on the carbon steel sample. In another study, the impact of fluid flow on the galvanic corrosion of a copper/stainless steel pair in a lithium bromide solution was investigated [152]. The study found that the galvanic current density initially rose with the Reynolds number (that is representative of flow velocity) but subsequently declined over time due to the accumulation of corrosion products on the copper surface. Other investigations focused on how flow conditions affected the galvanic corrosion of a carbon steel/brass pair in a sodium chloride solution [153]. It was found that the galvanic current density increased with flow velocity. This pattern was ascribed to the galvanic system being under mass transfer control, where an increase in flow velocity enhances the transportation of oxygen from the bulk solution to the metal surfaces. This, in turn, led to an acceleration in the rate of both cathodic and anodic reactions, thereby increasing the galvanic corrosion density. Similar findings (of galvanic corrosion due to mass transfer control) were also reported in the investigation of the flow effect on galvanic corrosion of copper/stainless steel pair in lithium bromide solutions [148].

Relevance to the present work

The flow-assisted galvanic corrosion was an important consideration in the present research work. As mentioned earlier in the technical brief (section 1.3), the isotopes of tungsten were found in the cooling water loop of the tantalum clad tungsten spallation target [8,9]. This target is an assembly, of tungsten core bonded with tantalum clad, enclosed in a tantalum cooling water sleeve [9]. Although there is no exposure of circulated cooling water to the core tungsten, the presence of two dissimilar metals with a flowing electrolyte demands an experimental investigation from the standpoint of galvanic corrosion. Furthermore, there is an absence of documented research on flow-assisted galvanic corrosion involving the interaction between tantalum and tungsten. All of

these aspects make the investigation of flow-assisted galvanic corrosion, between tantalum and tungsten, a highly relevant and significant undertaking.

2.4 Aqueous Erosion-Corrosion

Erosion-corrosion refers to the material degradation caused by the joint action of mechanical wear due to abrasive solid particles and corrosion due to the electrochemical process. The American Society for Testing and Materials (ASTM) defined it as “a synergistic process involving both erosion and corrosion, in which each of these processes is affected by the simultaneous action of the other, and in many cases is thereby accelerated” [154]. Erosion-corrosion is not an inherent characteristic of a material, but rather a property of the system as a whole. The magnitude of material loss is influenced by a multitude of factors associated with the tribological interaction, including the properties of the particle and target material, as well as the environmental conditions [17,155–157]. This phenomenon of erosion-corrosion is commonly observed in industries related to oil and gas, manufacturing, power plants, mining, and marine where the fluid handling equipment (such as pumps, impellers, turbines, valves, etc.) gets damaged and needs repair or replacement at a high cost [158].

2.4.1 Erosion-Corrosion processes

In the literature, it is widely recognised that the rate of erosion-corrosion is not merely the sum of erosion and corrosion rates [17,41,155–157,159]. Instead, these two processes interact with each other. This interaction is commonly known as synergy, details of which are described below.

Synergy

Various researchers have described the synergy between erosion and corrosion, as a phenomenon in which the combined wear rate exceeds the sum of pure erosion (in the absence of corrosion) and pure corrosion (in the absence of erosion) rates individually [160,161].

This synergy can appear due to two different interaction effects: additive and synergistic effects [12], details of these two effects are given in the following sections. The relationship used to describe the erosion-corrosion interaction is as follows [162],

$$K_{ec} = K_{eo} + K_{co} + \Delta K_{ec} \quad \text{Eq. (2.16)}$$

$$\Delta K_{ec} = K_{ec} - (K_{eo} + K_{co}) \quad \text{Eq. (2.17)}$$

where,

K_{ec} is total wastage rate of erosion-corrosion of a system.

K_{eo} is rate of erosion only (without corrosion).

K_{co} is rate of corrosion only (without erosion).

ΔK_{ec} is synergy or additional wastage rate.

Also,

$$\Delta K_{ec} = \Delta K_c + \Delta K_e \quad \text{Eq. (2.18) [162]}$$

where,

ΔK_c is the additive effect (described in section 2.4.2).

ΔK_e is the synergistic effect (described in section 2.4.3).

2.4.2 Erosion enhanced corrosion (ΔK_c): Additive effect

As stated earlier, the additive effect of erosion-corrosion arises when the corrosion rate is enhanced by the erosion process. This additive effect is dependent on process parameters. An earlier study reported that the extent of the additive effect is dependent on slurry concentration and velocity [163]. This observation was made on carbon steel pipelines transporting sand, iron ore, potash, limestone, and coal slurries at commercial concentrations and velocities. This additive effect has been observed due to two main reasons. Firstly, the higher concentration of solid particles in the slurry caused partial or complete removal of the protective oxide layer on the substrate. This resulted in a higher oxygen mass transport rate to the corroding surface. Secondly, plastic deformation of the surface increased passivation current requirements and favoured higher anodic dissolution due to the flow of oxygen which is consumed in the corrosion process. In another observation for pipelines carrying aerated slurry (30-50 μm silica mesh) with 3.13% NaCl at a velocity range of 2-6 ms^{-1} , it was found that the total wastage rate increased due to corrosion with the process under the control of oxygen mass transfer [164]. Moreover, in the same study, the relationship between wear rate and slurry velocity was established with the velocity coefficient ranging between 0.73 and 0.99. Other studies found similar results with the velocity exponent ranging between 0.5 and 1 [165].

The dependency of additive effect on slurry concentration and impact angle was also reported on the erosion of pure iron in HCl/NaOH slurry with silica sand (149-177 μm particle size) [166,167]. The erosion enhanced corrosion rate was found to be higher at a 60° angle as compared to a 20° impact angle. This was explained based on the formation of an oxide layer which was more stable at 20°, as compared to that at 60°. Consequently, the metallic substrate suffered less anodic dissolution and erosion at 20° as compared to the material loss at a 60° impact angle. Also, based on the general agreement, it can be concluded that the additive effect is the predominant erosion-corrosion mechanism once the protective oxide film is removed partially or completely and the material fails to re-passivate quickly [122,156,175,176,165,168–174].

2.4.3 Corrosion enhanced erosion (ΔK_e): Synergistic effect

As stated earlier, the synergistic effect of erosion-corrosion appears when the erosion rate is enhanced by the aqueous corrosion process. The synergistic effect can be triggered through various mechanisms. A previous study on erosion-corrosion of aluminium under aqueous silica (600-850 μm particle size) slurry containing acetic acid and sodium carbonate was reported [160]. This study reported a synergistic effect (corrosion enhanced erosion rate) in acetic acid and an antagonistic effect (corrosion impeded erosion rate) in sodium carbonate. The synergy mechanism was due to the detachment of metallic flakes through fragmental cracking because of the repeated impact of erodent particles. The corrosion process in this mechanism acted as a catalyst by initiating cracks at the root of metallic flakes thereby making them more susceptible to detachment. The selective dissolution of grain boundary and imperfections, as a mechanism for synergistic effect, were also reported [177–179]. In one of the erosion-corrosion experimental investigations on grey cast iron, it was found that the corrosive attacks at the graphite matrix interface caused the weakening of metallic grains and facilitated material removal upon particle impact [180]. A similar mechanism through intergranular corrosion was also reported in the erosion-corrosion of stainless steel [181]. Another study reported the synergistic effect which was observed in slurry erosion of mild steel in carbonate buffer solution containing alumina [170]. This synergistic effect was attributed to the environment induced fracture processes of intergranular corrosion and stress corrosion cracking.

Antagonistic effect

The antagonistic effect is observed when corrosion impedes erosion rate, which is contrary to the synergistic effect. The antagonistic effect mechanism is dependent on process conditions. A previous study on erosion-corrosion of high chromium cast iron and high carbon steel alloys, in alkaline slurries using quartz particles (74 – 147 μm particle size), has reported a clear mechanism for the antagonistic effect observed in the study [178]. This observation was based on the formation of stable passive films protecting the metal surface from particle erosion. Another study investigated the erosion-corrosion resistance of stainless steels in sodium chloride slurries using silica sand [122]. It was found that the addition of alloying elements, such as Cr, Mo, and N in high-alloy stainless steel improved its corrosion resistance. The addition of alloy elements led to firm oxide layer formation that reduced susceptibility to charge transfer, improved passivation behaviour, and decreased erosion-corrosion rate. Similar findings were reported in another study that investigated the effect of Mo on the passivation behavior of stainless steels [182].

The extensive use of all these interaction effects (additive, synergistic, and antagonistic) is also found in the strategic development of erosion-corrosion maps: regime maps and wastage maps [16,17,183]. These maps are highly significant in formulating a strategy for mitigating erosion-corrosion loss of materials in diverse engineering applications.

2.4.4 Erosion-corrosion test rigs

Various test rigs are available to measure the wear rate caused by the combined action of erosion and corrosion. Some of the commonly used test rigs include slurry pot apparatus [184,185], jet impingement apparatus [186,187], Coriolis apparatus [188], pipe flow loop [189,190], and rotating cylinder electrode apparatus [191,192].

Except for the jet impingement test rig, the other measuring apparatus suffered from structural limitations such as lack of impact angle control, high construction and maintenance costs, space restrictions, and high dependence on slurry concentration [193]. The advantage of jet impingement apparatus, in erosion-corrosion wear rate measurements in a controlled environment, is also reported elsewhere [186,187,194].

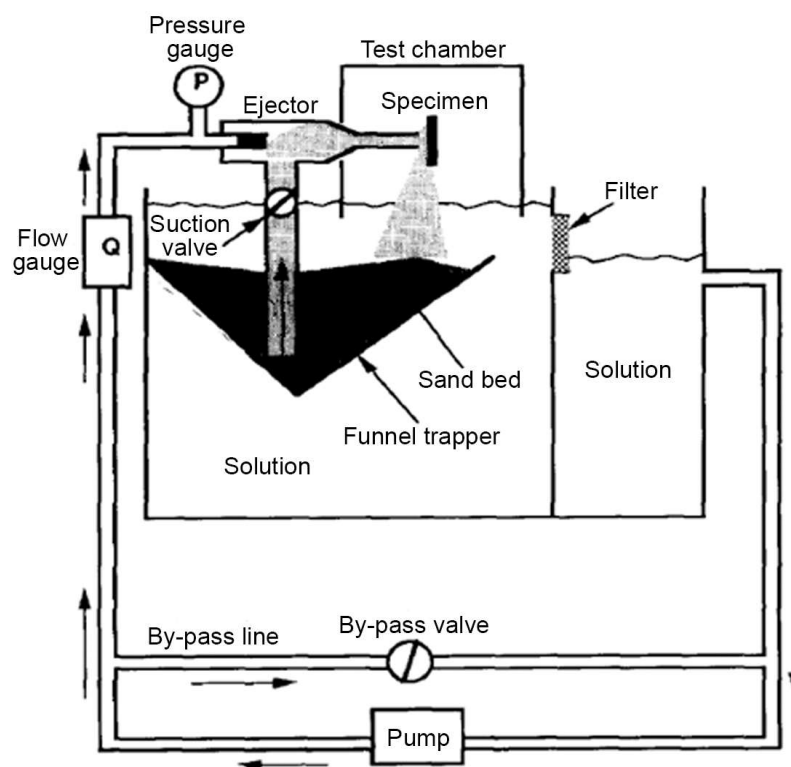


Figure 2.20 Schematic of jet impingement apparatus. [160]

Figure 2.20 shows the jet impingement apparatus schematic. The rig assembly includes an outer tank that contains electrolyte solution (filtered) which is pumped through an ejector to the specimen. The erodent particles (from the sand bed) are introduced into the electrolyte by pressure differentials (venturi effect) caused by the suction valve that allows the lifting of particles to the ejector. The resulting slurry (from the ejector) is then forced as a jet onto the specimen during an erosion experiment. After hitting the specimen, the slurry then falls into the inner tank and passes to the outer tank through the filter (which blocks particles and only allows solution to be collected into the outer tank) and the whole cycle repeats itself. The discharge and pressure readings are monitored through the installed flow gauge (Q) and pressure gauge (P), respectively. The electrochemical measurements of corrosion can also be performed by connecting this jet impingement apparatus to an external potentiostat that connects the reference electrode and counter electrode closer to the sample that acts as the working electrode [195].

2.5 Erosion-corrosion of tantalum and tungsten

This section reviews the erosion, corrosion, and erosion-corrosion behaviours of tantalum, tungsten, and tantalum-clad tungsten materials. The literature search was done extensively (from the year 1976 to 2022) through the ‘Clarivate Web of Science’ online platform, which is the world’s leading citation database of more than 34,000 peer-reviewed high-impact academic journals [196].

2.5.1 Erosion-corrosion of tantalum

There are no reported experimental studies on solid particle erosion, corrosion, and combined erosion-corrosion of tantalum under flow-assisted conditions until this study began.

Tantalum is a Group 5 metal in the periodic table and is characterised by its strong electronegativity which makes it more reactive [197]. Figure 2.21 depicts the tantalum Pourbaix diagram [198], which shows the thermodynamic stability of tantalum and its reaction products with water at 25°C.

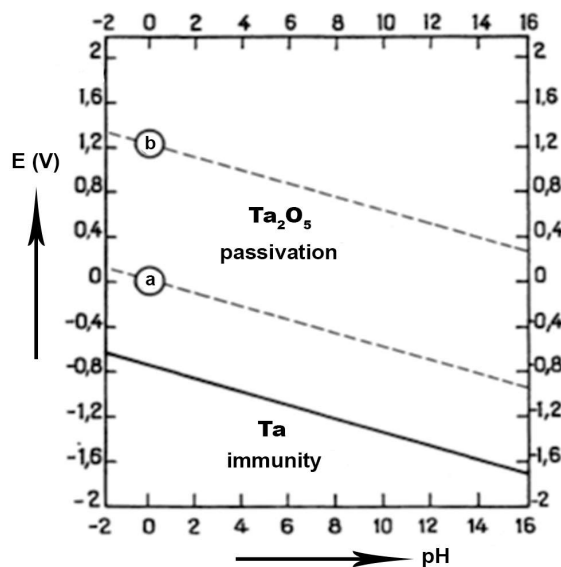


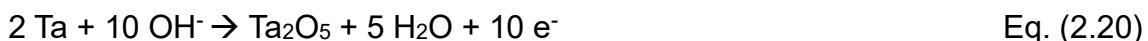
Figure 2.21 Pourbaix diagram for tantalum-water system at 25°C. [198]

Figure 2.21 shows that tantalum exhibits either immunity or passivation under the entire range of potential and pH. Under atmospheric conditions, tantalum forms a stable oxide film of tantalum pentoxide (Ta₂O₅), which provides passivity to the metal [199]. The previous studies on tantalum corrosion, using three electrode electrochemical cells in static conditions, reported the presence of this oxide film under both acidic and alkaline solutions [198,200–208].

The tantalum oxide film formation in an acidic solution takes place according to the following electrochemical reaction [198,200,201],



In alkaline solutions, the oxide film is formed due to the following electrochemical reaction [198,202,203],



This oxide film formation is commercially important for tantalum, which has found its application in chemical equipment construction, linings and shrouding of apparatus, surgical bone implants, heat exchangers, and many other applications where corrosion resistance is important [204,209]. Tantalum can resist corrosion from most acids and alkalis except for hydrofluoric acid, concentrated sulphuric acid at high temperatures, and fuming sodium hydroxide concentrated solution at 100°C [210]. Both hydrogen and hydrogen fluoride attack tantalum at temperatures ranging from 400°C to 800°C since at these temperatures the protective oxide layer dissolves. However, under high exposure to hydrogen gas at even lower temperatures, tantalum can be affected [204]. In borate buffer solutions, tantalum exhibited excellent passive behaviour in the pH ranges from 6.5 to 9 [205]. In alkaline solutions, the solubility of its protective oxide layer increased with the change of pH from 7 to 9.8 [206,207]. Another study investigated the polarisation behaviour of tantalum in sulphuric acid and seawater and found that tantalum was least resistant in seawater due to its extreme alkalinity while it was reasonably resistant to sulphuric acid in which it exhibited lower corrosion currents as compared to other metals [208].

2.5.2 Erosion-corrosion of tungsten

There are no reported experimental studies on the erosion, corrosion, and combined erosion-corrosion behaviour of tungsten under flow-assisted conditions until this study was commenced.

Tungsten displays passivation and is protected by its oxide layer in an acidic environment, as shown in its Pourbaix diagram [211], in Fig. 2.22. This figure shows that as the solution becomes alkaline, the corrosion of tungsten takes place with the liberation of its ions in the solution.

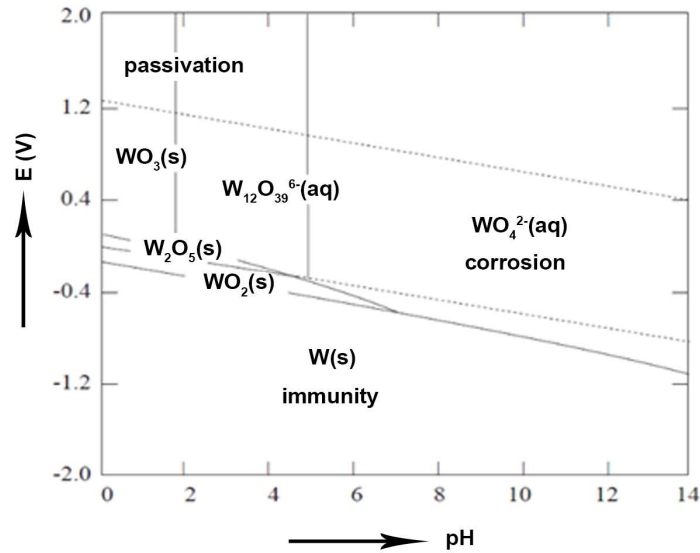


Figure 2.22 Pourbaix diagram for tungsten-water system at 25°C. [211]

The corrosion of tungsten in both acidic and alkaline solutions, under static conditions of three electrode cell, was previously reported [211–217]. These studies suggested that as solution alkalinity increases, the tungsten corrodes with its oxide layer dissolution assisted by hydroxyl ions. This happens due to the oxidation of the passive layer (WO_3) to higher valent tungsten oxides which are attacked (by the hydroxy ions in the alkaline solution) and liberated as polytungstate ions (WO_4^{2-}) in the solution. This tungsten corrosion is also shown by the following electrochemical reaction [215–217],



2.5.3 Erosion-corrosion of tantalum clad tungsten

The tantalum clad tungsten material is strategically important for its use as a source target material in neutron spallation applications [2,5,218–222]. As discussed earlier in Chapter 1, this target material is used in RAL and is speculated to be suffering from material degradation due to erosion-corrosion. Hence, this target material also demands a literature review from the standpoint of erosion, corrosion, and erosion-corrosion.

Apart from one erosion study, there are no reported experimental studies on corrosion and combined erosion-corrosion of tantalum clad tungsten under flow-assisted conditions. The only erosion study on tantalum clad tungsten under water impingement at an oblique angle (25°) did not report any erosion or pitting (under prolonged exposure) on the tantalum surface [223].

In neutron spallation applications, the target material is bonded with tantalum clad to protect the underlying core tungsten from the cooling water corrosive effect that can accelerate under irradiation conditions [224]. Figure 2.23 shows RAL's tantalum clad tungsten target assembly (TS2) and cooling water flow schematic [225].

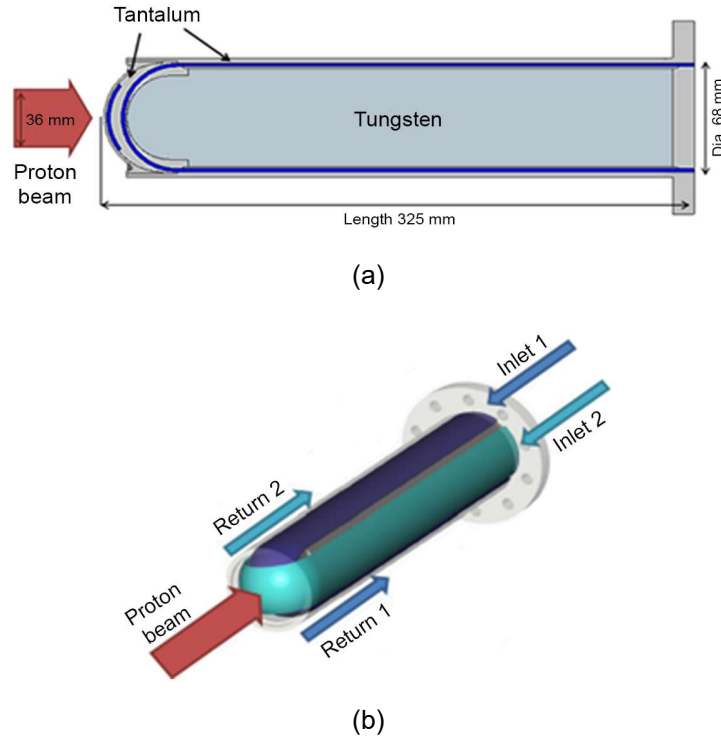


Figure 2.23 (a) TS2 2D target assembly cross-section showing incident proton beam and cooling water flow (blue stripes), (b) 3D image showing inlet and return water flow channels around the RAL target assembly. [225]

Table 2.2 Tantalum and Tungsten properties at room temperature. [8,226]

Property	Tantalum	Tungsten
Atomic Number	73	74
Density (kg m ⁻³)	16600	19250
Hardness at 20°C	220 (HV10)	460 (HV30)
Yield Strength (MPa) at 25°C	200	N/A (Brittle)
Ultimate Strength (MPa)	270	550
Modulus of Elasticity (GPa)	188	398
Coefficient of Thermal Conductivity (Wm ⁻¹ K ⁻¹)	57.2	174.9
Melting Point (°C)	3017	3422

Table 2.2 shows the room temperature properties of tantalum and tungsten. The electron beam welding and subsequent hot isostatic pressure bonding between

tantalum and tungsten (to achieve tantalum clad tungsten target) do not generally result in the build-up of any internal residual stresses in the target [8]. However, in neutron spallation conditions of high temperatures, both tantalum and tungsten experience irradiation hardening due to atomic dislocation mechanisms [227,228].

Chapter-3

Experimental Methods

3.1 Introduction

This chapter outlines the experimental methods used throughout the study. These methods are divided into the following three sections,

- (i) Material characterisation
- (ii) Erosion and electrochemical tests
- (iii) Analysis of test results

3.2 Material characterisation

3.2.1 Material source

The Tantalum (Ta) and Tungsten (W) samples used in this study were supplied by Rutherford Appleton Laboratory (RAL), UK. These were high-purity (99.9%) samples manufactured through the powder metallurgy (PM) route. The samples were received in the form of cylindrical shapes with a diameter of 30 mm and a thickness of 5 mm, as shown in Fig. 3.1.

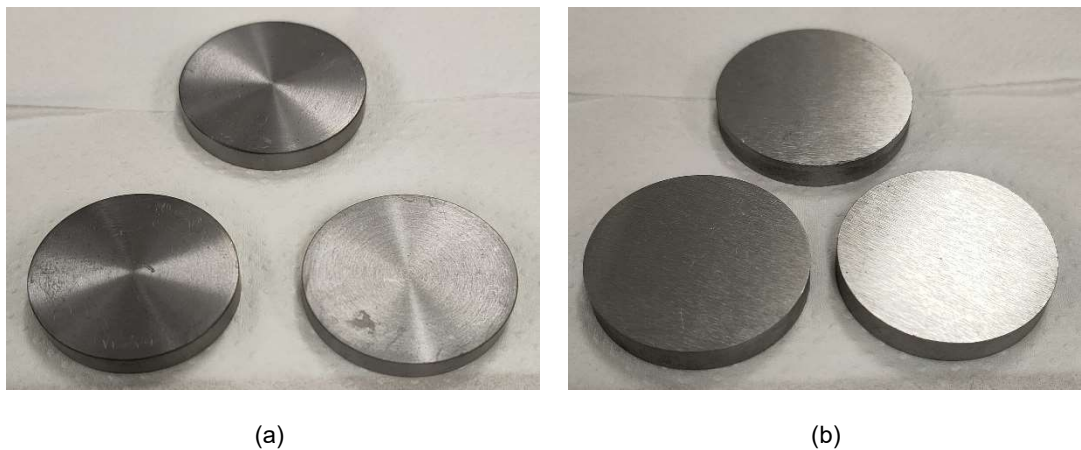


Figure 3.1 As-received samples; (a) Tantalum (b) Tungsten (diameter – 30 mm, thickness – 5 mm).

3.2.2 Surface preparation of the test samples

The surface preparation of the test samples was performed on the Buehler EcoMet 30 (Fig. 3.2a) grinding and polishing equipment and the process involved grinding with 600, 1200, and 2500 grit papers and polishing with polycrystalline diamond suspensions (6 μm and 1 μm). The samples were polished further on the chemically resistant synthetic polishing pad- ChemoMet (Fig. 3.2b) using non-crystallising amorphous colloidal silica suspension (0.02 μm particle size) to obtain a mirror-like surface finish, as shown in Fig. 3.3.

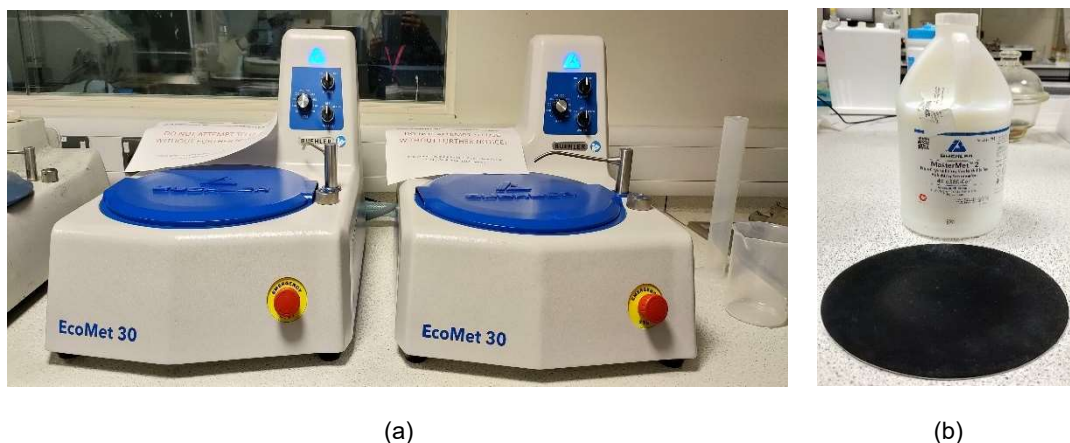


Figure 3.2 Specimen surface preparation; (a) Grinding-Polishing apparatus; EcoMet 30, Buehler, USA. (b) Final metallographic polishing; MasterMet-2 Non-Crystallising Colloidal Silica Polishing Suspension and ChemoMet Synthetic Polishing Pad.

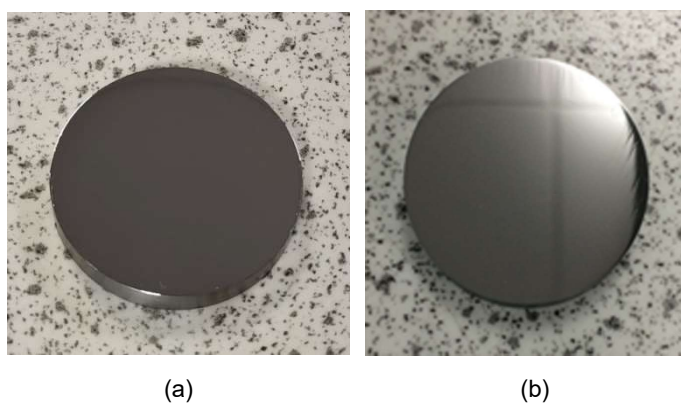


Figure 3.3 Polished samples; (a) Tantalum (b) Tungsten.

3.2.3 Metallographic sample preparation

The polished tantalum samples were etched using an etchant containing 30% HNO_3 of 48% + 70% HF of 48% strength, while the polished tungsten samples were etched using Sigma-Aldrich etchant (a mixture of tripotassium hexacyanoferrate and caustic potash) for microstructure analysis. The etched microstructure images were captured digitally using an optical microscope (Olympus BX51M).

3.2.4 Grain size measurement

The grain sizes of tantalum and tungsten samples were measured using an image processing software – Image J v1.53k [229]. These measurements were performed according to the linear intercept method described in ASTM standard E112-12 [230].

3.2.5 Surface roughness measurement

The surface roughness of tantalum and tungsten samples was measured using the Veeco Dektak 150 surface profilometer shown in Fig. 3.4.

Profilometer measurement process

A diamond stylus, with a 12.5 µm tip radius and 0.2 µm vertical resolution, was driven with a stylus force of 3 mg over the sample length of 6000 µm. A total of five measurements were conducted over the length in different directions. The arithmetic mean roughness value (R_a) in each measurement was calculated using Veeco Dektak 150 software (v9). An average of five measurements were considered for this study.

The software determines the R_a value based on the following equation [231],

$$R_a = \frac{(R_1 + R_2 + R_3 + R_4 + \dots)}{n} \quad \text{Eq. (3.1)}$$

where,

$R_1, R_2, R_3, R_4, R_5, \dots$ are the roughness values measured during stylus traversed sample length and n is the total number of readings.



Figure 3.4 Surface profilometer; Veeco Dektak 150, Veeco Instruments Inc. USA.

3.2.6 Hardness, Young's modulus, and density measurements

The hardness values of tantalum and tungsten samples were measured using Duramin Struers-40 AC3 Vickers hardness tester under an indenter load of 2 kgf. The tester is shown in Fig. 3.5. The average hardness of each specimen was determined from a total of 25 hardness measurements, in an area of 12 mm x 12 mm, with a dwell time of 10 sec. The selection of 2 kgf load was based on

additional hardness measurements that focused on a hardness load optimisation study at a range of indentation loads (ranging from 0.025 kgf to 10 kgf).



Figure 3.5 Hardness testing machine; Duramin Struers-40 AC3, USA.

The Young's modulus values of tantalum and tungsten samples were measured in a nanoindentation tester, namely, CSM Instruments SA, using Berkovich indenter (Fig. 3.6). Measurement was carried out under a normal indentation load of 500 mN, as per the procedure outlined in the Oliver-Pharr method [232,233].



Figure 3.6 Nano-hardness tester; CSM Anton Paar, Austria.

The densities of tantalum and tungsten samples were measured using the water displacement method in deionised water [234].

3.2.7 Elemental composition and crystal structure measurements

The crystallite size and composition of tantalum and tungsten specimens were determined following an X-ray diffraction (XRD) study conducted on Empyrean X-ray diffractometer (Fig. 3.7). The study used Co K α X-ray source (1.7890 Å

wavelength) to scan the samples using a Bragg-Brentano geometry (2θ ; 20 - 120°) with a step size of 0.013 ($^\circ 2\theta$) and step time of 34.17 s [235].



Figure 3.7 X-ray Diffractometer; Malvern Panalytical Empyrean, UK.

XRD measurement process

The XRD measurement is based on Bragg's law, which establishes a relationship between electromagnetic radiation wavelength, angle of diffraction, and atomic spacing in a crystal structure. This law is governed by the principles of constructive interference and diffraction. Figure 3.8 shows the X-ray diffraction by atomic planes. When the path difference between the incident beams is equal to an integral multiple of the beam wavelength then constructive interference of the reflected beam takes place and they reinforce each other as diffracted beams.

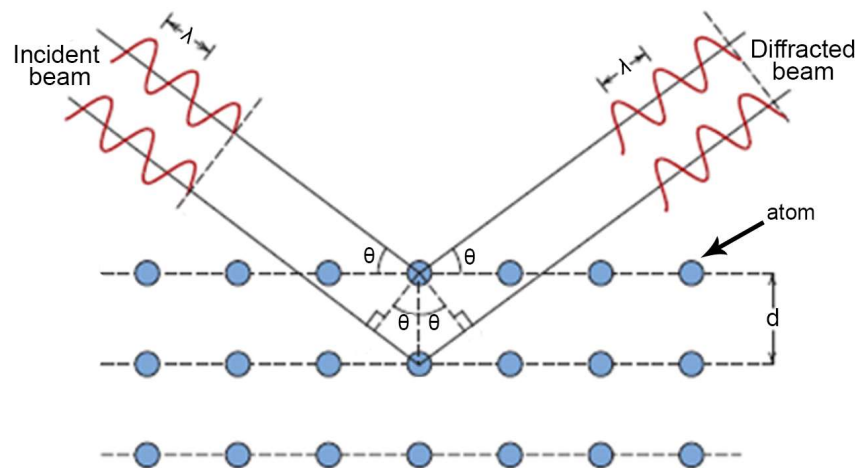


Figure 3.8 X-ray Diffraction by atomic planes. [236]

This constructive interference of reflected beam occurs when,

$$n_o \lambda = 2 d \sin \theta \quad \text{Eq. (3.2)}$$

where,

n_o is the order of reflection.

λ is the incident beam wavelength.

d is the distance between atomic planes.

θ is the incident angle of X-ray.

The sample diffractogram data registered peak signals of diffracted beams (due to constructive interference). This peak signal data was then matched with the powder diffraction files, available within the XRD software (Xpert HighScore Plus v4.5) to identify the material composition and crystallite size using the Scherrer equation [237–239]. To eliminate the machine error, tests were also performed on standard silicon samples. All deviations in the observed peak broadening at half the maximum intensity (FWHM) of the silicon sample were noted. These deviations were then discounted from observed FWHM data of tantalum and tungsten samples, for accurate determination of crystal sizes.

3.2.8 Erodent particle characterisation

The slurry erosion and erosion-corrosion testing were carried out using silicon carbide (SiC) erodent with particle sizes ranging from 500 to 710 μm . The SiC sand (98.5% purity), with a particle hardness of 25,500 MPa, was supplied by Hodge Clemco (UK). The high hardness, chemical inertness, and ease of availability made SiC an excellent choice of erodent material for erosion and erosion-corrosion experiments.

3.3 Erosion and electrochemical tests

3.3.1 Pure erosion test procedure

Prior to pure erosion (in the absence of corrosion) testing, the surface preparation of the samples was carried out as per the methodology outlined in section 3.2.2. These samples were further cleaned using both methanol and acetone. It was then followed with a circular inscription of 6.5 mm diameter which was meticulously executed to unveil a test area measuring 0.332 cm^2 for particle

impingement. The rest of the specimen (excluding test area) was masked using Caswell masking lacquer, as shown in Fig. 3.9.

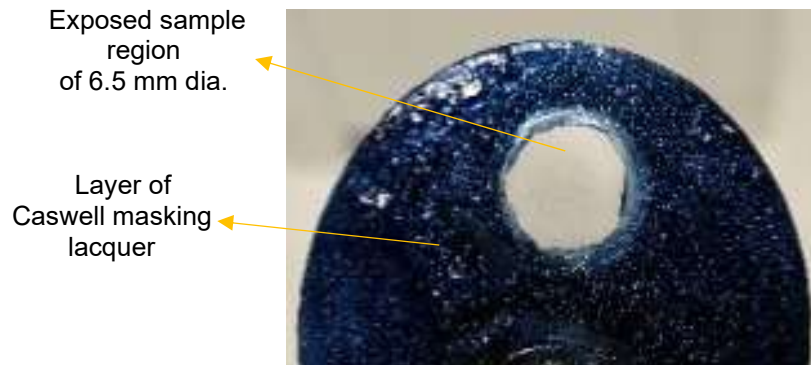


Figure 3.9 Image of masked tantalum sample with exposed zone.

The masking was done to ensure targeted slurry impingement to the exposed area. In addition, the specimen holder also provided additional protection by exposing only the desired specimen area (0.332 cm^2) to the oncoming particle slurry.

The slurry erosion testing was conducted, in ambient conditions, using the impinging jet aqueous erosion apparatus as described in section 3.3.1.1. This apparatus overcomes structural limitations imposed by other testing equipment and provides excellent erosion, corrosion and erosion-corrosion hydrodynamic conditions in a controlled environment [186,187,193,194].

3.3.1.1 Test apparatus description

The slurry erosion test equipment schematic and apparatus image are shown in Fig. 3.10 and Fig. 3.11, respectively. This apparatus was developed at Sheffield Hallam University and based on the design of an impinging slurry jet apparatus by Purandare et.al. [195] and Zu et.al. [186]. The rig consists of a slurry chamber (inner tank) and an outer tank referred to as the solution chamber. A slurry ejector, which forms the main part of the apparatus for mixing abrasive particles (SiC in this study) and the aqueous medium (deionised water in this study), is situated above the slurry chamber. The specimen is held in a specimen holder which can be rotated around its horizontal axis to facilitate experiments ranging from 20° to 90° slurry impact angles.

The solution (deionised water) is circulated from the solution chamber to the slurry ejector and back to the solution chamber with the help of a centrifugal pump (denoted as impinging jet pump in Fig. 3.10). The ejector functions as a mixing chamber where particles (sucked through a suction pipe due to venturi effect) are mixed with the solution to form a slurry. The solution in the solution chamber also circulates through another loop with the help of a centrifugal pump (shown as slurry chamber pump in Fig. 3.10). This pump draws solution from the outer tank into the slurry chamber and keeps it agitated to avoid segregation and lump formation of the abrasive particles. The jet of slurry, departing from the exit nozzle, impacts the specimen fitted in a specimen holder. Moreover, different concentrations (wt.%) of SiC sand particles in the slurry can be obtained by adjusting the linear distance between the inlet nozzle and the suction pipe in the slurry ejector. Further, by adjusting the frequencies of centrifugal pumps, different velocities of slurry jet impingement can be obtained.

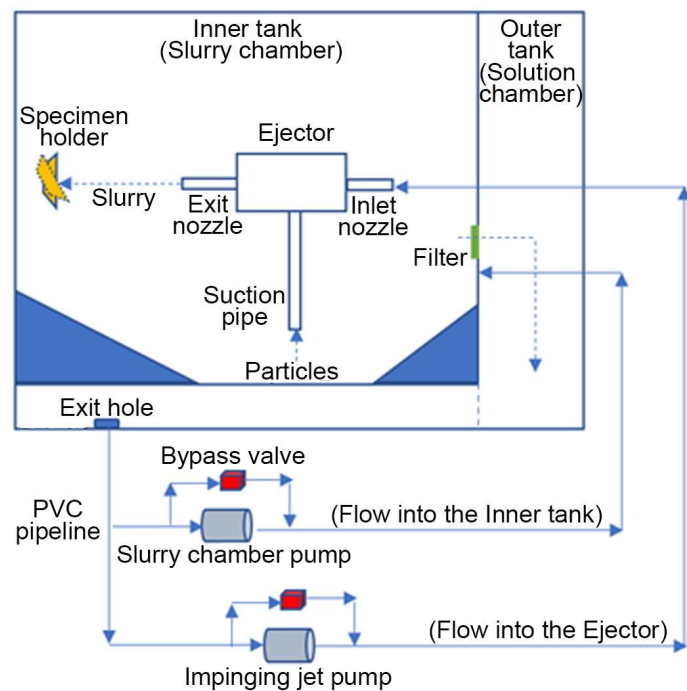


Figure 3.10 Schematic diagram of the impinging jet aqueous erosion apparatus.

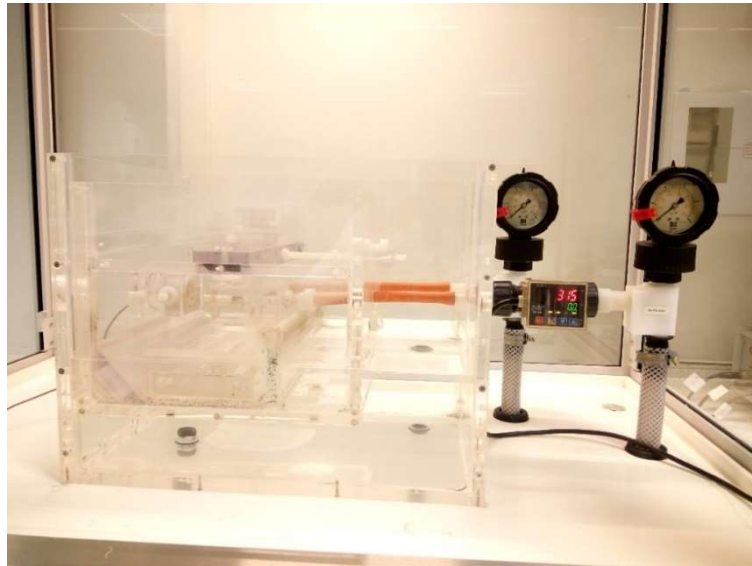


Figure 3.11 Impinging jet aqueous erosion apparatus; Thin Films Research Center, Sheffield Hallam University, UK.

3.3.1.2 Selection and description of test conditions

Numerous preliminary tests were performed to determine an appropriate testing condition that allows for the wear rate of Ta to be measured within an hour. The findings from these initial tests led to the selection of the following test parameters for this study: erodent size (500 – 710 μm), impact velocity (3, 4, and 5 ms^{-1}), and SiC concentration (3, 5, 7, and 10 wt.%).

Erosion experiments on tantalum were conducted in the following three sets. In all the experiments, a 6.5 mm diameter of exit nozzle was used, and a constant distance of 15 mm was maintained between the front end of the exit nozzle and the target surface.

In Set-1 experiments, the effect of impact angle on the erosion rate of Ta was evaluated. For these experiments, the SiC slurry concentration of 10 wt.% and impact velocity of 5 ms^{-1} were used, and the effect on mass erosion was analysed by varying the impingement angles (20, 30, 45, 60, and 90°).

In Set-2 experiments, the effect of slurry concentration on the erosion rate was evaluated. For these experiments, the impact velocity of 5 ms^{-1} , and impact angle of 30° (based on peak erosion observed in Set-1 experiments), and 90° were used, and the effect on mass erosion was analysed by varying the SiC slurry particle concentration (3, 5, 7, and 10 wt. %).

In Set-3 experiments, the effect of impact velocity on the erosion rate was evaluated. For these experiments, the slurry concentration of 7 wt.% (based on peak erosion observed in Set-2), impact angle of 30° and 90° were used, and the effect on mass erosion was analysed by varying the impact velocity (5, 4, and 3 ms⁻¹).

Table 3.1 summarises the experimental conditions which were used for the different sets of experiments.

Table 3.1 Test matrix* detailing various experimental sets.

Experimental Set	Impact Angle (deg.)					Impact Velocity (ms ⁻¹)			Sand Concentration (wt.%)			
	20	30	45	60	90	3	4	5	3	5	7	10
1	✓	✓	✓	✓	✓			✓				✓
2		✓			✓			✓	✓	✓	✓	✓
3		✓			✓	✓	✓	✓			✓	

*Silica sand size of 500-710 µm.

Following each experiment and before conducting weight loss measurements, specimens were carefully subjected to a thorough cleansing with Industrial Methylated Spirit (IMS), followed by Acetone, and subsequently, air-dried. Each material specimen was subjected to slurry erosion conditions for 1 hour and each erosion experiment was repeated three times to ensure data reproducibility and reliability. The mass loss of the eroded samples after each experiment was determined using an electronic microbalance (Fig. 3.12), which has a precision of 0.0001 g. A total of six measurements were conducted and an average of four readings was considered for mass loss after the exclusion of the first and last reading.



Figure 3.12 High precision analytical balance; OHAUS Pioneer, PA114C, Fisher Scientific, UK.

3.3.1.3 Calculation of dimensionless erosion rate

The erosion rate (E_R) was calculated based on the mass loss rate of target material (E_T) and the mass flow rate of slurry particles (E_P). The mass flow rate of slurry particles (E_P) was determined through a systematic procedure as follows: Initially, a slurry volume was collected over a precisely measured time duration of 10 seconds. Subsequently, the liquid component within this slurry was meticulously separated. The remaining particles were then weighed and their average mass over the defined time duration was calculated, thereby establishing the particle's mass flow rate (E_P). Mathematically, the dimensionless erosion rate is given by the following equation [41],

$$E_R (\text{gg}^{-1}) = \frac{E_T}{E_P} \quad \text{Eq. (3.3)}$$

To draw a comparison of erosion rates, erosion studies using aqueous slurry were also carried out on specimens of aluminium – Al (99.9% pure) that were 30 mm in diameter and 5 mm thick. Pure Al was selected due to its status as one of the most extensively researched metals for erosion, with a broad agreement on its performance and erosion mechanisms [85,87,159,240,241].

3.3.2 Electrochemical tests

3.3.2.1 Pure corrosion and erosion-corrosion test methods

3.3.2.1.1 Test apparatus description

The pure corrosion (in the absence of erosion) and erosion-corrosion tests were performed on the same impinging jet aqueous erosion apparatus as described in section 3.3.1.1. To measure the corrosion response of the samples under impinging jet conditions, a computer-controlled potentiostat (Gill AC, ACM Instruments) was connected to this apparatus, as shown in Fig. 3.13.

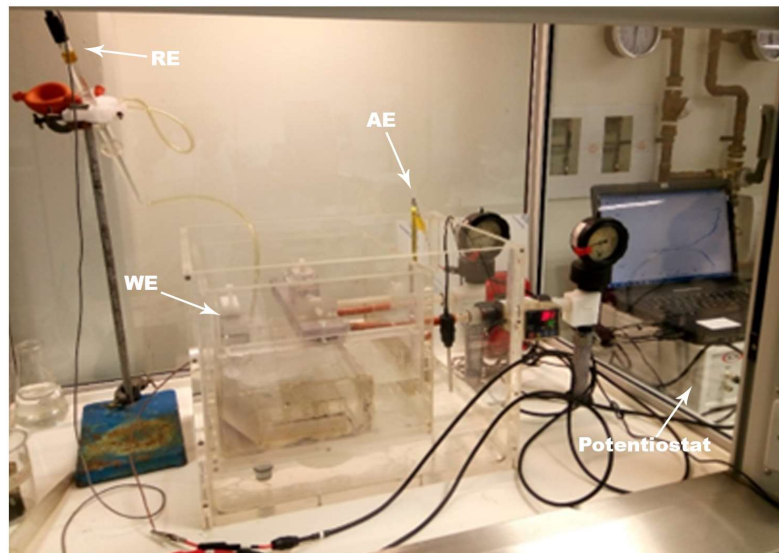


Figure 3.13 Impinging jet aqueous erosion-corrosion apparatus; Thins Films Research Center, Sheffield Hallam University, UK. (erosion apparatus connected with a Potentiostat, ACM Instruments, UK).

A conventional three-electrode electrochemical cell configuration was assembled using a graphite rod as the Auxillary Electrode (AE) and a saturated Ag/AgCl electrode as the Reference Electrode [242]. The working electrode (WE) in this setup was the exposed specimen. All electrochemical potentials discussed in this study henceforth are with respect to the Ag/AgCl reference electrode.

3.3.2.1.2 Selection of test technique

The corrosive action of the electrolyte solutions was facilitated by using the potentiodynamic polarisation method [243]. The potentiodynamic polarisation method allowed the metal specimen to act either as the anode or the cathode in an electrolytic cell. The resulting polarisation curves were used to obtain the steady-state equilibrium condition from the polarised condition through the application of mixed potential theory and the Tafel extrapolation method [110,120,121]. The polarisation curves (potential-current density plot) data obtained through the potentiostat software (ACM sequencer v5.1.4) were exported to data analysis software (Origin Pro v9.6.5) to determine the corrosion current densities and corrosion potentials for each corrosion and erosion-corrosion experiment.

The potentiodynamic polarisation method allows for the use of a broad spectrum of electrode potentials, ranging from -1000 mV to +1000 mV, enabling precise mapping of metallic behaviour. This makes it a superior choice compared to other

techniques such as linear polarisation and electrochemical impedance spectroscopy, which operate within limited potential ranges (-50 mV to +50 mV), are prone to errors, and involve high instrumentation costs [123,138].

3.3.2.1.3 Description of test conditions

Based on the results of erosion studies, experiments were conducted using two impact angles: 30°, which corresponds to the point of maximum slurry erosion rate, and 90°. All the experiments in this study were conducted under ambient conditions (22 – 24°C). Throughout the experiments, a constant slurry velocity and concentration were maintained at 5 ms⁻¹, representing an intermediate water circulation rate commonly employed for cooling spallation targets at RAL. These slurries were prepared by mixing the Silicon Carbide (SiC) particles with buffer solutions containing 7 ± 1 wt% concentration. To simulate corrosive conditions, solutions with three different pH values; 4, 7, and 10 were selected. Further details about the buffer solutions can be found in Table 3.2. The specimen holder's design enabled the exposure of a fixed area (0.332 cm²) on a masked sample positioned in front of the exit nozzle, which, as stated earlier, had a diameter of 6.5 mm and was located at a distance of 15 mm.

To assess the impact of erosion on corrosion, the flow corrosion experiments at 5 ms⁻¹ impact velocity were performed both in the absence and presence of erodent particles. The experiments in the absence of particles were performed under potentiodynamic conditions involving a potential sweep ranging from -1 V to +1 V at a rate of 0.6 mVs⁻¹. The experiments in the presence of particles were conducted under potentiostatic conditions with parameters derived from the polarisation curves. All tests were performed according to ASTM G119-09 standard [244] under ambient conditions. In each solution, the tests were conducted for 1 hour and were repeated three times for data reproducibility. Following each test, the specimens underwent a drying process and were then weighed using a precision balance (Ohaus PA114C, Fisher Scientific, UK), with the least count of 0.0001 g. Table 3.3 and Table 3.4 shows a summary of test operating conditions used in this investigation.

Table 3.2 Corrosive solutions used in the erosion-corrosion apparatus.

Type of solution	pH
0.5 M Citrate Buffer (Citric Acid and Sodium Citrate Dihydrate)	4
0.5 M Sodium Chloride	7
0.5 M Carbonate Buffer (Sodium Carbonate and Sodium Bicarbonate)	10

Table 3.3 Operating conditions for erosion, corrosion, and erosion-corrosion tests.

	Erosion	Corrosion	Erosion-Corrosion
Impact angle (°)	30, 90	30, 90	30, 90
Impact velocity (ms ⁻¹)	5	5	5
SiC concentration (wt.%)	7	-	7
Test duration (h)	1	1	1
Solution (0.5 M)	Deionised water	Citrate buffer, Sodium chloride, Carbonate buffer	Citrate buffer, Sodium chloride, Carbonate buffer
Temperature (°C)	22 - 24	22 - 24	22 - 24

Table 3.4 Operating conditions for potentiostatic experiments.

	Set Potential (mV):		
Impact angle (°)	pH 4	pH 7	pH 10
30	+ 230	- 125	+ 111
90	+ 60	- 80	- 35

3.3.2.2 Flow-assisted galvanic corrosion test procedure

Prior to galvanic corrosion testing, the polarisation tests were performed on tantalum and tungsten samples separately under flow conditions of normal impact at different pH and impact velocities; 5 ms⁻¹ and 9 ms⁻¹. Moreover, polarisation experiments on tungsten in static conditions of three-electrode cell were also performed at different pH solutions. Tantalum and tungsten polarisation tests were conducted to analyse the influence of different pH solutions at higher impact velocity (9 ms⁻¹) on both metals separately. Tungsten polarisation experiment results in static conditions were used with tantalum polarisation experiment results in flow conditions. This was done to estimate galvanic corrosion parameters based on mixed potential theory (MPT) which were then compared with the results of zero resistance ammeter galvanic measurements. This comparison provided a firm theoretical and empirical basis for the significance of galvanic corrosion between tantalum and tungsten.

Therefore, the flow-assisted galvanic corrosion between tantalum and tungsten was studied using applied mixed potential theory (MPT) and zero resistance ammeter (ZRA) measurements.

3.3.2.2.1 Applied mixed potential theory

After the above mentioned polarisation tests (as described in section 3.3.2.1.2), the flow-assisted galvanic corrosion was evaluated using mixed potential theory in which the potentiodynamic curves of both the materials (Ta and W) in their respective solutions (shown in Table 3.2) were superimposed to estimate the galvanic potential (E_{MPT}) and current density (i_{MPT}) of the coupled pair [245]. In the potentiodynamic experiments of tantalum, it was impacted by various flow velocities of different solutions using the impinging jet apparatus (shown in Fig. 3.13). On the other hand, potentiodynamic experiments of tungsten were performed in static conditions using different solutions in a three-electrode glass cell (connected to a computer-controlled potentiostat; Gill AC, ACM Instruments), as shown in Fig. 3.14. Tantalum was subjected to flow conditions while tungsten was evaluated in static conditions, to match the samples condition used in ZRA measurement process (described in section 3.3.2.2.2).



Figure 3.14 Three-electrode glass cell apparatus; Gamry Instruments, USA.

Figure 3.14 reveals that a traditional three-electrode glass cell setup was constructed, utilising a graphite rod as the Auxillary Electrode (AE) and a

saturated Ag/AgCl electrode as the Reference Electrode (RE) [242]. The tungsten specimen, which was masked and exposed to a fixed area of 0.332 cm² (as shown in Fig. 3.9), served as the Working Electrode (WE) in this arrangement.

Figure 3.15 illustrates the mixed potential theory (MPT) application to determine the galvanic corrosion parameters (galvanic corrosion potential (E_{MPT}) and galvanic current density (i_{MPT})) for Metal A and Metal B in an electrolyte solution.

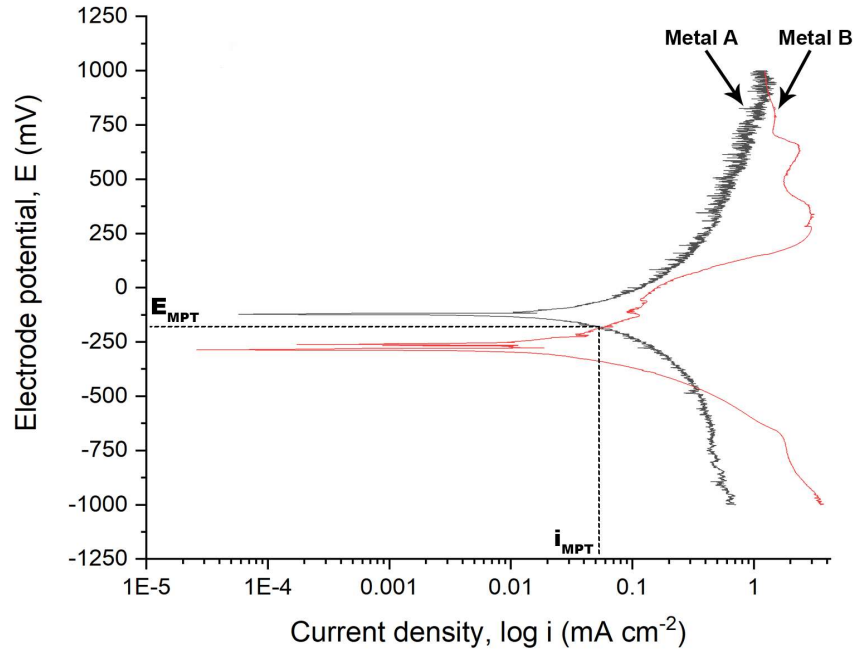


Figure 3.15 Bimetal galvanic couple illustrating the application of mixed potential theory through polarisation plots to estimate the galvanic corrosion parameters (E_{MPT} and i_{MPT}).

The sample with the most negative E_{corr} value acts as an anode and the most positive one acts as a cathode. E_{MPT} and i_{MPT} are derived through the intersection of an anodic branch of the anode polarisation curve (of Metal B in Fig. 3.15) and the cathodic branch of the cathode polarisation curve (of Metal A in Fig. 3.15). For tantalum and tungsten couple, the mean values of three such intersections (at each pH and flow velocity) were considered for analysis.

3.3.2.2.2 Zero resistance ammeter technique

The zero resistance ammeter (ZRA) galvanic tests were performed according to ASTM G71-81 standard [144] using an impinging jet apparatus connected to a potentiostat (as described in section 3.3.2.1.1.). During the ZRA test, the tantalum sample was subjected to a solution-impinging jet while tungsten was kept outside

the impact zone and submerged in the solution. The distance between the two samples was kept constant (14 mm) for each test. Tantalum was connected as the working electrode and tungsten was grounded. The current flowing between tantalum and tungsten as well as their galvanic potential were measured with respect to a silver-silver chloride (Ag/AgCl, 3 M KCl) reference electrode. The tests were conducted at two different impact velocities, 5 ms⁻¹ and 9 ms⁻¹. For each test, the galvanic current density (mA cm⁻²) and potential (mV) were determined for every 1 s for a total duration of 6 h.

3.3.3 Calculation of material removal rates (in kg m⁻² s⁻¹)

3.3.3.1 Pure erosion, erosion-corrosion, and pure corrosion rates

Determination of pure erosion (K_{eo}) and erosion-corrosion rates (K_{ec})

The pure erosion rate (K_{eo}) was calculated (in kg m⁻² s⁻¹) as follows:

sample mass loss, m (g) = initial sample mass – final sample mass (after 1h experiment)

$$\text{mass loss rate per unit area and time, } K_{eo} = \frac{m}{A \times 3600} \quad \text{Eq. (3.4)}$$

where,

A = 0.3322 × 10⁻⁴ m² (exposed area based on circular dia. of 6.5 mm).

Using the value of A in Eq. (3.4),

$$K_{eo} \text{ (kg m}^{-2} \text{ s}^{-1}\text{)} = \frac{m \text{ (g)} \times 10^{-3}}{0.332 \times 10^{-4} \times 3600} = \frac{m}{119.52} \quad \text{Eq. (3.5)}$$

Similarly, the erosion-corrosion rate (K_{ec}) was calculated as,

$$K_{ec} \text{ (kg m}^{-2} \text{ s}^{-1}\text{)} = \frac{m}{119.52} \quad \text{Eq. (3.6)}$$

Determination of pure corrosion rates (K_{co})

The pure corrosion rate (K_{co}) was calculated as follows:

According to Faraday's first and second laws [124], mass loss per unit area per unit time is given by,

$$K_{co} = \frac{(M \times i)}{(n \times F)} \quad \text{Eq. (3.7)}$$

where,

t = time (s).

M = molar mass (g mol⁻¹) (For Ta, M = 180.9479 g mol⁻¹ [246]).

i = current density (A cm⁻²).

n = number of electrons transferred in the oxidation reaction (For Ta, n = 5 [247,248]).

F = Faraday's constant (96485 C mol⁻¹).

Rearranging Eq. (3.7),

$$K_{co} = i \times \left(\frac{M}{n \times F} \right) \quad \text{Eq. (3.8)}$$

$$\begin{aligned} \text{For Ta, } \left(\frac{M}{n \times F} \right) &= \frac{180.9479}{(5 \times 96485)} \quad (\text{g C}^{-1}) \\ &= 3.75 \times 10^{-4} \quad (\text{g C}^{-1}) \end{aligned}$$

Using the value of $\left(\frac{M}{n \times F} \right)$ in Eq. (3.8),

$$K_{co} (\text{kg m}^{-2} \text{s}^{-1}) = i \times 3.75 \times 10^{-9} \quad \text{Eq. (3.9)}$$

where i = current density value in $\mu\text{A cm}^{-2}$.

3.3.3.2 Additive and synergistic effects, and synergy rates

The erosion-corrosion rate (K_{ec}) is given as [162],

$$K_{ec} = K_{eo} + K_{co} + \Delta K_{ec} \quad \text{Eq. (3.10)}$$

Also,

$$\Delta K_{ec} = \Delta K_c + \Delta K_e \quad \text{Eq. (3.11)}$$

where,

ΔK_c is the erosion enhanced corrosion rate (additive effect).

ΔK_e is the corrosion enhanced erosion rate (synergistic effect).

ΔK_{ec} is the synergy rate.

Calculation of synergy rates (ΔK_{ec})

The synergy rates (ΔK_{ec}) were obtained through the following steps –

1. The combined erosion-corrosion rates (K_{ec}) under potentiostatic experimental conditions (shown in Table 3.4) were calculated according to Eq. (3.6).

2. The pure erosion rates (K_{eo}) and pure corrosion rates (K_{co}) were calculated according to Eq. (3.5) and Eq. (3.9), respectively.
3. Using the values of K_{ec} , K_{eo} , and K_{co} in Eq. (3.10) and rearranging it,

$$\Delta K_{ec} = K_{ec} - (K_{eo} + K_{co}) \quad \text{Eq. (3.12)}$$

Calculation of erosion enhanced corrosion rates (ΔK_c)

The calculation ΔK_c values involved the following steps –

1. The anodic dissolution potentials for Ta, as shown in Table 3.4, were first identified from the potentiodynamic curves (in Fig. 4.15) under corrosion conditions.
2. At these identified potentials, the obtained potentiostatic curves (in Fig. 4.16) were used to determine the corrosion current density (i_{corr}) under erosion-corrosion conditions.
3. The determined i_{corr} values were then used in the following equation based on Faraday's first and second law [124], to determine ΔK_c as,

$$\Delta K_c = i_{corr} \times \left(\frac{M}{n \times F} \right) \quad \text{Eq. (3.13)}$$

Calculation of corrosion enhanced erosion rates (ΔK_e)

Using the values of ΔK_{ec} (from Eq. 3.12) and ΔK_c (from Eq. 3.13), ΔK_e was calculated from Eq. (3.11) and the final form of the equation is shown below,

$$\Delta K_e = \Delta K_{ec} - \Delta K_c \quad \text{Eq. (3.14)}$$

3.4 Analysis of test results

3.4.1 Optical microscopy

The sample surfaces were imaged suitably using a reflected light metallurgical microscope (Olympus BX51M, Japan) equipped with a range of objective lenses (UM PLAN FL 5x, 10x, 20x, 50x, 100x, and 500x) also shown in Fig. 3.16.

The optical microscope mainly consists of an eyepiece, objective lenses, a light source, a sample stage, focus control, a field aperture, and a condenser. It uses a light source for imaging and the magnification is achieved through suitable pairing between the eyepiece and objective lens [249]. A good-resolution image is obtained through a numerical aperture that allows the microscope to gather light and resolve fine sample details while working at a fixed object (sample)

distance. The samples before and after each test were examined under the microscope to identify any features (defects, scars etc.) before performing in-depth electron microscopy using a scanning electron microscope.



Figure 3.16 Optical microscope; Olympus BX51M, Japan.

3.4.2 Scanning electron microscopy

The scanning electron microscope imaging was performed using Quanta 650 SEM (Oxford Instruments), as shown in Fig. 3.17. This was used to investigate the wear scars on the test samples after performing erosion, corrosion and erosion-corrosion experiments. This SEM model is also equipped with Energy Dispersive X-ray Spectroscopy (EDX) capability, allowing for in-situ compositional analysis of the samples covering – point, elemental, and area composition. The EDX was performed using Aztech v4.0 – Nanoanalysis software. In the present work, the SEM electron beam accelerating voltages used were between 20 kV and 30 kV, while the working distance was maintained between 9 and 10 mm.

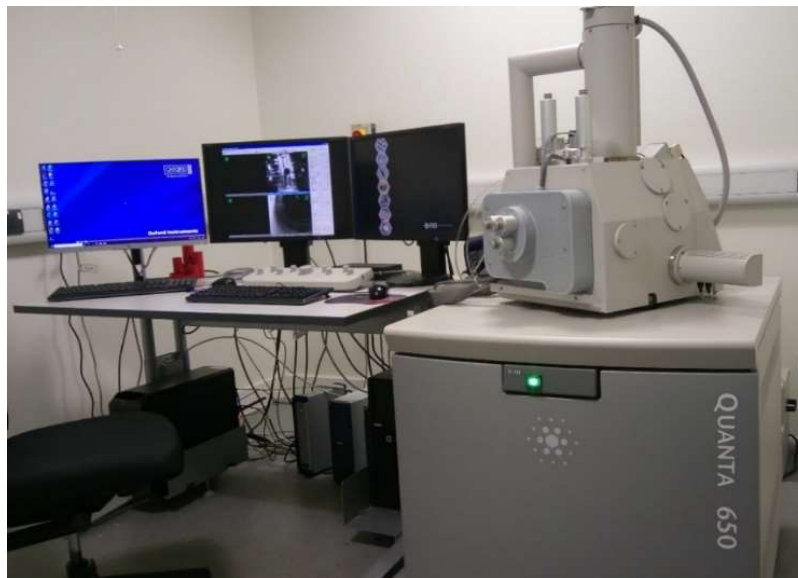


Figure 3.17 Scanning electron microscope (Quanta 650, Oxford Instruments) at Materials and Engineering Research Institute (MERI), Sheffield Hallam University.

As compared to an optical microscope, a scanning electron microscope provides a larger depth of field which allows precise analysis of the surface morphology of erosion-corrosion surface scars [250]. The SEM comprises various components such as an electron gun, electromagnetic condenser lens, objective lens, scanning coils, and display monitor screen. The main operating principle of SEM is the generation of high-energy electron beams, with energies ranging from 1 to 30 keV, by a field emission gun. This electron beam is collimated by the electromagnetic condenser, and it is then focused over the sample surface using an objective lens. The beam is then deflected either linearly or in a raster array through a set of scanning coils. The interaction of the incident electron beam with that of the sample surface results in further generation of electrons which are detected by various detectors equipped with the microscope. Figure 3.18 shows this interaction in which a variety of signals can be detected and measured such as high-energy backscattered electrons, low-energy secondary electrons, characteristic x-rays etc. [251].

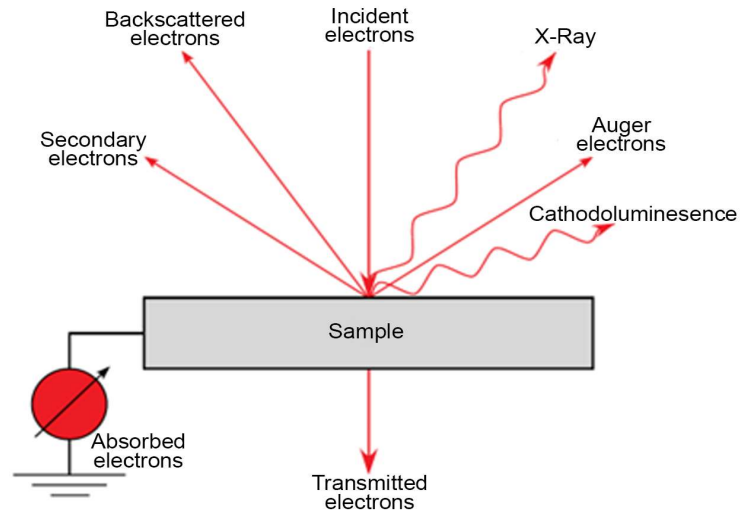


Figure 3.18 Schematic of signals generated due to beam-specimen interaction. [251]

Simultaneously, a charge-coupled device (CCD) displays the image on the screen by converting electrons (from the electron beam) to photons. The spot brightness is modulated by the current which has been amplified by the detector [250].

Chapter-4

Results

4.1 Introduction

This chapter presents the results of this study in the following three sections:

1. Erosion of tantalum.
2. Erosion-corrosion of tantalum.
3. Flow-assisted galvanic corrosion of tantalum and tungsten.

4.2 Erosion of tantalum

This section is divided into two parts. The first part presents the material characterisation results obtained for both tantalum and SiC erodent particles. The second part presents the results of the erosion studies on tantalum under deionised aqueous slurry conditions, which avoided the effect of corrosion. This second part covers specifically the following results: erosion versus impact angle, erosion versus particle concentration, erosion versus impact velocity, and the electron micrographs of wear scars. The erosion mass loss and erosion rate data tables can be found in the Appendix section (Table A.1 to Table A.8).

4.2.1 Material characterisation

4.2.1.1 Microstructure of tantalum

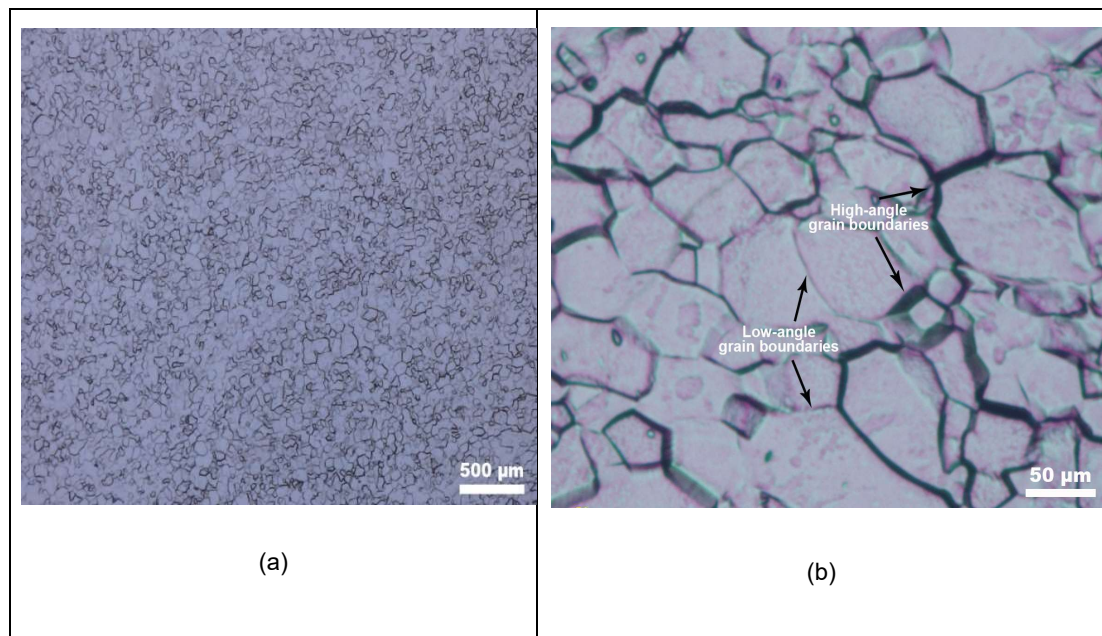


Figure 4.1 Optical micrographs of etched tantalum sample at different magnifications; (a) x50 (b) x500.

Figure 4.1 shows optical microstructures of the etched tantalum specimen, which reveals a non-uniform grain distribution with a measured mean grain size of $65 \pm 15 \mu\text{m}$ (equivalent to ASTM grain size no. (G) of 4.6 ± 0.55).

Figure 4.1 also shows the presence of both low-angle and high-angle grain boundaries, indicated by arrows. Additionally, the microstructure appears to be completely free of porosity. This aligns with tantalum's measured density value of 16.65 g cm^{-3} , which is nearly identical to its theoretical density of 16.67 g cm^{-3} [252].

4.2.1.2 Surface roughness and mechanical properties

Roughness

Table 4.1 shows the mean surface roughness values (R_a) that were obtained based on five multidirectional profilometer scans on the metallurgically polished tantalum sample surface.

Table 4.1 Surface roughness data for tantalum sample.

S.No.	$R_a (\mu\text{m})$ Standard Scan-1	$R_a (\mu\text{m})$ Standard Scan-2	$R_a (\mu\text{m})$ Standard Scan-3	$R_a (\mu\text{m})$ Standard Scan-4	$R_a (\mu\text{m})$ Standard Scan-5	$R_a (\mu\text{m})$ (Mean)	Standard deviation
1	0.277	0.340	0.200	0.357	0.336	0.302	0.058

The tantalum surface roughness was determined by calculating the arithmetic mean of the 5 average roughness values, listed in Table 4.1, and was found to be $0.302 \pm 0.058 \mu\text{m}$.

Hardness

In order to identify a suitable load for hardness measurement, hardness load optimisation studies were performed on the tantalum sample. The results of these studies are shown in Fig. 4.2.

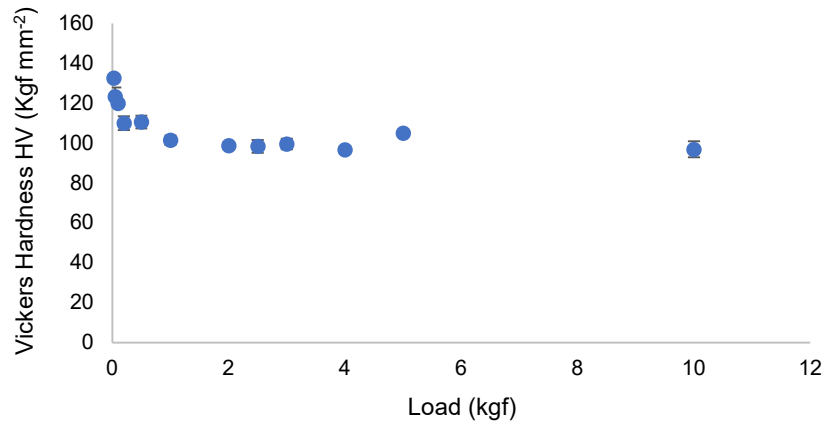


Figure 4.2 Vickers indenter load-hardness optimisation plot for tantalum sample.

As shown in Fig. 4.2, the hardness-load curve remains unchanged after an indenter load of approximately 1 kgf. In addition, it was found that the standard deviation (of the hardness values) was minimum at a 2 kgf indenter load. Consequently, a 2 kgf load was chosen for the hardness measurement.

Following the optimisation studies, hardness of tantalum was measured using a 2 kgf indenter load at 25 different points (in a 5 x 5 matrix), as shown in Fig. 4.3. The measured hardness at each point is shown in Table 4.2, and its variation over the sample surface is also shown graphically in Fig. 4.4. As shown in the figure, the mean hardness value was found to be $HV_2\ 89 \pm 3$ (approx.).



Figure 4.3 Image of polished tantalum sample after Vickers hardness test under the load of 2 kgf on 25 indents (5 x 5 matrix) visible on the sample surface.

Table 4.2 Vickers hardness data of tantalum sample under indenter load of 2 kgf.

Point No.	Hardness (HV ₂)
1	91.68
2	88.86
3	91.40
4	84.07
5	88.43
6	90.25
7	89.31
8	86.65
9	91.68
10	88.63
11	87.53
12	87.98
13	90.03
14	89.11
15	92.14
16	85.33
17	85.98
18	88.88
19	91.68
20	88.87
21	81.21
22	85.57
23	87.30
24	91.18
25	92.63
Mean	88.66
Standard deviation	2.73

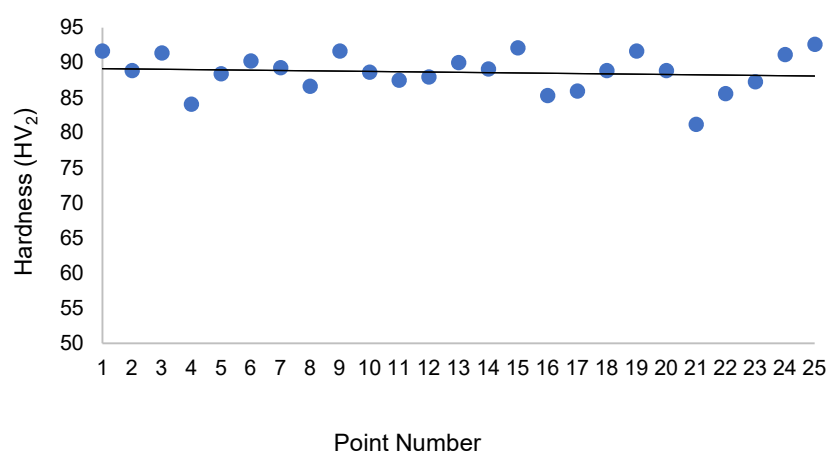


Figure 4.4 Vickers hardness measurement data for 25 indents on tantalum sample under 2 kgf indenter load, 3 mm indent separation, and 10 s dwell time.

Young's modulus

The Young's modulus of the tantalum sample was measured using a CSM nanoindentation tester (Berkovich indenter) and it was found to be 195 ± 6 GPa.

Reference aluminium samples

High purity (99.9%) aluminium samples were used as reference material for comparison of the erosion performance of tantalum. In contrast to the tantalum specimen, which was powder metallurgically manufactured, these aluminium samples were manufactured through the melting and casting process.

Table 4.3 summarises data measurement for both aluminium and tantalum samples.

Table 4.3 Measured properties mean data summary for tantalum and aluminium.

Property	Tantalum	Aluminium
Density (g cm ³)	16.65 ± 0.01	2.7 ± 0.02
Hardness (HV)	89 ± 3 (HV ₂)	100 ± 1.8 (HV ₅)
Young's modulus (GPa)	195 ± 6	87 ± 1
Roughness (μm)	0.302 ± 0.06	0.640 ± 0.06

4.2.1.3 X-ray diffraction analysis

Figure 4.5 shows the diffractogram of tantalum obtained using XRD technique. All the peaks in the diffractogram matched perfectly with the peaks of the corresponding powder diffraction file (PDF Card Ref. 00-004-0788) which is also labelled in the figure. This suggested that the analysed tantalum sample had a body centred cubic (BCC) crystal structure of 100% tantalum.

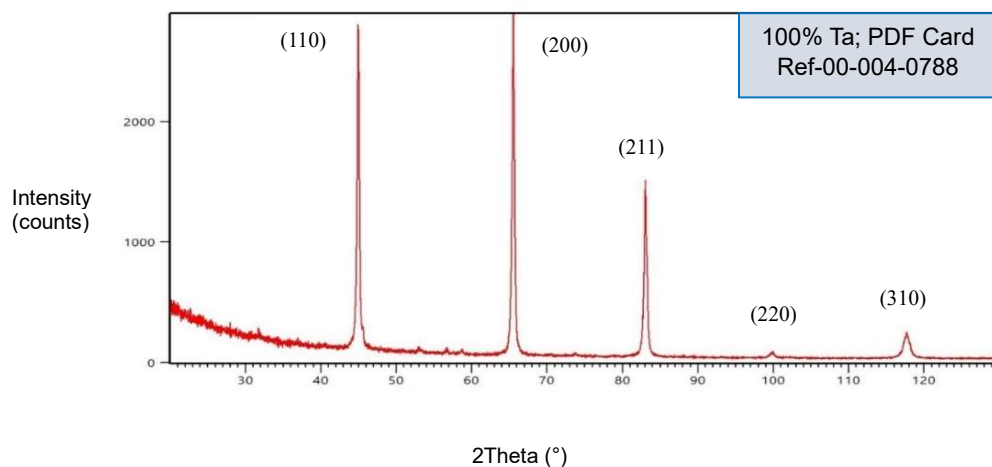


Figure 4.5 X-ray diffraction (XRD) pattern of tantalum.

The diffractogram exhibits dominating peaks at (110) and (200) orientations and a significant contribution at (211) orientation. The angles ($^{\circ}2\theta$) of the peaks are strikingly similar to those found in the corresponding powder diffraction file (PDF Card Ref 00-004-0788). The XRD software (X'Pert Highscore Plus) was used to process the diffractogram for resolving positions of the observed peaks and to measure their broadening (full width at half maximum - FWHM). This data was further processed using the Scherrer equation [238] to obtain crystal sizes as shown in Table 4.4.

Table 4.4 Tantalum crystallite size data summary.

S.No.	FWHM ($^{\circ}2\theta$)	Error ($^{\circ}2\theta$)	Peak Position ($^{\circ}2\theta$)	FWHM – Error ($^{\circ}2\theta$)	Crystallite size (using Scherrer equation [238]) (Å)
1	0.280	0.080	44.930	0.199	500.391
2	0.333	0.093	65.479	0.239	458.703
3	0.343	0.105	82.996	0.239	516.009
4	0.671	0.132	99.735	0.538	265.883
5	0.817	0.154	117.567	0.662	268.719

The mean crystallite size for tantalum was found to be 402 ± 112 Å.

4.2.1.4 Electron microscopy of erodent particles

Figure 4.6 shows a scanning electron microscope (SEM) image of the SiC erodent particles used in this study. It is evident that the SiC particles were angular in shape (with varying angularity), and ranged in size between 500 to 710 μm .

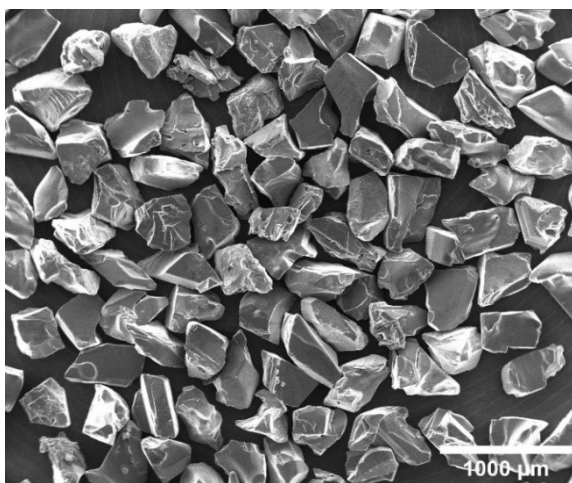


Figure 4.6 SEM image of SiC erodent particles.

4.2.2 Deionised aqueous slurry erosion

4.2.2.1 Erosion versus impact angle

Figure 4.7 illustrates the relationship between erosion rate and impact angles for tantalum when tested under slurry concentration of 10 wt.% and impact velocity of 5 ms^{-1} .

The erosion rate (in Fig. 4.7) was calculated based on the ratio of the rate of target material mass loss to the rate of particle mass flow (as described in section 3.3.1.3). As shown in Fig. 4.7, the erosion rate was highest at 30° impact angle (among the tested angles of 20° , 30° , 45° , 60° , and 90°). Following this peak, the erosion rate decreased to less than half of its maximum value at normal impact angle (90°).

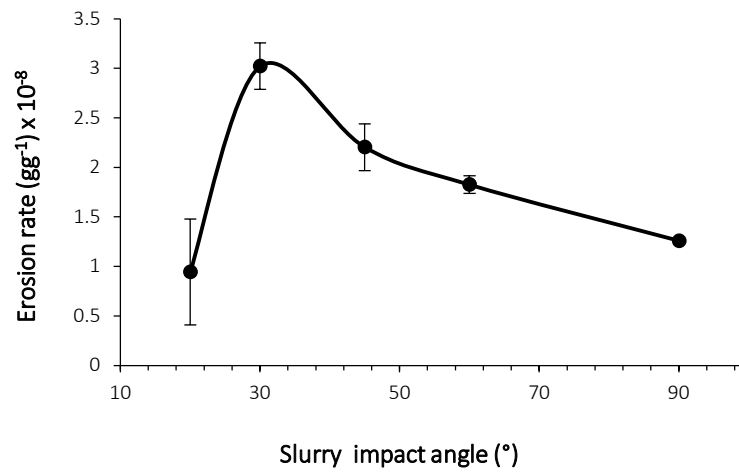


Figure 4.7 Tantalum erosion rate versus slurry impact angle (SiC slurry concentration 10 wt. %; impact velocity 5 ms^{-1}).

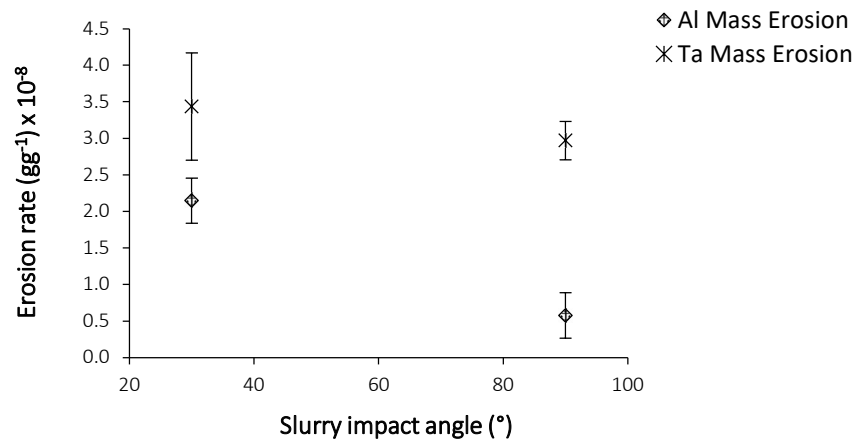


Figure 4.8 Erosion rate versus slurry impact angle for Ta and Al samples. (SiC slurry concentration 7 wt. %; impact velocity 5 ms^{-1} ; impact angles 30° and 90°).

Figure 4.8 shows a comparison of the measured erosion rate for tantalum and aluminium (reference sample) at 30° and 90° impact angles. In this study, the slurry concentration and impact velocity were maintained at 10 wt.% and 5 ms⁻¹, respectively. At both impact angles studied, tantalum eroded at a significantly higher rate compared to aluminium – five times higher at 90° and one and a half times higher at 30° impact angle.

4.2.2.2 Erosion versus particle concentration

Figure 4.9 shows the erosion rate of tantalum as a function of slurry concentration (wt.%), at both 30° and 90° impact angles.

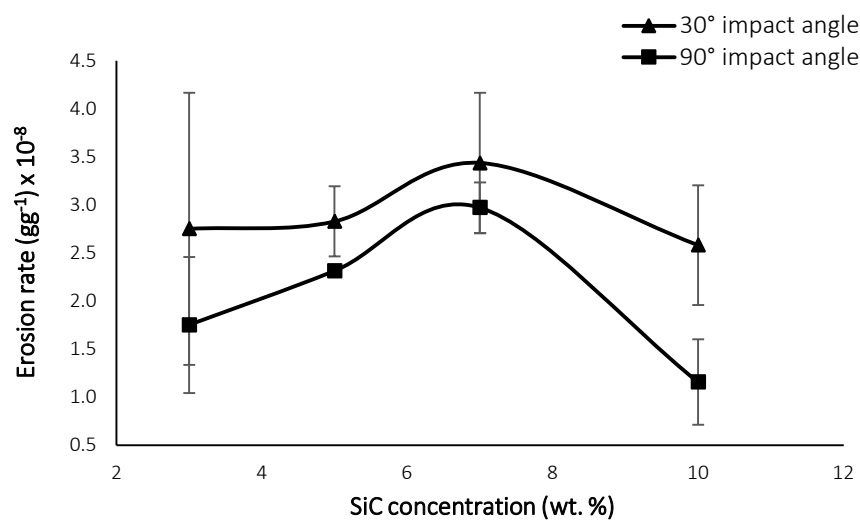


Figure 4.9 Tantalum erosion rate versus SiC slurry concentration (impact velocity 5 ms⁻¹).

The SiC slurry concentrations were 3%, 5%, 7%, and 10% (wt.%). These experiments (categorised under Set-2 experiments as mentioned in Table 3.1) were performed under 30° and 90° impact angles, and 5 ms⁻¹ impact velocity. As shown in Fig. 4.9, a similar trend was observed for both impact angles; the erosion rate initially rose, peaking at a median concentration of 7 wt.%. However, as the concentration reached 10 wt.%, the erosion rate began to decline. Based on these results, slurry concentration of 7 wt.% was chosen for further experiments.

4.2.2.3 Erosion versus impact velocity

Figure 4.10 displays the erosion rate of tantalum at various impact velocities. These experiments were performed at 30° and 90° impact angles using SiC slurry

concentration of 7 wt. %. Details of these experimental conditions can be found in Table 3.1, under Set-3.

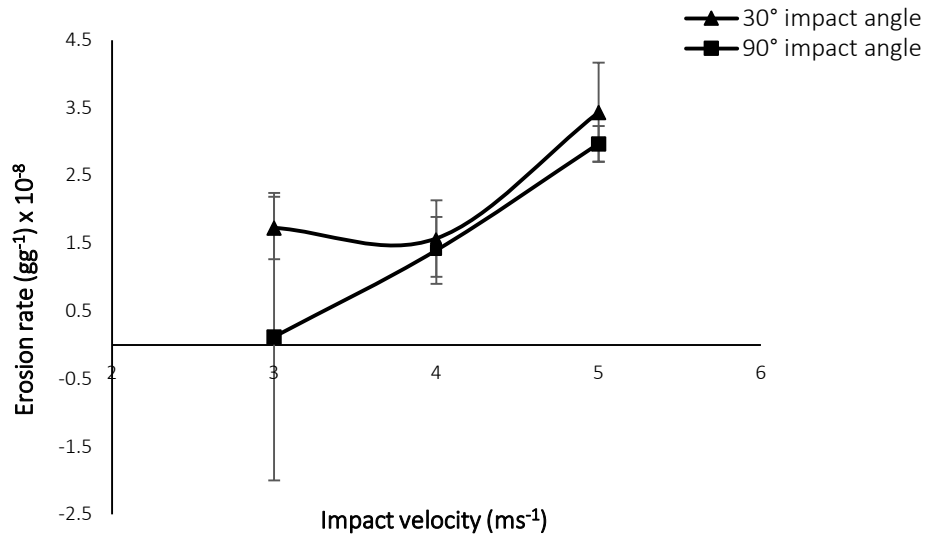


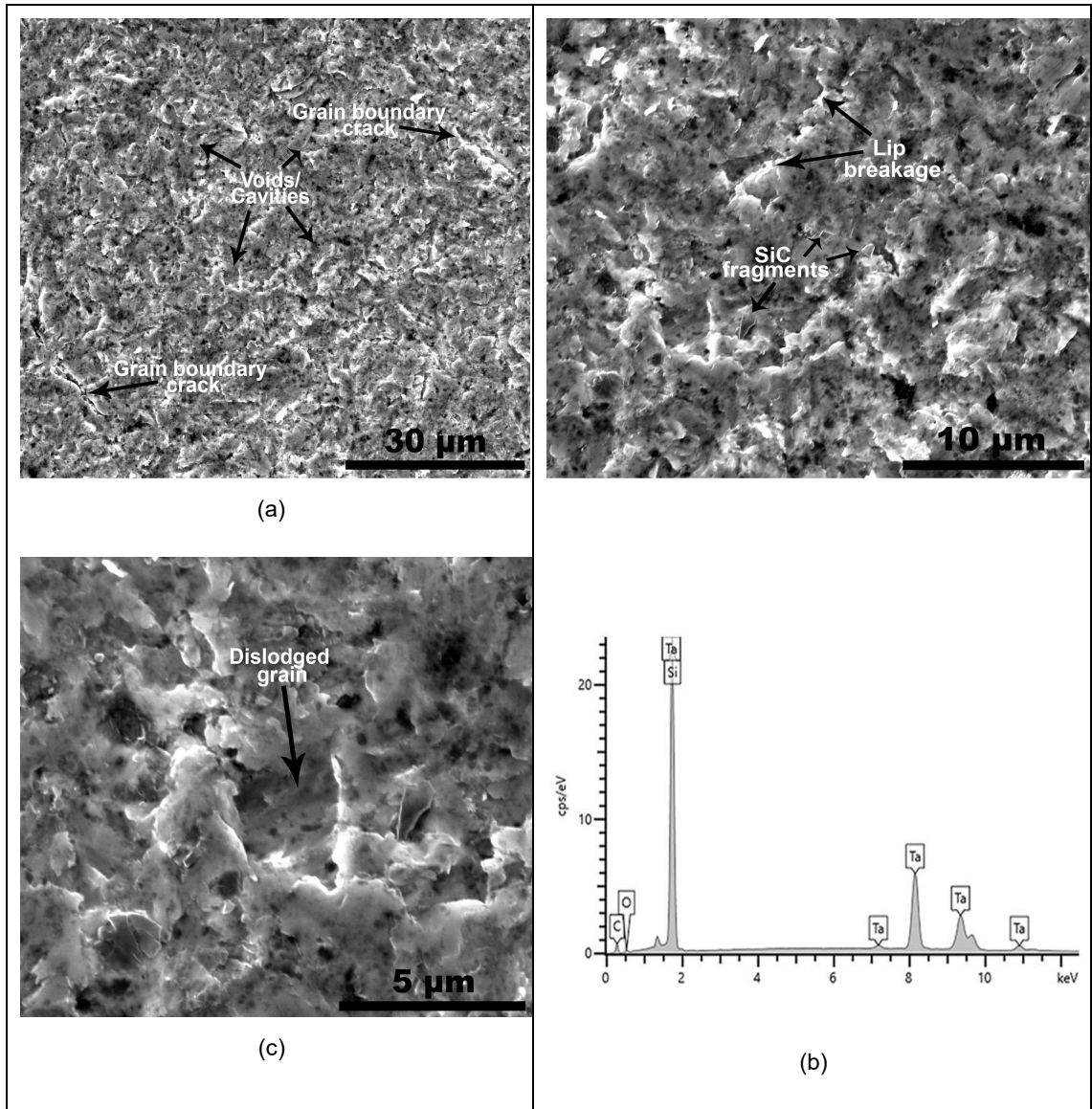
Figure 4.10 Tantalum erosion rate versus impact velocities (SiC slurry concentration 7 wt.%; impact angles 30° and 90°).

As shown in Fig. 4.10, the rate of erosion increases linearly with impact velocity, regardless of the particle impact angle considered. However, an anomaly was noted at an impact velocity of 3 ms⁻¹ for a 30° impact. These results are described in section 5.2 using relevant underpinning theories.

4.2.2.4 SEM and optical micrographs

Fig. 4.11 and Fig. 4.12 show the SEM micrographs of wear scars formed on the tantalum and aluminium samples, respectively. The effect of impact angle is also visible on these micrographs. When the tantalum samples were subjected to particle impact at 90°, the resulting wear scars (as shown in Fig. 4.11(a), Fig. 4.11(b), and Fig. 4.11(c)) exhibited several distinct characteristics: (i) a topography resembling hills and valleys spread across the entire surface, (ii) cracks along the grain boundaries, (iii) damage to the lip area, (iv) fragments of the eroding agent (SiC) particles embedded within the erosion scar, (v) voids or cavities scattered across the whole surface, covering both the hills and valleys. The bright contrast areas in the images are due to sample surface valence electrons which were displaced by the SEM electron beam and detected by the SEM secondary electron detector.

Wear scars formed on tantalum samples at 30° impact angle (shown in Fig. 4.11(d), Fig. 4.11(e), and Fig. 4.11(f)) were dominated by features such as craters with and without lips. In addition, similar to 90° impact, the presence of grain boundary cracks and voids/cavities can also be seen at 30° impact. Section 5.2.7 provides a detailed description of the material removal mechanism for erosion of tantalum based on the wear scar features observed here.



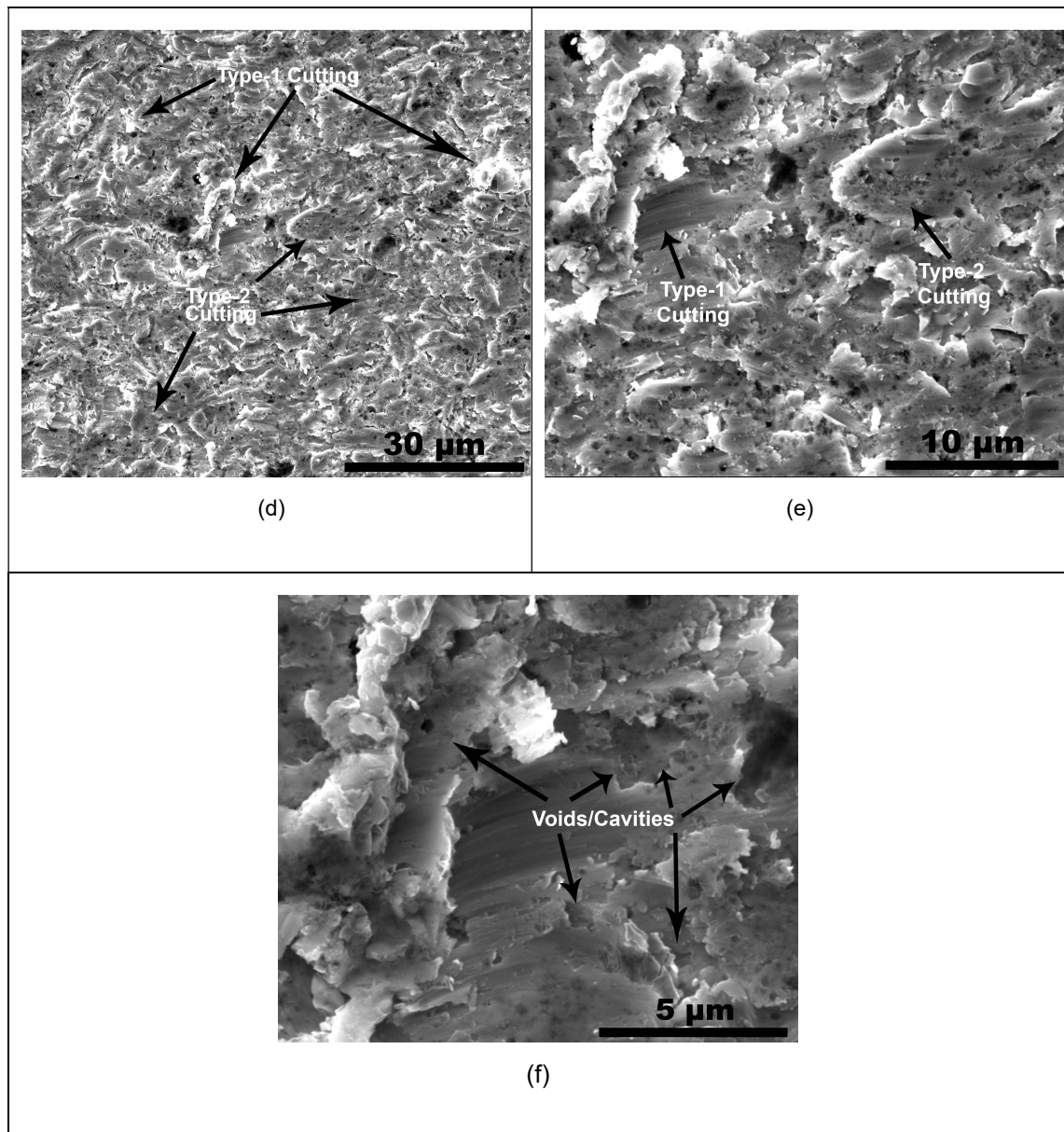


Figure 4.11 SEM images of tantalum specimens wear scars after erosion experiments: impact velocity 5 ms^{-1} ; slurry concentration 7 wt.%; impact angle 90° - (a) Ta (x2500), (b) Ta (x7000); EDX of a SiC fragment, (c) Ta (x15000); impact angle 30° - (d) Ta (x2500), (e) Ta (x7000), (f) Ta (x15000).

Wear scars formed on the aluminium reference sample at 90° impact angle (as shown in Fig. 4.12(a) and Fig. 4.12(b)) displayed a topography resembling hills and valleys, along with the presence of extruded lip fracture, and traces of shattered erodent particles embedded within the wear scars. While wear scars formed at 30° impact angle demonstrated signs of crater formation with and without lip formation, as shown in Fig. 4.12(c) and Fig. 4.12(d).

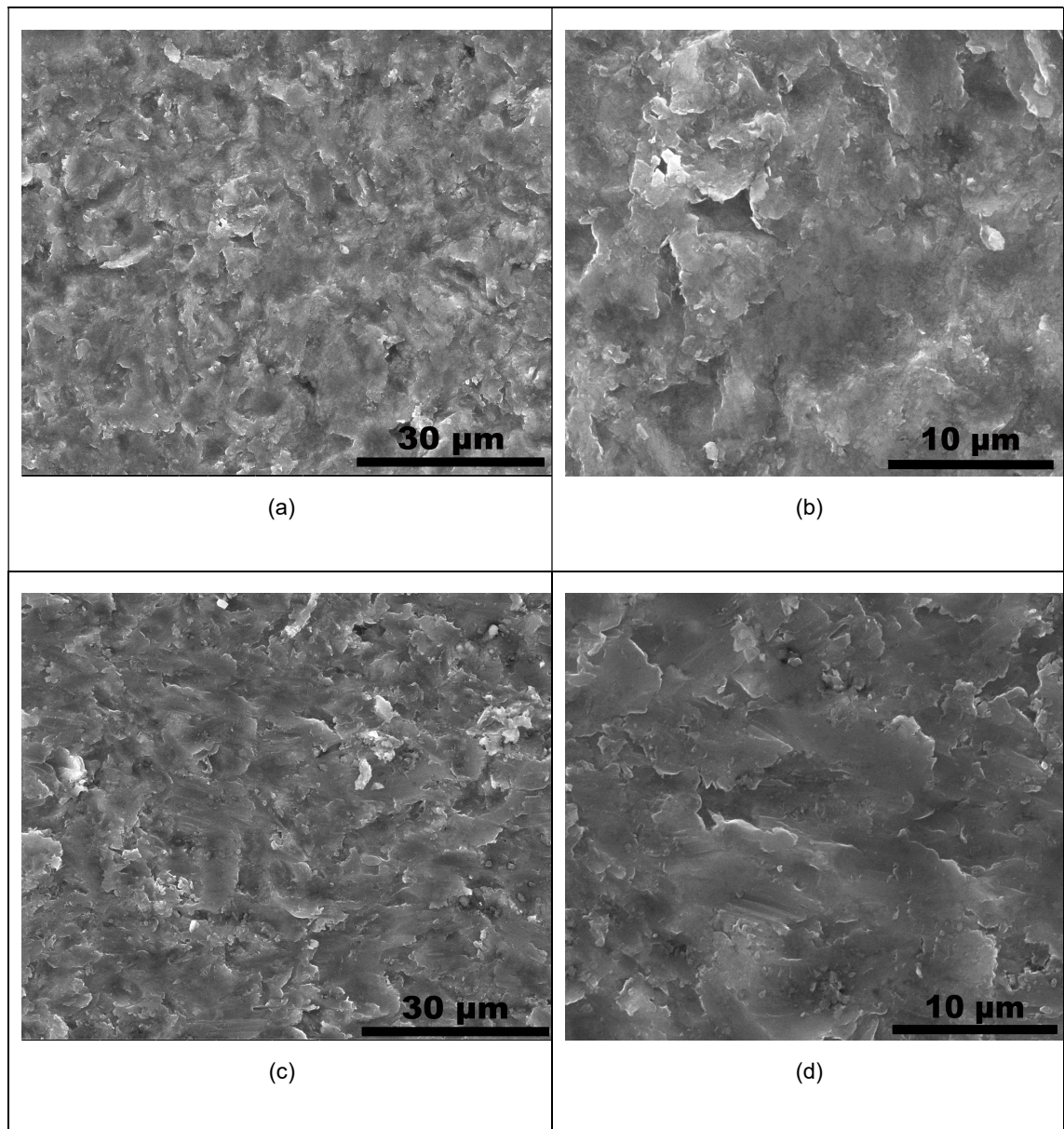


Figure 4.12 SEM images of aluminium specimens wear scars after erosion experiments:

impact velocity 5 ms^{-1} ; slurry concentration 7 wt.%;
 impact angle 90° - (a) Ta (x2500) and (b) Ta (x7000);
 impact angle 30° - (c) Ta (x2500) and (d) Ta (x7000).

Figure 4.13 shows SEM micrographs of tantalum wear scars after erosion experiments; 90° and 30° impact angles, 5 ms^{-1} impact velocity, and 5 wt.% SiC concentration. The abundance of voids/cavities along with hill-and-valley topography was observed in wear scars under normal impact, as shown in Fig. 4.13(a) and Fig. 4.13(b). At 30° impact angle, the dominant feature was the presence of craters with extruded lips, all around wear scars as shown in Fig. 4.13(c) and Fig. 4.13(d). Section 5.2.5 provides a detailed description of wear

scar features observed here on the basis of different slurry concentrations; 5 wt.% and 7 wt.%, as shown in Fig. 4.13 and Fig. 4.11, respectively.

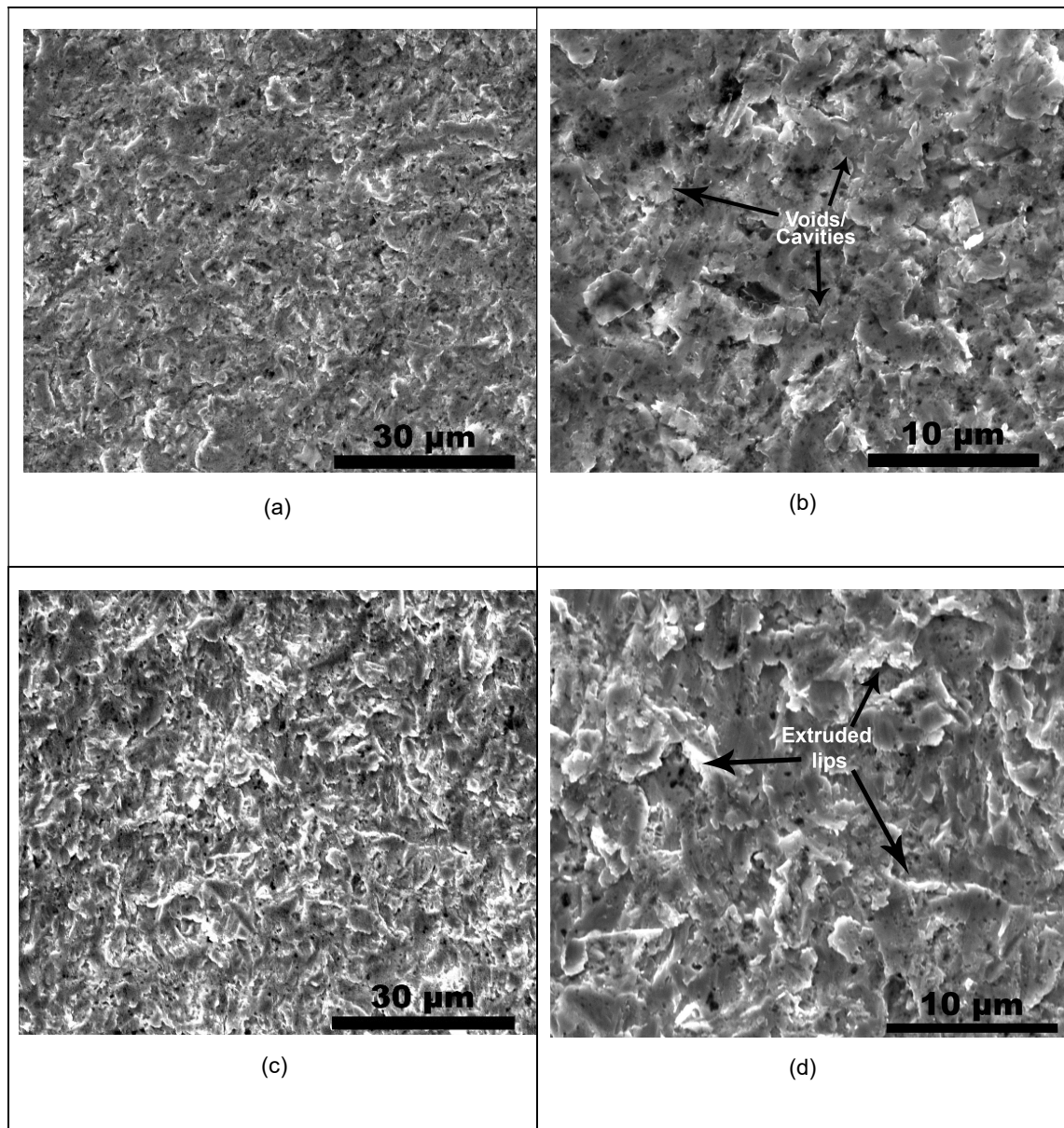


Figure 4.13 SEM images of tantalum specimens wear scars after erosion experiments: impact velocity 5 ms^{-1} ; slurry concentration 5 wt.%; impact angle 90° - (a) Ta (x 2500) and (b) Ta (x 7000); impact angle 30° - (c) Ta (x 2500) and (d) Ta (x 5500).

Figure 4.14 shows the optical micrographs of polished tantalum specimen deformed under various indentation loads (1, 3, and 5 kgf) using Vickers hardness tester. These additional tests were performed to assess the material behaviour under indentation loading.

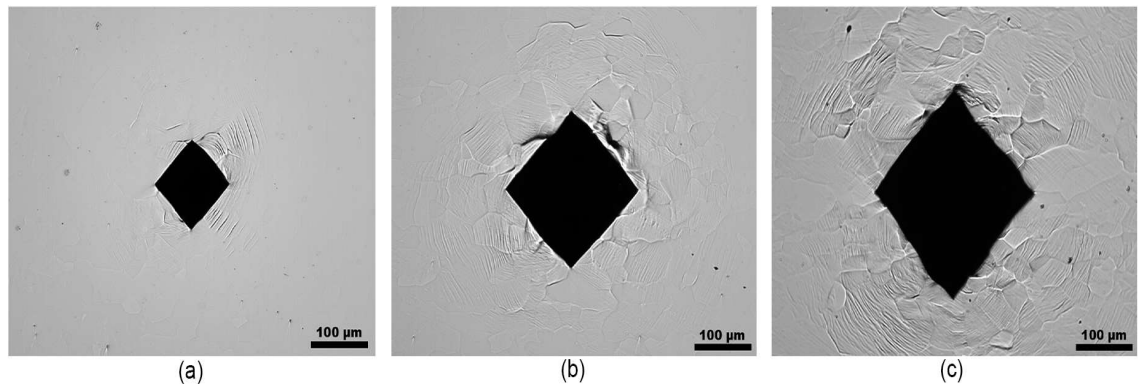


Figure 4.14 Optical micrographs of Vickers indentation on polished tantalum specimen under various loads; (a) 1 kgf, (b) 3 kgf, and (c) 5 kgf.

As evident in Fig. 4.14, the indentation load plastically deformed the tantalum substrate and the severity of the deformation increases with the indentation load. This plastic deformation pattern was found to be contributory to the material removal mechanism for tantalum and this aspect is discussed further in section 5.2.7.1.

4.3 Erosion-corrosion of tantalum

This section is divided into the following six parts.

The first part presents potentiodynamic polarisation plots for tantalum obtained under impinging-jet conditions (with and without erodent particles) at different pH solutions. The second part presents the results of the erosion-corrosion experiments conducted under different pH solutions and impact angles.

The third, fourth, and fifth parts present the rate of various erosion-corrosion interactions at different pH solutions and impact angles. These rates were calculated from the relevant data obtained from the first and second part, and they are presented as the synergy rate, the erosion enhanced corrosion rate (also known as additive effect), and the corrosion enhanced erosion rate (also known as synergistic effect). Finally, the sixth part presents SEM images of wear scars obtained during erosion-corrosion experiments at different pH solutions and impact angles.

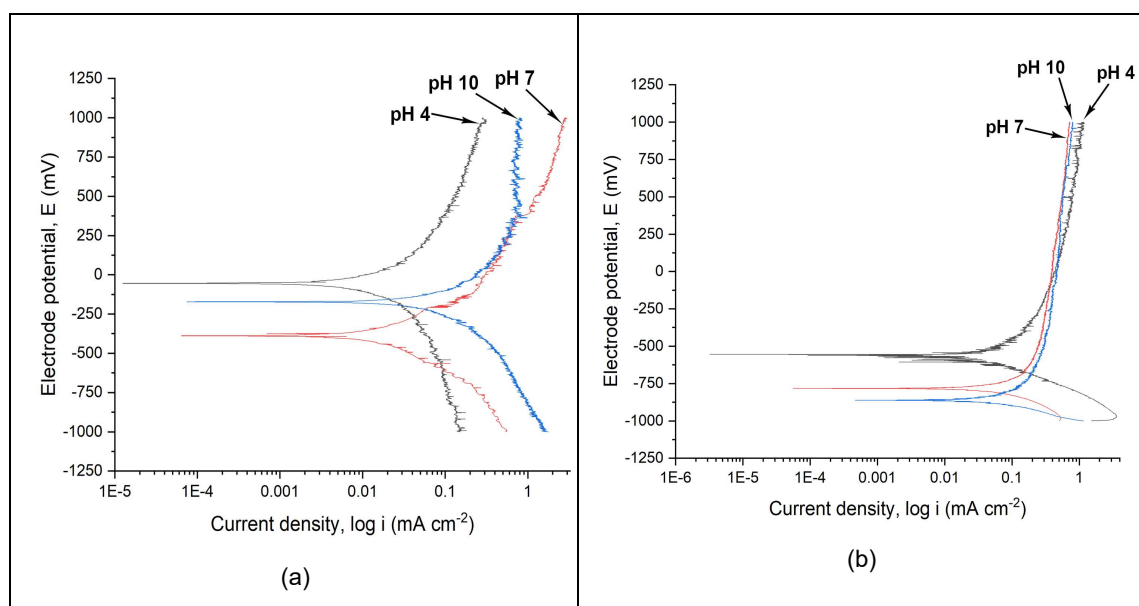
All experiments were repeated at least three times (for data repeatability and reliability). In this chapter, representative results (and, in some cases, average results) out of the three repeat experiments are shown. The remaining results

from the repeat experiments can be found in the Appendix section (Fig. A.1 to Fig. A.6).

4.3.1 Potentiodynamic plots

Figure 4.15 shows the potentiodynamic polarisation plots of tantalum specimens obtained under impinging-jet conditions at different pH solutions with and without particles. These tests were conducted at of 30° and 90° impact angles. Relevant corrosion parameters obtained from the polarisation plots (Fig. 4.15) are presented in Table 4.5.

At both 30° and 90° impact angles, the effect of particle impact on electrode potential and current density is evident in Fig. 4.15(a-d). In the presence of particles, the corrosion potentials at all the pH values moved towards the active side (with more negative values), as shown in Fig. 4.15(b) and Fig. 4.15(d), whereas in the absence of particles, it became nobler (with more positive values), as shown in Fig. 4.15(a) and Fig. 4.15(c). This effect of particle impact is also visible in the data shown in Table 4.5, which reveals that, in the presence of particles, the corrosion current density (i_{corr}) increased with solution pH. Whereas in the absence of particles, i_{corr} first increased with the change of pH from 4 to 7, and it then decreased as solution pH changed from 7 to 10. This trend was found at both 30° and 90° impact angles.



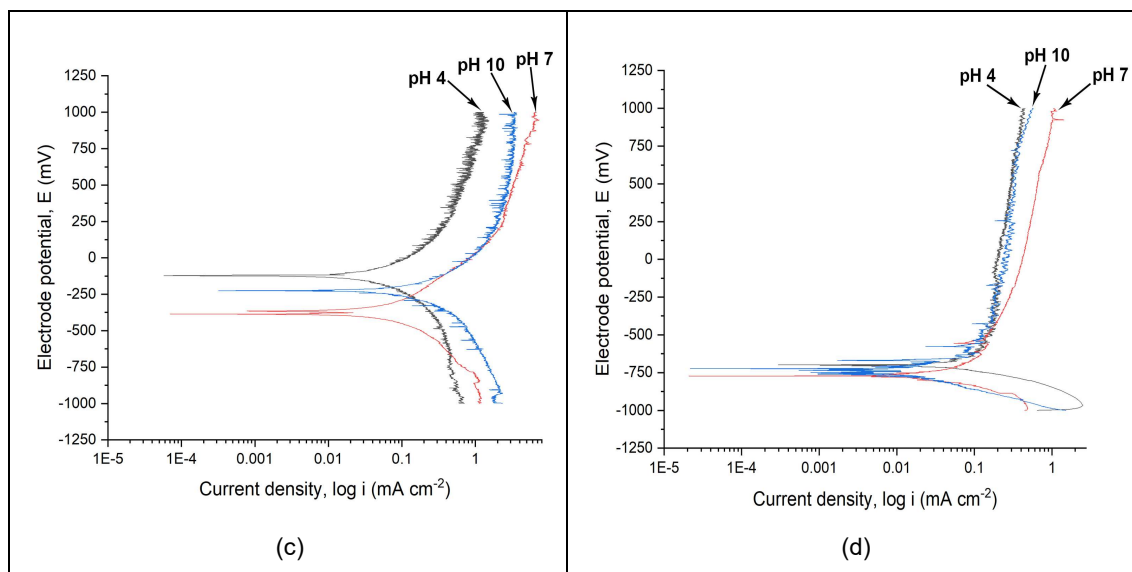


Figure 4.15 Tantalum potentiodynamic polarisation plots after erosion-corrosion experiments at 5 ms^{-1} impact velocity and different pH solutions: (a) without particles at 30° impact angle, (b) with 7 wt.% SiC particles at 30° impact angle, (c) without particles at 90° impact angle, (d) with 7 wt.% SiC particles at 90° impact angle.

Table 4.5 Mean corrosion potentials (E_{corr}) and current densities (i_{corr}) obtained from polarisation plots at different pH and impact angles.

Operating parameters	pH	Corrosion potential E_{corr} (V)	Corrosion current density i_{corr} ($\mu\text{A cm}^{-2}$)
30° , Without SiC	4	-0.064 ± 0.01	9 ± 1.70
	7	-0.358 ± 0.03	17 ± 1.99
	10	-0.170 ± 0.01	163 ± 0.91
30° , 7 wt.% SiC	4	-0.593 ± 0.08	23 ± 2.49
	7	-0.780 ± 0.01	57 ± 4.99
	10	-0.871 ± 0.01	36 ± 2.94
90° , Without SiC	4	-0.127 ± 0.03	24 ± 1.89
	7	-0.376 ± 0.02	66 ± 0.80
	10	-0.260 ± 0.02	116 ± 2.45
90° , 7 wt.% SiC	4	-0.680 ± 0.01	33 ± 1.70
	7	-0.763 ± 0.01	60 ± 5.35
	10	-0.709 ± 0.02	15 ± 2.05

4.3.2 Erosion-corrosion rate versus pH and impact angle

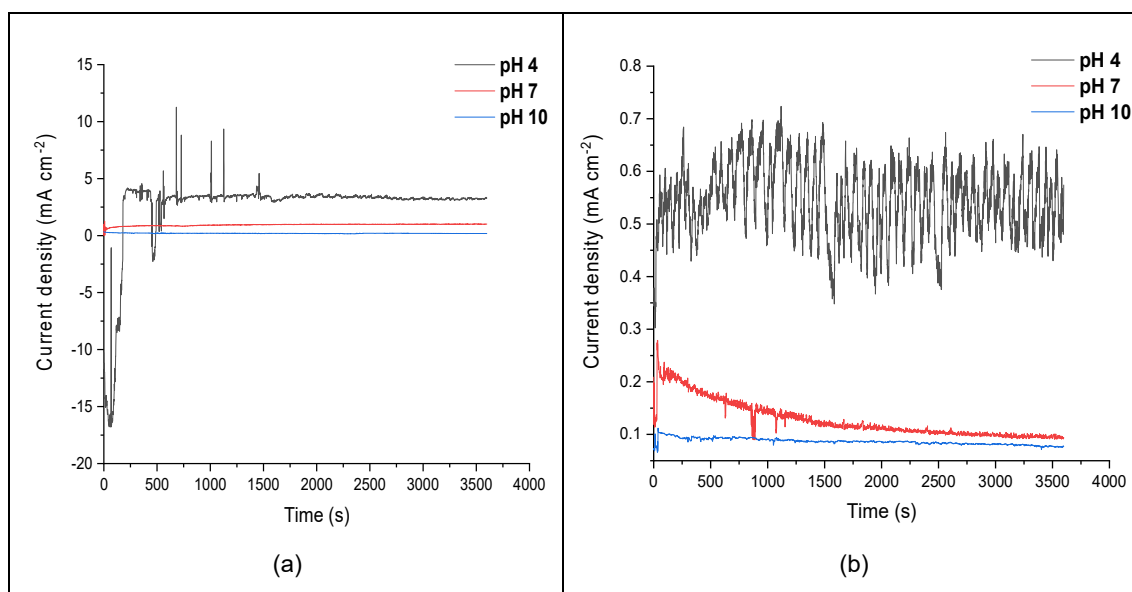


Figure 4.16 Tantalum potentiostatic plots obtained in different pH solutions with 7 wt.% SiC concentration at 5 ms⁻¹ impact velocity and different impact angles; (a) 30°, (b) 90°.

Fig. 4.16(a) and Fig. 4.16(b) show the potentiostatic polarisation plots for erosion-corrosion at 30° and 90° impact angles, respectively (details of potentiostatic conditions can be found in Table 3.3 and Table 3.4, section 3.3.2.1.3). It is visible that the current density decreased with the increase in solution pH at both the impact angles studied. As a result, the current density was maximum at pH 4 and minimum at pH 10.

In addition to the current density data (Fig. 4.16), the tantalum mass loss data was also obtained in these potentiostatic polarisation experiments which can be found in the Appendix section (Table A.9). This mass loss data was used to calculate the erosion-corrosion rate (K_{ec}) using Eq. (3.6), as explained in section 3.3.3.1. The calculated K_{ec} values are shown in Table 4.6. For simplicity, the data from this table is also shown as a bar chart in Fig. 4.17, which shows K_{ec} variation with pH at 30° and 90° impact angles. The bar chart shows higher K_{ec} values at 30° as compared to their values at 90° impact angle, for all pH solutions. In addition, at both impact angles, K_{ec} declined as the solution pH changed from pH 4 to pH 10; K_{ec} was maximum at pH 4 and minimum at pH 10. A large fluctuation in current density, at pH 4 under normal impact, was also observed in Fig. 4.16(b). These results are further examined in the Discussion section which can be found in section 5.3.2.

Table 4.6 Tantalum erosion-corrosion rate data obtained after erosion-corrosion experiments in different pH solutions at 5 ms⁻¹ under 30° and 90° impact angles.

Impact angle (°)	Solution pH	Sample mass before experiment (g)	Mean sample mass after experiment (g)	Mean sample mass loss (g)	Erosion-Corrosion rate, K_{ec} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Mean K_{ec} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Standard deviation (kg m ⁻² s ⁻¹) x 10 ⁻⁵
30	4	58.7920	58.7877	0.0044	3.64	3.47	0.17
		59.1690	59.1651	0.0039	3.30		
		59.3240	59.3212	0.0028	2.38		
	7	59.3200	59.3173	0.0027	2.28	2.27	0.08
		58.0265	58.0239	0.0026	2.18		
		59.3173	59.3145	0.0028	2.36		
	10	59.1652	59.1605	0.0047	3.95	1.98	0.14
		59.1605	59.1580	0.0025	2.11		
		57.9050	57.9028	0.0022	1.84		
90	4	58.7877	58.7859	0.0018	1.55	1.22	0.24
		58.0277	58.0264	0.0014	1.13		
		59.3212	59.3200	0.0012	0.98		
	7	59.1276	59.1265	0.0011	0.94	0.90	0.06
		59.1256	59.1245	0.0011	0.94		
		59.1245	59.1235	0.0010	0.82		
	10	59.1580	59.1565	0.0016	1.30	0.83	0.03
		57.9028	57.9019	0.0010	0.80		
		58.6216	58.6206	0.0010	0.86		

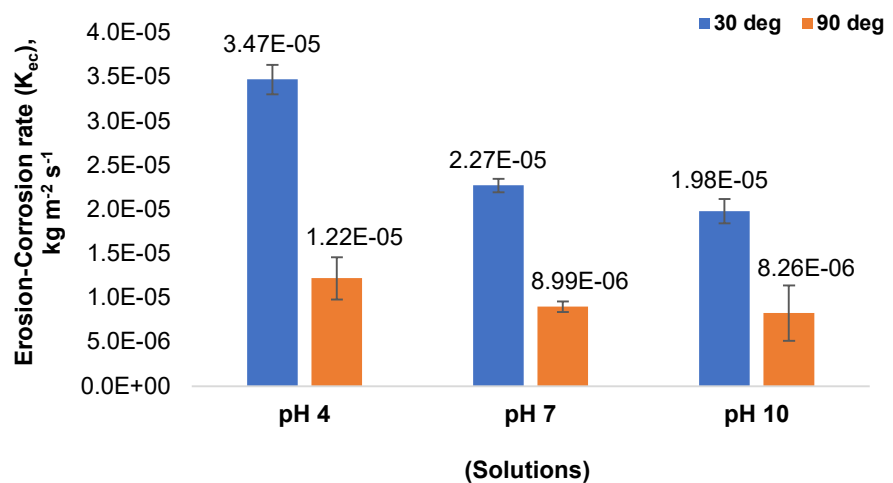


Figure 4.17 Bar chart showing tantalum erosion-corrosion rate variation with pH under 30° and 90° impact angles.

4.3.3 Synergy rate versus pH and impact angle

The synergy rate (ΔK_{ec}) of tantalum was calculated using Eq. (3.12), which is shown in section 3.3.3.2. To aid the understanding, the equation is presented here again as,

$$\Delta K_{ec} = K_{ec} - (K_{eo} + K_{co}) \quad \text{Eq. (4.1)}$$

Using Eq. (4.1), the erosion-corrosion rate (K_{ec}) was obtained using the calculation methodology described in the previous section 4.3.2. The pure erosion rate (K_{eo}) and pure corrosion rate (K_{co}) were obtained using Eq. (3.5) and Eq. (3.9), respectively, as per the methodology stated in section 3.3.3.1.

The calculated pure erosion rate (K_{eo}) and pure corrosion rate (K_{co}) values are shown in Table 4.7 and Table 4.8, respectively, and their simplified representation as bar charts is also shown in Fig. 4.18. The calculated ΔK_{ec} values are shown in Table 4.9 and their simplified representation as a bar chart is also shown in Fig. 4.19.

Figure 4.18(a) shows higher K_{eo} values at 30° as compared to that at 90° impact. Fig. 4.18(b) shows, under both the impact angles studied, K_{co} increased with pH and its maximum was noted at pH 10 and minimum at pH 4.

An opposite trend was observed for the synergy rate (ΔK_{ec}), as shown in Fig. 4.19. Under both 30° and 90° impact angles, ΔK_{ec} decreased with the increase in pH, and were found to be maximum at pH 4 and minimum at pH 10. Please note, negative ΔK_{ec} values were observed at pH 7 and pH 10.

Table 4.7 Tantalum pure erosion rate (K_{eo}) data obtained after erosion experiments in deionised water slurry (7 wt.% SiC) at 5 ms⁻¹ under 30° and 90° impact angles.

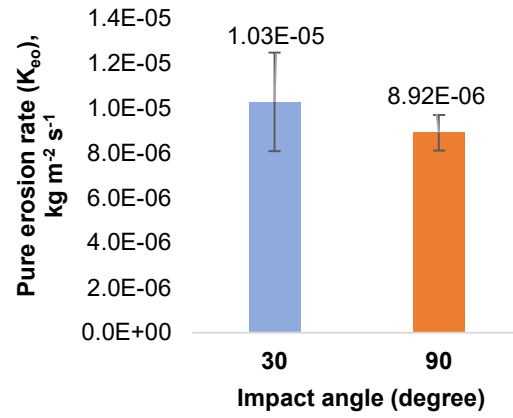
Impact angle (°)	Sample mass before experiment (g)	Mean sample mass after experiment (g)	Mean sample mass loss (g)	Pure erosion rate, K_{eo} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Mean K_{eo} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Standard deviation (kg m ⁻² s ⁻¹) x 10 ⁻⁵
30	59.6876	58.6866	0.0011	0.92	1.03	0.22
	59.6864	59.6855	0.0010	0.84		
	59.6857	59.6841	0.0016	1.34		
90	58.8999	58.8989	0.0010	0.84	0.89	0.08
	58.8992	58.8982	0.0010	0.84		
	58.8984	58.8972	0.0012	1.00		

Table 4.8 Tantalum pure corrosion rate (K_{co}) data obtained after corrosion experiments in different pH solutions at 5 ms⁻¹ under 30° and 90° impact angles.

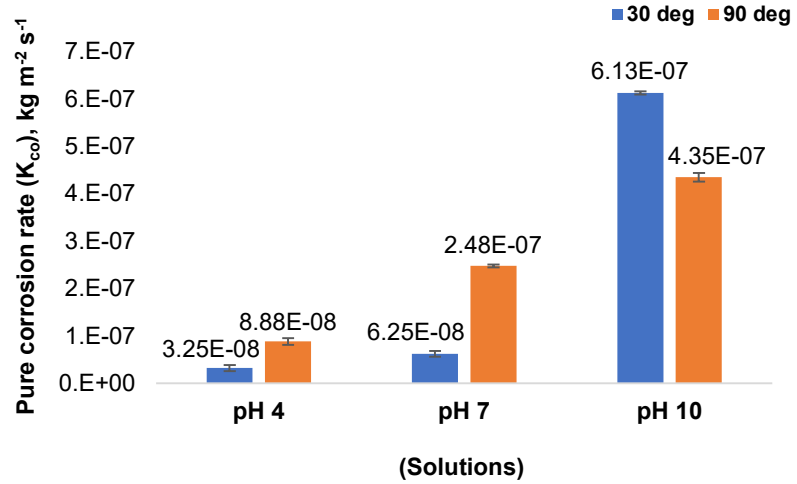
Impact angle (°)	Solution pH	Current density, i (μA cm ⁻²)	Pure corrosion rate, K_{co} (kg m ⁻² s ⁻¹) x 10 ⁻⁷	Mean K_{co} (kg m ⁻² s ⁻¹) x 10 ⁻⁷	Standard deviation (kg m ⁻² s ⁻¹) x 10 ⁻⁷
30	4	11	0.41	0.33	0.06
		8	0.30		
		7	0.26		
	7	19	0.71	0.63	0.06
		15	0.56		
		16	0.60		
	10	162	6.08	6.13	0.04
		164	6.15		
		164	6.15		
90	4	25	0.94	0.89	0.07
		21	0.79		
		25	0.94		
	7	67	2.51	2.48	0.03
		66	2.48		
		65	2.44		
	10	116	4.35	4.35	0.09
		119	4.46		
		113	4.24		

Table 4.9 Tantalum synergy rate (ΔK_{ec}) data based on pure erosion rate (K_{eo}), pure corrosion rate (K_{co}), and combined erosion-corrosion rate (K_{ec}).

Impact angle (°)	Solution pH	Mean K_{ec} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Mean K_{eo} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Mean K_{co} (kg m ⁻² s ⁻¹) x 10 ⁻⁵	Mean Synergy rate ΔK_{ec} $\Delta K_{ec} = K_{ec} - (K_{eo} + K_{co})$ (kg m ⁻² s ⁻¹) x 10 ⁻⁵
30	4	3.47 ± 0.20	1.03 ± 0.22	0.003 ± 0.06	2.44
	7	2.27 ± 0.08	1.03 ± 0.22	0.006 ± 0.06	1.24
	10	1.98 ± 0.10	1.03 ± 0.22	0.061 ± 0.04	0.89
90	4	1.22 ± 0.20	0.89 ± 0.08	0.009 ± 0.07	0.32
	7	0.90 ± 0.06	0.89 ± 0.08	0.025 ± 0.03	-0.02
	10	0.83 ± 0.03	0.89 ± 0.08	0.044 ± 0.09	-0.11



(a)



(b)

Figure 4.18 Bar charts showing variation of (a) pure erosion rate (b) pure corrosion rate with pH under 30° and 90° impact angles.

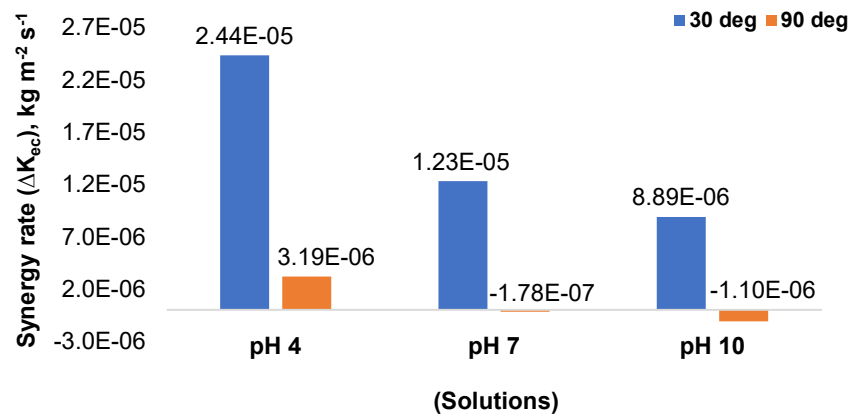


Figure 4.19 Bar chart showing tantalum synergy rate variation with pH under 30° and 90° impact angles.

4.3.4 Erosion enhanced corrosion rate versus pH and impact angle

The effect of erosion on corrosion rate (also known as erosion enhanced corrosion rate, ΔK_c or additive effect) was calculated, from the corrosion current density (i_{corr}) values, using Eq. (3.13) as shown in section 3.3.3.2. These i_{corr} values were measured through the erosion-corrosion experiments under potentiostatic conditions at 30° and 90° impact angles (as shown in Table 3.3 and Table 3.4, section 3.3.2.1.3).

The calculated ΔK_c values are shown in Table 4.10, and their simplified representation as a bar chart is also shown in Fig. 4.20.

Figure 4.20 shows higher ΔK_c values at 30° as compared to their values at 90° impact. For both the impact angles studied, ΔK_c decreased with the increase in pH and was found to be maximum at pH 4 and minimum at pH 10.

Table 4.10 Tantalum erosion enhanced corrosion rate (ΔK_c) data obtained after potentiostatic experiments in different pH solutions at 5 ms⁻¹ under 30° and 90° impact.

Impact angle (°)	Solution pH	Set Potential (mV)	Current density, i ($\mu\text{A cm}^{-2}$)	ΔK_c ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-6}$	Mean ΔK_c ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-6}$	Standard deviation ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-6}$
30	4	+ 230	2083	7.81	10.30	2.40
			3389	12.70		
			1915	7.18		
	7	- 125	916	3.43	3.18	0.44
			944	3.54		
			685	2.57		
	10	+ 111	181	0.68	0.67	0.04
			168	0.63		
			191	0.72		
90	4	+ 60	547	2.05	2.00	0.12
			491	1.84		
			563	2.11		
	7	- 80	152	0.57	0.50	0.05
			128	0.48		
			122	0.46		
	10	- 35	79	0.30	0.28	0.03
			69	0.26		
			82	0.31		

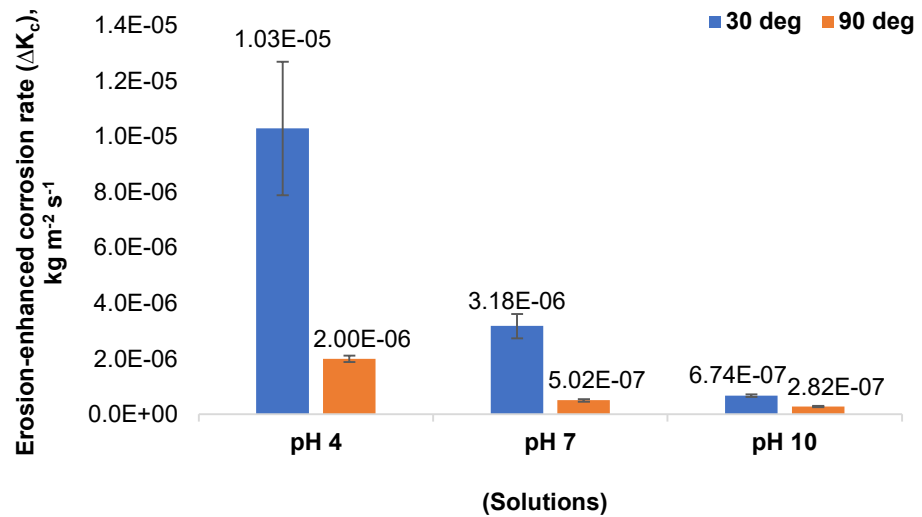


Figure 4.20 Bar chart showing tantalum erosion enhanced corrosion rate variation with pH under 30° and 90° impact angles.

4.3.5 Corrosion enhanced erosion rate versus pH and impact angle

The effect of corrosion on erosion (also known as corrosion enhanced erosion rate, ΔK_e or synergistic effect) was calculated using Eq. (3.14) described in section 3.3.3.2. To aid the understanding, this equation is presented here again as,

$$\Delta K_e = \Delta K_{ec} - \Delta K_c \quad \text{Eq. (4.2)}$$

In this equation, the synergy rate (ΔK_{ec}) and erosion enhanced corrosion rate (ΔK_c) were obtained as per the calculation methodology described in section 4.3.3 and section 4.3.4, respectively. The ΔK_{ec} and ΔK_c values thus obtained were used in Eq. (4.2) to calculate ΔK_e .

The calculated ΔK_e values are shown in Table 4.11, and their simplified representation as a bar chart is also shown in Fig. 4.21.

Figure 4.21 shows higher ΔK_e values at 30° as compared to their values at 90° impact. For both the impact angles studied, ΔK_e values were found to be maximum at pH 4 and minimum at pH 10. In addition, ΔK_e decreased significantly as the solution pH increased from pH 4 to pH 10, a trend which was similar under both impact angles. The negative ΔK_e values at pH 7 and pH 10 show that ΔK_c values were higher than ΔK_{ec} values under these pH conditions. These findings are further discussed in the next chapter (section 5.3.4).

Table 4.11 Tantalum corrosion enhanced erosion rate (ΔK_e) data based on synergy rate (ΔK_{ec}) and erosion enhanced corrosion rate (ΔK_c).

Impact angle (°)	Solution pH	ΔK_{ec} ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$	ΔK_c ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$	ΔK_e ($\Delta K_e = \Delta K_{ec} - \Delta K_c$) ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$
30	4	2.44	1.03 ± 0.20	1.41
	7	1.24	0.32 ± 0.04	0.92
	10	0.89	0.07 ± 0.004	0.82
90	4	0.32	0.20 ± 0.01	0.12
	7	-0.02	0.05 ± 0.005	- 0.07
	10	-0.11	0.03 ± 0.003	- 0.14

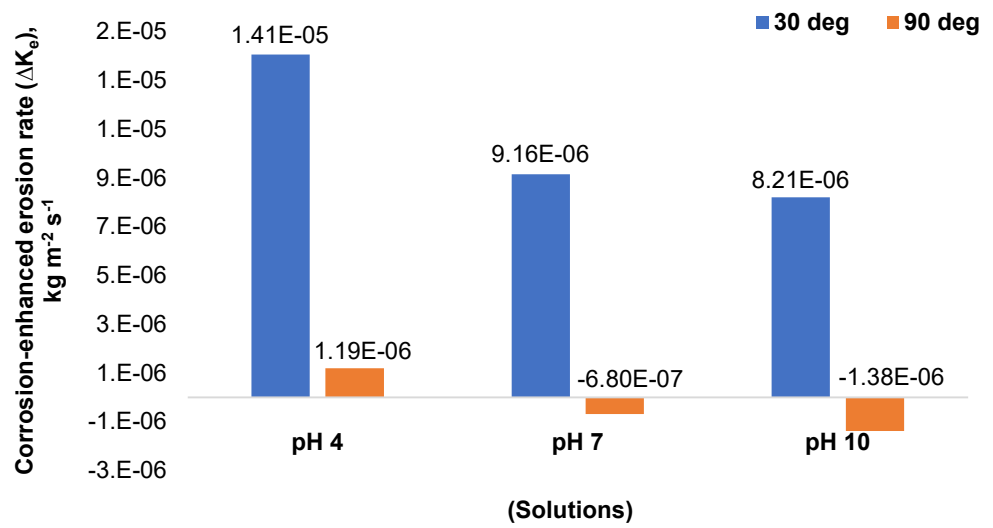


Figure 4.21 Bar chart showing tantalum corrosion enhanced erosion rate variation with pH under 30° and 90° impact angles.

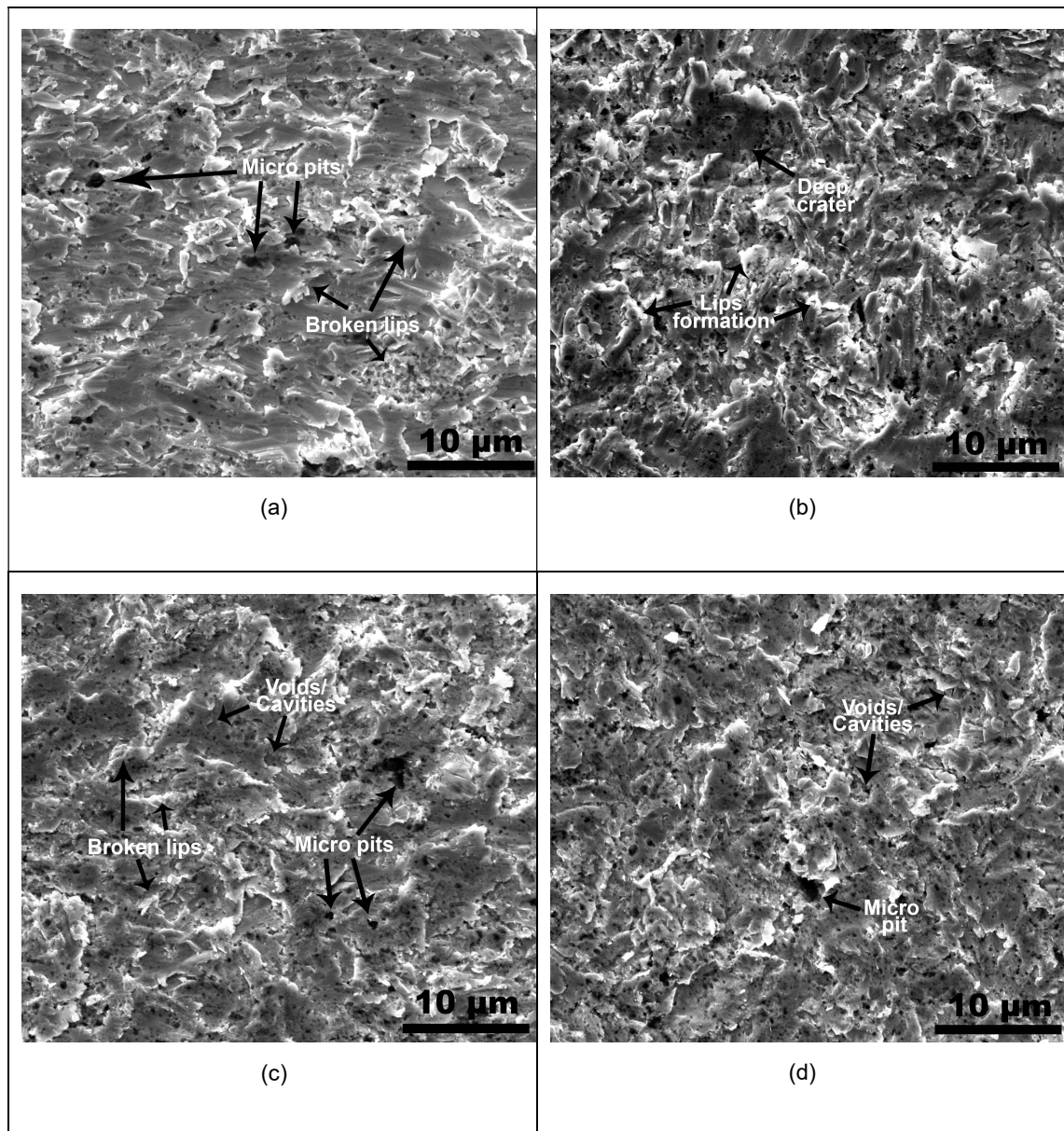
4.3.6 SEM micrographs

Figure 4.22 shows SEM micrographs of wear scars on tantalum formed after erosion-corrosion experiments using various pH solution slurries (7 wt.% SiC) at 5 ms^{-1} impact velocity under 30° and 90° impact angles. These wear scars were found to be largely similar to those obtained earlier for pure erosion of tantalum (as shown in Fig. 4.11 and 4.13 in section 4.2.2.4), except the material removal mechanism was further aided by the effect of corrosion.

Upon close examination of the wear scars presented in Fig. 4.22, it is evident that the material removal mechanism was facilitated by the ploughing mechanism at a 30° impact angle, while it was supported by plastic deformation at a 90° impact angle. Extruded lips and lip fractures were evident at both impact angles. Under

both the impact angles studied, the formation of voids/cavities and micro pits are also visible on wear scars.

The effect of solution pH on the wear scar was less apparent and generally undistinguished. However, the wear scar at pH 4 under 30° is characterised by broken lips (as shown in Fig. 4.22(a)), which are mostly intact at pH 10 under 90° impact angle (as shown in Fig. 4.22(f)).



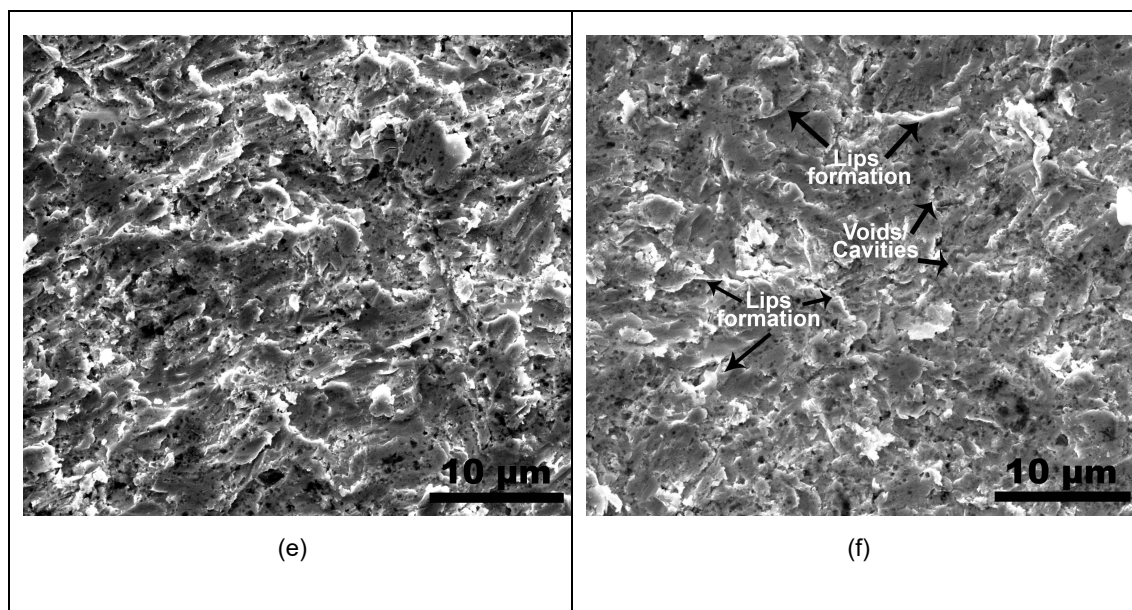


Figure 4.22 SEM images (x5000) of tantalum specimens wear scars after erosion-corrosion experiments at 5 ms^{-1} impact velocity, 7 wt.% slurry concentration, at:
 (a) 30° impact, pH 4 (b) 90° impact, pH 4
 (c) 30° impact, pH 7 (d) 90° impact, pH 7
 (e) 30° impact, pH 10 (f) 90° impact, pH 10.

4.4 Flow-assisted galvanic corrosion of tantalum and tungsten

This section is divided into two parts. The first part presents the material characterisation results obtained for the tungsten specimen. The second part presents the results of the electrochemical tests conducted on both tantalum and tungsten under normal impact at different pH solutions and impact velocities.

All experiments were repeated at least three times (for data repeatability and reliability). In this chapter, representative results (and, in some cases, average results) out of the three repeat experiments are shown. The remaining results from the repeat experiments can be found in the Appendix section (Fig. A.7 to Fig. A.13)

4.4.1 Tungsten material characterisation

Microstructure

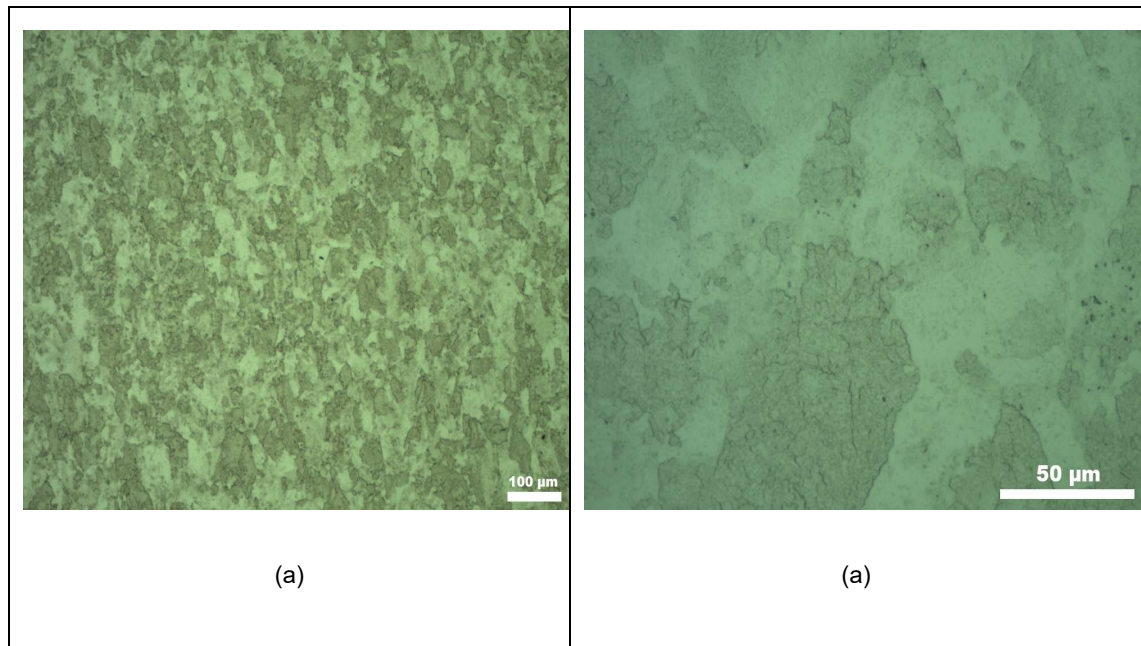


Figure 4.23 Optical micrographs of etched tungsten specimen at different magnifications; (a) x100 (b) x500.

Figure 4.23 shows the optical microstructures of the etched tungsten specimen. Similar to tantalum (in Fig. 4.1), the microstructure of tungsten (in Fig. 4.23) reveals a non-uniform grain distribution and appears to be free of porosity. This also aligns with tungsten's measured density value of 19.38 g cm^{-3} , which is close to its theoretical density of 19.25 g cm^{-3} [253].

The measured mean grain size of tungsten was $53 \pm 8 \text{ µm}$ (equivalent to ASTM grain size no. (G) of 5.2 ± 0.36). This grain size was found to be smaller than their measured values for tantalum (Grain size: $65 \pm 15 \text{ µm}$; G: 4.6 ± 0.55), as shown in section 4.2.1.1.

Roughness

Table 4.12 shows the mean roughness values (R_a) that were obtained based on five multidirectional profilometer scans on the sample surface.

Table 4.12 Surface roughness data for tungsten sample.

S.No.	R _a (μm) Standard Scan-1	R _a (μm) Standard Scan-2	R _a (μm) Standard Scan-3	R _a (μm) Standard Scan-4	R _a (μm) Standard Scan-5	R _a (μm) (Mean)	Standard deviation
1	0.300	0.160	0.120	0.177	0.178	0.187	0.06

The tungsten surface roughness was determined by calculating the arithmetic mean of the 5 average roughness values, listed in Table 4.12, and was found to be $0.187 \pm 0.06 \mu\text{m}$.

Hardness

The hardness of tungsten specimens was measured using a 2 kgf indenter load at 10 different points (in a 1 x 10 matrix). The measured hardness at each indentation point is shown in Table 4.13, while its variation over the sample surface is shown in Fig. 4.24. From this figure, the mean hardness value was calculated as $\text{HV}_2 489 \pm 2$ (approx.).

Table 4.13 Vickers hardness data of tungsten sample under indenter load of 2 kgf.

Point No.	Hardness (HV ₂)
1	487.66
2	490.53
3	487.69
4	487.66
5	490.53
6	487.56
7	490.64
8	487.53
9	493.58
10	490.61
Mean	489.40
Standard deviation	1.97

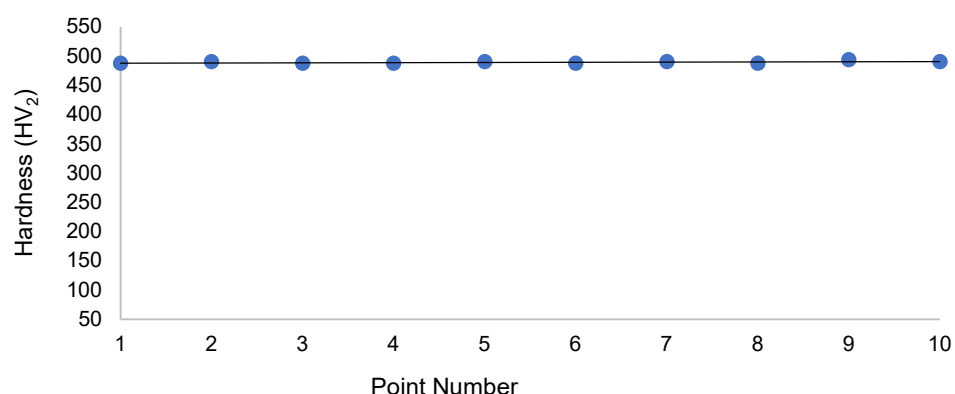


Figure 4.24 Vickers hardness measurement data for 10 indents on tungsten sample under 2 kgf indenter load, 3 mm indent separation, and 10 s dwell time.

Young's modulus

The Young's modulus of the tungsten sample was measured using a CSM nanoindentation tester (Berkovich indenter) and it was found to be 568 ± 27 GPa.

Table 4.14 summarises the data measurement for tungsten samples.

Table 4.14 Measured properties mean data summary for tungsten.

Property	Tungsten
Density (g cm ³)	19.38 ± 0.05
Hardness (HV)	489 ± 2 (HV ₂)
Young's modulus (GPa)	568 ± 27
Roughness (μm)	0.187 ± 0.06

X-ray diffraction analysis

Figure 4.25 shows the XRD diffractogram of tungsten. All the peaks in the diffractogram matched perfectly with the peaks of the corresponding powder diffraction file (PDF Ref. 04-004-7097) which is also labelled in the figure. This suggested that the analysed sample was body centred cubic (BCC) crystal structure of 100% tungsten.

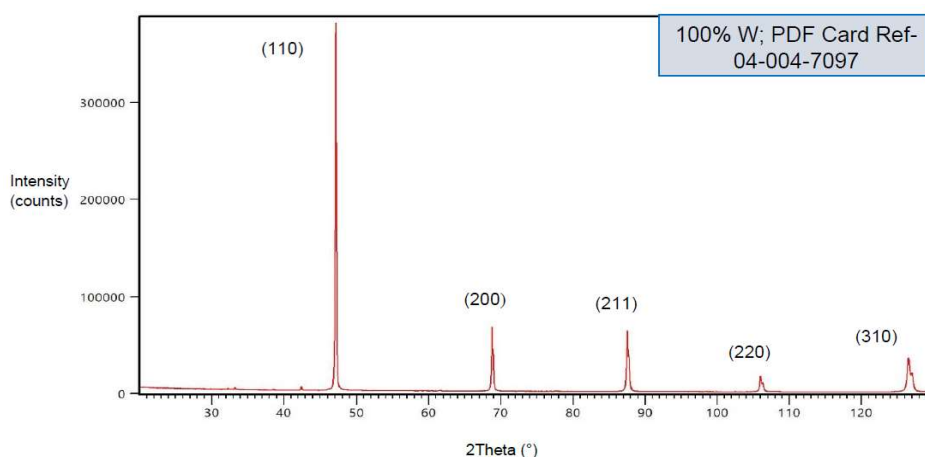


Figure 4.25 X-ray diffraction (XRD) pattern of tungsten.

The diffractogram shows a dominant peak at (110) orientation and similar intensity peaks at (200) and (211) orientations. The angles ($^{\circ}2\theta$) of the peaks are strikingly similar to those found in the corresponding powder diffraction file (PDF Card Ref 04-004-7097). The XRD software (X'Pert Highscore Plus) processed the diffractogram and computed peak positioning and broadening (full width at half maximum - FWHM) data. This data was further processed using the Scherrer equation [238] to obtain crystal sizes which are shown in Table 4.15.

Table 4.15 Tungsten crystallite size data summary.

S.No.	FWHM ($^{\circ}2\theta$)	Error ($^{\circ}2\theta$)	Peak Position ($^{\circ}2\theta$)	FWHM – Error ($^{\circ}2\theta$)	Crystallite size (using Scherrer equation [238]) (Å)
1	0.114	0.084	47.067	0.030	3365.269
2	0.142	0.084	68.770	0.057	1950.887
3	0.196	0.108	87.532	0.087	1461.593
4	0.247	0.135	106.031	0.112	1374.071
5	0.361	0.166	126.540	0.196	1049.113

The mean crystallite size for tungsten was found to be 1840 ± 815 Å.

4.4.2 Electrochemical tests

4.4.2.1 Potentiodynamic plots

Fig. 4.26(a) and Fig. 4.26(b) show open circuit potential (OCP) plots for tantalum and tungsten specimens, respectively, obtained at different pH solutions in static conditions of a 3-electrode glass cell. The potential values obtained from these OCP plots are shown in Table 4.16.

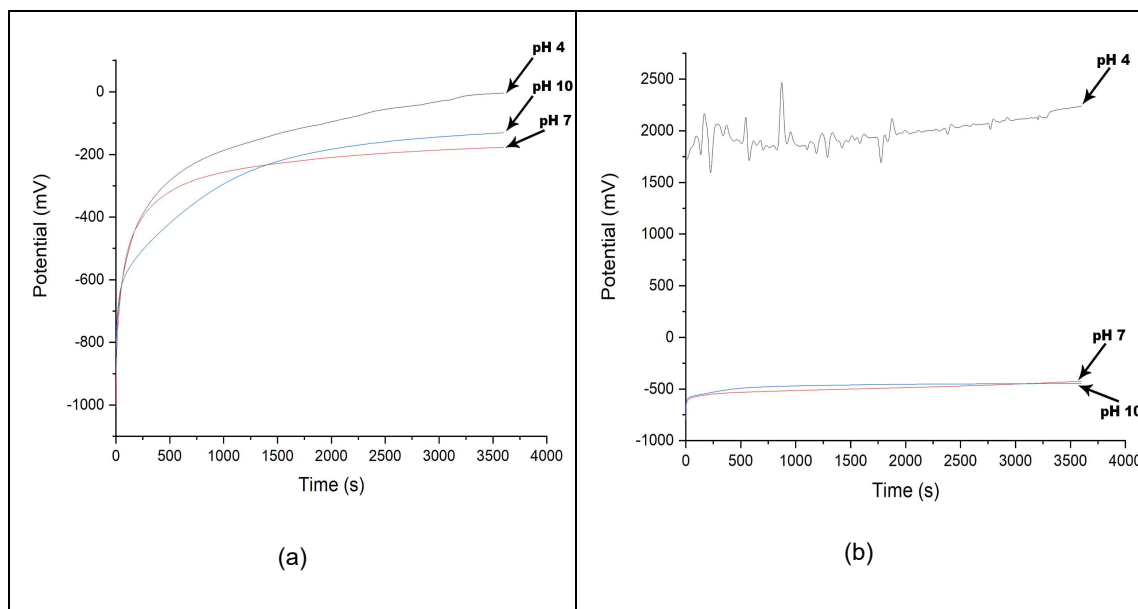


Figure 4.26 Potential-time plots obtained in OCP experiments conducted for 1 h in different pH solutions for: (a) Tantalum (b) Tungsten.

Table 4.16 Open circuit potentials for tantalum and tungsten specimens in static conditions.

Material	pH 4	pH 7	pH 10
Tantalum	-0.079 V	-0.207 V	-0.180 V
Tungsten	+2.018 V	-0.476 V	-0.455 V

Table 4.16 shows that the OCP was most noble (with maximum positive value) at pH 4 and it became most active (with maximum negative value) at pH 7. However, it again shifted to less active potentials at pH 10, a trend which was similar for both metals.

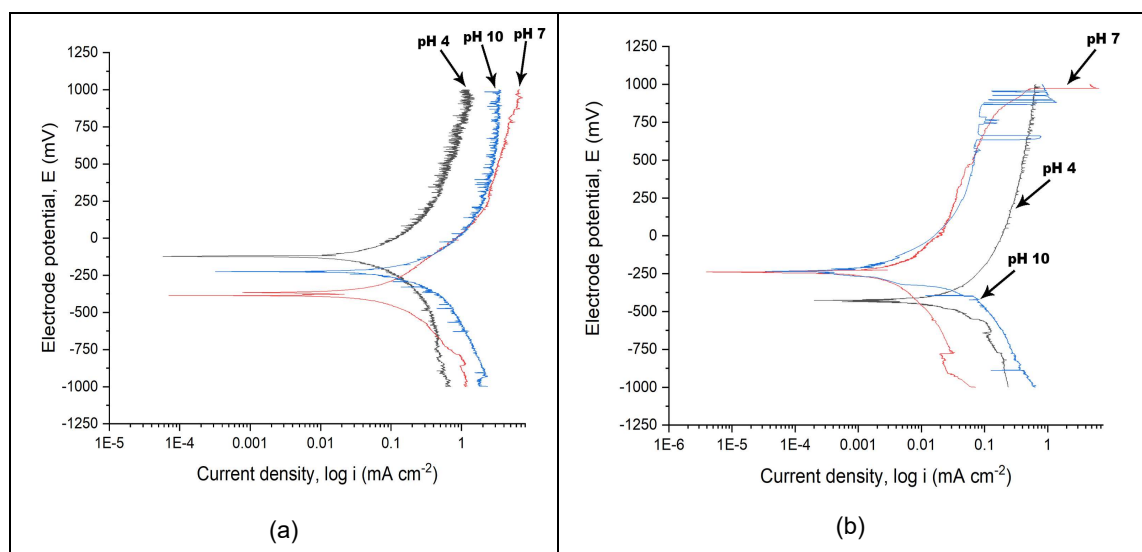
After OCP experiments, potentiodynamic polarisation experiments were conducted on tantalum and tungsten at different pH solutions and impact velocities.

Figure 4.27 shows the potentiodynamic polarisation plots of tantalum and tungsten specimens under impinging-jet conditions of normal impact at different pH solutions for 5 ms⁻¹ and 9 ms⁻¹ impact velocities.

Please note that the polarisation plots of tantalum (in Fig.4.27(a)) have already been shown in section 4.3.1 for analysis of its erosion-corrosion performance; however, they are being repeated here to help understand its galvanic effect with tungsten. Relevant important corrosion parameters obtained from the polarisation plots (shown in Fig. 4.27) are shown in Table 4.17 and they are presented in graphical form in Fig. 4.28.

Figure 4.28(c) shows the effect of higher impact velocity (9 ms⁻¹) on tantalum; at pH 4, its corrosion potential significantly shifted to a more negative value as compared to that at 5 ms⁻¹ as shown in Fig. 4.28(a). On the contrary, at pH 7 and pH 10, the corrosion potential shifted to more positive values as shown in Fig. 4.28(c).

Figure 4.28(c) also shows the effect of higher impact velocity (9 ms⁻¹) on tungsten; at pH 10, its corrosion potential shifted to a more negative value as compared to that at 5 ms⁻¹ as shown in Fig. 4.28(a). On the contrary, at pH 4 and pH 7, the corrosion potential shifted to more positive values as shown in Fig. 4.28(c).



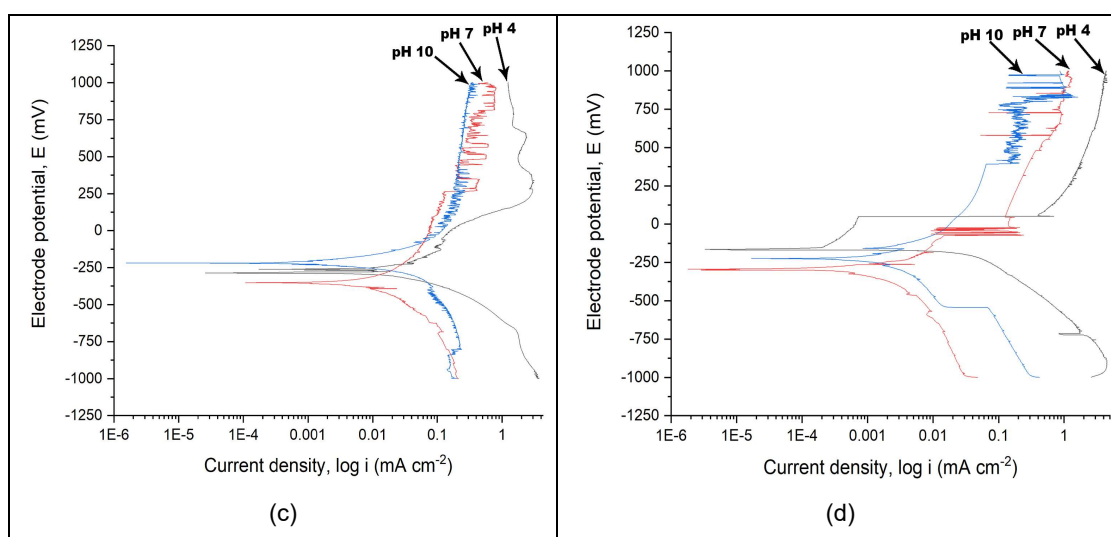
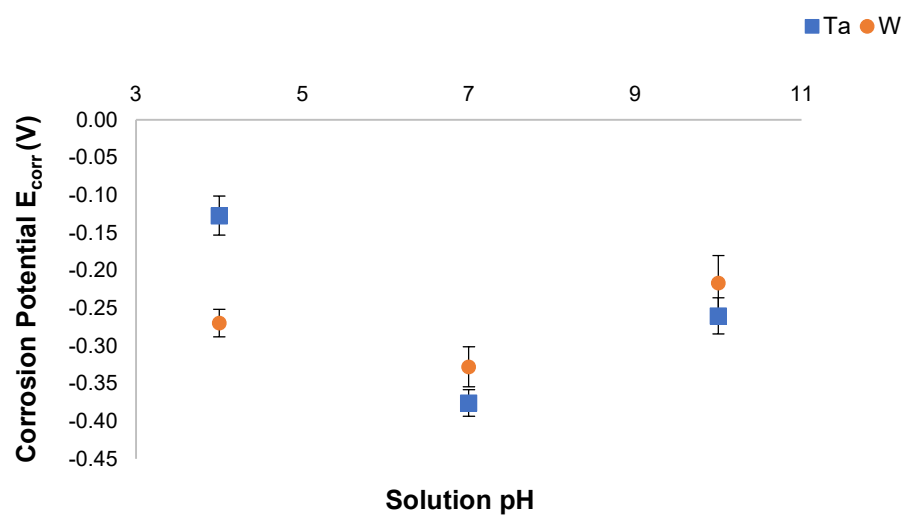


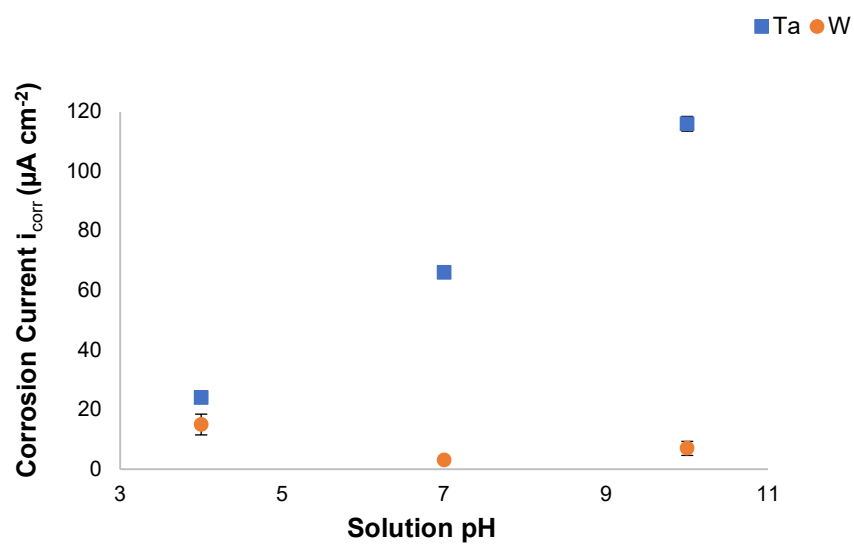
Figure 4.27 Potentiodynamic polarisation plots of tantalum and tungsten under normal impact at different pH solutions and impact velocities:
Ta – (a) 5 ms⁻¹ (b) 9 ms⁻¹;
W – (c) 5 ms⁻¹ (d) 9 ms⁻¹.

Table 4.17 Mean corrosion potentials (E_{corr}) and current densities (i_{corr}) obtained from polarisation plots as shown in Fig. 4.27.

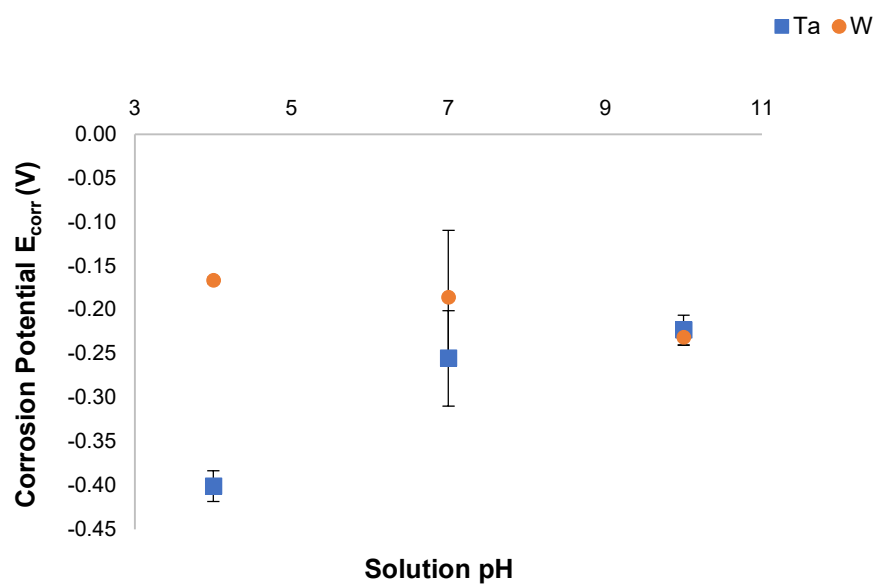
Material	Impact velocity (ms ⁻¹)	pH	Corrosion potential E_{corr} (V)	Corrosion current density i_{corr} (μA cm ⁻²)	Tafel slopes (mV decade ⁻¹)	
					β_a	β_c
Ta	5	4	-0.1271 ± 0.03	24 ± 1.89	232 ± 12	-266 ± 14
		7	-0.3758 ± 0.02	66 ± 0.80	328 ± 42	-230 ± 10
		10	-0.2601 ± 0.02	116 ± 2.45	398 ± 50	-360 ± 91
	9	4	-0.4008 ± 0.02	8 ± 2.36	71 ± 16	-61 ± 10
		7	-0.2552 ± 0.05	2 ± 1.75	59 ± 14	-47 ± 3
		10	-0.2228 ± 0.02	0.3 ± 0.09	34 ± 13	-36 ± 0.4
W	5	4	-0.2696 ± 0.02	15 ± 3.50	172 ± 3	-108 ± 0.2
		7	-0.3278 ± 0.03	3 ± 0.47	73 ± 8	-61 ± 14
		10	-0.2165 ± 0.04	7 ± 2.38	88 ± 26	-57 ± 15
	9	4	-0.1664 ± 0.01	15 ± 1.50	31 ± 0.1	-52 ± 3
		7	-0.1857 ± 0.08	0.1 ± 0.03	37 ± 4	-50 ± 10
		10	-0.2314 ± 0.01	1.4 ± 1.17	42 ± 5	-58 ± 8



(a)



(b)



(c)

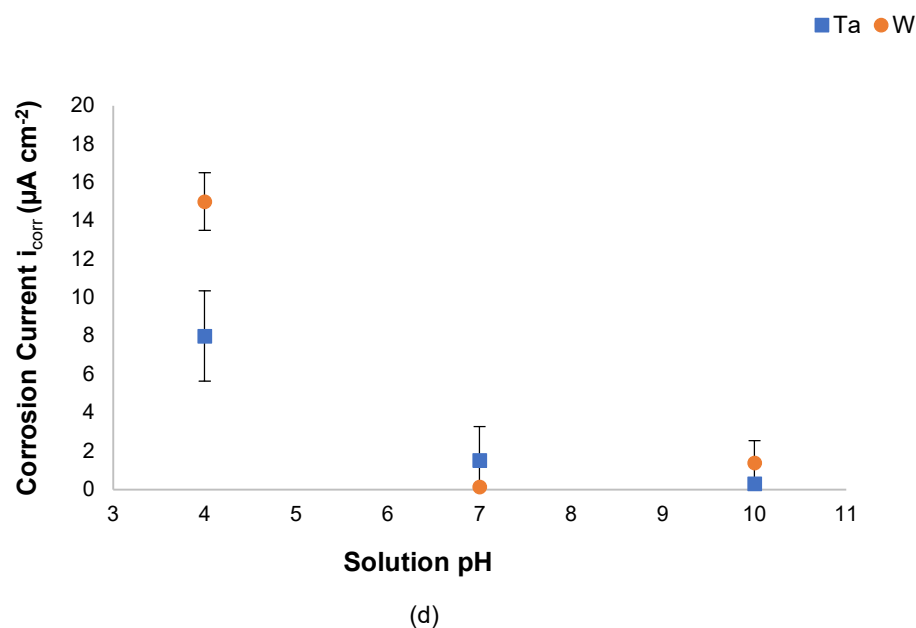


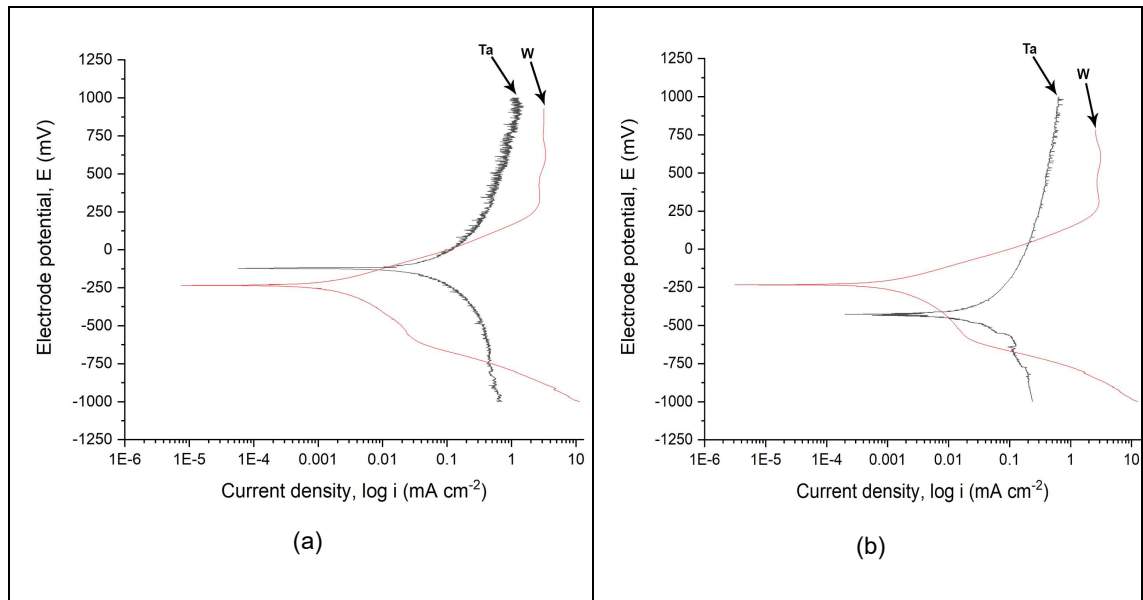
Figure 4.28 Corrosion potential (E_{corr}) and current density (i_{corr}) variation for tantalum and tungsten in various pH solutions under normal impact at:
 5 ms^{-1} – (a) and (b);
 9 ms^{-1} – (c) and (d)

Table 4.17 and Fig. 4.28 shows that under all pH solutions, the tantalum corrosion current densities (i_{corr}) were significantly reduced at 9 ms^{-1} (Fig. 4.28(d)), as compared to their values at 5 ms^{-1} (Fig. 4.28(b)). At pH 4, the i_{corr} value of tungsten remained similar under both impact velocities, while at pH 7 and pH 10, it reduced significantly as the impact velocity changed from 5 ms^{-1} to 9 ms^{-1} (Fig. 4.28(d)).

Table 4.17 also shows Tafel slope values (anodic (β_a) and cathodic (β_c) Tafel slopes), which were obtained from the tantalum and tungsten polarisation plots presented in Fig. 4.27. The Tafel slope values were found to be different at individual experimental conditions. At 5 ms^{-1} , for tantalum, both β_a and β_c values were maximum at pH 10, whereas for tungsten, they were maximum at pH 4. On the contrary, an opposite trend was observed at 9 ms^{-1} , in which, for tantalum, both β_a and β_c values were minimum at pH 10, whereas for tungsten, they were minimum at pH 4.

4.4.2.2 Galvanic measurements based on mixed potential theory

Figure 4.29 shows polarisation plots of tantalum and tungsten obtained under normal impact at different pH solutions and impact velocities. These polarisation plots were obtained separately for tantalum and tungsten, under similar conditions of galvanic (ZRA) experiments, in which tantalum was tested under impinging-jet flow and tungsten under static solution. The separate polarisation plots thus obtained were superimposed to apply mixed potential theory (MPT) [245] to obtain galvanic corrosion potentials (E_{MPT}) and current densities (i_{corr}). Table 4.18 shows mean E_{MPT} and i_{corr} values derived from these superimposed plots; these values are also presented in graphical form in Fig. 4.30.



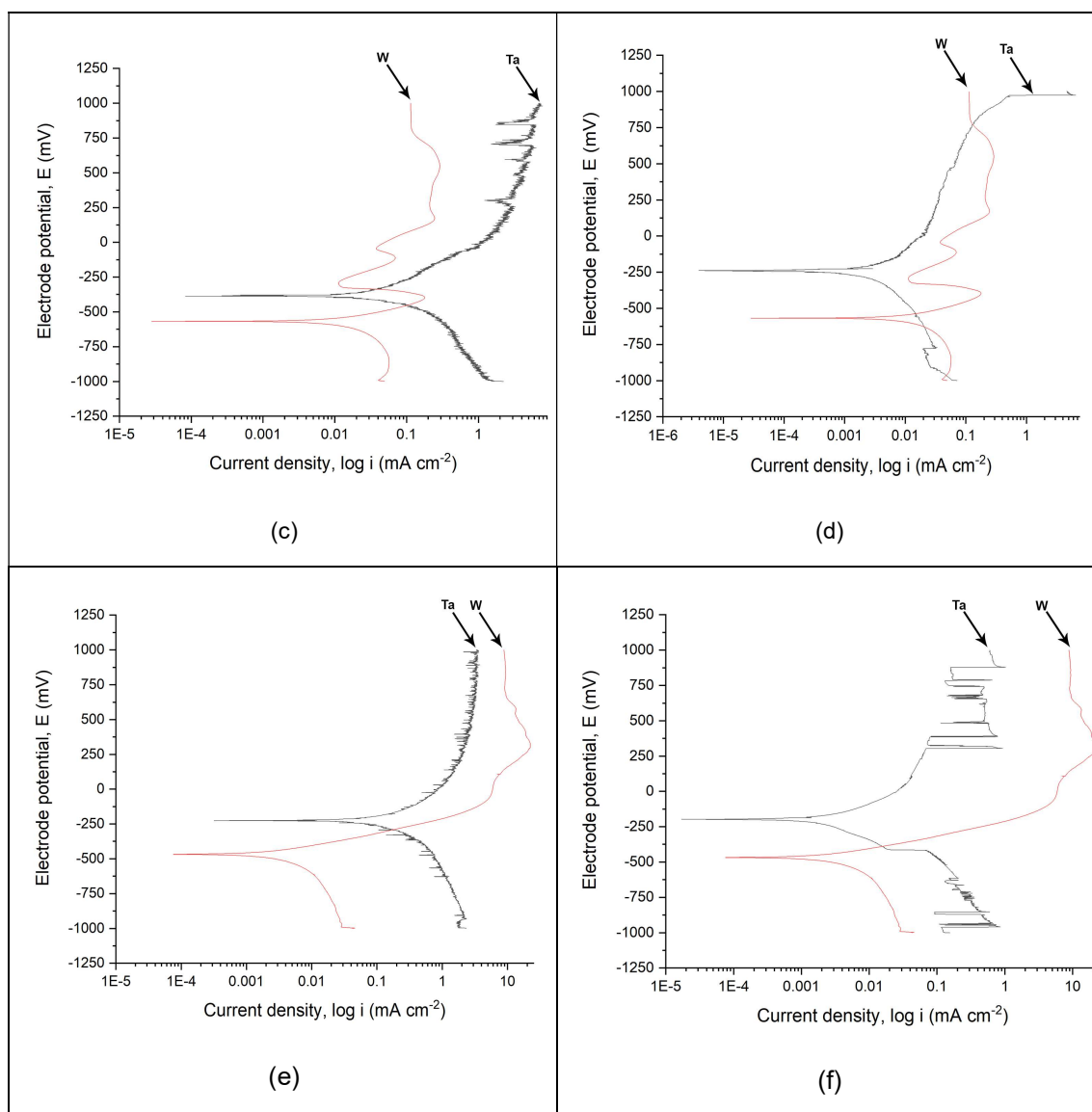
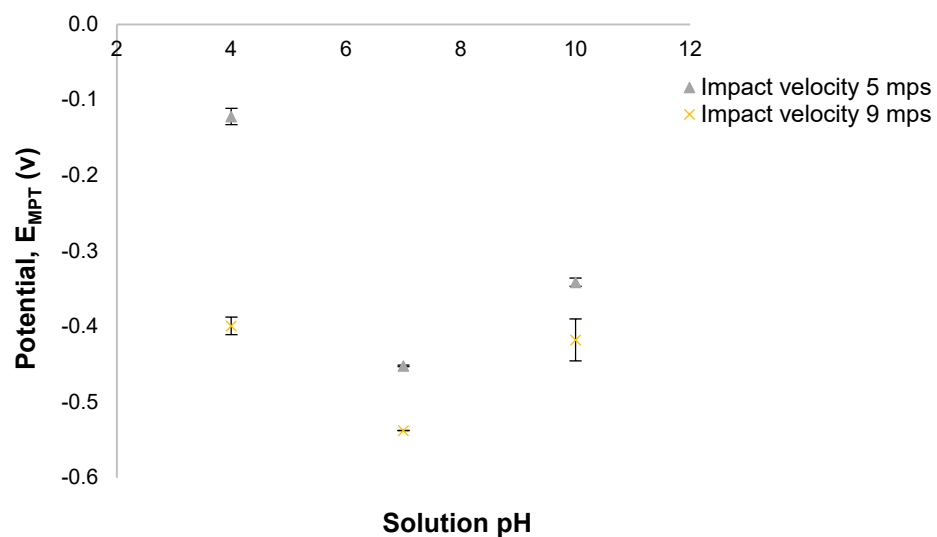


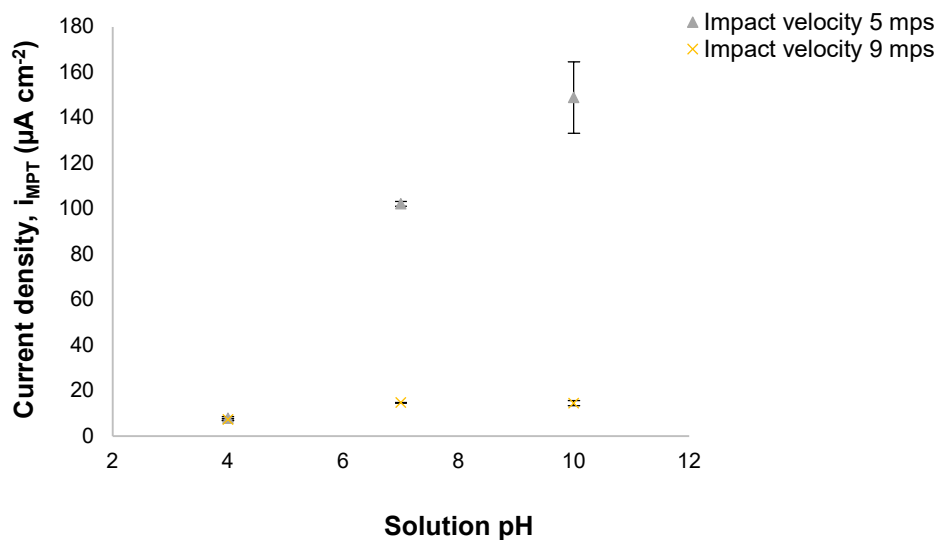
Figure 4.29 Tantalum and tungsten polarisation plots superimposed to obtain galvanic parameters (E_{MPT} and i_{MPT}) under impinging-jet conditions:
 5 ms^{-1} – (a) pH 4 (c) pH 7 (e) pH 10;
 9 ms^{-1} – (b) pH 4 (d) pH 7 (f) pH 10.

Table 4.18 Mean corrosion potentials (E_{MPT}) and current densities (i_{MPT}) obtained from polarisation plots as shown in Fig. 4.28.

Impact velocity (ms^{-1})	Galvanic parameter	pH 4	pH 7	pH 10
5	E_{MPT} (V)	-0.122 ± 0.01	-0.452 ± 0.01	-0.341 ± 0.01
	i_{MPT} ($\mu\text{A cm}^{-2}$)	8 ± 0.75	102 ± 1.05	149 ± 15.65
9	E_{MPT} (V)	-0.399 ± 0.01	-0.538 ± 0.01	-0.418 ± 0.03
	i_{MPT} ($\mu\text{A cm}^{-2}$)	7 ± 0.49	15 ± 0.14	14 ± 1.15



(a)



(b)

Figure 4.30 Variation of galvanic parameters; (a) E_{MPT} (b) i_{MPT} at different pH and impact velocities.

Table 4.18 and Fig. 4.30 show that E_{MPT} was most active (with maximum negative value) in pH 7 and most noble (with maximum positive value) in pH 4, a trend which was similar under both impact velocities. At $5 ms^{-1}$, i_{MPT} was maximum in pH 10, and at $9 ms^{-1}$, it was maximum in pH 7. Under both impact velocities, i_{MPT} was minimum at pH 4. At $5 ms^{-1}$, the i_{MPT} increased significantly with an increased solution pH, a trend which was similar at $9 ms^{-1}$ up to pH 7; i_{MPT} reduced as pH changed from pH 7 to pH 10.

4.4.2.3 Galvanic measurements based on zero resistance ammeter

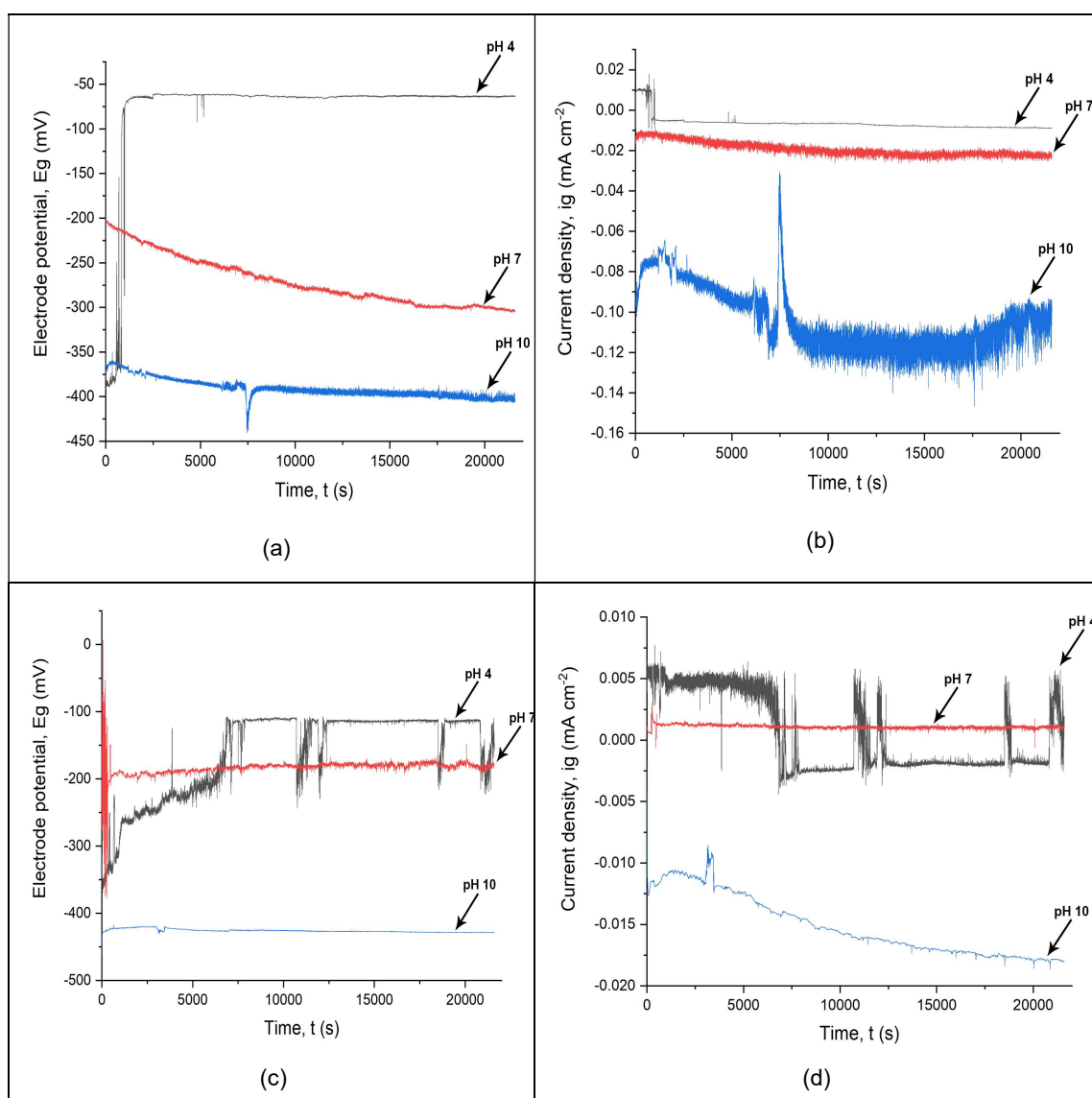


Figure 4.31 Galvanic potentials (E_g) and current densities (i_g) obtained in ZRA experiments at different pH solutions and impact velocities:
 5 ms^{-1} – (a) and (b);
 9 ms^{-1} – (c) and (d).

Table 4.19 Mean galvanic potentials (E_g) and absolute current densities $|i_g|$ obtained from ZRA plots as shown in Fig. 4.29.

Impact velocity (ms^{-1})	Galvanic parameter	pH 4	pH 7	pH 10
5	E_g (V)	-0.072 ± 0.01	-0.270 ± 0.01	-0.390 ± 0.01
	$ i_g $ ($\mu\text{A cm}^{-2}$)	8 ± 1.50	20 ± 0.73	113 ± 9
9	E_g (V)	-0.266 ± 0.04	-0.189 ± 0.01	-0.422 ± 0.01
	$ i_g $ ($\mu\text{A cm}^{-2}$)	7 ± 1.50	1 ± 0.07	18 ± 0.50

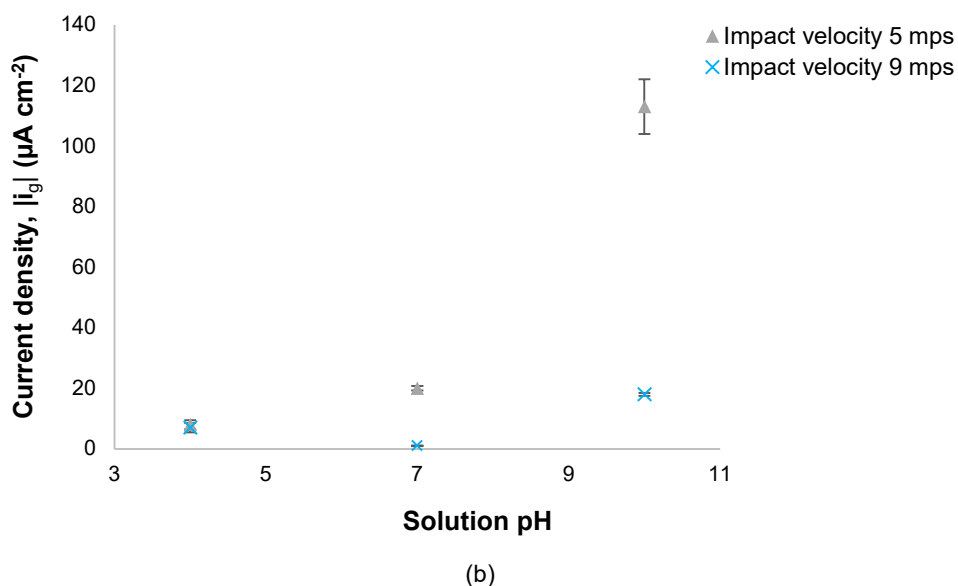
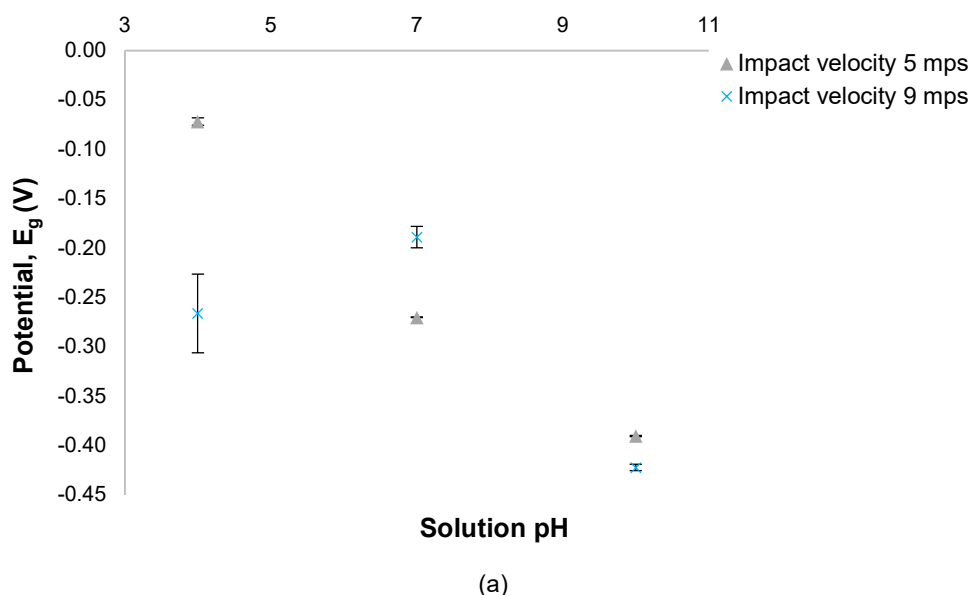


Figure 4.32 Variation of galvanic parameters; (a) E_g (b) i_g at different pH and impact velocities.

Figure 4.31 shows potential and current profiles for tantalum and tungsten couple, obtained at different pH and impact velocities in ZRA experiments. The figure shows low and high amplitude signals (current/voltage) in short and long period transients. The mean galvanic potential (E_g) and absolute current density ($|i_g|$) values, obtained for whole experimental duration (6 h), are shown in Table 4.19. For ease of understanding, these values are also presented in graphical form in Fig. 4.32.

Table 4.19 and Fig. 4.32 show that galvanic potential (E_g) was most noble (with lower negative value) at pH 4 and 5 ms^{-1} and it was also most noble at pH 7 and

9 ms⁻¹. Further examination of Table 4.19 reveals that at 5 ms⁻¹, E_g became active (with higher negative values) as the solution pH continually increased from pH 4 to pH 10. Whereas at 9 ms⁻¹, a mixed trend was observed; E_g became noble at pH 7 and then active at pH 10. Under both impact velocities, absolute current density ($|i_g|$) was maximum at pH 10. At 5 ms⁻¹, $|i_g|$ was minimum at pH 4, and at 9 ms⁻¹, it was minimum at pH 7. At 5 ms⁻¹, $|i_g|$ increased significantly with an increased solution pH, however, at all pH, $|i_g|$ reduced as impact velocity changed to 9 ms⁻¹.

Table 4.20 summarises data obtained in potentiodynamic and galvanic corrosion measurements (MPT and ZRA) for tantalum and tungsten. The Table shows one of the parameters as (E_{corr_c} – E_{corr_a}), in which E_{corr_c} and E_{corr_a} denote the corrosion potentials of the cathode and anode, respectively. For the tantalum-tungsten galvanic couple considered here, the anode and cathode material in the galvanic couple was determined based on the potentiodynamic polarisation behaviour for the individual metal, as shown in Fig. 4.27. The differences of E_{corr_c} – E_{corr_a}, in the range of 0.10 to 0.13 V are necessary indicators for a significant galvanic impact [254,255]. Table 4.20 indicates that the (E_{corr_c} – E_{corr_a}) value is significant only at pH 4 not at pH 7 and pH 10. This trend was consistent for both 5 ms⁻¹ and 9 ms⁻¹ impact velocities.

Table 4.20 also shows the ratio $\frac{|i_g|}{|i_{corr_a}|}$ in which $|i_{corr_a}|$ is the absolute current density of the anodic member of the galvanic couple. This ratio value of less than 5 indicates the compatibility between the members in a galvanic couple [254,256,257]. As shown in the Table, at 9 ms⁻¹ and pH 10, the $\frac{|i_g|}{|i_{corr_a}|}$ value was more than 5 which indicates incompatibility between tantalum and tungsten pair; therefore the galvanic corrosion between the pair will be severe. For all other conditions, $\frac{|i_g|}{|i_{corr_a}|}$ value was less than 5 which indicates tantalum and tungsten are compatible and galvanic corrosion was not severe between them.

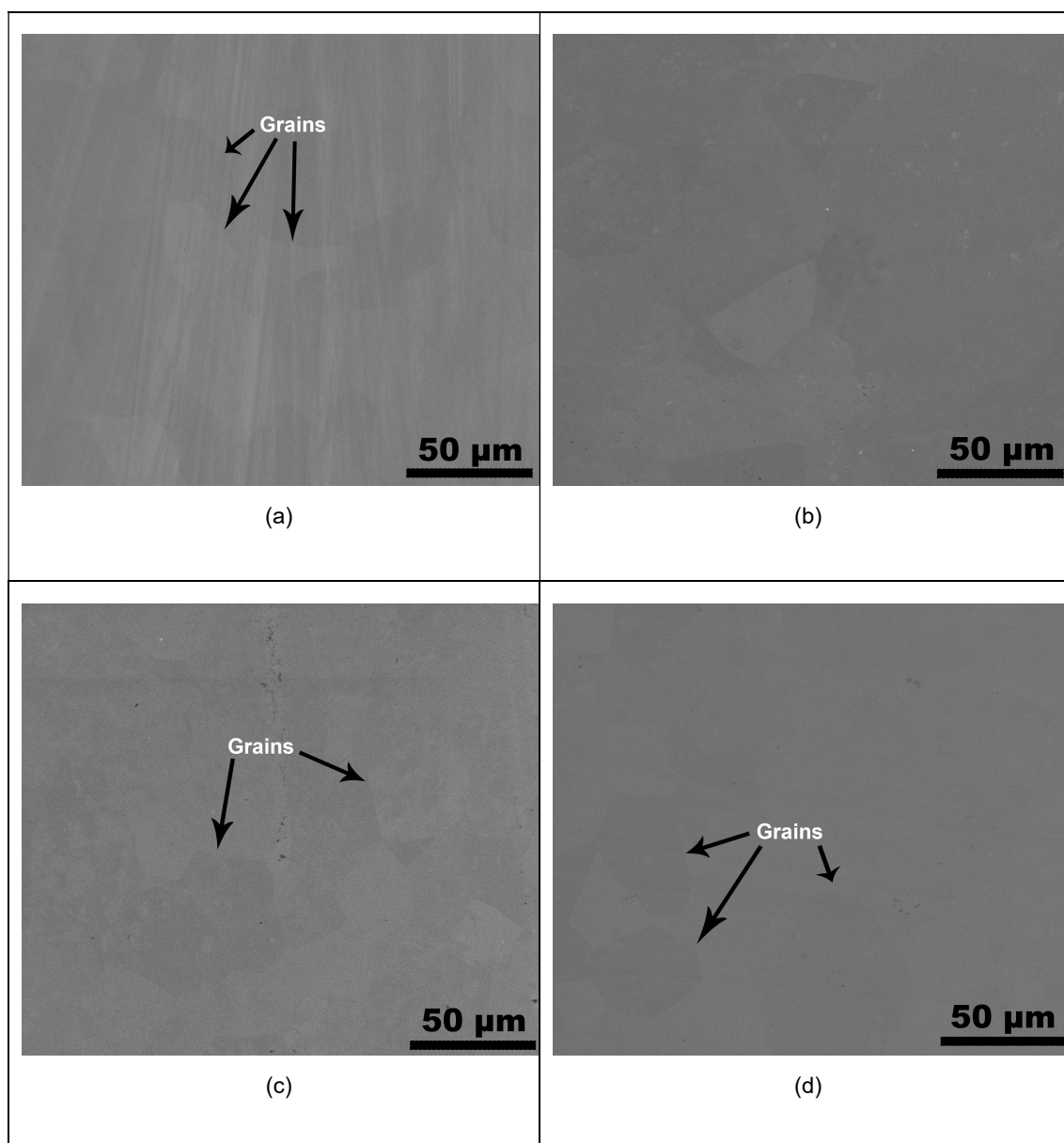
Table 4.20 Potentiodynamic and galvanic data summary for tantalum and tungsten under normal impact at different pH solutions and impact velocities.

Impact velocity (ms ⁻¹)	Parameter	pH 4	pH 7	pH 10
5	E _{corr-Ta} (V)	-0.127 ± 0.03	-0.376 ± 0.02	-0.260 ± 0.02
	E _{corr-W} (V)	-0.270 ± 0.02	-0.328 ± 0.03	-0.217 ± 0.04
	E _{MP} (V)	-0.122 ± 0.01	-0.452 ± 0.01	-0.341 ± 0.01
	E _g (V)	-0.072 ± 0.01	-0.270 ± 0.01	-0.390 ± 0.01
	E _{corr_c} – E _{corr_a} (V)	0.143	0.048	0.044
	i _{corr-Ta} (μA cm ⁻²)	24 ± 1.89	66 ± 0.80	116 ± 2.45
	i _{corr-W} (μA cm ⁻²)	15 ± 3.50	3 ± 0.47	7 ± 2.38
	i _{MP} (μA cm ⁻²)	8 ± 0.75	102 ± 1.05	149 ± 15.65
	i _g (μA cm ⁻²)	8 ± 1.50	20 ± 0.73	113 ± 9
	$\frac{ i_g }{ i_{corr,a} }$	0.5	0.3	1
9	E _{corr-Ta} (V)	-0.401 ± 0.02	-0.255 ± 0.05	-0.223 ± 0.02
	E _{corr-W} (V)	-0.166 ± 0.01	-0.186 ± 0.08	-0.231 ± 0.01
	E _{MP} (V)	-0.399 ± 0.01	-0.538 ± 0.01	-0.418 ± 0.03
	E _g (V)	-0.266 ± 0.04	-0.189 ± 0.01	-0.422 ± 0.01
	E _{corr_c} – E _{corr_a} (V)	0.234	0.070	0.009
	i _{corr-Ta} (μA cm ⁻²)	8 ± 2.36	2 ± 1.75	0.3 ± 0.09
	i _{corr-W} (μA cm ⁻²)	15 ± 1.50	0.1 ± 0.03	1.4 ± 1.17
	i _{MP} (μA cm ⁻²)	7 ± 0.49	15 ± 0.14	14 ± 1.15
	i _g (μA cm ⁻²)	7 ± 1.50	1 ± 0.07	18 ± 0.50
	$\frac{ i_g }{ i_{corr,a} }$	0.9	0.7	13

4.4.2.4 SEM micrographs and mass loss measurements

Fig. 4.33 and Fig. 4.34 show the SEM images of tantalum and tungsten samples after galvanic corrosion experiments (ZRA) at different pH solutions and impact velocities. Figure 4.33 shows that the effect of galvanic corrosion on tantalum was less pronounced with grains visible under all conditions of pH and impact velocities. On the other hand, Fig. 4.34 shows that tungsten was significantly affected by the galvanic corrosion and revealed various features such as grain boundary attack and dissolution damage (indicated by arrows). At both 5 ms⁻¹ and 9 ms⁻¹ impact velocities, these features were dominant at pH 4 and pH 10, but not at pH 7.

Fig. 4.33(f) and Fig. 4.34(f) show that on both tantalum and tungsten samples, respectively, there exist some visible stains which may be the result of incomplete cleaning that led to the drying marks of residual final polishing suspension (colloidal silica).



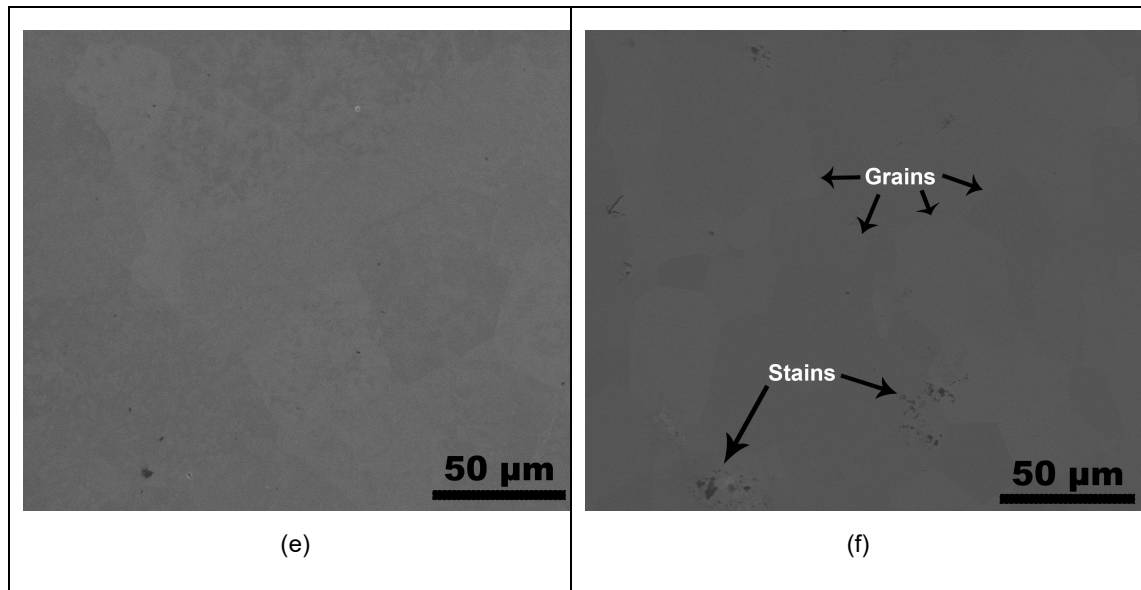
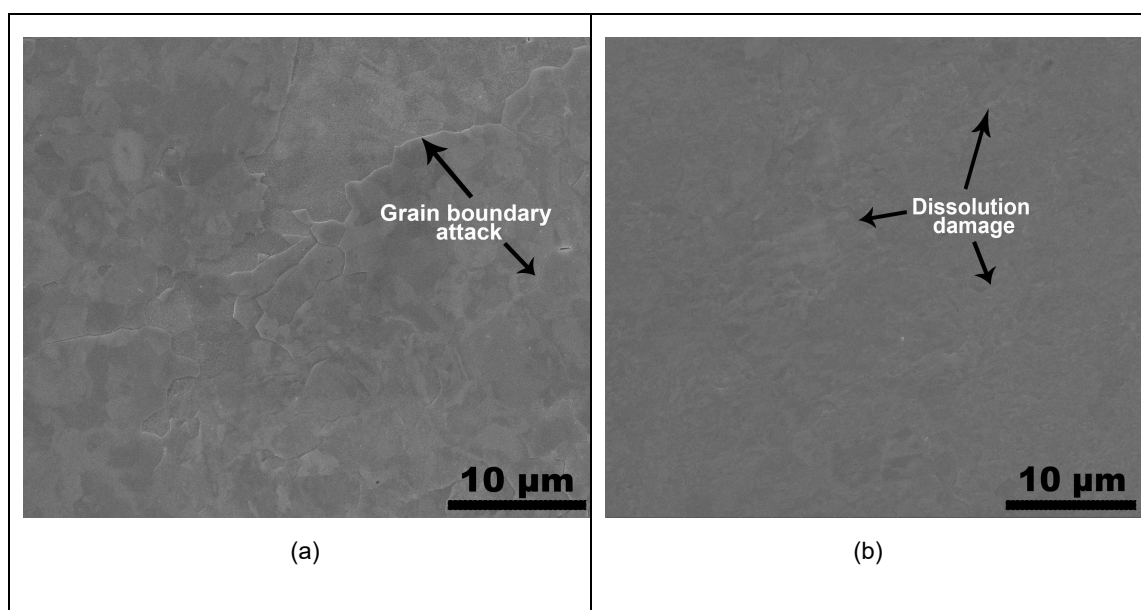


Figure 4.33 SEM images of tantalum specimens after ZRA experiments at different pH solutions and impact velocities:
 5 ms⁻¹ – (a) pH 4 (c) pH 7 (e) pH 10;
 9 ms⁻¹ – (b) pH 4 (d) pH 7 (f) pH 10.



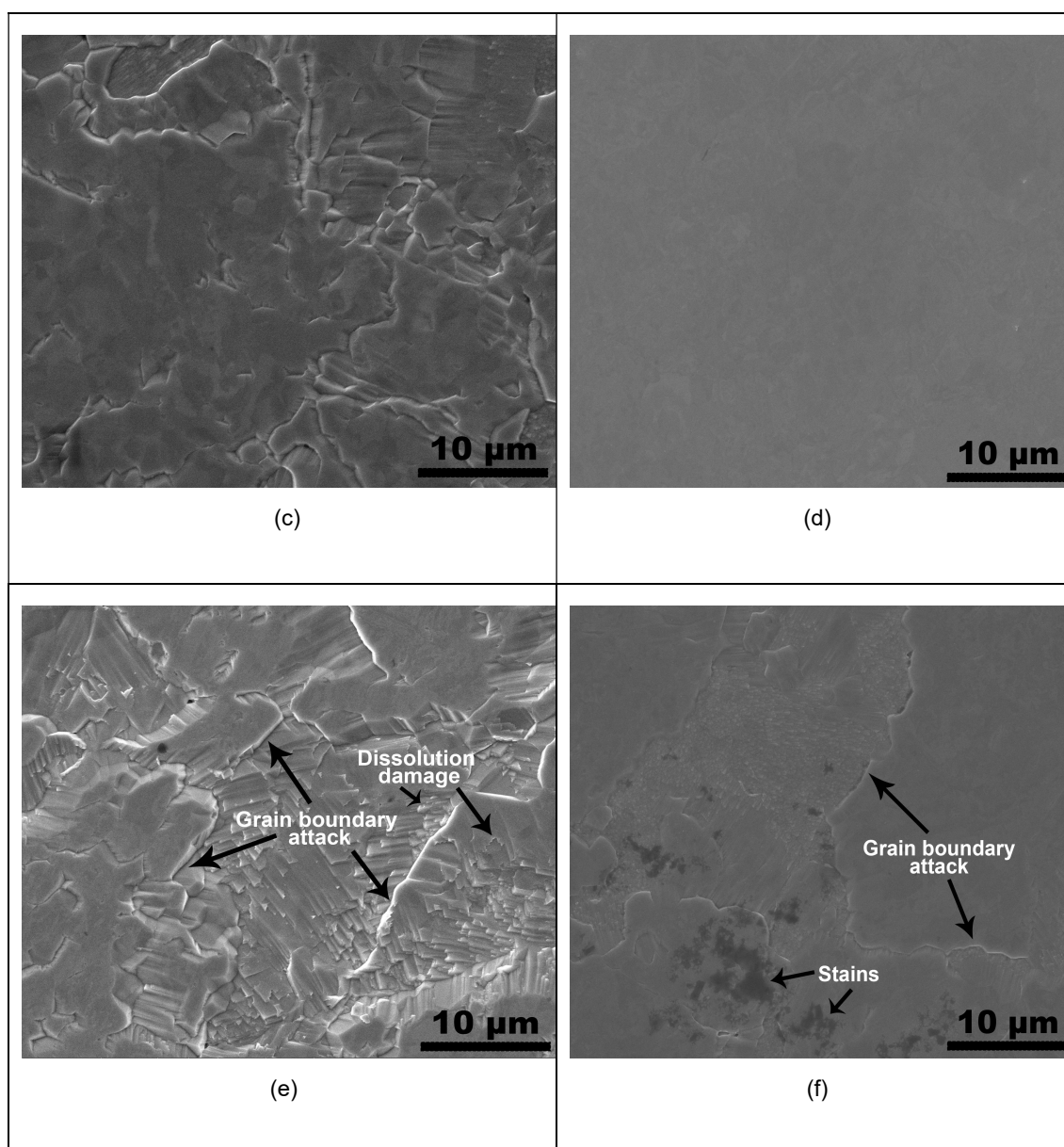


Figure 4.34 SEM images of tungsten specimens after ZRA experiments at different pH solutions and impact velocities:
 5 ms^{-1} – (a) pH 4 (c) pH 7 (e) pH 10;
 9 ms^{-1} – (b) pH 4 (d) pH 7 (f) pH 10.

Table 4.21 Mass loss measurements of tantalum and tungsten specimens.

Impact velocity (ms^{-1})	Material	Mass loss (g) $\times 10^{-4}$ (in pH 4)	Mass loss (g) $\times 10^{-4}$ (in pH 7)	Mass loss (g) $\times 10^{-4}$ (in pH 10)
5	Tantalum	1 ± 0.1	1 ± 0.1	1 ± 0.1
	Tungsten	2 ± 0.3	1 ± 0.3	6 ± 0.4
9	Tantalum	0 ± 0.1	1 ± 0.1	1 ± 0.1
	Tungsten	4 ± 0.2	2 ± 0.2	2 ± 0.2

Table 4.21 shows mass loss measurements which were performed on tantalum and tungsten specimens, after the ZRA experiments. As shown in the table, at 5 ms⁻¹, tungsten suffered a maximum mass loss at pH 10; whereas at 9 ms⁻¹, it suffered a maximum mass loss at pH 4. On the contrary, at all pH and impact velocities, tantalum suffered minimum damage which clearly shows it being cathodically protected during galvanic corrosion with tungsten in ZRA experiments.

Chapter-5

Discussion

5.1 Introduction

The results of this study are discussed in the following three sections:

1. Erosion of tantalum.
2. Erosion-corrosion of tantalum.
3. Flow-assisted galvanic corrosion of tantalum and tungsten.

Several interesting features have been identified from the results shown in the previous chapter. This chapter discusses their relevance in the context of published literature.

5.2 Erosion of tantalum

5.2.1 Effect of impact angle

As observed in Fig. 4.7 (erosion rate versus slurry impact angle), the peak erosion rate was obtained at 30° impact angle. As the impact angle was further increased, the erosion rate declined with a significant reduction at 90° as compared to that at 30°. This finding is in line with the published data available in the literature for the erosion of ductile metals under dry particulate erosion conditions [30,258]. This literature data typically shows that the peak erosion rate occurs at an impact angle between 20-30° and that its value falls to one-half to one-third at 90° impact angle.

5.2.2 Effect of particle concentration

As observed in Fig. 4.9 (erosion rate versus SiC slurry concentration), under both 30° and 90° impact angles, the erosion initially increased until it reached a concentration of 7 wt.%, after which it declined at 10 wt.%. Although one might anticipate the erosion rate to rise with the increase in slurry concentration [259,260], the observed decrease in erosion at higher slurry concentrations of 10 wt.% could be attributed to a mix of test geometry effects and/or a 'shielding effect' [54,56,58,59]. Despite the rise in the particle concentration and the consistent sample distance of 15 mm from the exit nozzle, not all particles are expected to make contact with the sample surface. The SiC particles that hit the target material surface at any given time may protect or shield the same surface from the impacts of subsequent particles [54]. This 'shielding effect', coupled with some particle interaction (stemming from the change of a lamellar jet to a turbulent one at the surface), could account for the decrease in erosion rate. At a lower impact angle (30°) conditions, the test geometry leads to a noticeable

sliding action of the particles, as opposed to a full-on surface-particle interaction. This could explain the decrease in the erosion rate and the larger error margins under these conditions.

5.2.3 Effect of impact velocity

As observed in Fig. 4.10 (erosion rate versus impact velocity), the rate of erosion increased linearly with impact velocity except for conditions with 30° impact angle and 3 ms⁻¹ impact velocity. In contrast to dry erosion tests, which typically occur at a high strain rate, slurry erosion occurs at significantly lower strain rate, particularly for the velocity range (up to 5 ms⁻¹) examined in this study [261,262]. As a result, thermal induced deformation is not expected in the mechanism of slurry erosion, rather the mechanism was solely governed by local mechanical deformation at the impact point, which increases with impact velocity. Hence, the erosion rate also increased with impact velocity, as shown in Fig. 4.10.

Further scrutiny of Fig. 4.3 reveals that the erosion rate deviated from the general trend at 3 ms⁻¹, for both 30° and 90° impact angles. Under these conditions, the test samples might have some fractured erodent particles embedded in the matrix or caught beneath the plastically deformed materials and voids, leading to an apparent mass gain. This could potentially account for the substantial error margins observed in these test conditions. The mass gain was notably more pronounced at a lower impact velocity of 3 ms⁻¹ and impact angle of 30°. This could be associated with the distinct erosion mechanism observed for the tantalum specimens (elaborated in the following sections). Figure 4.10 also indicates that the intensity of the erosion loss is greater at 30° compared to 90° impact. This aligns with the trend seen earlier for erosion loss as a function of impact angle (Fig. 4.7).

5.2.4 Comparison with reference aluminium sample

As observed in Fig. 4.8 (erosion rate versus impact angle for tantalum and aluminium reference material), the erosion rate of tantalum was found to be significantly higher than that of aluminium at both impact angles tested. This could be attributed to the fact that the measured hardness of aluminium (100 HV₅) was higher than that of tantalum (89 HV₂), by a factor of 1.1. Therefore, it is expected that aluminium would exhibit higher erosion resistance. However, the high

erosion loss for tantalum specimens can also be attributed to its unique material removal mechanisms, as described in subsequent sections.

5.2.5 SEM micrographs - wear scar analysis

5.2.5.1 Effect of impact angles

Fig. 4.11 and Fig. 4.12 show SEM images of wear scars formed on both tantalum and aluminium samples at 30° and 90° impact angles, respectively.

At 30° impact angle, the wear scars were primarily influenced by the cutting and ploughing mechanisms [41]. The cutting mechanism was categorised into Type-1 and Type-2 by angular erodent particles with sharp edges. Type-1 cutting occurs when particles hit the target surface and roll forward, resulting in an indentation and a raised lip. On the other hand, Type-2 cutting happens when erodent particles roll backwards, leading to micromachining of the target surface and forming a smooth wear scar. Additionally, ploughing occurs when the blunt edges of the erodent particles push material to the sides and front, resulting in a raised or extruded lip.

At 30° impact angle, the wear scars formed on the tantalum specimens, as shown in Fig. 4.11(d) and Fig. 4.11(e), showed Type-1 cutting (with visible raised lips) and Type-2 cutting along the path of erodent impact. In addition, there were abundant voids present on the tantalum samples. Whereas, the wear scars on the aluminium specimen, as shown in Fig. 4.12(c) and Fig. 4.12(d), displayed signs of cutting (both Type-1 and 2) and ploughing, but no traces of voids or cavities were observed.

At 90° impact angle, the wear scars formed on both tantalum and aluminium samples, as shown in Fig. 4.11(a-c) and Fig. 4.12(a-b), revealed signs of plastic deformation and formation of hill-and-valley surface topology, which align with the erosion mechanism for typical ductile materials at normal impact angles [241,263]. These mechanisms are further described in section 5.2.7.

5.2.5.2 Effect of slurry concentration

Figure 4.13 shows the effect of slurry concentration on the formation of wear scars for both tantalum and aluminium at 90° and 30° impact angles. At 90°, when

slurry concentration was increased from 5 wt.% to 7 wt.%, as seen in Fig. 4.13(a-b) and Fig. 4.11(a-b), respectively, the wear scars appear smoother at higher concentrations (7 wt.%) due to increased lip breakage, as shown in Fig. 4.11(b). This excessive lip breakage also contributes to the greater erosion loss observed at 7 wt.% compared to 5 wt.% (Fig. 4.9). As anticipated, wear mechanisms at both 5 wt.% and 7 wt.% were dominated by plastic deformation (featuring hill-and-valley surface topology), however, the grain boundary cracks are more noticeable at 7 wt.% than at 5 wt.% for 90° impact.

The effect of slurry concentration at 30° impact angle is also more pronounced (in terms of lip breakage severity) when the SiC concentration is increased from 5 wt.% to 7 wt.%, as seen in Fig. 4.13(c-d) and Fig. 4.11(d-e), respectively. As anticipated, the wear scars formed under both concentrations exhibit similar cutting and ploughing mechanisms with numerous voids/cavities. However, along the cutting/ploughing path, more extruded lips are observed at a lower concentration of 5 wt.%, as seen in Fig. 4.13(c) and Fig. 4.13(d), than at 7 wt.%, as seen in Fig. 4.11(a) and Fig. 4.11(b); this suggests that the severity of lip breakage increases with SiC concentration. Consequently, a higher mass loss is recorded at 7 wt.% compared to 5 wt.% for 30° impact angles.

5.2.6 Erosion mechanisms

5.2.6.1 Formation of voids/cavities

In the context of slurry erosion, particularly at lower velocities (up to 5 ms⁻¹), a significant particle rebound effect is anticipated [264]. As a result, the slurry erosion process is likely to involve a low strain rate, leading to a condition akin to quasi-static indentation. Therefore, tantalum was assessed under different static Vickers hardness loads, as shown in Fig. 4.14.

Figure 4.14 provides a clear evidence of grain boundary sliding, which escalated as the indentation load increased from 1 kgf to 5 kgf. This grain boundary sliding can be attributed to the movement of high-angle grain boundaries present in the tantalum microstructure (Fig. 4.1). The creation of voids/cavities due to grain boundary sliding has been the subject of extensive prior research; it is believed to occur only under a low strain rate condition [265]. In this study, given the test conditions involved a low strain rate associated with the slurry impact velocity of

only up to 5 ms^{-1} , grain boundary sliding is suggested to be the primary mechanism for the formation of most voids/cavities at both 90° and 30° impact angles.

The growth and coalescence of voids due to repeated slurry impacts were visible, particularly in the area where a complete grain had been dislodged, as shown in the high-resolution SEM micrographs (indicated in Fig. 4.11(c)). The areas where grains were dislodged appeared as cavities when viewed at lower magnification (Fig. 4.13(a) and Fig. 4.13(b)). The expansion and merging of these voids also led to the large cracks observed along the grain boundaries in the SEM images (Fig. 4.11(a)). The dislodgement of grains played a significant role in the total erosion loss of the tantalum specimens examined in this study (this will be further discussed in the following sections).

A closer examination of the high-resolution SEM images (Fig. 4.11(c) and Fig. 4.11(f)) revealed that these voids/cavities were distributed across the eroded surface, including the raised areas (or extruded lips) and the depressions (or impact craters), regardless of the impact angle. This indicates that some of these voids remained microscopically small under the test conditions and did not grow sufficiently to cause void merging and subsequent grain dislodgement. The direct impact of 'lip weakening' due to these voids and its removal due to subsequent impacts was challenging to measure.

It is also known that voids/cavities in deformed metals can form due to the movement of low-angle grain boundaries, particularly at the triple point [266]. However, this mechanism typically operates at high strain rates, much higher than those available for slurry erosion, and is therefore not anticipated under the slurry erosion conditions used in this study.

5.2.6.2 Material removal mechanisms

The primary mechanisms for removing material from the surface of tantalum were identified as plastic deformation at normal impact angles, and cutting and ploughing at oblique impact angles. Additionally, grain dislodgement due to void coalescence was a significant material removal mechanism at both impact angles. However, the individual contributions of these mechanisms could not be quantified in this study.

Fig. 4.11(a) and Fig. 4.11(b) revealed that plastic deformation at normal impact angles resulted in a hill-and-valley surface topology on the tantalum specimens. This is similar to the classical ductile material erosion mechanism observed on the reference aluminium specimen (see Fig. 4.12(a) and Fig. 4.12(b)). However, voids/cavities were an additional feature unique to the tantalum specimens.

Material removal under normal impact can occur through several well-established theories [51,84,85]. The primary mechanism of material removal from the tantalum specimens was identified as lip breakage from the “hills” region, particularly noticeable when the SiC concentration increased from 5 wt.% (see Fig. 4.13(a) and Fig. 4.13(b)) to 7 wt.% (see Fig. 4.12(a) and Fig. 4.12(b)). The removal of material from the “valleys” can be a possibility, however, it was not evident in this study. Additionally, complete grain dislodgement was observed at normal impact angles (see Fig. 4.11(c)), likely due to void nucleation and coalescence, especially at the high-angle grain boundary.

At oblique impact angles, the mechanism was identified as cutting and ploughing, as seen in the SEM images for the tantalum specimen (see Fig. 4.11(d) and Fig. 4.11(e)). This is similar to the typical ductile material erosion observed for the reference aluminium specimen (see Fig. 4.12(c) and Fig. 4.12(d) [41]). However, voids/cavities were again a prominent feature unique to tantalum at oblique impact angles (see Fig. 4.11(f)). The mechanisms that prevailed at oblique impact angles are described earlier in detail in section 5.2.5.1.

5.2.6.3 Eroducts embedment in the substrate

The hardness of the tantalum specimens used in this study was 873 MPa, while the SiC particles had a hardness of 25,500 MPa. Therefore, it is speculated that the impact of the particle on particle breakage would be minimal. However, small quantities and sizes of fragmented erodent particles, a few hundred nanometers in dimension, were found embedded in the target, leading to some mass gain by the specimen under certain test conditions (see Fig. 4.10). Other researchers have also reported mass gain due to erodent embedment [266,267]. In this study, fragmented SiC erodents were discovered locked in the grain boundary cavities/voids (see Fig. 4.11(b)). Given the size of the voids (around 1–2 μm) compared to the erodent (500–710 μm), the embedded particles were fragmented erodent particles, likely generated due to particle interactions within

the rig. The fragmented erodents could also become embedded inside the subsurface of a healthy grain, considering the hardness difference between the two [266]. However, it was not possible to identify any such entrapment of sharp and minuscule particles in this study.

5.3 Erosion-corrosion of tantalum

5.3.1 Effect of particle bombardment on polarisation curves

Figure 4.15 (electrode potential versus current density) and Table 4.5 show that both solution pH and the impact of particles considerably influenced corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values.

As observed in Fig. 4.15(a) at 30° impact angle of the solution jet (without particles), E_{corr} is least negative (or most noble) at pH 4, whereas, it is most negative (or most active) at pH 7. And a value in between these E_{corr} values was observed at pH 10. These E_{corr} and corresponding i_{corr} values, as shown in Table 4.5, are representative of the stability of the tantalum pentoxide (Ta_2O_5) passive layer formed on the tantalum surface, which is a few nanometres in range [268]. The evidence of passive layer stability is further supported by the polarisation curve (Fig. 4.15(a)) obtained in this study, which indicated that under anodic conditions, the corrosion of the sample occurred either through the removal of the inherent passive layer by the flowing solution or the dissolution of the passive layer/substrate.

As observed in the polarisation curves (Fig. 4.15(b)) at 30° impact angle of aqueous slurry (with particle), a noticeable decrease in corrosion resistance was found, with a substantial cathodic shift in the E_{corr} values (ranging from –400 mV to –500 mV) seen across all pH levels (Table 4.5). This negative shift in the E_{corr} values is likely due to the erosion of the inherent passive layer caused by particle bombardment, similar to the negative shift seen in OCP values for passive metals under tribocorrosive conditions as reported in the literature [269,270]. As the anodic potentials rose from –250 mV to +1000 mV, there was a steady increase in current densities, though the shape and slope of the curves remained relatively unchanged across different pH levels. This suggests that the mechanical component, i.e., material removal through particle bombardment, was predominant, significantly inhibiting the repassivation of the material surface.

As observed in the polarisation curves (Fig. 4.15(c)) at 90° impact angle of solution jet (without particles), the E_{corr} values and the trends it followed were nearly identical to those observed for experiments at 30° impact angle without particles (Fig. 4.15(a)), indicating that the angle of impact did not significantly influence the E_{corr} values when particle bombardment was not involved.

As observed in the polarisation curves (Fig. 4.15(d)) at 90° impact angle of aqueous slurry (with particle), a significant cathodic shift in the E_{corr} values (also within the -400 mV to -500 mV range) was noted, however, the variation in their absolute values across different pH solutions was less noticeable. The findings suggest that the synergistic or additive interaction between the erosion and corrosion processes of material removal due to particle bombardment (i.e. the mechanical component of erosion) at 90° impact angle was less pronounced compared to that at 30° impact angle. This reduced synergy between erosion and corrosion processes could be responsible for the lower erosion rates observed at 90° impact angle; hence the mixed trends were observed in the E_{corr} values.

Table 4.5 shows the i_{corr} values measured at different solution pH, and these were found to be rather complex and indistinct.

At 30° impact angle for pH 4 and pH 7, a significant increase in i_{corr} values was found for erosion-corrosion conditions (with particles in solution), compared to that at pure corrosion conditions (without particles in solution). Conversely, at pH 10, there was a significant reduction in i_{corr} value relative to pure corrosion conditions, the cause of which is unknown. In general, corrosion current densities at 90° impact (for both with and without particles) were higher than those at 30° impact. The findings imply that the tests geometries may have significantly influenced the corrosion current densities. For example, in pure corrosion conditions, at 90° impact, the exposed area of the specimen would have been subjected to the full force of the solution, receiving a higher concentration of corrosive species compared to 30° impact angle. As a result, higher corrosion current densities were observed in pH 4 and pH 7 at 90° impact, as compared to that at 30° impact.

5.3.2 Effect of pH on erosion-corrosion rate

As observed in Fig.4.17 (erosion-corrosion rate versus pH and impact angle), the erosion-corrosion rate (K_{ec}) is dependent on both solution pH and impact angles. At 30° impact angle, K_{ec} values were significantly higher as compared to that at 90° impact angle. This aligns with the ductile erosion behaviour of tantalum as reported in Fig. 4.7. The results for 30° impact angle also showed a dependency on the solution pH. The K_{ec} values for pH 7 and pH 10 were lower compared to pH 4. The higher K_{ec} value for pH 4 was noteworthy, especially considering that under pure corrosion conditions (without particles), this pH value had the most noble E_{corr} value (Fig. 4.15(a)). However, pH 4 also exhibited higher current densities for tantalum under particle bombardment, as shown in Table 4.5. These findings suggest that at pH 4, the passive layer(s) formed in the potential range studied (–150 mV to +250 mV) were not sufficient in providing adequate corrosion protection; they were either porous or mechanically weak and were easily removed by particle bombardment. The K_{ec} values for pH 7 and pH 10 were in a similar range indicating that passive layers formed under these conditions had similar electrochemical and physiochemical properties. In comparison to pure erosion rates of tantalum (as shown in Fig. 4.19(a) at 30°), the erosion-corrosion rate (as shown in Fig. 4.17 at 30°) was 3.3 times higher for pH 4, 2.2 times higher for pH 7, and 1.9 times higher for pH 10.

At 90° impact angle, the effect of K_{ec} on pH was less noticeable as compared to that at 30° impact angle. At smaller impact angles (< 45°), the cutting mechanism was a primary factor, leading to greater material removal. However, for larger and normal impact angles, plastic deformation was the main factor, requiring multiple particle impacts to eventually dislodge the material through fatigue or fracture [41,51,271]. In addition, the substrate material is likely to undergo work-hardening at normal impact, causing reduced material loss [271].

These findings suggested that the erosion of the material surface layer(s), including any passive layers formed, was more effective at 30° impact angle than at 90°. As a result, the K_{ec} values at 90° showed a minimal dependency on pH value, indicating that the damage caused by the bombarding particles was not sufficient to proficiently remove the surface layers, thereby reducing the interaction between erosion and corrosion.

5.3.3 Erosion-corrosion mechanisms

Figure 4.22 shows SEM images of the wear scars formed on the tantalum surface after erosion-corrosion experiments at different pH solution slurries and impact angles; 30° and 90°. The SEM images in Fig. 4.22a (pH 4), Fig. 4.22c (pH 7), and Fig. 4.22e (pH 10) depict the scars formed at 30° impact angle, while Fig. 4.22b (pH 4), Fig. 4.22d (pH 7), and Fig. 4.22f (pH 10) illustrate the scars formed at 90° impact angle. The observed surface features on the wear scars are consistent with the results obtained for pure erosion of tantalum (as shown in Fig. 4.11) and are commonly seen in ductile materials.

At 30° impact angle, the observed features on wear scars were surface topology resembling Type-1 and Type-2 cutting action [41], broken lips, micro pits, and micro-sized voids/cavities due to the grain boundary sliding typically associated with lower strain rates. The dominant material removal mechanism appeared to be the coalescence of these voids, lip fracture due to repeated particle impacts, and grain dislodgement. The pH value did not significantly affect these features, however, the wear scar for pH 4 (Fig. 4.22(a)) appeared smoother compared to the scars of pH 7 and pH 10 (Fig. 4.22(c) and Fig. 4.22(e), respectively). This suggested an accelerated dissolution of the already weakened areas may have assisted the mechanical action of bombarding particles in dislodging the strained feature, leading to a smoother surface finish (electropolishing effect) at pH 4 as compared to other pH levels.

At 90° impact angle, the wear scars showed typical features such as hills and valleys surface topology and deep craters with intact lips. This is due to the plastic deformation mechanism for tantalum as discussed earlier in section 5.2.6.2. Extensive and ubiquitous micro-voids and pitting, similar to those observed at 30° impact angle, were also visible for scars created at 90° impact. The number, shape, and sizes of the microvoids and pits formed in the wear scar were similar to those observed for pure erosion of tantalum, for both impact angles and all solutions, making the role of corrosion in their formation unclear.

As observed in Fig. 4.22, the mostly intact lips at 90° and broken lips at 30°, correspond well with lower K_{ec} (due to less material removed at 90°) and higher K_{ec} (due to more material removed at 30°) as shown in Fig. 4.17.

5.3.4 Effect of synergy

The combined effect of erosion and corrosion, as discussed earlier in erosion-corrosion mechanisms, can lead to a total material loss that exceeds the individual losses caused by each mechanism when they operate independently [272–275]. This synergy (ΔK_{ec}) between erosion and corrosion, which exceeds material loss [12] is shown by Eq. (3.12) and Eq. (3.11) in section 3.3.3.2. To aid the discussion, these equations are presented here again as follows,

$$\Delta K_{ec} = K_{ec} - (K_{eo} + K_{co}) \quad \text{Eq. (5.1)}$$

$$\Delta K_{ec} = \Delta K_e + \Delta K_c \quad \text{Eq. (5.2)}$$

ΔK_{ec} can be positive [276–279] or it can also be negative [280–282] depending on dominating mechanism: additive, synergistic, or antagonistic effect.

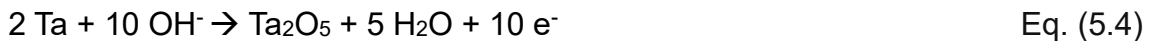
Figure 4.19 illustrates the calculated synergy rate (ΔK_{ec}) from Eq. (5.1) for 30° and 90° impact angles in different pH solutions.

At 30° impact angle and for pH 4, a positive synergy rate (measured in $\text{kg m}^{-2} \text{s}^{-1}$) was observed which decreased at pH 7 and further reduced at pH 10. At 90° impact angle, the synergy rate was reduced by an order of magnitude at pH 4 and by two orders of magnitude at pH 10. For both pH 7 and pH 10, the corrosion seemed to have a counteractive effect resulting in negative synergy rates as seen in Table 4.9.

As described in section 2.5.1, some previous studies have indicated that in an acidic environment, an oxide layer of tantalum pentoxide (Ta_2O_5) is formed on the surface of tantalum through the following electrochemical reaction [198,200,201],

$$2 \text{Ta} + 5 \text{H}_2\text{O} \rightarrow \text{Ta}_2\text{O}_5 + 10 \text{H}^+ + 10 \text{e}^- \quad \text{Eq. (5.3)}$$

In alkaline environments, this oxide layer is formed according to the following electrochemical reaction [198,202,203],



This Ta_2O_5 oxide layer offers passivity to the tantalum surface under various electrode potentials. At pH 7 and pH 10, for 90° impact angle and 5 ms^{-1} impact velocity, the findings (in Fig. 4.19) suggest that the impact energy of the particles was not sufficient enough to remove the protective oxide layers from the tantalum surface. It may also be the case that the formation rate of this layer was faster than its removal rate. Therefore, this oxide layer could have provided some

resistance to erosion by the impacting particles. In stark contrast to the negative synergy rates at pH 7 and pH 10, a relatively high positive synergy rate at pH 4 indicated less effective surface protection.

As shown in Eq. (5.2), synergy rate (ΔK_{ec}) comprises of erosion enhanced corrosion rate (or additive effect, ΔK_c) and corrosion enhanced erosion rate (or synergistic effect, ΔK_e). Fig. 4.20 and Fig. 4.21 depict the changes in ΔK_c and ΔK_e , respectively, under different pH solutions for 30° and 90° impact angles. The data in these figures indicates that for all pH, at 90° impact angle, ΔK_c values were greater than ΔK_e , however, at 30° impact angle, ΔK_e values were significantly higher than ΔK_c . As observed in Fig. 4.20, ΔK_c decreased as the solution became alkaline at both 30° and 90° impact angles. This reduction in ΔK_c is attributed to the formation of protective surface layers on tantalum in alkaline solutions, as previously discussed, due to the rapid repassivation of newly exposed areas (and/or thickening of undisturbed passive layers). Under both impact angles, ΔK_e follows a similar trend, decreasing as pH changes from 4 to 10 (Fig. 4.21), with a decrease in value as the solution became alkaline with the change in pH from pH 4 to pH 10.

A concise table that summarises the dominant contributor of ΔK_{ec} , based on ΔK_c and ΔK_e , is shown in Table 5.1.

Table 5.1 Summary of calculated mean erosion-corrosion parameters and major contributors of synergy rate (ΔK_{ec}).

Impact angle (°)	pH	K_{ec} ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$	ΔK_{ec} ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$	ΔK_c ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$	ΔK_e ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{-5}$	Major contributor (ΔK_c or ΔK_e)
30	4	3.47 ± 0.2	2.44	1.03 ± 0.2	1.41	Synergistic effect (ΔK_e)
	7	2.27 ± 0.08	1.24	0.32 ± 0.04	0.92	Synergistic effect (ΔK_e)
	10	1.98 ± 0.1	0.89	0.07 ± 0.004	0.82	Synergistic effect (ΔK_e)
90	4	1.22 ± 0.2	0.32	0.20 ± 0.01	0.12	Additive effect (ΔK_c)
	7	0.90 ± 0.06	-0.02	0.05 ± 0.005	-0.07	Antagonistic effect ($-\Delta K_e$)
	10	0.83 ± 0.03	-0.11	0.03 ± 0.003	-0.14	Antagonistic effect ($-\Delta K_e$)

Table 5 clearly shows that at 30° impact angle, synergistic effect (ΔK_e) was the dominant contributor of synergy at all pH levels. However, at 90° impact angle,

additive effect (ΔK_c) was responsible for synergy at pH 4, and antagonistic effect ($-\Delta K_e$) was the major contributor of synergy at pH 7 and pH 10.

5.4 Flow-assisted galvanic corrosion of tantalum and tungsten

5.4.1 Effect of impact velocity on polarisation curves

Figure 4.27 (electrode potential versus current density) and Table 4.17 show a considerable influence of impact velocity on corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values.

Tantalum polarisation curves

As observed in Table 4.17 and Fig. 4.28(a), at 5 ms^{-1} impact velocity, E_{corr} registered a three-fold shift to active potential as solution pH changed from pH 4 to pH 7. A further increase to pH 10 resulted in E_{corr} being shifted to a less active potential which shows a passivation tendency for tantalum in alkaline solution that correlates well with the findings in the literature [198]. Concerning i_{corr} , as observed in Fig. 4.28(b), it increased significantly as the solution pH changed from pH 4 to pH 10. The lower i_{corr} at pH 4 signifies the existence of a protective oxide film which is also confirmed by the most noble OCP value at pH 4 in static conditions for tantalum, as shown in Table 4.16. However, as the solution became alkaline with increased pH from pH 4 to pH 10 (Table 4.17), the increased i_{corr} suggests substantial dissolution of this oxide film at pH 10 under 5 ms^{-1} impact velocity, and consequently substantial corrosion in this condition.

As observed in Table 4.17 and Fig. 4.28(c), at pH 4, E_{corr} registered around three times more active potential at 9 ms^{-1} as compared to that at 5 ms^{-1} . However, at 9 ms^{-1} , E_{corr} shifted to less active potential as the solution pH changed from pH 4 to pH 7 and then to pH 10. At 9 ms^{-1} , i_{corr} values decreased with pH, and there was a substantial reduction in these values when compared to that for respective pH at 5 ms^{-1} impact velocity.

It is clearly evident that a higher impact velocity of 9 ms^{-1} caused higher passivation of tantalum surface with increased pH and hence explains the significant reduction of i_{corr} at pH 10. This passivation was caused by higher oxygen concentration in alkaline solutions ($\geq \text{pH } 7$) that enabled hydroxy ions (OH^-) generation and subsequent passive film formation on the tantalum surface [198,202,203]. The electrochemical reactions responsible for the formation of this

film on tantalum surface in both alkaline and acidic solutions have been discussed in previous sections; Eq. (5.3) and Eq. (5.4).

Tungsten polarisation curves

As observed in Table 4.17 and Fig. 4.28(a), at 5 ms⁻¹ impact velocity, E_{corr} shifted to active potential as solution pH changed from pH 4 to pH 7. A further increase to pH 10 resulted in E_{corr} being shifted to a least active potential. This shifting of E_{corr} to active potential and then being least active suggests tungsten's corrosion tendency which contradicts its i_{corr} response under these conditions. The i_{corr} was highest at pH 4 and it then dropped significantly as the solution pH changed from pH 4 to pH 7. It then increased with a further change from pH 7 to pH 10. At pH 4, the highest i_{corr} was attributed to the rapid dissolution of tungsten surface oxide layer assisted by hydroxyl ions [283]. As pH changed towards alkaline levels at pH 7, this enabled the formation of a tungsten trioxide (WO₃) layer [198,284] which inhibited the binding of anions (Cl⁻) [285] and remained stable under flow conditions at pH 7. This stable oxide layer (WO₃) at pH 7 explains signification reduction in i_{corr} as observed earlier at this pH level. At pH 10, the WO₃ layer (which was formed at pH 7) was oxidised to higher valent tungsten oxides (WO₄²⁻) resulting in oxide film dissolution assisted by hydroxyl ions and hence explains increased i_{corr} at pH 10. This increase in i_{corr} can also be represented by the following electrochemical reaction which is shown by Eq. (2.21) in section 2.5.2,



As observed in Table 4.17 and Fig. 4.28(c), at 9 ms⁻¹ impact velocity, E_{corr} shifted to active potentials as solution pH changed from pH 4 to pH 7 and then to pH 10. This suggests tungsten's corrosion tendency which increased as the solution became alkaline. Concerning i_{corr} , it was highest at pH 4 and then reduced significantly to lower values at pH 7 and pH 10. The hydroxy ions assisted oxide dissolution, at pH 4, as discussed earlier at 5 ms⁻¹, was independent of impact velocities and as a result at this pH level, i_{corr} remained highest and unchanged at 9 ms⁻¹. The reduced i_{corr} at pH 7 and pH 10 was attributed to the increased participation of oxygen (due to higher velocity) in anodic passivation reactions at the tungsten surface. In addition, this trend corresponds well with the findings on

other metals (13Cr stainless steel) in alkaline solution at higher impact velocities [286].

5.4.2 Effect of pH and impact velocity on galvanic parameters

5.4.2.1 Predicted galvanic potential (E_{MPT}) and current density (i_{MPT})

As observed in Fig. 4.30(a) and Table 4.18, at 5 ms^{-1} impact velocity, galvanic potential calculated based on Mixed Potential Theory (E_{MPT}) registered a four-fold shift to active potential as solution pH changed from pH 4 to pH 7. A further increase to pH 10 resulted in E_{MPT} being shifted to a less active potential. At all pH levels, E_{MPT} lies closer to E_{corr} of tantalum than E_{corr} of tungsten, as seen in Table 4.17 and Table 4.18. Therefore, MPT analysis predicted that tantalum polarised tungsten to less active potentials at pH 4, however, on the contrary, it polarised tungsten to more active potentials at pH 7 and pH 10. Consequently, the lowest value of i_{MPT} was predicted at pH 4 and a significant value of that was predicted at pH 7 and pH 10. Furthermore, as observed in Table 4.17, at 5 ms^{-1} for all pH levels, the i_{corr} values obtained for tungsten is comparatively lower than that for tantalum. However, when tungsten was coupled to tantalum, the findings of MPT analysis and its comparison with polarisation data of tantalum and tungsten suggested that tungsten would corrode more than tantalum at pH 7 and pH 10 under 5 ms^{-1} impact velocity.

As observed in Fig. 4.30(b) and Table 4.18, at 9 ms^{-1} impact velocity, the variation of E_{MPT} with pH followed a similar trend as observed at 5 ms^{-1} . However, for all pH levels, E_{MPT} registered a more active potential at 9 ms^{-1} as compared to that at 5 ms^{-1} . At pH 4 and pH 7, E_{MPT} lies closer to E_{corr} of tantalum than E_{corr} of tungsten, and the converse was true at pH 10, as seen in Table 4.17 and Table 4.18. Therefore, MPT analysis predicted that tungsten when coupled with tantalum became more active at pH 7 and pH 10, and less active at pH 4. Consequently, the lowest value of i_{MPT} was predicted at pH 4 and a significant higher value of that was predicted at pH 7, which then reduced at pH 10. Furthermore, as observed in Table 4.17, at 9 ms^{-1} for pH 4 and pH 10, the i_{corr} of tungsten is comparatively higher in values than the i_{corr} of tantalum, however, at pH 7, the i_{corr} of tantalum is higher than the i_{corr} of tungsten. This means when tungsten was coupled to tantalum, the findings of MPT analysis and its

comparison with polarisation data of tantalum and tungsten suggested that tungsten would be corroding less at pH 4, however, it would expect significant corrosion at pH 7 and pH 10 under 9 ms^{-1} impact velocity.

5.4.2.2 Experimental galvanic potential (E_g) and current density (i_g)

Curve profiles and polarity indicator

At both 5 ms^{-1} and 9 ms^{-1} impact velocities, the galvanic potential (E_g) and galvanic current density (i_g) profiles show mixed responses depicted by short-period transients (in Fig. 4.31(a) and Fig. 4.31(c)) and more significant transients (in Fig. 4.31(b) and Fig. 4.31(d)). A low amplitude potential and current signals in a short-period transient are associated with uniform corrosion processes [287,288] while localised damage would be expected through stable pits nucleation in a longer-period transient [289].

As observed in Fig. 4.31(b) at 5 ms^{-1} impact velocity, the galvanic current density (i_g) values were negative at all pH levels. These negative i_g values signify that tungsten behaved as an anode and tantalum behaved as a cathode, during all tests at different pH. On the contrary, in Fig. 4.31(d) at 9 ms^{-1} impact velocity, i_g registered positive values at pH 4 and pH 7 which shows that tantalum behaved as an anode and tungsten behaved as a cathode under these conditions.

Impact of flow velocity on E_g and i_g

As observed in Table 4.19 and Fig. 4.32, at 5 ms^{-1} impact velocity, the galvanic potential (E_g) shifted to more active potentials as solution pH changed from pH 4 to pH 7 and then to pH 10. Consequently, from anodic tungsten, the lowest value of absolute galvanic current density ($|i_g|$) was observed at pH 4 and a significant value of that was observed at pH 10. At 9 ms^{-1} impact velocity, E_g shifted to less active potential as solution pH changed from pH 4 to pH 7. A further increase to pH 10 resulted in E_g being shifted significantly to a more active potential. Consequently, from anodic tantalum, the lower values of $|i_g|$ were observed at pH 4 and pH 7, while from anodic tungsten, a significantly higher value of $|i_g|$ was observed at pH 10.

As also observed in Table 4.19 for all pH levels, $|i_g|$ at 5 ms^{-1} was reduced to lower values at 9 ms^{-1} . These reductions in $|i_g|$ values clearly show higher passivation of the anode surface when impacted at a higher impact velocity of 9 ms^{-1} .

Assessment of galvanic effect

The galvanic effect between tantalum and tungsten is discussed in the subsequent sections based on the galvanic polarity map, potential difference, and galvanic ratio.

Galvanic polarity map

In this study a galvanic polarity map was devised to identify the polarity for the members of a galvanic couple (tantalum/tungsten) in different pH solutions and impact velocities and it is shown in Table 5.2. The polarity of galvanic couple members was evaluated in both mixed potential theory (MPT) and zero resistance ammeter (ZRA) measurements of galvanic corrosion. For the polarity of the members in MPT measurement (as observed in Table 4.20), the member with most negative E_{corr} value was anode and other member with less negative E_{corr} value was cathode. For polarity of members in ZRA measurement (as observed in Fig. 4.31(b) and Fig. 4.31(d)), the negative value of i_g indicated that tantalum was cathode and tungsten was anode. Conversely, the positive value of i_g indicated that tantalum was anode and tungsten was cathode. The evaluated polarity (anode/cathode) through MPT and ZRA, for respective members (tantalum and tungsten) of galvanic couple, thus noted for each experimental conditions of pH and impact velocity and a table of galvanic polarity map was constructed (Table 5.2).

With the help of this galvanic polarity map, the identified polarity of tantalum and tungsten was used to analyse the electron microscopy and gravimetry data of ZRA samples and to assess their galvanic corrosion behaviour. The galvanic polarity map is a very useful tool to analyse large datasets which was the case in the present study.

Table 5.2 Galvanic polarity map of tantalum and tungsten at different pH and impact velocities.

Impact velocity (ms ⁻¹)	Polarity evaluation technique	Material	pH 4	pH 7	pH 10
5	MPT	Tantalum	Cathode	Anode	Anode
		Tungsten	Anode	Cathode	Cathode
	ZRA	Tantalum	Cathode	Cathode	Cathode
		Tungsten	Anode	Anode	Anode
9	MPT	Tantalum	Anode	Anode	Cathode
		Tungsten	Cathode	Cathode	Anode
	ZRA	Tantalum	Anode	Anode	Cathode
		Tungsten	Cathode	Cathode	Anode

The ‘Anode’ polarity is marked in red colour as it signifies a damaging condition of material loss due to oxide film depletion/dissolution which is also responsible for anodic current densities. A green-coloured ‘Cathode’ polarity signifies a protective condition of reduction reactions that take place on cathode due to sacrificial anode.

ZRA evaluated polarity is a somewhat better representation than that of MPT. This is because MPT is only a useful ‘predictor’ of galvanic currents between the members of a galvanic couple. However, MPT galvanic parameters are theoretically determined based on polarisation experiments conducted independently on each member of the galvanic couple. Moreover, in those polarisation experiments, each metal (tantalum or tungsten) behaved as a working electrode (anode or cathode) and the determined current densities were not affected by the presence of an inert auxiliary electrode (graphite). However, in practice, galvanic currents affect both anode and cathode simultaneously [152,153,254]. On the other hand, the ZRA technique determined the ‘actual’ galvanic parameters based on the behaviour/reactions of individual members

(anode or cathode) placed together as a galvanic couple in ZRA experiments. This way ZRA also better justifies the significance of anode/cathode colour marking as described earlier in the galvanic polarity map where damage to the anode and protection to the cathode are expected to happen simultaneously.

Table 5.2 shows that MPT and ZRA techniques are in perfect agreement of the tantalum/tungsten galvanic polarity for pH 4 at 5 ms⁻¹ and for all pH levels at 9 ms⁻¹. A polarity reversal is seen for pH 7 and pH 10, at 5 ms⁻¹ impact velocity. In addition, as observed in Table 4.20, i_{MPT} and $|i_g|$ values are significantly different at pH 7 and pH 10 under both impact velocities. The practical limitations of MPT, as pointed out and discussed earlier, justify the polarity reversal and differences between i_{MPT} and $|i_g|$ values, at pH 7 and pH 10.

Potential difference

As mentioned in section 4.4.2.3, the significance of the galvanic effect is considered through the difference between the corrosion potentials of the cathode and the anode of the galvanic pair ($E_{\text{corr}_c} - E_{\text{corr}_a}$). Minimum differences ranging from 0.10 to 0.13 V are necessary indicators of a significant galvanic impact [254,255]. Table 4.20, which includes these differences, shows that under both impact velocities (5 and 9 ms⁻¹), the galvanic effect of the tantalum/tungsten pair was significant at pH 4 and it was insignificant at pH 7 and pH 10 solutions since the galvanic pair differences ($E_{\text{corr}_c} - E_{\text{corr}_a}$) fall below 0.10 V in these solutions. This analysis of the differences in potentials is useful from a thermodynamic perspective that can only predict the direction of the flow of galvanic current; from anode to cathode. However, the extent of galvanic corrosion cannot be assessed reliably based on these differences in potentials [149].

Galvanic ratio

As also mentioned in section 4.4.2.3, a more reliable approach to assess the severity of the galvanic effect is through the galvanic ratio, $\frac{|i_g|}{|i_{\text{corr}_a}|}$ [254,256,257], where $|i_g|$ is the absolute galvanic current density and $|i_{\text{corr}_a}|$ is the corrosion current density of the uncoupled anodic member. The ratio value of less than 5 signifies the compatibility of the members in a galvanic couple [147,256]. As observed in Table 4.20, at 5 ms⁻¹ for all pH and at 9 ms⁻¹ for pH 4 and pH 7, $\frac{|i_g|}{|i_{\text{corr}_a}|}$

values are less than 5, whereas, at 9 ms^{-1} for pH 10, its value is greater than 5. This means severity of galvanic corrosion between Ta and W pair was significantly higher for pH 10 at 9 ms^{-1} impact velocity, whereas, it was insignificant for other velocities and pH conditions studied.

5.4.3 Analysis of SEM images and mass loss measurements

Surface morphology

As observed in SEM images of tantalum in Fig. 4.33 after ZRA experiments, the tantalum surface showed no visible damage to the grains under all the conditions studied (i.e. different pH and impact velocities). This is despite of the different galvanic corrosion behaviour of tantalum/tungsten observed under various conditions studied. As seen in the galvanic polarity map of ZRA shown in Table 5.2, at 5 ms^{-1} for all pH levels and at 9 ms^{-1} for pH 10, tantalum was cathodically protected; therefore no corrosive attack was visible in the SEM images. However, at 9 ms^{-1} for pH 4 and pH 7, although the anodic polarity of tantalum was observed, the severity of the corrosion attack was not high enough to be observed under SEM images.

As observed in SEM images for tungsten in Fig. 4.34(a), Fig. 4.34(c), and Fig. 4.34(e) after ZRA experiments at 5 ms^{-1} impact velocity, the tungsten surface exhibited grain boundary attack and dissolution damage for all conditions studied at this velocity. This behaviour of tungsten is justified through its anodic polarity as confirmed by the galvanic polarity map of ZRA, as shown in Table 5.2. At 9 ms^{-1} impact velocity, surface features, similar to those observed at 5 ms^{-1} , were mostly visible on the tungsten surface at pH 4 and pH 10 (Fig. 4.34(b) and Fig. 4.34(f), respectively), however, noticeable to a lesser extent as compared to that at 5 ms^{-1} . Moreover, these features were not evident in the SEM image in Fig. 4.34(d) at pH 7 for 9 ms^{-1} impact velocity. This is because at 9 ms^{-1} , based on the galvanic polarity map of ZRA as shown in Table 5.2, the tungsten surface was cathodically protected at both pH 4 and pH 7, however, it still suffered from corrosive damage which was minimum due to the formation of a very thin film of corrosion products [198,284,285]. However, at pH 10, the anodic dissolution of this film, assisted by hydroxyl ions [283], resulted in a more damaging corrosive surface as observed in Fig. 4.34(f).

The surface morphology of tantalum and tungsten specimens were explained further through their mass losses which are discussed in following section.

Mass loss measurements

As observed in Table 4.21 for mass loss of tantalum and tungsten in ZRA experiments, except for tantalum mass loss for pH 4 at 9 ms⁻¹, the tantalum material loss remained the same ($1 \pm 0.1 \times 10^{-4}$ g) at all experimental conditions of different pH and impact velocities. On the other hand, except for tungsten mass loss for pH 7 at 5 ms⁻¹, the tungsten suffered mass loss at least twice in magnitude as compared to that for tantalum in all experimental conditions.

At 5 ms⁻¹ for pH 4 and pH 10, the mass loss values were lower for tantalum as compared to tungsten. This effect is in good agreement with the polarity indication of the galvanic polarity map of ZRA in Table 5.2 (i.e. cathodic tantalum and anodic tungsten). Table 5.2 (under ZRA) also showed anodic polarity for tungsten at 5 ms⁻¹ under pH 7, however, its mass loss ($1 \pm 0.1 \times 10^{-4}$ g), which was similar to that of tantalum, also suggested the presence of oxide film which reduced anodic damage of tungsten and hence resulted in its minimum mass loss at pH 7.

At 9 ms⁻¹, tantalum, despite being at anodic polarity under pH 4 and pH 7 (as observed in Table 5.2 for ZRA), its mass loss was negligible at pH 4 and remained the same at pH 7 and pH 10. This indicates firm passivation on the tantalum surface at pH 4 and the existence of an oxide film which was mostly stable on its surface at all pH levels under both the impact velocities studied. At 9 ms⁻¹, tungsten, despite being at cathodic polarity under pH 4 and pH 7 (as observed in Table 5.2 for ZRA), suffered a mass loss which was significantly higher as compared to that at similar conditions of 5 ms⁻¹. This indicates poor surface protection due to the existence of an oxide film which became porous and unstable as the impact velocity changed from 5 ms⁻¹ to 9 ms⁻¹.

As observed in Table 4.21, the maximum mass loss of tungsten occurred at 5 ms⁻¹ for pH 10. As observed in Table 4.20, the severe galvanic effect, due to the highest galvanic ratio (of 13), occurred at 9 ms⁻¹ for pH 10. This maximum mass loss and highest galvanic ratio suggest the severity of tantalum-tungsten galvanic corrosion at pH 10 solutions in which tungsten anodically suffered

maximum damage as confirmed by the galvanic polarity map in Table 5.2 and evident in SEM images of Fig. 4.34(e) and Fig. 4.34(f).

Chapter-6

Conclusions and Recommendations

6.1 Conclusions

In this work, the erosion and erosion-corrosion behaviour of tantalum, and the flow-assisted galvanic corrosion behaviour of tantalum and tungsten were investigated under impinging-jet conditions. Based on the data-intensive results and interesting findings which were discussed in previous chapter, the following conclusions can be drawn:

Erosion of Tantalum

1. The tantalum specimens exhibited a typical ductile material erosion response with greater erosion mass loss at oblique impact angles (at 30°), which increased with velocity.
2. For the given experimental conditions (velocities, particle type, shape, and size), the erosion mass loss of tantalum increased with slurry concentrations up to an intermediate concentration of 7 wt.% and then decreased. The reduced mass loss at higher concentrations is attributed to the increased particle interaction.
3. SEM micrographs revealed the presence of numerous voids/cavities dispersed across the eroded surface of the tantalum specimens. These voids were proposed to originate primarily from high-angle grain boundary sliding. Notably, the high-angle grain boundary represents a distinctive microstructural attribute of the tantalum specimens produced through the powder metallurgy (PM) route.
4. Wear scar analysis of the tantalum specimens revealed a hill-and-valley surface topology at 90° impact angle, whereas a cutting/ploughing topology was observed at 30° impact angle.
5. The material removal mechanism in tantalum specimens was found to be supported by (i) lip breakage due to repeated erodent impacts at 90° impact angle, (ii) micro-cutting and ploughing at 30° impact angle, and (iii) dislodgement of grains due to grain boundary void coalescence at both 90° and 30° impact angles.

Erosion-Corrosion of Tantalum

1. The corrosion resistance of tantalum was found to decrease significantly under particle bombardment conditions, as evidenced by a marked reduction in corrosion potential (E_{corr}) values in the range of -400 mV to -500 mV.
2. The erosion-corrosion rate of tantalum was found to be more than twice as high at 30° impact angle compared to that at 90° impact angle, regardless of the type of corrosive solution used in this study. Additionally, the erosion-corrosion rate was higher at pH 4 than at pH 7 and pH 10.
3. The erosion-corrosion mechanisms observed were dominated by micro-cutting at 30° impact angle. At 90° impact angle, the dominant mechanism was plastic deformation resulting in lip formation followed by their removal by additional particle impacts. The corrosion mechanisms included the dissolution of weakened areas due to plastic deformation under anodic potentials, as well as the continuous removal/formation of passive layers under passivating potentials.
4. At 90° impact angle, an additive effect was observed for pH 4, where erosion enhanced the corrosion rate. Conversely, an antagonistic effect was observed for pH 7 and pH 10 solutions, where corrosion impaired the erosion rate. At 30° impact angle, irrespective of pH value, a synergistic effect was observed, where corrosion enhanced the erosion rate.

Flow-assisted Galvanic Corrosion of Tantalum and Tungsten

1. Based on the potentiodynamic polarisation results obtained for tantalum and tungsten separately, the impact velocity (5 ms^{-1} and 9 ms^{-1}) significantly influenced corrosion current density (i_{corr}) for all the pH levels studied. In case of tantalum, the i_{corr} values were significantly reduced at higher impact velocity (9 ms^{-1}) for all pH levels and this is due to greater oxygen transport at higher velocity resulting accelerated surface passivation. This trend was also observed for tungsten, except for pH 4 at both velocities, where i_{corr} remained unchanged. This indicates the

presence of firm passive layer unaffected by the flow conditions at this particular pH level.

2. The mixed potential theory (MPT) analysis and Zero resistance ammeter (ZRA) tests revealed that with the increase in solution pH, as compared to the uncoupled state, the galvanic coupling (between tantalum and tungsten) significantly increased the corrosion rate of tungsten for pH 7 and pH 10 at both impact velocities (5 ms^{-1} and 9 ms^{-1}). On the contrary, a significant reduction in its corrosion rate was found at pH 4 at both impact velocities. This reaffirms the existence of passive layer at pH 4. These observations were further supported by electron microscopy and mass loss measurements.
3. At 5 ms^{-1} impact velocity, tantalum was cathodically protected and therefore suffered minimum corrosion at all pH levels. At 9 ms^{-1} impact velocity, although tantalum displayed anodic polarity at pH 4 and pH 7, it still suffered minimum damage in these conditions and the damage was unidentifiable under SEM examination.
4. The galvanic ratio ($\frac{|i_g|}{|i_{\text{corr.al}}|}$) showed that galvanic corrosion was significant only for pH 10 at 9 ms^{-1} . And the ratio remained insignificant for all other pH and velocity conditions studied.

6.2 Recommendations for future work

1. The present study utilised a maximum impact velocity of 5 ms^{-1} for the erosion and erosion-corrosion experiments conducted on tantalum specimens. A velocity higher than 5 ms^{-1} was not possible due to the limitation of the erosion-corrosion apparatus used in this study. Future studies on erosion and erosion-corrosion of tantalum can make use of impact velocity around 9 ms^{-1} which represents the flow conditions of RAL's target. Although this high velocity is not likely to change the mechanism of material removal, future studies are recommended to verify the material removal mechanism at higher velocities.

2. This study only considered pH values of 4, 7, and 10. Future studies are recommended to include more pH values and to check the effect of pH on erosion-corrosion behaviour of tantalum.
3. The tantalum specimen used in this study were manufactured through powder metallurgy method which requires compaction and sintering of tantalum powder at specific temperature and pressure. Future studies can examine how changes in these process parameters can influence the erosion and erosion-corrosion response of tantalum.
4. Although, due to safety reasons, the present study was conducted on RAL-supplied unirradiated tantalum and tungsten samples, the effect of proton beam irradiation also needs to be considered in future work as some literature (as mentioned in literature review section 2.5.3) reported that this effect can alter mechanical properties of target materials and chemical composition of cooling water for the target [224,227,228].
5. Future research work can venture into investigation on the tantalum-tungsten interface location, which is formed by electron beam welding leading to diffusion bonding of the interface. It would be particularly useful to observe how the interface behaves under flow-assisted galvanic conditions and compare the results with the benchmark results of the current study to draw meaningful conclusions.
6. Future research work can also include an investigation on the oxide layers formed on tantalum and tungsten, particularly with an aim to understand how these oxide layers influence the erosion-corrosion synergy rate under different pH levels and slurry concentrations.
7. Future study can also include development of predictive mathematical models for erosion and erosion-corrosion of tantalum and validate those using the results obtained in this study.
8. From the material selection viewpoint, based on the findings of this study, the tantalum manufactured through powder metallurgy routes (as was used in this study) may not be an ideal material option for a neutron spallation target used by RAL. This is due to its adverse performance

under erosion-corrosion conditions, which is caused by a distinct material removal mechanism facilitated by the presence of extensive high-angle grain boundaries in its microstructure. From an operational viewpoint, based on this study, the galvanic corrosion interaction between tantalum and tungsten is minimum at pH 7, which can be targeted for the cooling water used for the spallation target. In addition, it is also recommended that the tantalum-tungsten interface rupture should be avoided, so that formation of a galvanic circuit between the two metals is prevented.

9. Although this research was targeted to improve the life of Ta-W spallation targets used by RAL, the findings presented here can also be useful in other applications of Ta, such as chemical processing, nuclear, and biomedical.

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Appendix

Table A.1 Tantalum mass loss data table for erosion experiments
(Erosion rate vs Impact angle)

Tantalum sample No.	Impact angle (deg)	Wear scar No.	Mass of sample before experiment (g)	Mass of sample (g) after 60 min. erosion experiment at 5 ms ⁻¹ impact velocity and 10 wt.% SiC concentration.				Mean mass of sample after experiment (g)	Mass loss (g)	Mean Mass loss (g)
				R1	R2	R3	R4			
B2Ta6	90	1	59.8271	59.8263	59.8264	59.8264	59.8266	59.8264	0.0007	0.0007
B2Ta6		2	59.8266	59.8256	59.8258	59.8260	59.8261	59.8259	0.0007	
B2Ta6		3	59.8261	59.8253	59.8256	59.8256	59.8256	59.8255	0.0006	
B2Ta6	60	4	59.8256	59.8245	59.8250	59.8249	59.8250	59.8249	0.0008	0.0009
B2Ta6		5	59.8250	59.8238	59.8240	59.8241	59.8242	59.8240	0.0010	
B2Ta4		1	59.8261	59.8247	59.8250	59.8252	59.8251	59.8250	0.0011	
B2Ta6	45	1	59.9191	59.9175	59.9177	59.9179	59.9179	59.9178	0.0013	0.0012
B2Ta4		2	59.9649	59.9633	59.9637	59.9638	59.9639	59.9637	0.0012	
B2Ta5		3	59.7975	59.7963	59.7966	59.7966	59.7966	59.7965	0.0010	
B2Ta4	30	2	59.8251	59.8235	59.8236	59.8237	59.8238	59.8237	0.0014	0.0016
B2Ta4		3	59.8238	59.8216	59.8219	59.8218	59.8218	59.8218	0.0020	
B2Ta4		4	59.8218	59.8202	59.8204	59.8206	59.8205	59.8204	0.0014	
B2Ta4	20	5	59.8205	59.8200	59.8204	59.8205	59.8203	59.8203	0.0002	0.0005
B2Ta5		1	59.6886	59.6875	59.6879	59.6881	59.6881	59.6879	0.0007	
B2Ta5		2	59.6881	59.6872	59.6876	59.6876	59.6876	59.6875	0.0006	

Table A.2 Tantalum mean erosion rate data for different impact angles.

Impact angle (deg)	Erosion rate (gg ⁻¹) x 10 ⁻⁸ under erodent mean flow rate of 14.7 gs ⁻¹			Mean erosion rate (gg ⁻¹) x 10 ⁻⁸	Standard deviation
	Expt.-1	Expt.-2	Expt.-3		
20	0.3779	1.3228	1.1338	0.9448	0.4082
30	2.6455	3.7793	2.6455	3.0234	0.5345
45	2.4565	2.2676	1.8896	2.2046	0.2357
60	1.5117	1.8896	2.0786	1.8266	0.2357
90	1.3228	1.3228	1.1338	1.2598	0.0891

Table A.3 Aluminium mass loss data table for erosion experiments at 30° and 90° impact angles.

Sample	Impact angle (deg)	Wear scar No.	Mass of sample before experiment (g)	Mass of sample (g) after 60 min. erosion experiment at 5 ms ⁻¹ impact velocity and 7 wt.% SiC concentration.				Mean mass of sample after experiment (g)	Mass loss (g)	Mean mass loss (g)
				R1	R2	R3	R4			
Aluminium	90	1	7.7244	7.7240	7.7242	7.7240	7.7240	7.7241	0.0004	0.0002
		2	7.7240	7.7240	7.7238	7.7238	7.7238	7.7239	0.0001	
		3	7.7238	7.7236	7.7236	7.7236	7.7237	7.7236	0.0002	
	30	1	7.7235	7.7227	7.7229	7.7229	7.7228	7.7228	0.0007	0.0009
		2	7.6509	7.6498	7.6501	7.6499	7.6499	7.6499	0.0010	
		3	7.6499	7.6489	7.6489	7.6491	7.6489	7.6490	0.0009	

Table A.4 Aluminium mean erosion rate data for 30° and 90° impact angles.

Impact angle (deg)	Aluminium erosion rate (gg ⁻¹) x 10 ⁻⁸ under erodent mean flow rate of 11.2 gs ⁻¹			Mean erosion rate (gg ⁻¹) x 10 ⁻⁸	Standard deviation
	Expt.-1	Expt.-2	Expt.-3		
30	1.7361	2.4802	2.2321	2.1495	0.3093
90	0.9921	0.2480	0.4960	0.5787	0.3093

Table A.5 Tantalum mass loss data table for erosion experiments.
(Erosion rate vs SiC slurry concentration)

Ta sample No.	Impact angle (deg)	SiC conc. (wt.%)	Wear scar No.	Mass of sample before experiment (g)	Mass of sample (g) after 60 min. erosion experiment at 5 ms ⁻¹ impact velocity.				Mean mass of sample after experiment (g)	Mass loss (g)	Mean mass loss (g)
					R1	R2	R3	R4			
B2Ta2	30	10	3	58.7829	58.7809	58.7811	58.7813	58.7813	58.7812	0.0018	0.0014
B2Ta2			4	58.7813	58.7800	58.7800	58.7803	58.7803	58.7802	0.0011	
B2Ta6			3	59.8218	59.8202	59.8204	59.8206	59.8205	59.8204	0.0014	
B2Ta5		7	3	59.6876	59.6864	59.6867	59.6867	59.6864	59.6866	0.0011	0.0012
B2Ta5			4	59.6864	59.6851	59.6854	59.6856	59.6857	59.6855	0.0010	
B2Ta5			5	59.6857	59.6838	59.6841	59.6842	59.6843	59.6841	0.0016	
B2Ta2		5	4	58.8974	58.8964	58.8965	58.8966	58.8967	58.8966	0.0008	0.0007
B2Ta2			5	58.8967	58.8959	58.8961	58.8962	58.8962	58.8961	0.0006	
B2Ta6			1	59.7480	59.7469	59.7472	59.7473	59.7474	59.7472	0.0008	
B2Ta4		3	3	59.7364	59.7358	59.7360	59.7360	59.7360	59.7360	0.0005	0.0004
B2Ta4			4	59.7360	59.7360	59.7358	59.7359	59.7358	59.7359	0.0001	
B2Ta4			5	59.7358	59.7350	59.7353	59.7354	59.7354	59.7353	0.0005	
B2Ta2	90	10	1	58.7840	58.7834	58.7834	58.7837	58.7837	58.7836	0.0004	0.0007
B2Ta2			2	58.7837	58.7825	58.7828	58.7830	58.7829	58.7828	0.0009	
B2Ta6			3	59.8261	59.8253	59.8256	59.8256	59.8256	59.8255	0.0006	
B2Ta2		7	1	58.8999	58.8986	58.8988	58.8990	58.8992	58.8989	0.0010	0.0011
B2Ta2			2	58.8992	58.8978	58.8984	58.8981	58.8984	58.8982	0.0010	
B2Ta2			3	58.8984	58.8968	58.8973	58.8974	58.8974	58.8972	0.0012	
B2Ta6		5	1	59.7474	59.7465	59.7468	59.7469	59.7471	59.7468	0.0006	0.0006
B2Ta6			2	59.7471	59.7461	59.7465	59.7467	59.7468	59.7465	0.0006	
B2Ta6			3	59.7468	59.7460	59.7462	59.7462	59.7464	59.7462	0.0006	
B2Ta6		3	5	59.7464	59.7460	59.7463	59.7465	59.7465	59.7463	0.0001	0.0002
B2Ta4			1	59.7369	59.7364	59.7366	59.7367	59.7366	59.7366	0.0003	
B2Ta4			2	59.7366	59.7361	59.7363	59.7366	59.7364	59.7364	0.0003	

Table A.6 Tantalum mean erosion rate data for different SiC concentration at 30° and 90° impact angles.

SiC conc. (wt.%)	Erosion rate (gg ⁻¹) x10 ⁻⁸ at 30° impact angle			Mean erosion rate at 30° (gg ⁻¹) x 10 ⁻⁸	Standard deviation	Erosion rate (gg ⁻¹) x10 ⁻⁸ at 90° impact angle			Mean erosion rate at 90° (gg ⁻¹) x 10 ⁻⁸	Standard deviation
	Expt.-1	Expt.-2	Expt.-3			Expt.-1	Expt.-2	Expt.-3		
3	3.7538	0.7508	3.7538	2.7528	1.4156	0.7508	2.2523	2.2523	1.7518	0.7078
5	3.0864	2.3148	3.0864	2.8292	0.3637	2.3148	2.3148	2.3148	2.3148	0.0000
7	3.0647	2.7861	4.4578	3.4362	0.7313	2.7861	2.7861	3.3434	2.9719	0.2627
10	3.2051	1.9587	2.4930	2.5523	0.5106	0.7123	1.6026	1.0684	1.1278	0.3659

Table A.7 Tantalum mass loss data table for erosion experiments.
(Erosion rate vs Impact velocity)

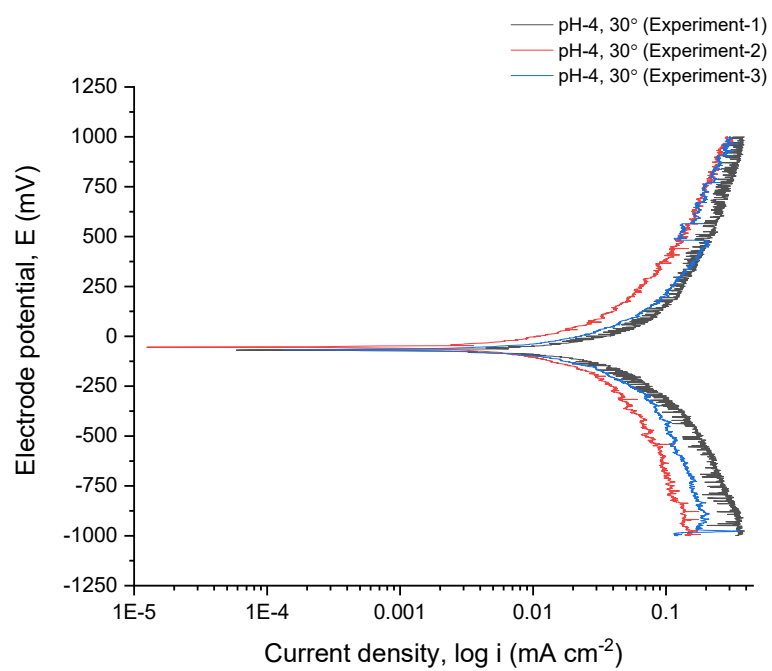
Ta sample No.	Impact angle (deg)	Impact velocity (ms ⁻¹)	Wear scar No.	Mass of sample before expt. (g)	Mass of sample (g) after 60 min. erosion experiment at 7 wt.% SiC concentration.				Mean mass of sample after expt. (g)	Mass loss (g)	Mean mass loss (g)
					R1	R2	R3	R4			
B2Ta4	30	3	5	59.6431	59.6424	59.6426	59.6428	59.6428	59.6427	0.0005	0.0005
B2Ta6			1	59.6468	59.6463	59.6460	59.6462	59.6462	59.6462	0.0006	
B2Ta6			2	59.6462	59.6456	59.6460	59.6460	59.6461	59.6459	0.0003	
B2Ta5		4	4	59.5484	59.5476	59.5482	59.5482	59.5482	59.5481	0.0003	0.0006
B2Ta5			5	59.5482	59.5472	59.5474	59.5476	59.5476	59.5475	0.0008	
B2Ta4			1	59.6432	59.6421	59.6427	59.6426	59.6426	59.6425	0.0007	
B2Ta5		5	3	59.6876	59.6864	59.6867	59.6867	59.6864	59.6866	0.0011	0.0012
B2Ta5			4	59.6864	59.6851	59.6854	59.6856	59.6857	59.6855	0.0010	
B2Ta5			5	59.6857	59.6838	59.6841	59.6842	59.6843	59.6841	0.0016	
B2Ta4	90	3	2	59.6426	59.6432	59.6432	59.6434	59.6435	59.6433	-0.0007	0.0000
B2Ta4			3	59.6435	59.6426	59.6427	59.6431	59.6430	59.6429	0.0007	
B2Ta4			4	59.6430	59.6426	59.6429	59.6430	59.6431	59.6429	0.0001	
B2Ta5		4	1	59.5496	59.5491	59.5492	59.5492	59.5494	59.5492	0.0004	0.0005
B2Ta5			2	59.5494	59.5487	59.5490	59.5490	59.5491	59.5490	0.0004	
B2Ta5			3	59.5491	59.5481	59.5484	59.5485	59.5484	59.5484	0.0008	
B2Ta2		5	1	58.8999	58.8986	58.8988	58.8990	58.8992	58.8989	0.0010	0.0011
B2Ta2			2	58.8992	58.8978	58.8984	58.8981	58.8984	58.8982	0.0010	
B2Ta2			3	58.8984	58.8968	58.8973	58.8974	58.8974	58.8972	0.0012	

Table A.8 Tantalum mean erosion rate data for different impact velocity at 30° and 90° impact angles.

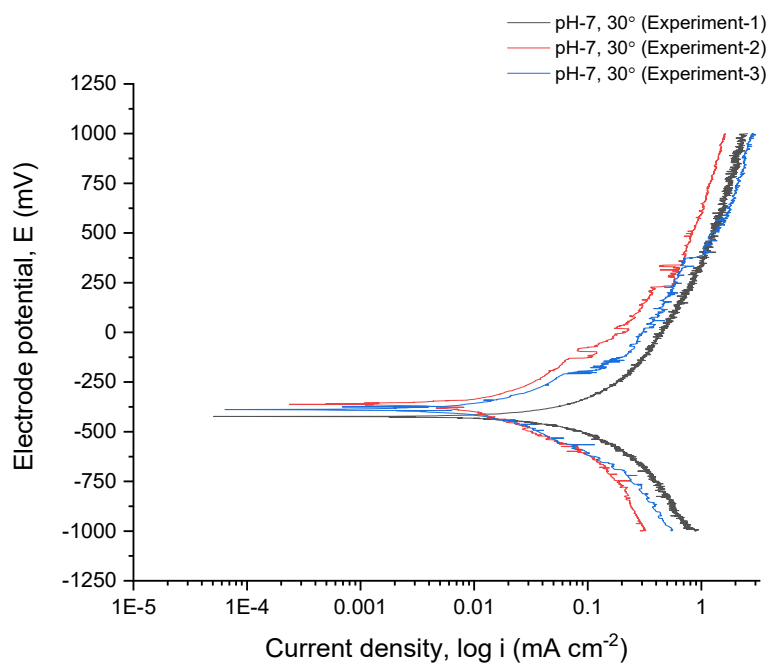
Impact velocity (ms ⁻¹)	Erosion rate (gg ⁻¹) x 10 ⁻⁸ at 30° impact angle.			Mean erosion rate at 30° (gg ⁻¹) x 10 ⁻⁸	Std. Dev.	Erosion rate (gg ⁻¹) x 10 ⁻⁸ at 90° impact angle.			Mean erosion rate at 90° (gg ⁻¹) x 10 ⁻⁸	Std. Dev.
	Expt.-1	Expt.-2	Expt.-3			Expt.-1	Expt.-2	Expt.-3		
3	1.8519	2.2222	1.1111	1.7284	0.4619	-2.5926	2.5926	0.3704	0.1235	2.1240
4	0.7862	2.0964	1.8344	1.5723	0.5661	1.0482	1.0482	2.0964	1.3976	0.4941
5	3.0647	2.7861	4.4578	3.4362	0.7313	2.7861	2.7861	3.3434	2.9719	0.2627

Table A.9 Tantalum mass loss data table for potentiostatic erosion-corrosion experiments in different pH solutions at 30° and 90° impact angles.

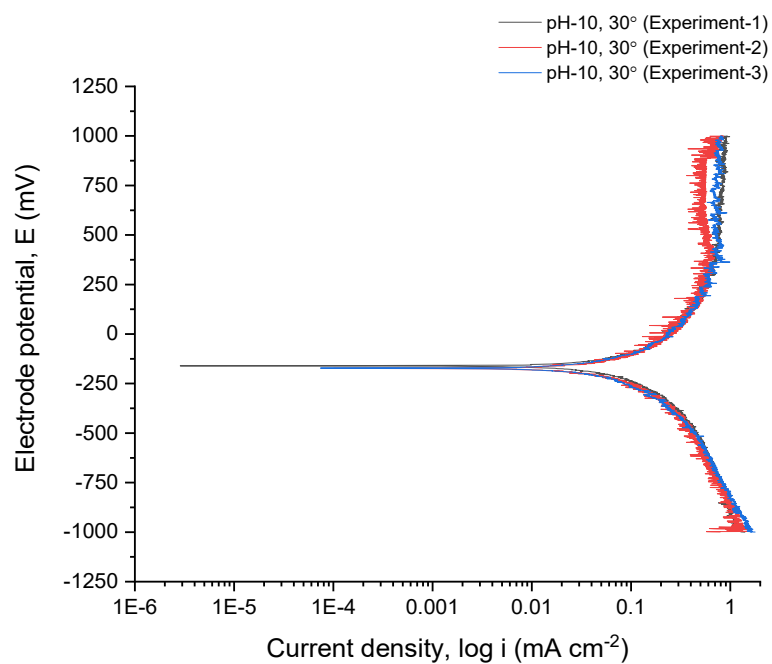
Ta sample No.	Impact angle (deg)	Solution pH	Wear scar No.	Mass of sample before expt. (g)	Mass of sample (g) after 60 min. erosion-corrosion experiment at 5 ms ⁻¹ impact velocity and 7 wt.% SiC concentration.				Mean mass of sample after expt. (g)	Mass loss (g)	Mean mass loss (g)	Set potential (mV)
					R1	R2	R3	R4				
B2Ta3	30	0.5M Citrate Buffer pH 4	3	58.7920	58.7876	58.7876	58.7877	58.7877	58.7877	0.0044	0.0037	+230
B2Ta4			1	59.1690	59.1650	59.1651	59.1651	59.1650	59.1651	0.0039		
B2Ta6			1	59.3240	59.3211	59.3212	59.3212	59.3211	59.3212	0.0028		
B2Ta6		0.5M NaCl pH 7	3	59.3200	59.3172	59.3172	59.3173	59.3174	59.3173	0.0027	0.0027	-125
B2Ta2			4	58.0265	58.0239	58.0239	58.0239	58.0239	58.0239	0.0026		
B2Ta6			4	59.3173	59.3145	59.3145	59.3144	59.315	59.3145	0.0028		
B2Ta4		0.5M Carbonate Buffer pH 10	3	59.1652	59.1605	59.1603	59.161	59.1605	59.1605	0.0047	0.0032	+111
B2Ta4			4	59.1605	59.1579	59.1580	59.1581	59.158	59.1580	0.0025		
B2Ta2			1	57.9050	57.9029	57.9028	57.9027	57.903	57.9028	0.0022		
B2Ta3	90	0.5M Citrate Buffer pH 4	4	58.7877	58.7858	58.7858	58.786	58.786	58.7859	0.0018	0.0015	+60
B2Ta2			2	58.0277	58.0263	58.0263	58.026	58.026	58.0264	0.0014		
B2Ta6			2	59.3212	59.3199	59.3200	59.3201	59.3201	59.3200	0.0012		
B2Ta6		0.5M NaCl pH 7	1	59.1276	59.1266	59.1264	59.1265	59.1264	59.1265	0.0011	0.0011	-80
B2Ta6			3	59.1256	59.1245	59.1245	59.1245	59.1244	59.1245	0.0011		
B2Ta6			4	59.1245	59.1235	59.1235	59.1236	59.1235	59.1235	0.0010		
B2Ta4		0.5M Carbonate Buffer pH 10	4	59.1580	59.1566	59.1563	59.1564	59.1565	59.1565	0.0016	0.0012	-35
B2Ta2			2	57.9028	57.9018	57.9019	57.9018	57.902	57.9019	0.0010		
B2Ta3			1	58.6216	58.6205	58.6206	58.6206	58.6206	58.6206	0.0010		



(a)

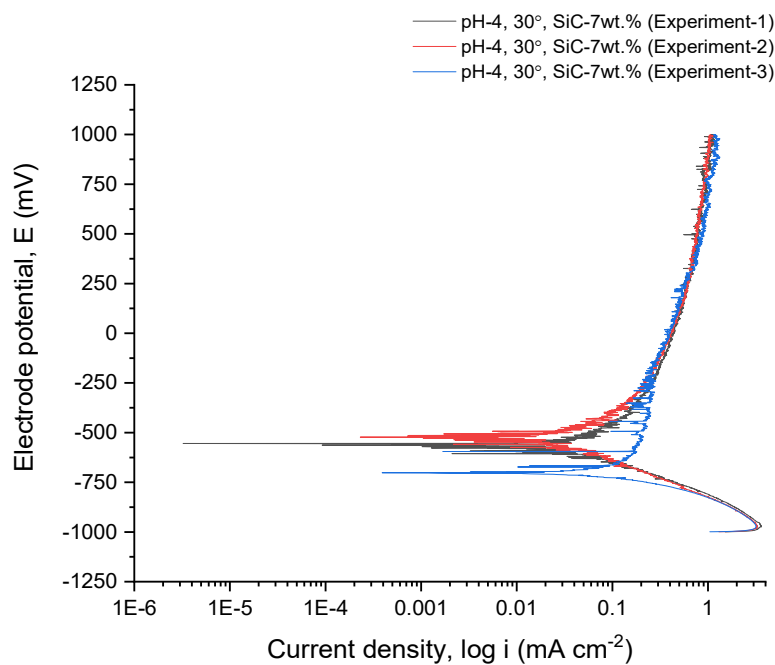


(b)

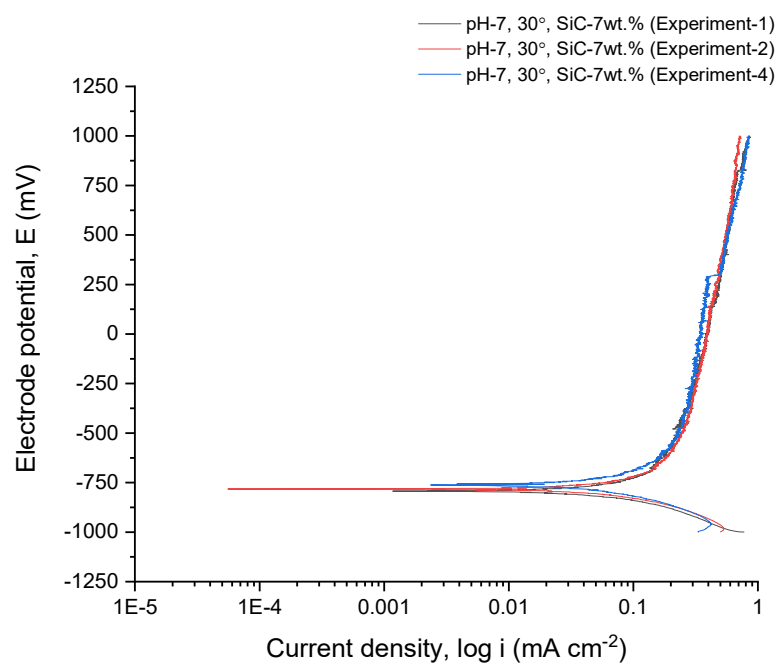


(c)

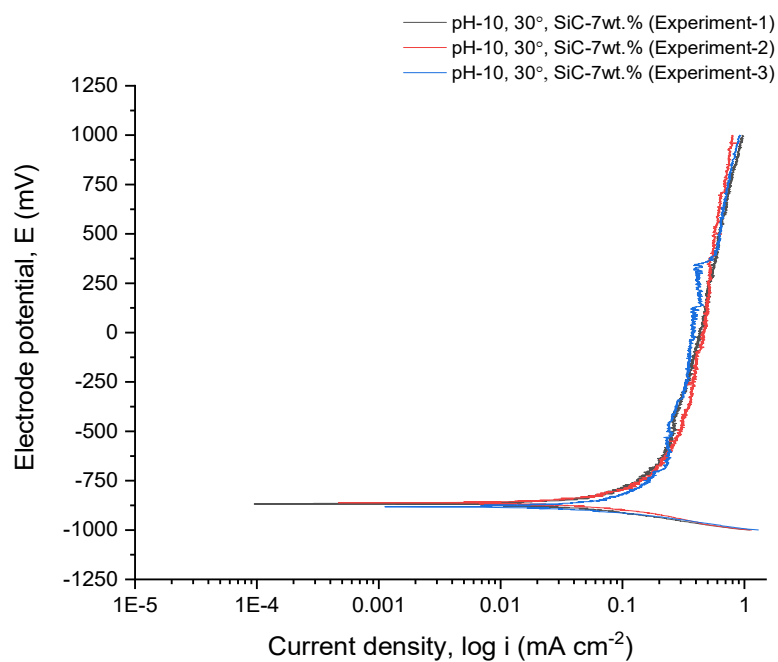
Figure A.1 Tantalum potentiodynamic polarisation curves after corrosion experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 30°)



(a)

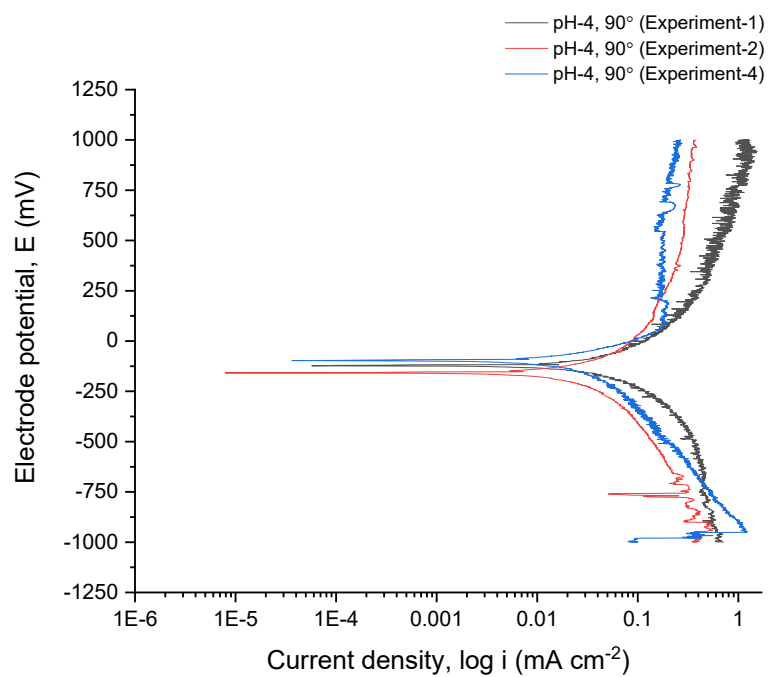


(b)

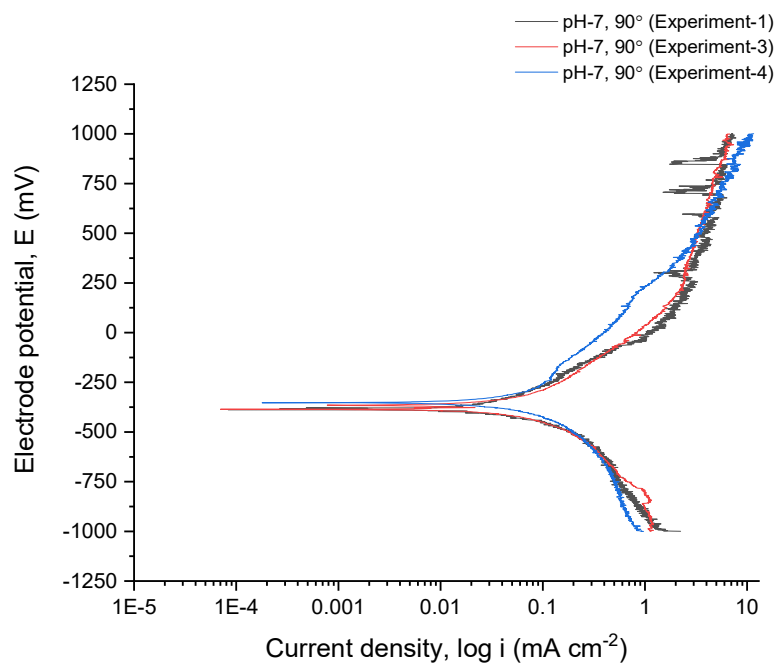


(c)

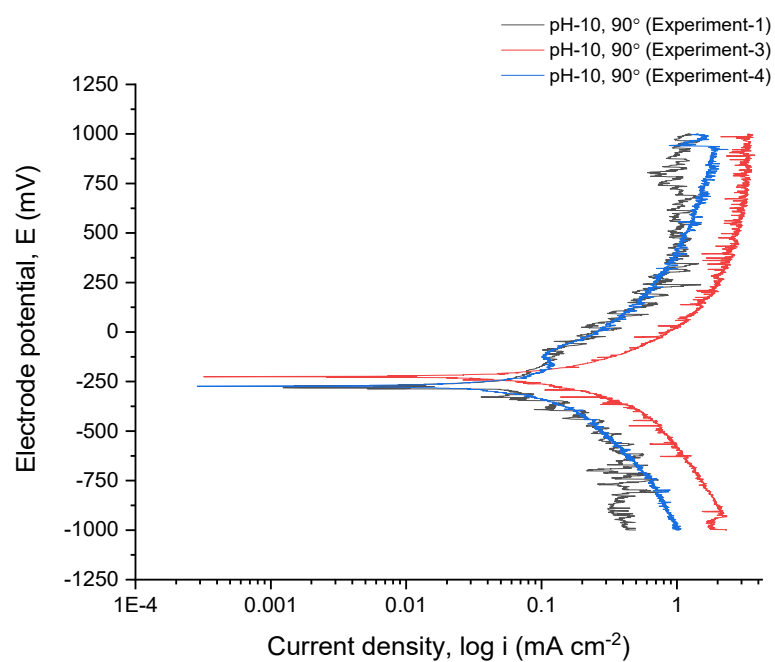
Figure A.2 Tantalum potentiodynamic polarisation curves after corrosion experiments with particles (7 wt.% SiC) in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 30°)



(a)

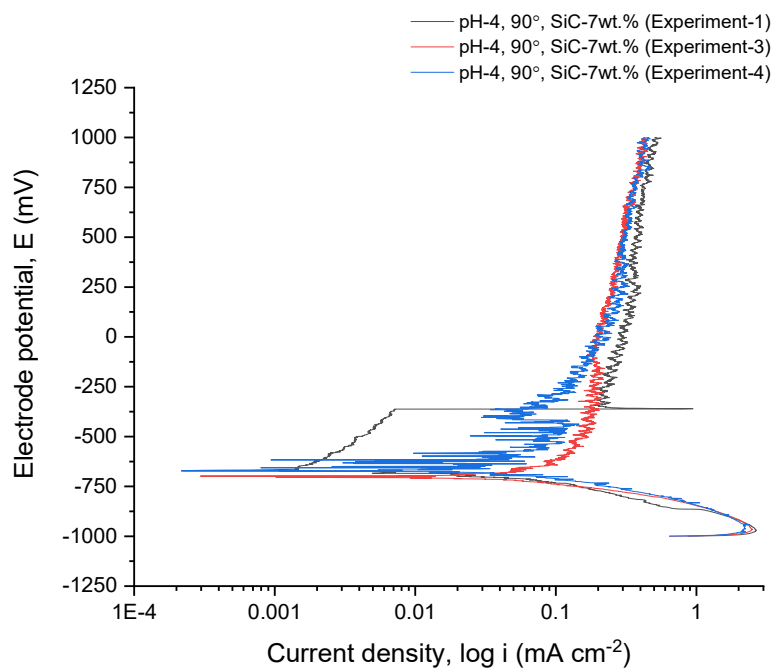


(b)

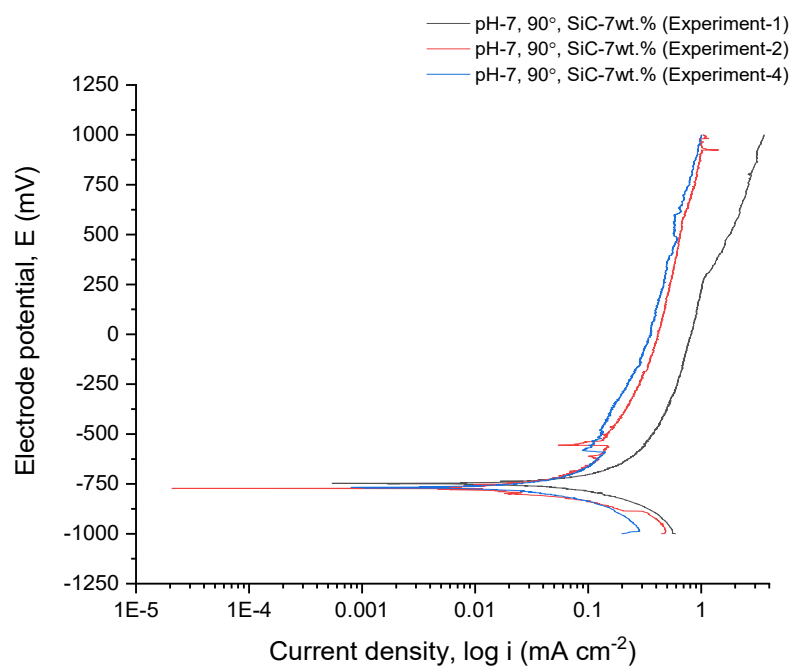


(c)

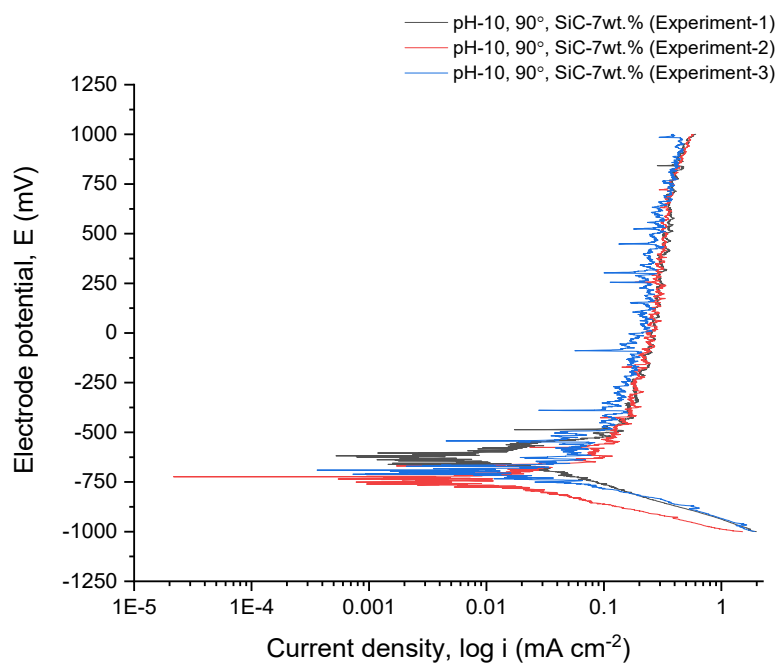
Figure A.3 Tantalum potentiodynamic polarisation curves after corrosion experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 90°)



(a)

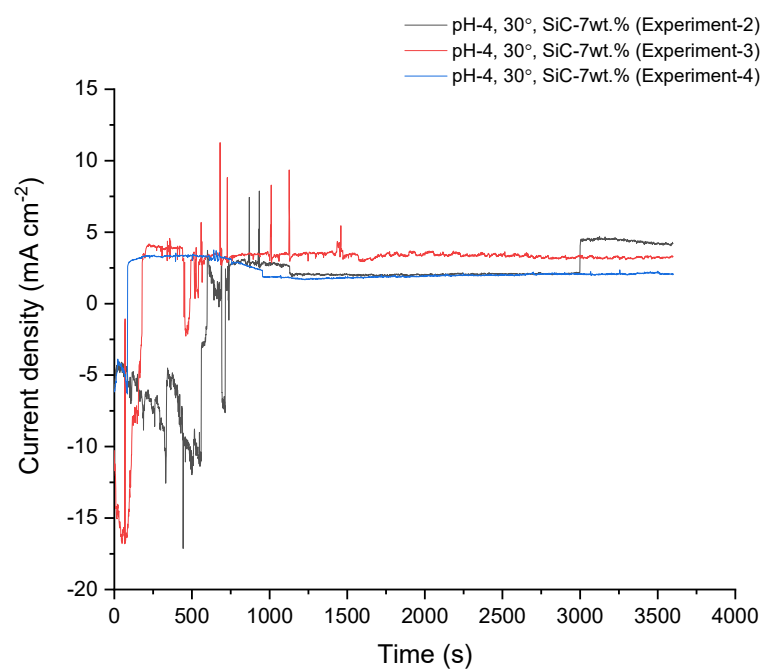


(b)

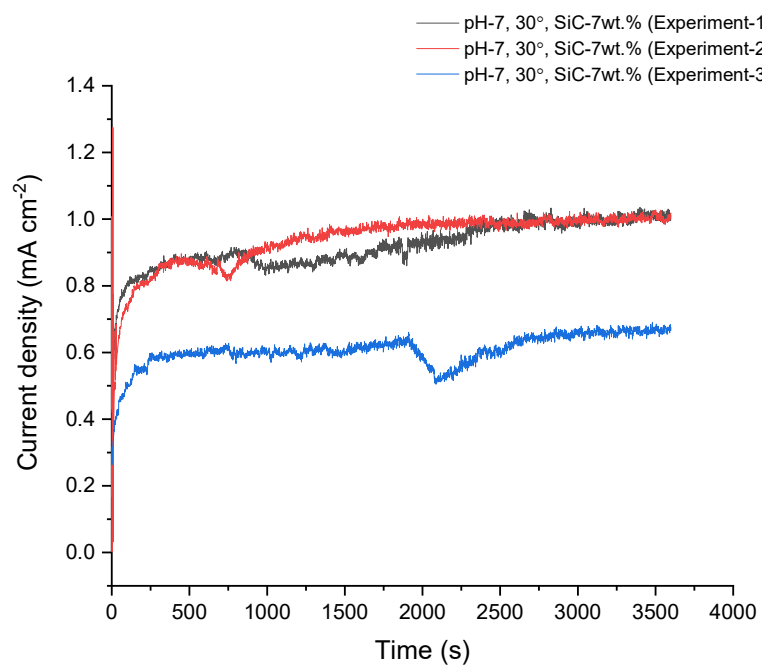


(c)

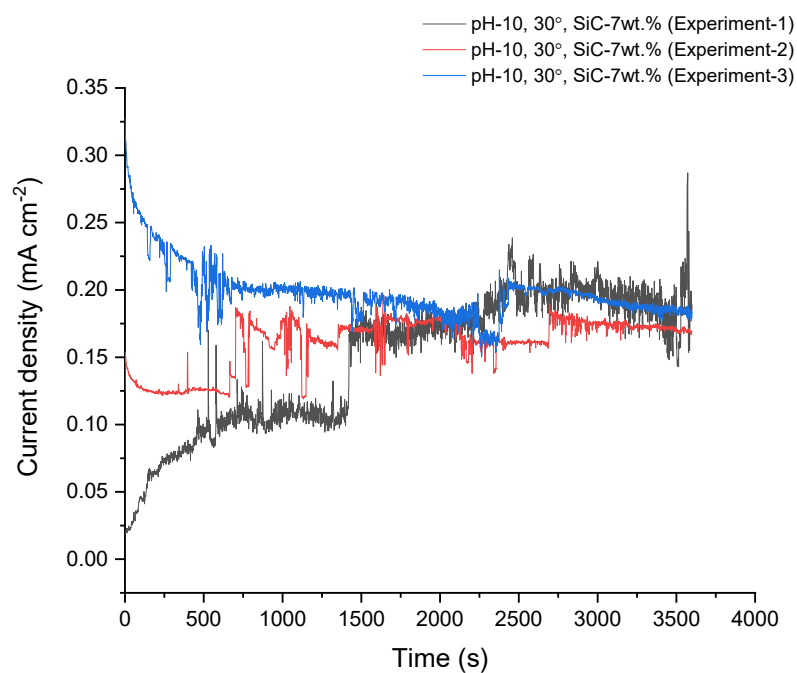
Figure A.4 Tantalum potentiodynamic polarisation curves after corrosion experiments with particles (7 wt.% SiC) in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms⁻¹; impact angle 90°)



(a)

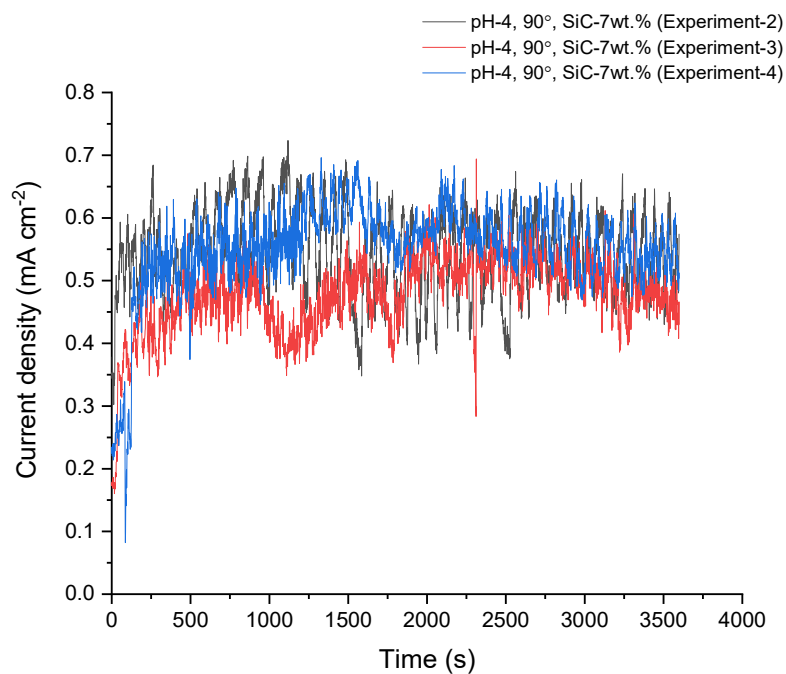


(b)

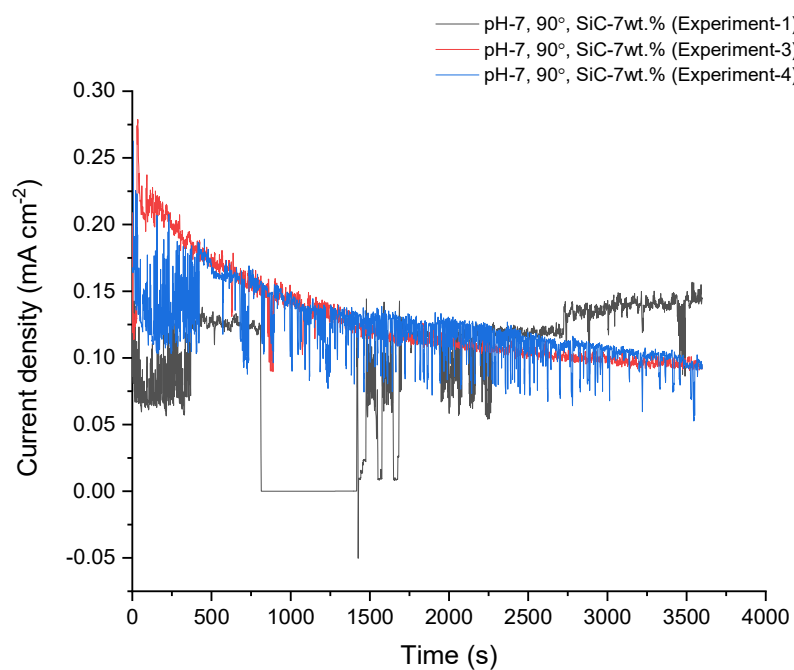


(c)

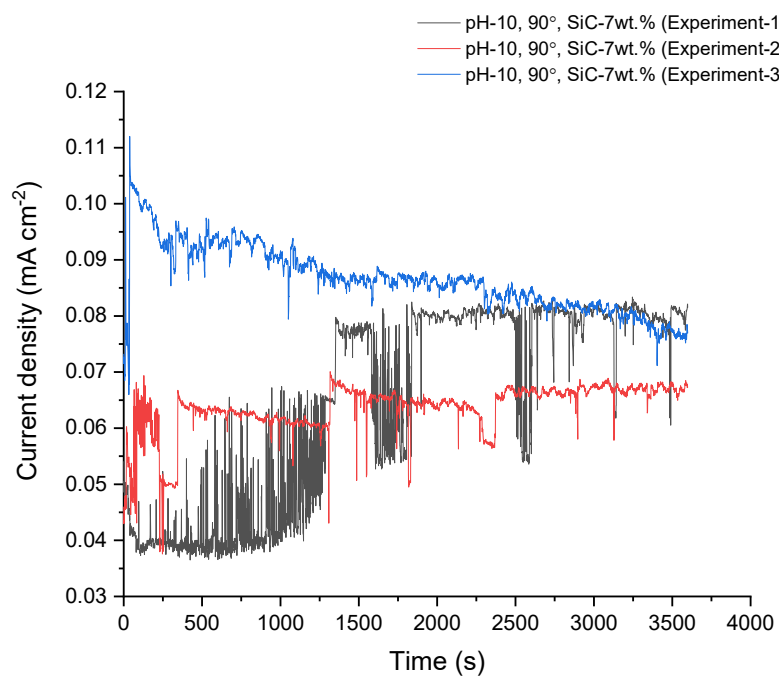
Figure A.5 Tantalum potentiostatic polarisation curves after erosion-corrosion experiments in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 30° ; Slurry concentration 7 wt.%)



(a)

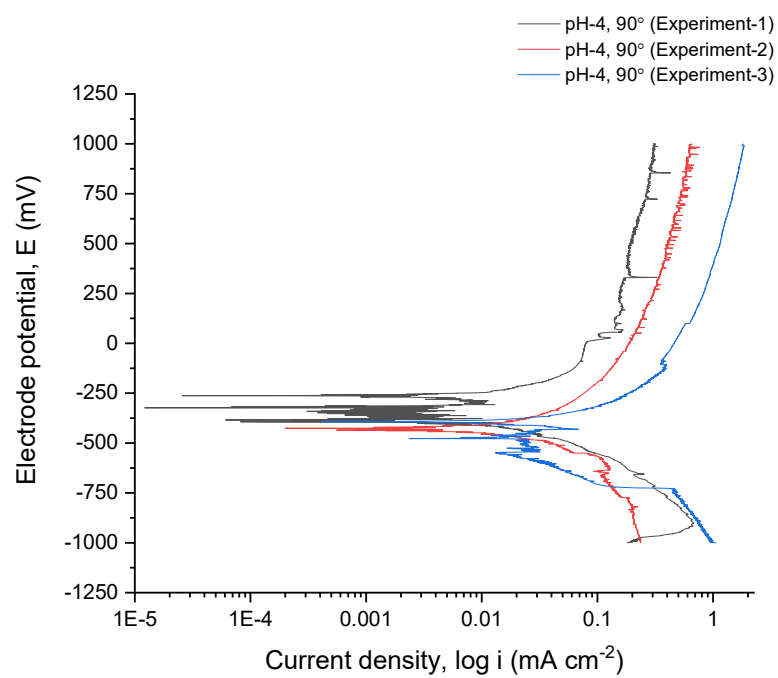


(b)

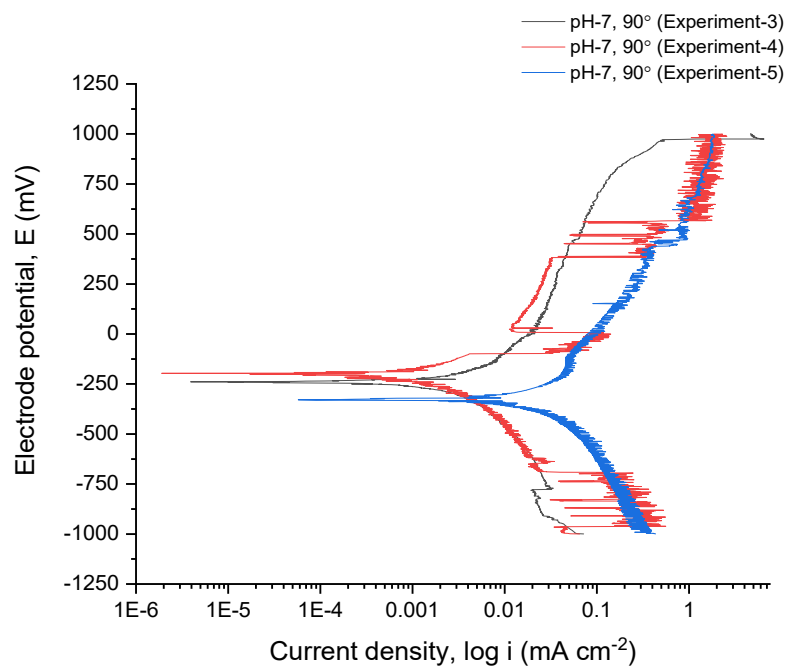


(c)

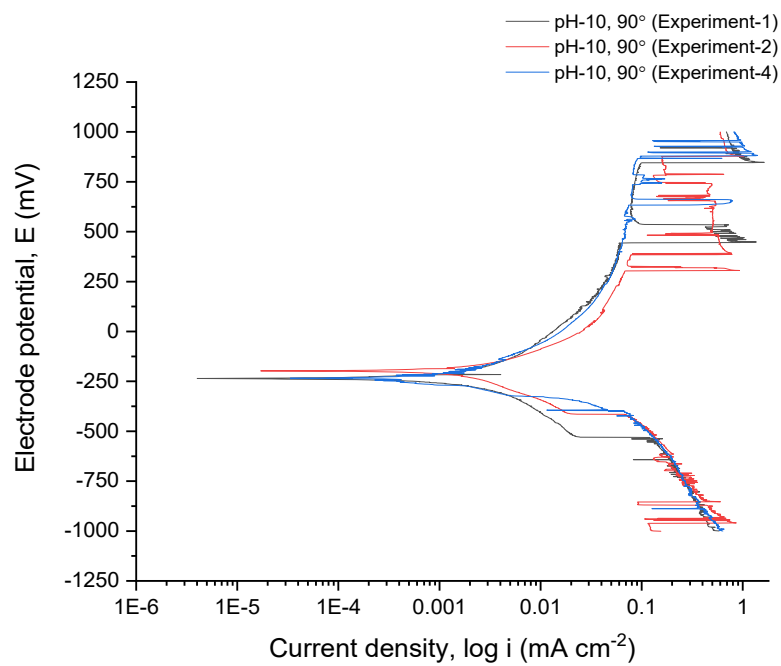
Figure A.6 Tantalum potentiostatic polarisation curves after erosion-corrosion experiments in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 90° ; Slurry concentration 7 wt.%)



(a)

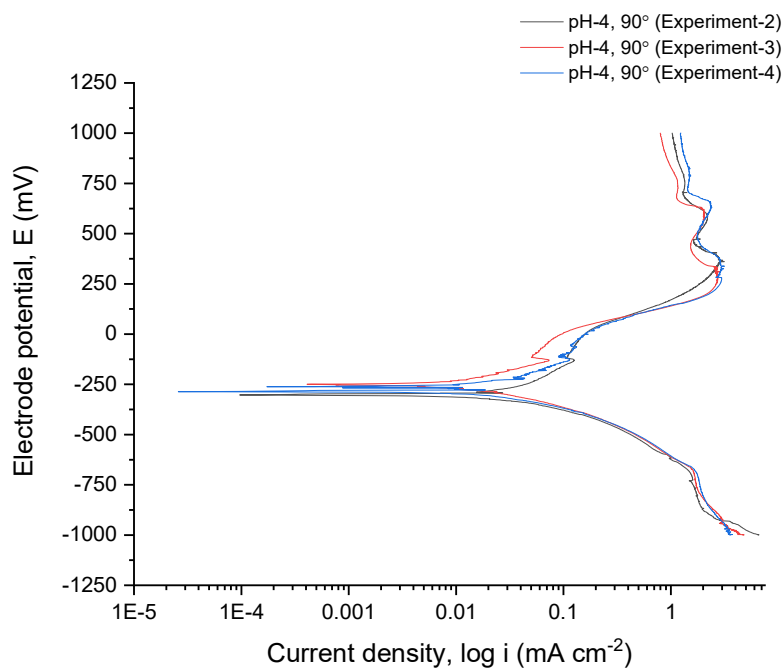


(b)

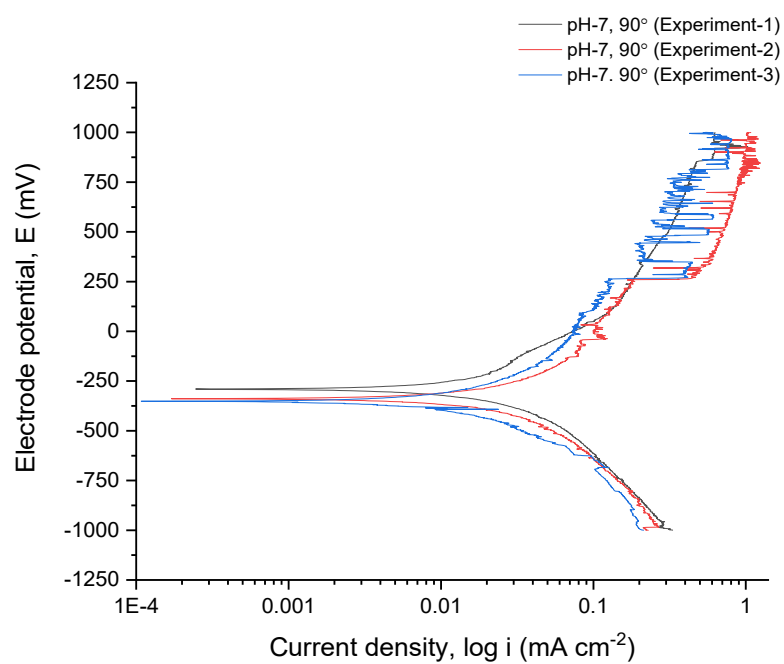


(c)

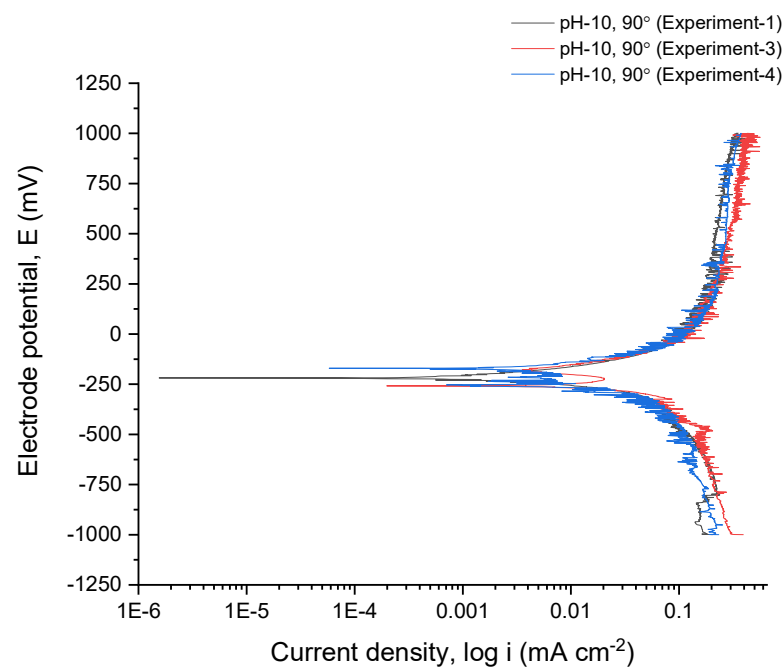
Figure A.7 Tantalum potentiodynamic polarisation curves after corrosion experiments in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 9 ms⁻¹; impact angle 90°)



(a)

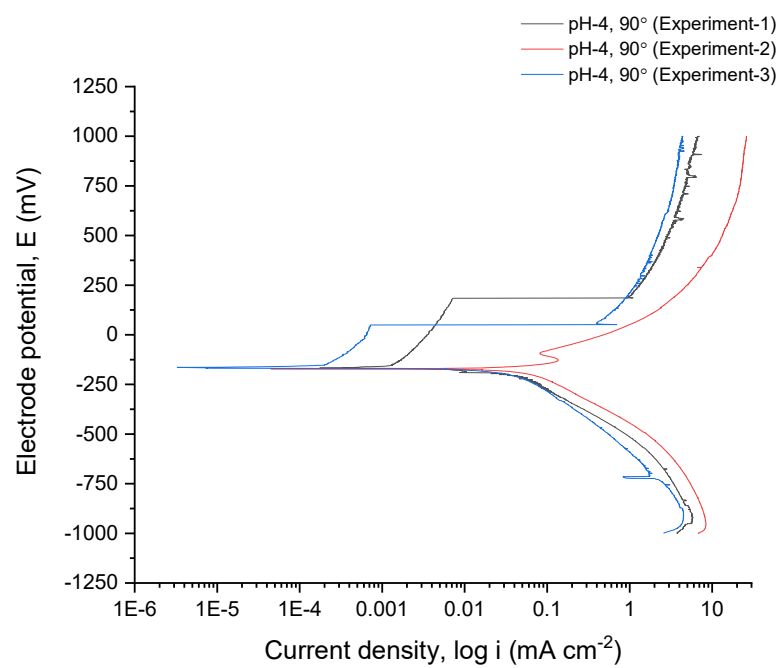


(b)

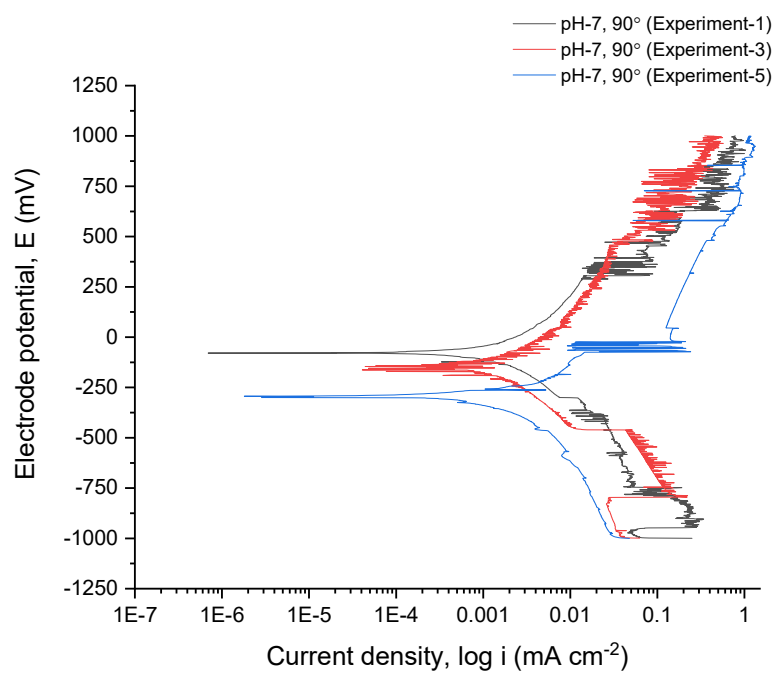


(c)

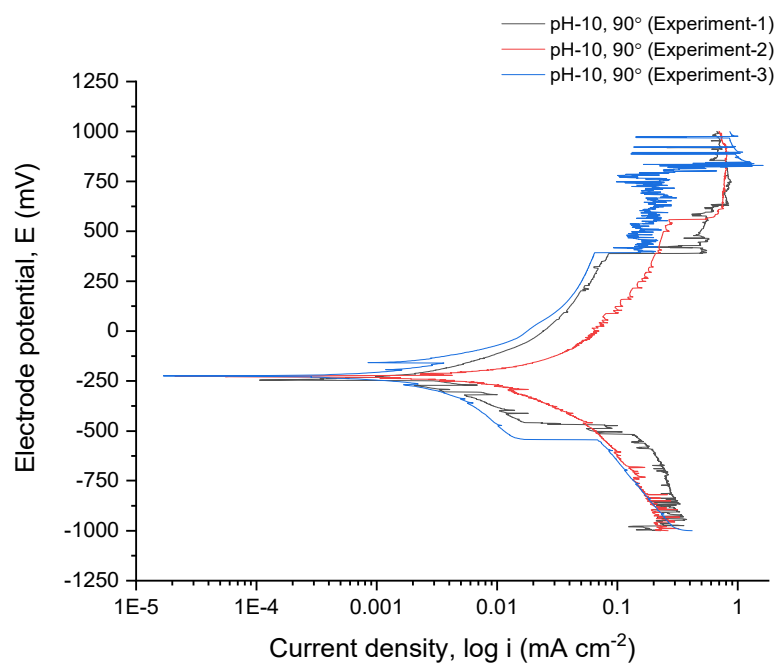
Figure A.8 Tungsten potentiodynamic polarisation curves after corrosion experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms⁻¹; impact angle 90°)



(a)

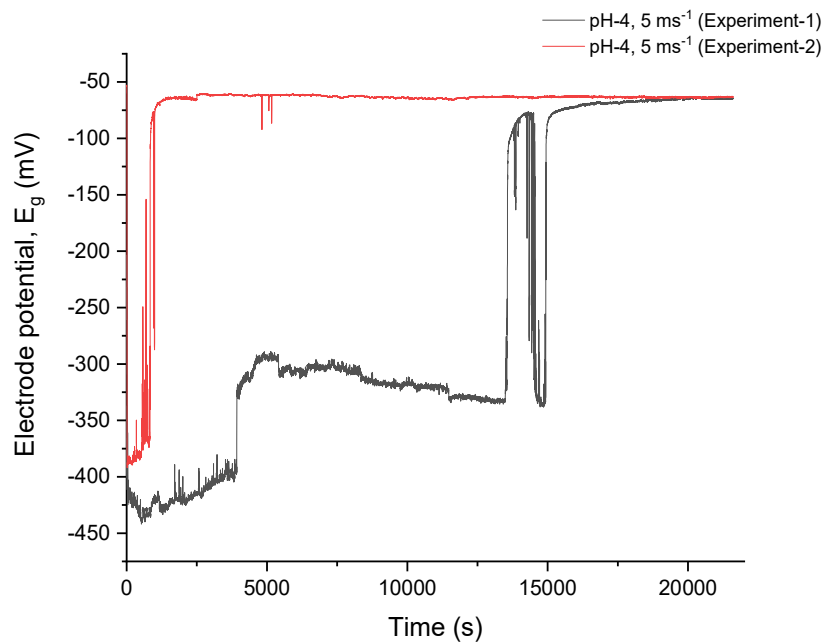


(b)

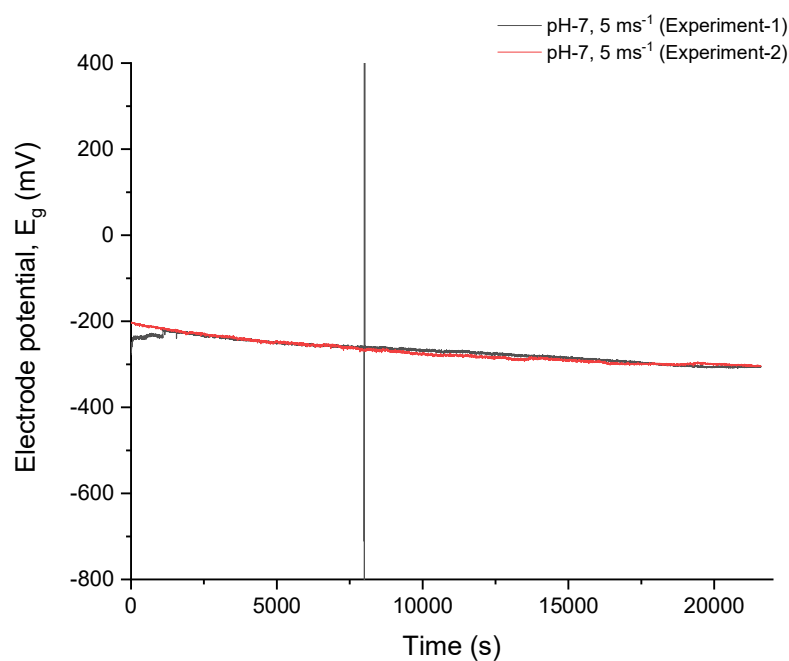


(c)

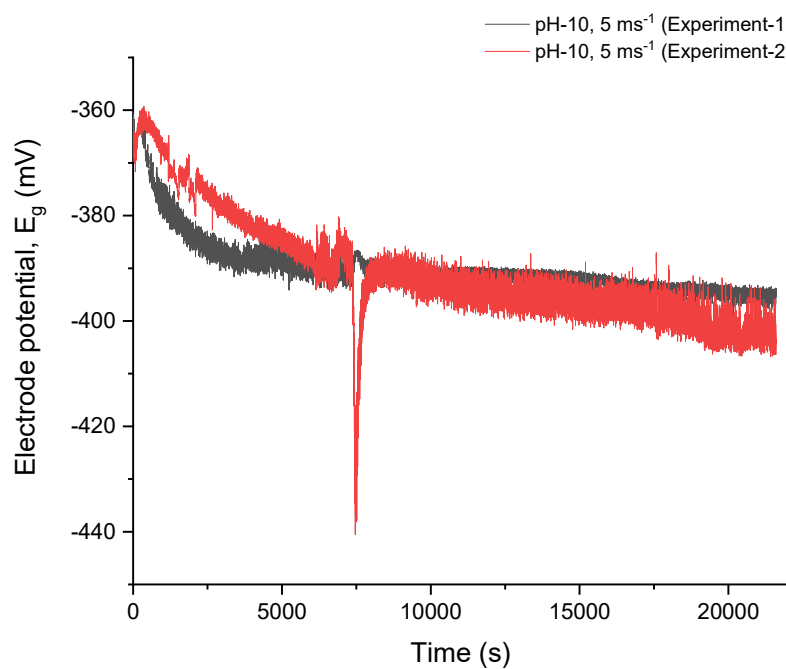
Figure A.9 Tungsten potentiodynamic polarisation curves after corrosion experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 9 ms^{-1} ; impact angle 90°)



(a)

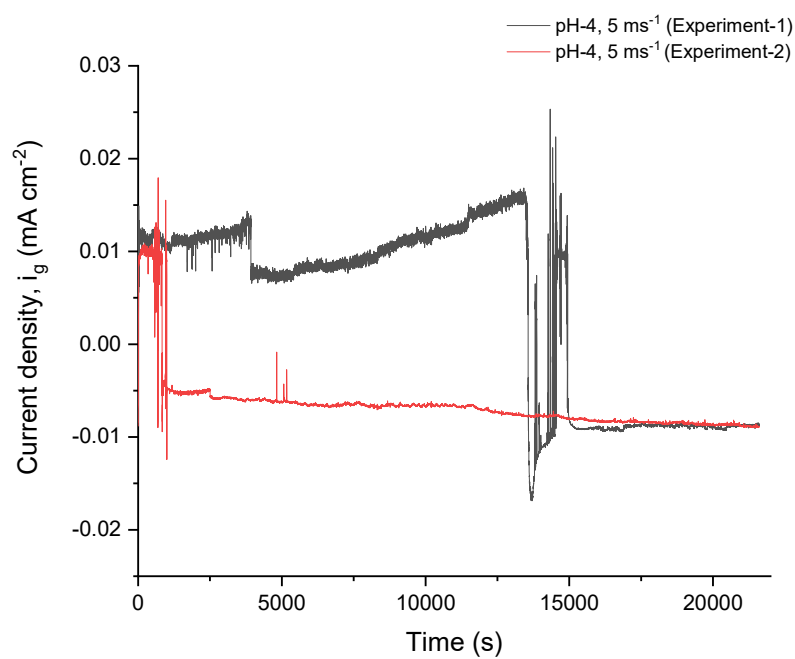


(b)

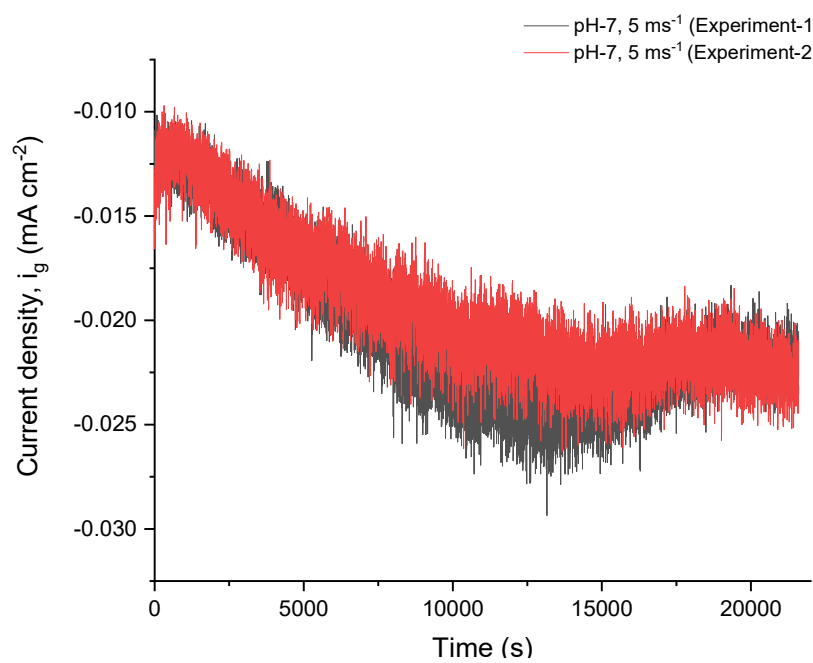


(c)

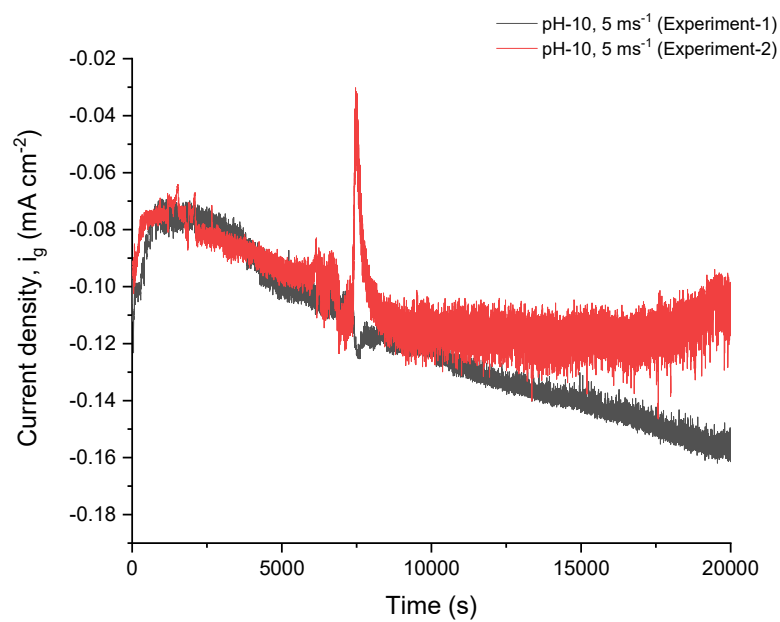
Figure A.10 Galvanic potential (E_g) curves obtained in ZRA experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 90°)



(a)

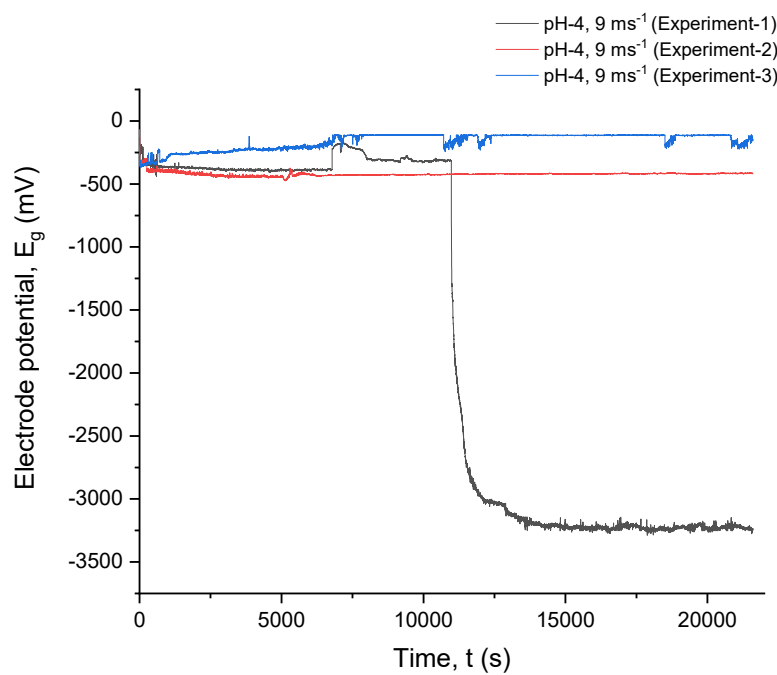


(b)

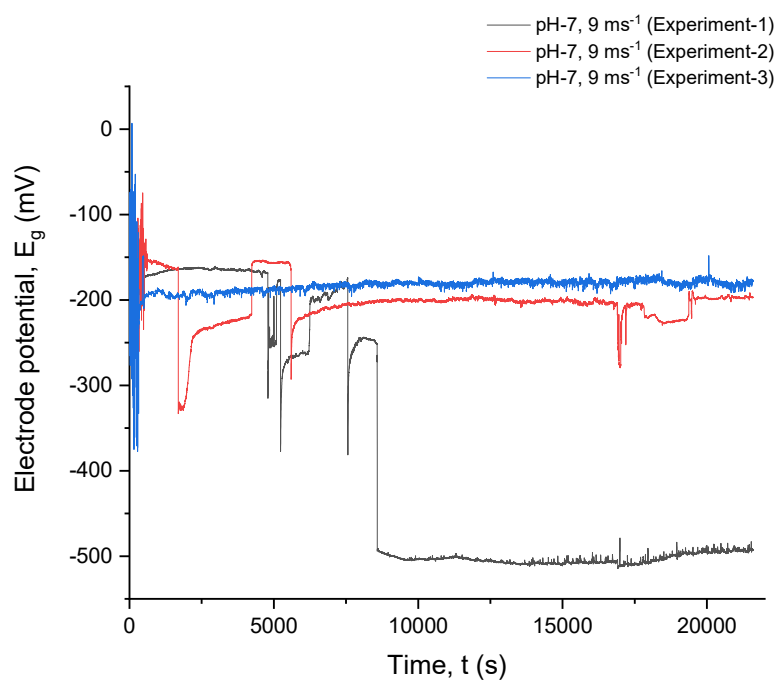


(c)

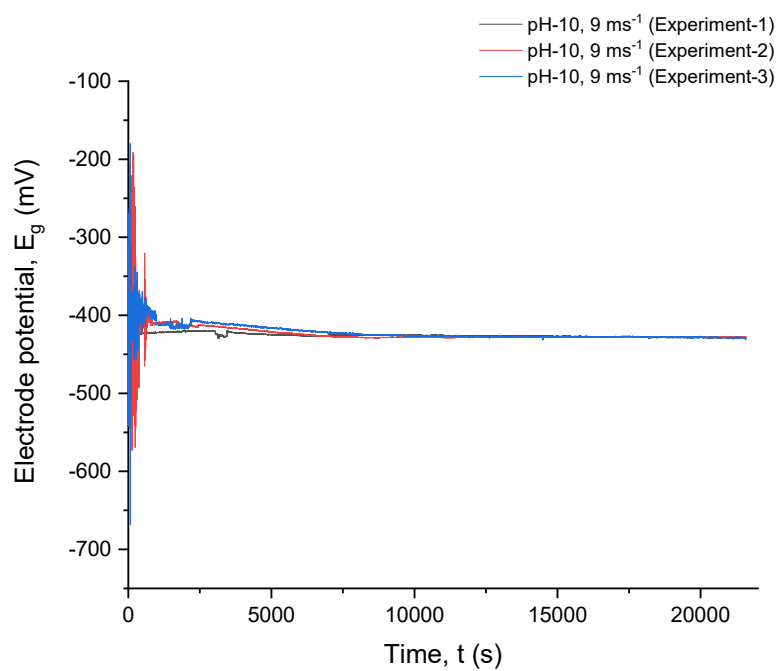
Figure A.11 Galvanic current density (i_g) curves obtained in ZRA experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 5 ms^{-1} ; impact angle 90°)



(a)

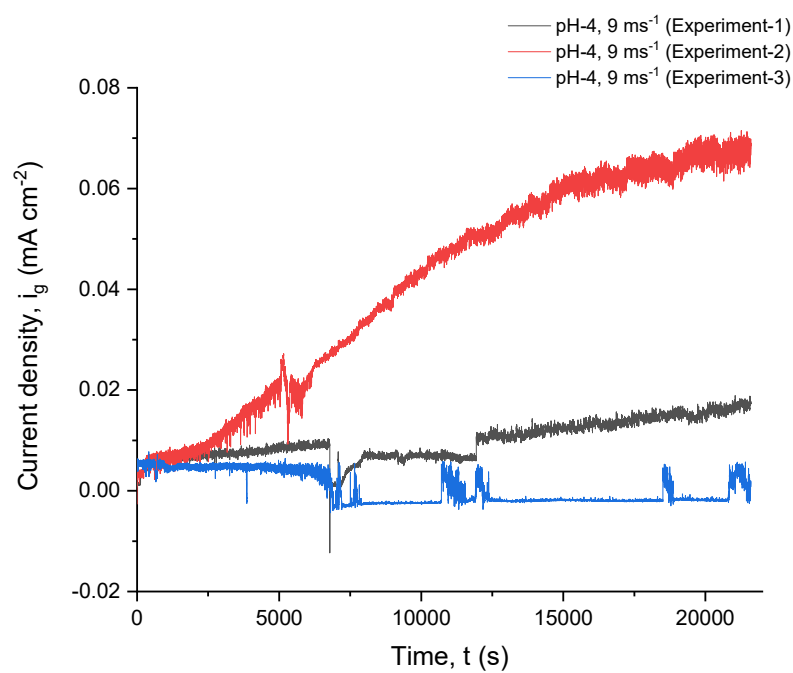


(b)

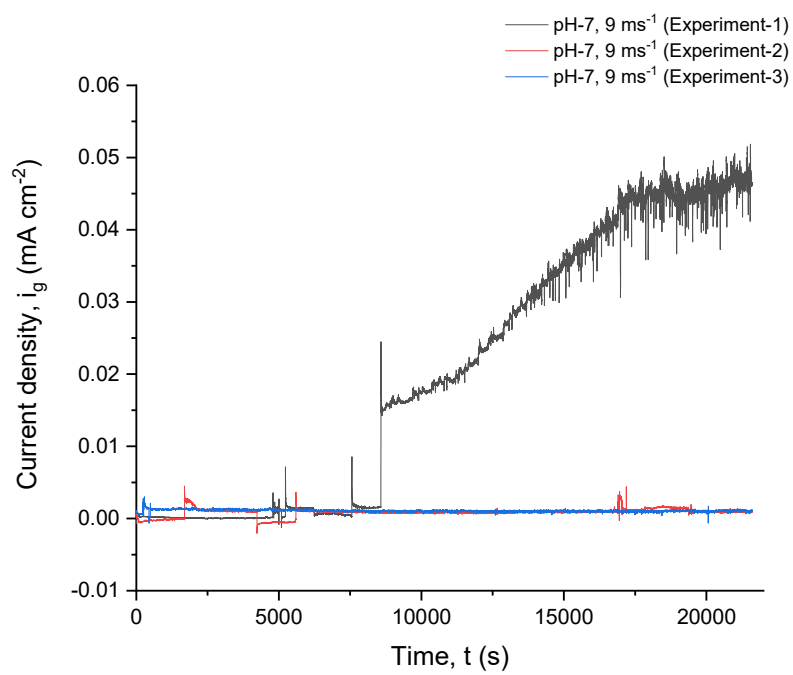


(c)

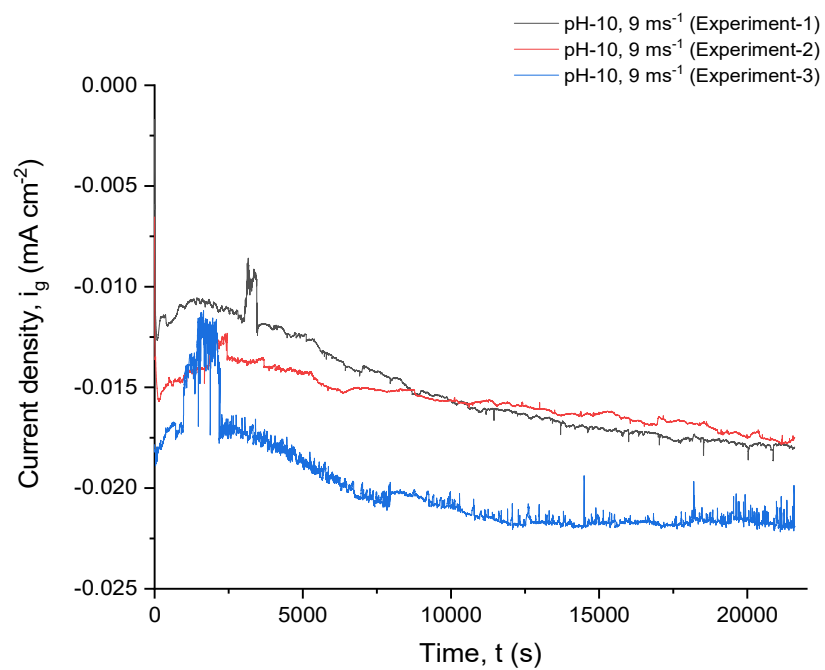
Figure A.12 Galvanic potential (E_g) curves obtained in ZRA experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 9 ms^{-1} ; impact angle 90°)



(a)



(b)



(c)

Figure A.13 Galvanic current density (i_g) curves obtained in ZRA experiments without particles in various solutions: (a) pH 4 (b) pH 7 (c) pH 10. (impact velocity 9 ms⁻¹; impact angle 90°)