

CHAPTER 3

Characterisation of Thermal Oxide Scales on Stainless Steels

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Abstract. This chapter aims at reviewing the characterisation techniques that are commonly used for high temperature oxidation study, especially on stainless steels. In addition, the experimental studies about the high temperature oxidation i.e. thermogravimetric method and chromium volatilisation measurement are explained. The various kinds of characterisation techniques for physico-chemical and electronic properties of thermal oxide scales are reviewed, starting from optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), focused ion beam coupled with scanning electron microscope (FIB/SEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), and photoelectrochemical characterisation (PEC). The review focuses on the basic concepts and shows how the characterising tools can be applied to thermal oxide characterisation.

3.1 Introduction

In high temperature corrosion study, thermal oxide scales are interested in many aspects such as interfaces, morphologies, species, semiconducting types, and growth mechanisms, because they affect lifetime of material. The various techniques are used to characterise the materials.

The surface morphology of thermal oxide grown on alloy can be simply observed by optical microscope and scanning electron microscope. The literature [1–5] always reports the oxide morphology obtained from electron micrographs because it helps visualise the oxide morphology and topography. The focused ion beam coupled with scanning electron microscope is the superior technique because the focused ion beam is used for the cross-sectioning preparation inside the vacuum chamber when the electron microscope is operated, allowing to reveal the information of matter from surface to the desired depth such as morphology [6–7]. Chemical compositions of oxides are generally analysed by energy dispersive X-ray spectroscopy [8–10] and X-ray photoelectron spectroscopy [11–14]. The oxide phases are widely identified by X-ray diffractometer [12–16] and Raman spectroscopy [17–19]. Photoelectrochemical technique, which is generally used for finding electronic characteristics of matter, can be applied to identify thermal oxide phases with a high performance and a superior local analysis [20, 21].

Apart from the characterisation techniques, the experimental methods for simulating oxidation conditions are also important. The set-up generally consists of a furnace and a gas system. A simple set-up uses a typical furnace such as a tubular furnace and the mass gain can be subsequently calculated by weighting outside the furnace. Thermobalance is a superior method because a balance

is equipped with a furnace, providing a real-time weighting during oxidation and permitting an oxidation kinetic study. In addition, the experiments can be set-up depending on the study aspects such as the study of chromium volatilisation. In some oxidising conditions, trivalent chromium compound (Cr^{3+}) is oxidised to the hexavalent chromium (Cr^{6+}) compound, which can be volatile such as the oxyhydroxyde $\text{CrO}_2(\text{OH})_2$, leading to a low chromium/iron ratio in the scale. Both of the experimental methods and the characterisation techniques will be reviewed in this chapter.

3.2 Analysis of Gas Composition in the Furnace: a Case of Humidified Oxygen

The types of the oxide formed at high temperatures can be varied depending on many parameters particularly the atmospheres the metal is exposed to. The analysis of gas composition in the atmosphere is important to predict thermodynamic stability and oxidation kinetics of the metal. One of the gases that could significantly affect the oxide formation and will be treated here is water vapour. This gas is typically present in the ambient atmosphere of the industrial processes [22–27] or in the cathode side of the solid oxide fuel cells [28–31]. The experimental set-up to produce the gas mixture containing water vapour can be done by purging oxygen into a flask containing water, giving oxygen with water vapour at the outlet of the flask. The water vapour content is controlled by water temperature in the flask according to the Clausius-Clapeyron equation [32]:

$$\ln \left(\frac{p_{\text{H}_2\text{O}(\text{g}),T}}{p_{\text{H}_2\text{O}(\text{g})}} \right) = -\frac{\Delta H^{1 \rightarrow v}}{R} \left(\frac{1}{T} - \frac{1}{373.15} \right) \quad (3.1)$$

where $p_{\text{H}_2\text{O}(\text{g}),T}$ is the partial pressure of water vapour at temperature T , $p_{\text{H}_2\text{O}(\text{g})}$ is the partial pressure of water vapour at 100 °C (1 bar), $\Delta H^{1 \rightarrow v}$ is the enthalpy of vaporisation (J mol^{-1}), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the considered temperature in K.

At ambient temperatures of 15–20 °C, the water vapour pressure might be calculated by assuming that $\Delta H^{1 \rightarrow v}$ is constant with the value of 40893 J mol^{-1} [33]. In this case, the water vapour pressure is in the range of 0.020–0.027 bar. In the condition where water vapour exists in the atmosphere with other gases i.e. H_2 and O_2 , these three gases can be in equilibrium according to Reaction 3.2.



As an example for the case when the oxidising atmosphere contains $A\%$ of H_2O in argon inert gas, Table 3.1 shows the calculation method to determine a partial pressure of each gas in the atmosphere. From this table, A mol of water vapour is in the initial state. When the reaction occurs, $2x$ mol of A is consumed while $2x$ mol of hydrogen gas and x mol of oxygen gas are formed. This gives at equilibrium $A - 2x$ mol of water vapour, $2x$ mol of hydrogen gas, and x mol of oxygen, giving the total number of mole of $100 + x$. If the total pressure is 1 bar, a mole fraction equals the partial pressure. The partial pressure of each gas can then be expressed as follows:

$$p_{\text{H}_2\text{O}} = \frac{A - 2x}{100 + x} \quad (3.3)$$

$$p_{\text{H}_2} = \frac{2x}{100 + x} \quad (3.4)$$

$$p_{O_2} = \frac{x}{100+x} \quad (3.5)$$

where x can be found out from the equilibrium constant of Reaction 3.2 which is

$$K = \exp\left(\frac{-\Delta_r G_{3.2}^\circ}{RT}\right) = \left(\frac{p_{H_2}^2 \cdot p_{O_2}}{p_{H_2O}^2}\right)_{eq} = \frac{\left(\frac{2x}{100+x}\right)^2 \left(\frac{x}{100+x}\right)}{\left(\frac{A-2x}{100+x}\right)^2} \quad (3.6)$$

By assuming that $x \ll A$ and $x \ll 100$, it can be obtained that

$$x = (25A^2 K)^{1/3} \quad (3.7)$$

Table 3.1 Determination of partial pressure of gases in water dissociation reaction.

	$2H_2O_{(g)}$	$=$	$2H_{2(g)}$	$+$	$O_{2(g)}$	Ar	Total mole
Initial number of mole	A		0		0	$100-A$	100
Reacted number of mole	$-2x$		$2x$		x		
Final number of mole at equilibrium	$A-2x$		$2x$		x	$100-A$	$100+x$
Mole fraction	$\frac{A-2x}{100+x}$		$\frac{2x}{100+x}$		$\frac{x}{100+x}$		

For example, at 900 °C in argon with 20% of water vapour, by using [32]

$$\Delta_r G_{3.2}^\circ = 117800 - 26.2T \text{ cal} \quad (3.8)$$

it can be obtained that $x = 8.45 \times 10^{-5}$ and $p_{O_2} = 8.45 \times 10^{-7}$ bar [34]. It is noted that, in pure water vapour, the oxygen dissociation from water vapour is essentially small. Thus the role of water vapour on steel oxidation is not only mainly from the oxygen dissociated but from other mechanisms which will be explained in Chapter 5.

Furthermore, after the oxidation test, mass gain or scale thickness can be measured. Such mass gain is in fact from the oxygen gas consumed by the oxidation reaction. Once the mass gain is measured, the oxide thickness can be calculated using Eq. 1.28. The calculated thickness can be used to compare with the measured oxide thickness. For example, when AISI 441 stainless steel is oxidised in air at 850 °C for 1 h, mass gain was measured and calculated to be 0.03 mg cm^{-2} and then oxide thickness was calculated to be $0.18 \text{ }\mu\text{m}$ by assuming that the oxide formed is chromia and has the density of 5.21 g cm^{-3} [35]. The measured oxide thickness gives the value of $0.16 \text{ }\mu\text{m}$. This case shows that the scale thickness calculated from the measured mass gain is similar to the thickness measured directly from the sample.

3.3 Chromium Species Volatilisation Measurement

In order to measure chromium species volatilisation from the alloys, the experimental set-up as shown in Fig. 3.1 is invented. The oxygen tank is connected to the flow meter which is continuously connected to the humidifier set. The role of humidifier set is to adjust the humidity in the gas. After this section, the humidified O_2 is flowed to the quartz column installed inside the furnace. The specimen is hung in the quartz column at the position “S”. At the end of the column, the condenser is installed and immersed in the thermos cryostat where the temperature is set to be 7°C in order to condense the chromium volatile species from the specimen. Before venting the outlet gas to the atmosphere, the gas is flowed through the water-containing Erlenmeyer flask which is the second bubbler of the setup for making sure that all chromium volatile species are captured into the solution. After the experiment, the temperature is cooled down to room temperature. The column is cleaned by 0.1 M HCl. The cleaning acid solution together with the solutions collected from the condenser and the second bubbler are then analysed by inductively coupled plasma (ICP) to measure the amount of chromium volatile from the specimen.

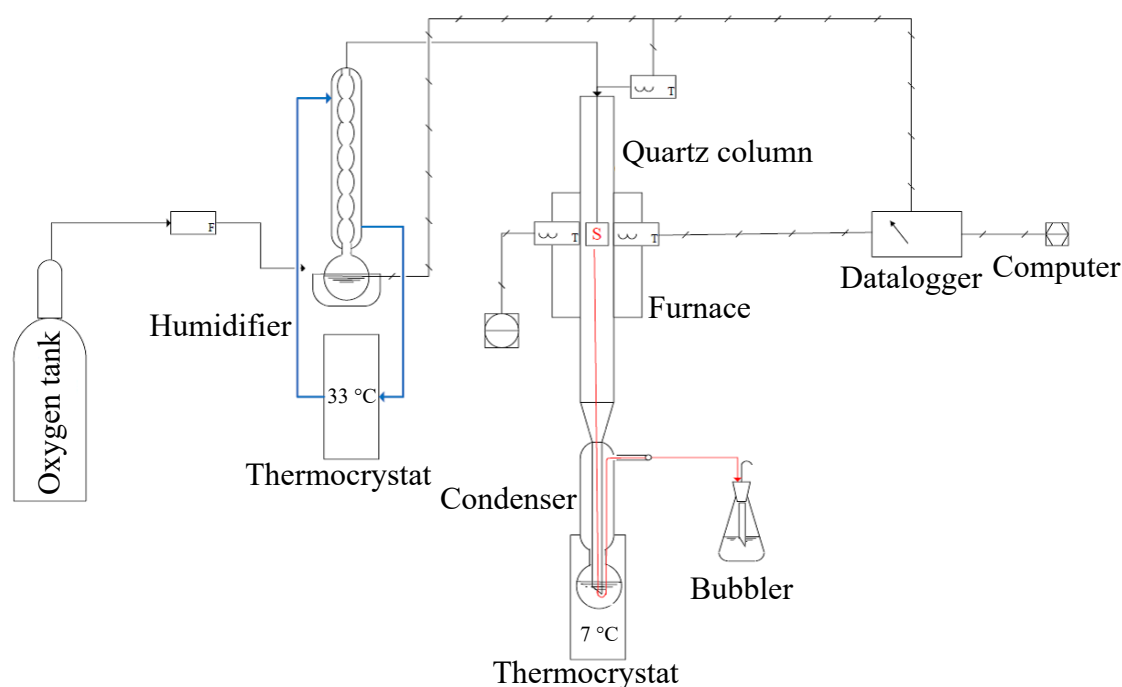


Fig. 3.1. Schematic sketch of chromium volatilisation experimental set-up. Reproduced from W. Wongpromrat et al., *Corros. Sci.* 106 (2016) 172–178 [28].

3.4 Physico-Chemical Characterisation

Physico-chemical properties of materials can be characterised by various techniques. The sources that are used in these techniques can be photon, electron, or ion. Microscopy is a basic technique for physical property observation that the image is usually performed by photon (visible light or X-ray or laser) or electron as optical microscopy or electron microscopy, respectively. Apart from benefits in image performing, when photons or electrons or ions interact with matter, the various signals can be produced.

In the case of photon, X-ray is broadly used to be the source for characterisation techniques. When X-ray is illuminated on matter, the photoelectron and secondary X-ray can be generated. For X-ray photoelectron spectroscopy (XPS) technique, the binding energy of photoelectron, which is the fingerprint of matter, can be evaluated to identify element and its chemical environment. X-ray diffraction (XRD) is one of the techniques that use X-ray as a source and analyse diffracted X-ray to generally identify a phase of matter by finding the lattice spacing and crystal structure. Laser source,

which is a monochromatic and intense light, is also typically used as in Raman spectroscopy where matter is characterised from the frequency change of light.

In the case of electron, the interaction of electron beam on matter might generate secondary electron, backscattered electron, Auger electron, and X-ray. These kinds of signals are useful for characterisation. Scanning electron microscopy (SEM) uses secondary and backscattered electrons to perform image that reveals surface topography. Auger electron, which is produced at a very near surface, is the important one of surface analysis techniques, named Auger spectroscopy (AES). The energy dispersive X-ray spectroscopy (EDS or EDX), which is typically equipped with SEM, utilises the characteristic X-ray for elemental analysis technique. Besides, some electrons that can pass through the thin matter are utilised to find many characteristics by transmission electron microscopy (TEM). Nowadays, many techniques with electron source are developed such as scanning transmission electron microscopy (STEM) which combines the principles of SEM and TEM. Moreover, some techniques are developed to support and enhance performance of other techniques such as focused ion-beam (FIB) instrument that is equipped with SEM.

In the case of ion, the energetic ion beam focused on matter can generate sputtered atoms or molecules. The charge of these species might be neutral, negative or positive, according to momentum transfer from the primary ion to the sample surface. In secondary ion mass spectroscopy (SIMS), the intensity of the obtained secondary ion is measured and reported.

Most of the techniques mentioned above will be presented in more detail concerning the principles, applications, advantages, disadvantages and limitations in the following parts.

3.4.1 Optical Microscopy

Microscopy is a technique for image performing. The technique is generally used to observe morphology of materials. The typical microscopes can be categorised by sources as optical microscope and electron microscope. Magnification and resolution of the image obtained from optical microscope is low, comparing with the image obtained from electron microscope. However, optical microscope is still useful and widely used because the operation is simple and fast. In addition, the optical microscope is inexpensive and affordable.

Optical microscopy or OM is generally referred to an optical instrument containing lenses that produce an enlarged image of an object placed in the focal plane of the lenses using light source. Typically, visible light with 400 to 700 nm in wavelength is used to study the microstructure of materials, leading to resolution limitation in submicron scale. Magnification of the image is also limited at around 1500 times. Apart from morphology, optical microscopes can be used to determine other characteristics of materials, depending on model or set-up, such as phase distribution, transparency or opacity, colour, refractive indices, dispersion of refractive indices, crystal system, degree of crystallinity, and polymorphism.

The conventional optical microscope could be operated in two modes as transmission and reflection mode, depending on the path of light. Transmission is suitable for the transparent sample, whereas reflection is suitable for the opaque sample. Hence, the use of reflective light is appropriate for metallurgy and the oxide grown on surface of alloys studies. The image colours of the reflected light microscope depend on amounts of collected light reflected from surface. If the area reflects more light to objective lenses, a lighter tone is presented on image.

Fig. 3.2 illustrates the example of optical micrographs obtained from the 2205 duplex stainless steel surface before and after oxidation at 850 °C under water vapour during 5 min. Since the duplex stainless steel consists of two phases of ferrite and austenite, the micrographs reveal the different phases with some defects in structure as twin. Moreover, in Fig. 3.2(b), micrograph illustrates the different oxide morphology between oxides grown on ferritic phase (dark area) and on austenitic phase (light area). However the technique still has a limit. It cannot provide the perfect oxide morphology image because one shot of image is obtained from only one focal plane, resulting in some blur area in the image when the high magnification image is performed as illustrated in Fig. 3.3. The light microscope previously mentioned is generally used in high temperature oxidation

and is sometimes specifically called a bright field microscope. However, other light microscopes for the other particular functions are evolved such as a dark field microscope, ultraviolet microscope, fluorescence microscope, and phase-contrast microscope.

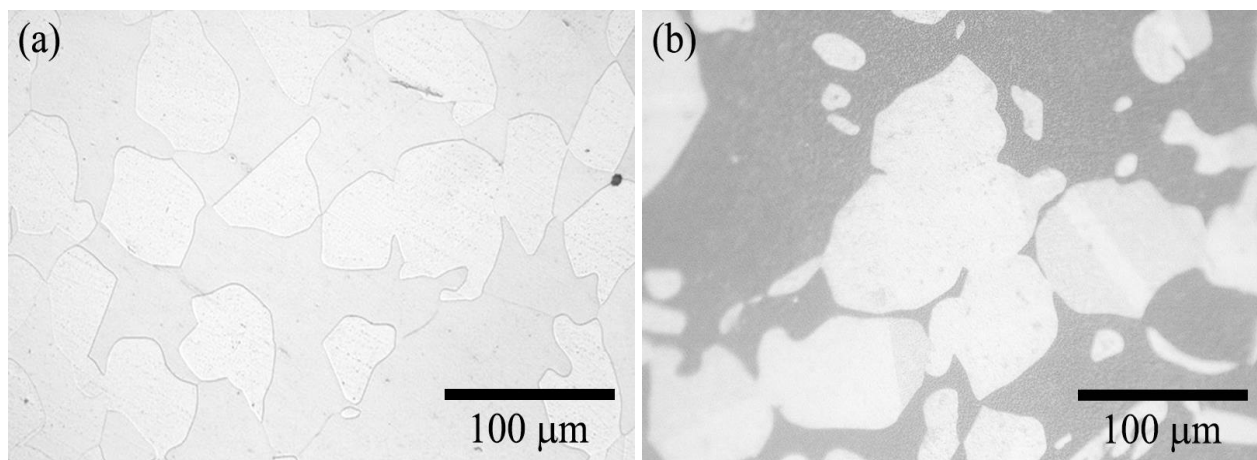


Fig. 3.2. Optical micrographs of the 2205 duplex stainless steel surface (a) before and (b) after oxidation at 850 °C under water vapour in nitrogen gas during 5 min [36].

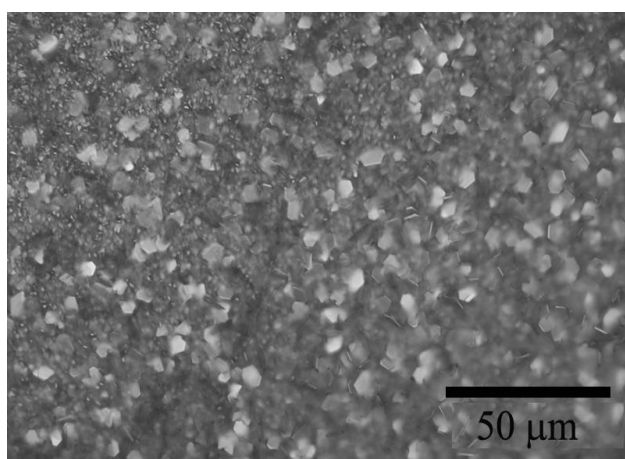


Fig. 3.3. Optical micrograph of the AISI 304 austenitic stainless steel oxidised at 800 °C in laboratory air during 25 h [36].

3.4.2 Scanning Electron Microscopy

As already mentioned in the previous part, electron microscopy is one of microscopy techniques that the images are performed by electron source. The technique is also mainly categorised in scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 3.4 shows signals obtained from materials interacted with incident electron beam. The signals are achieved from both quasi-elastic and inelastic events. For the quasi-elastic event that the trajectory of incident electron is affected while the kinetic energy of incident electron is not affected, some incident electrons can pass through materials either with or without diffraction that are called diffracted electrons or transmitted electrons respectively. The other incident electrons which cannot pass through material are retarded by the electromagnetic field of the nucleus and scattered back from the matter surface, giving backscattered electrons. For the inelastic event that the electron energy is transferred to the matter, the secondary electron, the characteristic X-ray and the Auger electron are generated with different phenomena.

Scanning electron microscopy mainly utilises signals of the secondary electron (SE) and the backscattered electron (BSE) that escape from the surface. The interaction volume of an incident electron beam on a sample in Fig. 3.5 illustrates that the secondary electron comes from the shallow depth and small volume compared with the backscattered electron because the energy of the secondary electron is very low compared with the energy of the backscattered electron. Therefore the secondary electron provides near-surface information with the small volume, leading to the higher image resolution compared with the backscattered electron image. Fig. 3.6 shows the high resolution secondary electron micrographs at different magnifications of 2205 duplex stainless steel oxidised at 850 °C under water vapour in nitrogen gas during 2 h. The different surface morphology is clearly revealed between the oxide grown on ferritic and austenitic phases. The electron micrographs obtained from secondary electrons and backscattered electrons of 2205 duplex stainless steel oxidised at 850 °C under hydrogen gas during 5 min is shown in Fig. 3.7. It is obviously seen that the secondary electron micrograph provides the better information about morphology.

However, the backscattered electron micrograph is still useful because the backscattered electron can provide the superior information about atomic number of matter. The backscattered electron yield obtained from the interaction between incident electron and material strongly depends on atomic number when the atomic number is less than 40. In this range of atomic number, a higher amount of backscattered electron is emitted from a heavier element sample. In Fig. 3.7(b), the backscattered electron micrograph reveals phases of ferrite (α) and austenite (γ). The presence of nickel (Ni) element in austenite phase leads to a lighter zone at austenitic grain because the atomic number of nickel is higher than iron and chromium. Moreover, according to the ferrite phase, the darker zone on the top left area implies that the oxide composes of a higher chromium content, comparing to the lighter zone.

Therefore, scanning electron microscope provides not only topography and morphology of matter but also element distribution recognition. Secondary electron micrograph is more preferable for morphology observation, whereas backscattered electron micrograph is preferred when the phase contrast or phase distribution is needed.

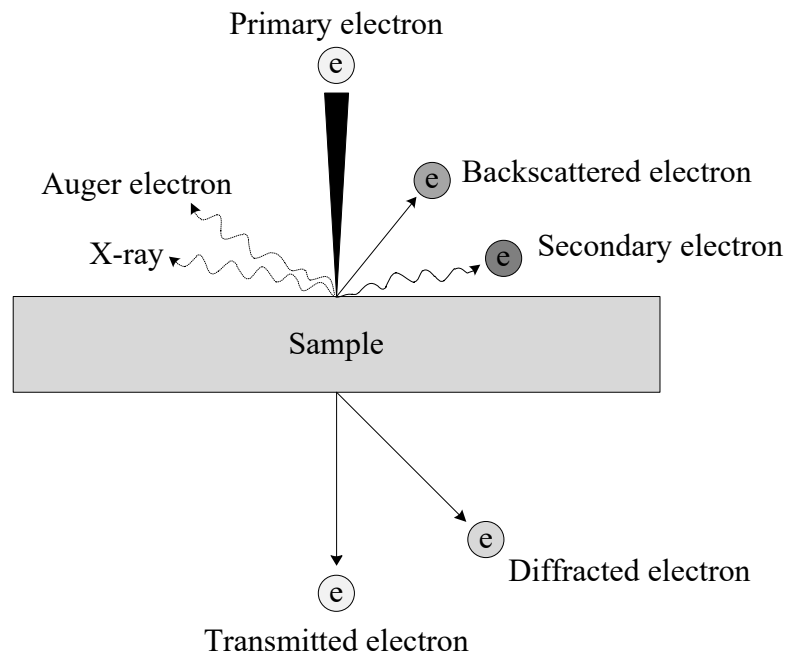


Fig. 3.4. Signals obtained from material interacted with electron beam. Redrawn and adapted from P. Sarrazin et al., *Mechanisms of High Temperature Corrosion: A Kinetic Approach*, Trans Tech Publications, Switzerland, 2008 [37].

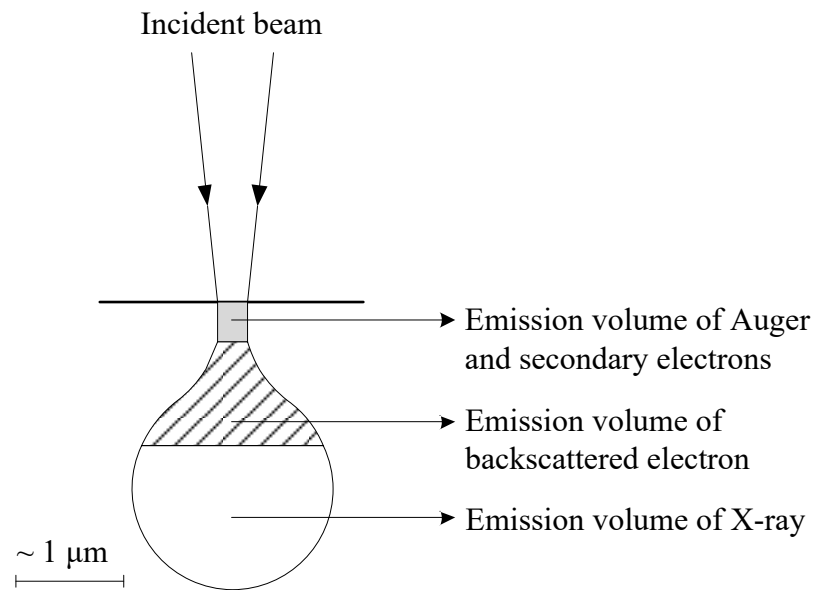


Fig. 3.5. Interaction volume of an incident electron beam on a sample. Redrawn and adapted from P. Sarrazin et al., *Mechanisms of High Temperature Corrosion: A Kinetic Approach*, Trans Tech Publications, Switzerland, 2008 [37].

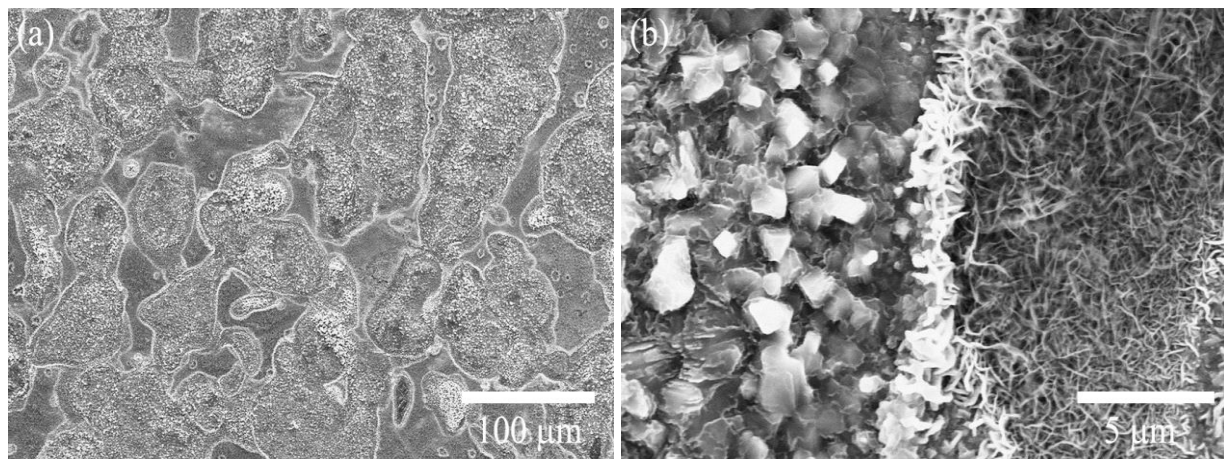


Fig. 3.6. Secondary electron micrographs of the 2205 duplex stainless steel oxidised at 850 °C under water vapour in nitrogen gas during 2 h (a) 250 × and (b) 5000 × magnification [36].

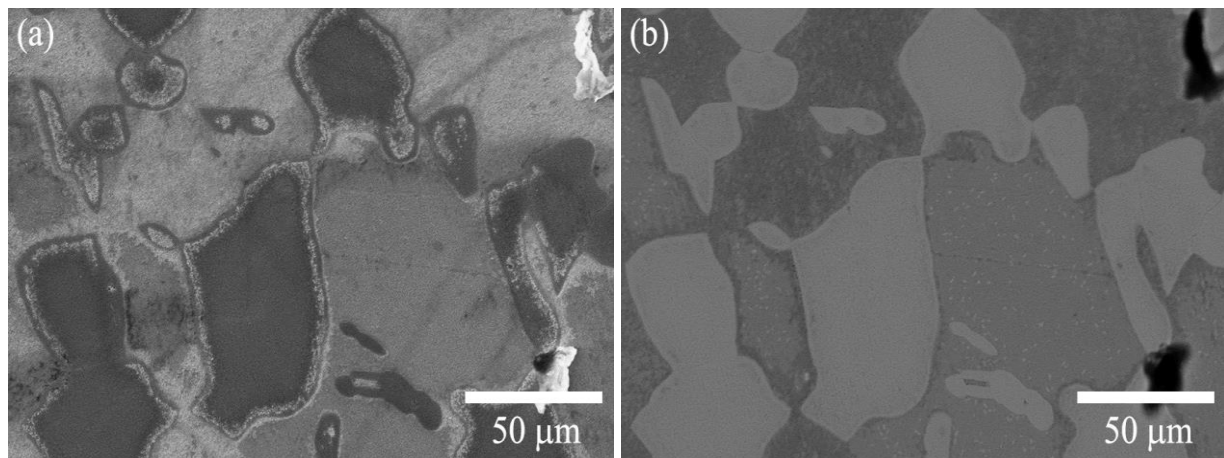


Fig. 3.7. Electron micrographs obtained from (a) secondary electrons and (b) backscattered electrons of the 2205 duplex stainless steel oxidised at 850 °C under hydrogen gas during 5 min [36].

3.4.3 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy is generally known as EDX or EDS. This technique utilises the X-ray signal obtained from the interaction between incident electron and matter as presented in Fig. 3.4. Hence, the energy dispersive X-ray spectroscopy is often found as a supplementary technique combined with the scanning electron microscopy. The obtained X-ray radiation composes of continuous X-ray and characteristic X-ray as presented in Fig. 3.8(a). Only characteristic X-ray, which is emitted from electron transition between the different atomic energy levels as in Fig. 3.8(b), is used for the energy dispersive X-ray spectroscopy technique. Since energy of the characteristic X-ray is unique depending on element, the spectroscopy is used for elemental analysis and reported as the intensity *versus* the characteristic X-ray energy.

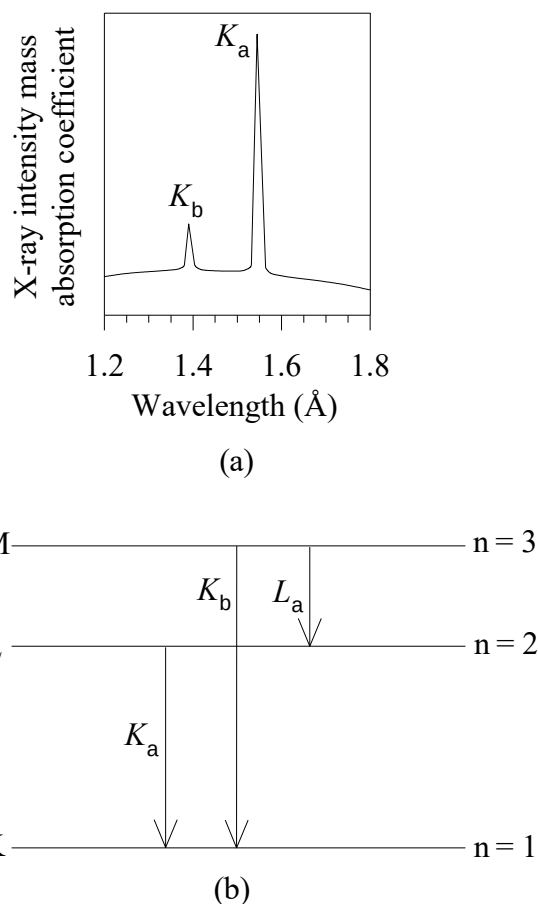


Fig. 3.8. (a) X-ray radiation of copper target and (b) characteristic X-ray emission. Redrawn and adapted from B.D. Cullity, S.R. Stock, Elements of X-Ray Diffraction, third ed., Prentice Hall, USA, 2001 [38].

Fig. 3.9 shows EDS spectrum obtained from austenitic phase of 2205 duplex stainless steel oxidised at 850 °C in water vapour for 60 min. The pattern shows the presence of iron (Fe), chromium (Cr), nickel (Ni), manganese (Mn), molybdenum (Mo) and oxygen (O) elements. Since the analysis volume of EDS is not small, the analysis signal comes from not only surface oxide but also the bulk alloy, allowing the presence of the signals of nickel and molybdenum. In addition, the quantitative analysis of elements shown in Fig. 3.9 can be quantified in terms of weight percent (wt.%) and atomic percent (at.%) as reported in Table 3.2. The technique typically has the limitation to detect the elements with atomic number less than 11. Because oxygen is a constituent of the oxide and has the atomic number of 8, the quantitative analysis is then unfavorable for high temperature oxidation field. However, the technique provides the idea about the elemental components in the oxide phases. Moreover, X-ray mapping of individual element can be performed to observe the element distribution of sample.

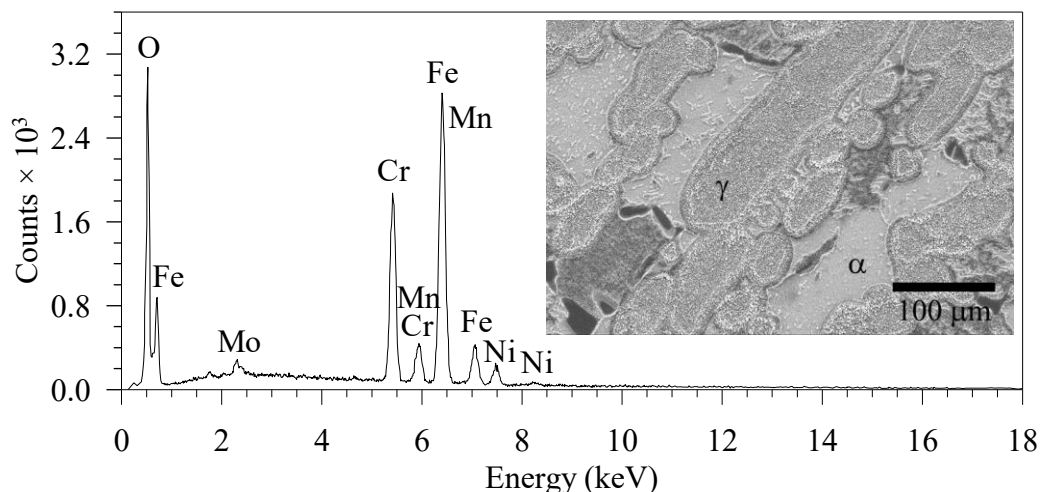


Fig. 3.9. EDS spectrum obtained from austenitic phase of the 2205 duplex stainless steel oxidised at 850 °C in water vapour for 60 min [36].

Table 3.2 Quantitative analysis of EDS spectrum in Fig. 3.9 [36].

Element	O K	Mo L	Cr K	Mn K	Fe K	Ni K	Total
wt.%	24.87	2.22	19.19	2.26	46.77	4.69	100.00
at.%	53.51	0.80	12.70	1.42	28.83	2.75	100.00

3.4.4 Focused Ion Beam Coupled with Scanning Electron Microscope

The focused ion beam coupled with scanning electron microscope or FIB-SEM consists of 2 columns that are FIB and SEM columns. They are installed with the intercolumn angle of 54 ° as shown in Fig. 3.10. FIB is the perpendicular column to the specimen surface. Gallium ion (Ga^+) source installed inside FIB column is used for cutting, technically called milling, the localised area while SEM records the image of such area. However, the specimen can be damaged due to the milling process. Thus, before milling, the interesting surface needs to be protected usually by coating with carbon.

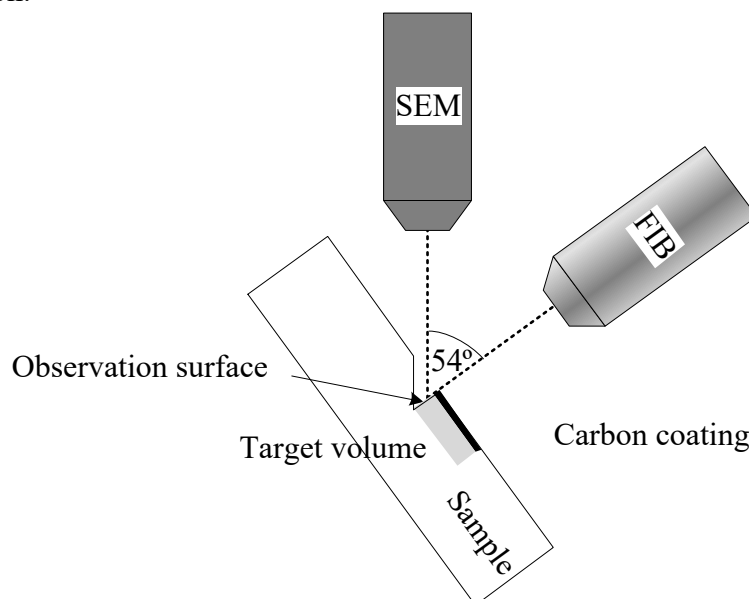


Fig. 3.10. Schematic sketch of FIB-SEM. Redrawn and adapted from H. Iwai et. al., J. Power Sources, 195 (2010) 955–961 [39].

Normally, FIB-SEM has been used for many purposes in the study of high temperature oxidation of alloys. The first one is to make a thin lamella. Before characterising the specimen by TEM, thin lamella with the thickness of 100–150 nm is prepared by FIB in order to observe the transmission of electron. Moreover, the characterisation of alloys by SEM and EDX has one big problem concerning the too deep penetration depth of electron beam. For example, if the penetration depth of electron beam is about 10 μm but the depth of interested oxide layer is 5 μm , the characterisation obtained from SEM and EDX would be disturbed from phases under the interested oxide layer. In order to get rid of this effect, thin lamella from FIB may be prepared to limit the area of characterisation. The preparation of thin lamella is shown in Fig. 3.11 [40]. First, carbon is deposited on the surface in order to protect the surface from the milling process as shown in Fig. 3.11(a). After that, the FIB-boxes are made at both sides of the lamella as shown in Fig. 3.11(b). The right and left sides as well as beneath the lamella are cut (the red dash lines refer to the cutting lines) while the small connection bridge at the left side is still remained in order to maintain the lamella as shown in Figs. 3.11 (c) and (d). Later, the lamella is connected with a pin by carbon-deposition as illustrated in Fig. 3.11(e) and then the small bridge can now be cut as illustrated in Fig. 3.11(f). The lamella is moved and connected to the copper grid as shown in Figs. 3.11 (g) and (h), and then the pin is disconnected. Finally, the lamella is slenderised to be 100–150 nm thick. After this preparation, the thin lamella can be characterised by TEM, SEM or other techniques. The example of the advantage of thin lamella is shown in Fig. 3.12 showing the cartography and EDX localised analysis of AISI 441 after oxidation at 800 $^{\circ}\text{C}$ in 5% $\text{H}_2\text{O}-\text{O}_2$ for 24 h [40].

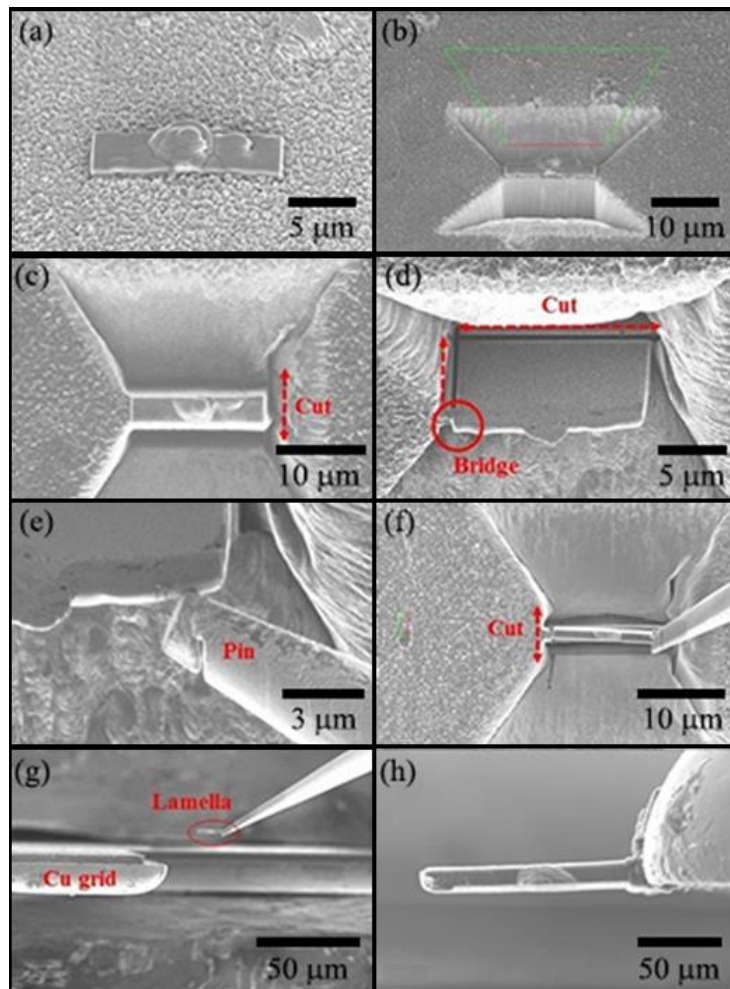


Fig. 3.11. Thin lamella preparation from FIB. Reproduced and adapted from W. Wongpromrat, PhD Thesis, Université Grenoble Alpes, France, and King Mongkut's Institute of Technology Ladkrabang, Thailand, 2015 [40].

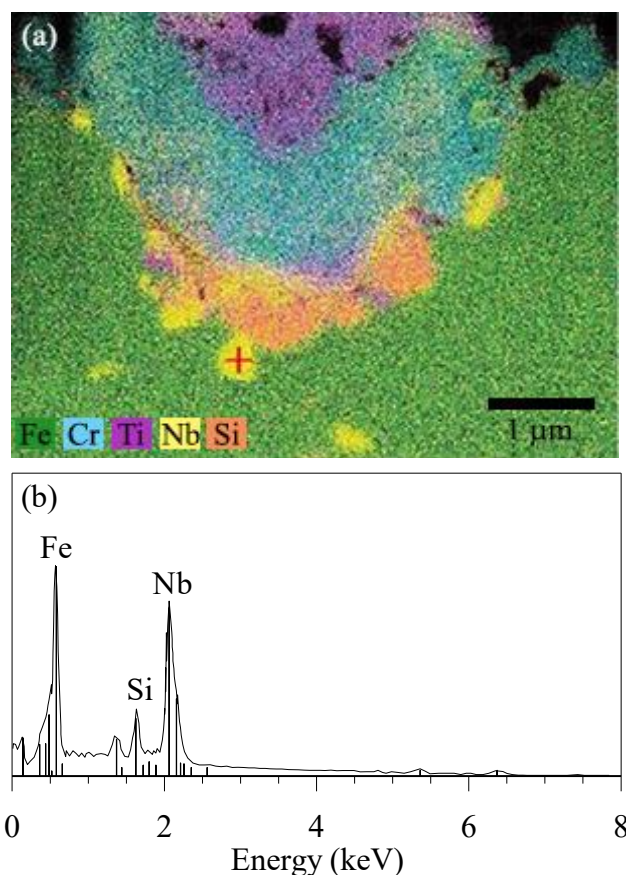


Fig. 3.12. (a) Cartography and (b) EDX of the localised area of the nodule grown during oxidation at 800 °C in 5% H₂O-O₂ for 24 h. Reproduced from W. Wongpromrat, PhD Thesis, Université Grenoble Alpes, France, and King Mongkut's Institute of Technology Ladkrabang, Thailand, 2015 [40].

The FIB-SEM technique can also be applied to observe the cross section of the small localised area where other techniques are unable. For example, in the recent work of Parry et al. [29], FIB was used to observe the revolution of the nodule grown on AISI 441 ferritic steel after oxidation at 800 °C in 5% H₂O-O₂ for 4, 14 and 24 h as shown in Fig. 3.13. Furthermore, the FIB-SEM technique can also be used to reconstruct the area of interest. In this case, the FIB and SEM columns would work iterately in milling and capturing the images of the scoped area. All images were then combined in the software. The results attained from this process may be the revolution of the area of interest as shown in Figs. 3.13 and 3.14 and the reconstruction of phase(s) on the specimens as shown in Fig. 3.15.

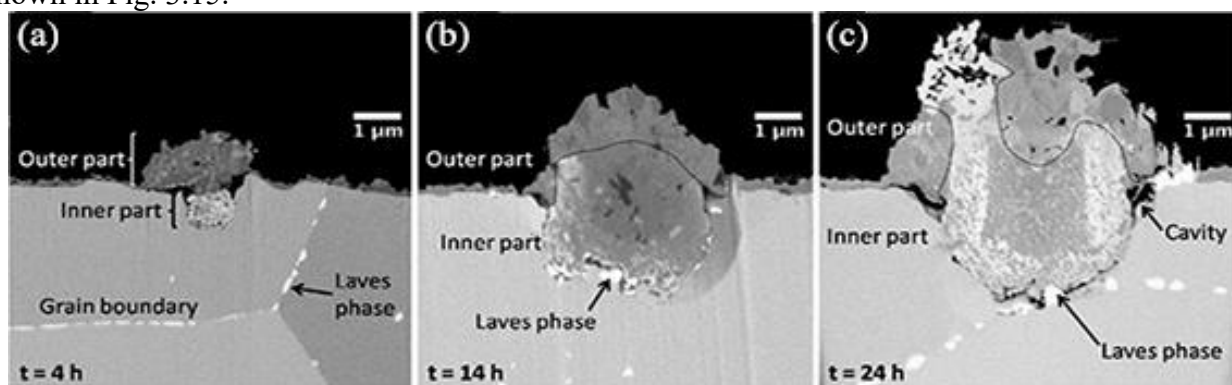


Fig. 3.13. FIB cross sections of the nodule grown on AISI 441 after oxidation at 800 °C in 5% H₂O-O₂ for (a) 4 h, (b) 14 h and (c) 24 h. Reproduced from V. Parry et al., Corros. Sci. 141 (2018) 255–263 [29].

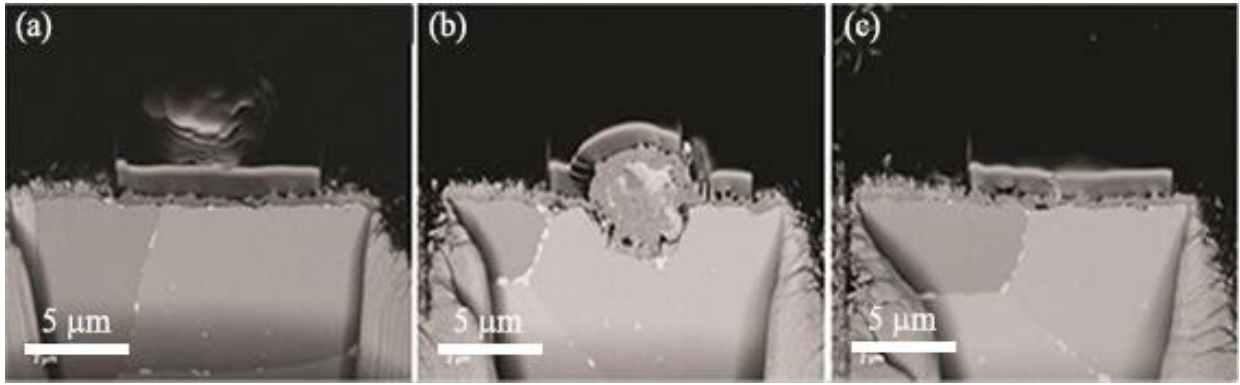


Fig. 3.14. The revolution of the nodule extracted from stack of 330 SEM-images where Fig. (a), (b) and (c) correspond to image stack numbers of 1, 165 and 330 respectively. Reproduced from W. Wongpromrat et al., *Mater. High Temp.* 32 (2015) 22–27 [30].

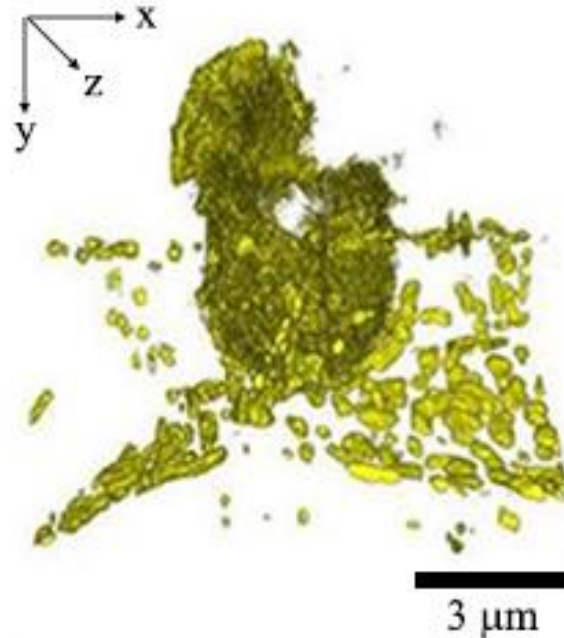


Fig. 3.15. Reconstruction of niobium phases, including NbC and intermetallic niobium, above the metallic grain boundary of AISI 441 oxidised at 800 °C in O₂-5% H₂O for 24 h. Reproduced from W. Wongpromrat, PhD Thesis, Université Grenoble Alpes, France, and King Mongkut's Institute of Technology Ladkrabang, Thailand, 2015 [40].

3.4.5 X-ray Diffractometer

X-ray diffractometer or XRD is used to observe the crystalline information of the solid samples that can be used to identify the phase of matter such as oxide species. The diffraction pattern produced by X-ray through the lattice in a crystal is recorded and interpreted to determine the nature of the lattice [41]. When X-ray is applied to the crystal, the diffraction occurs on the lattice plane. The incident X-ray primarily interacts with electron in the atom. Some photons of X-ray are deflected from the incident direction. This diffraction phenomenon is illustrated in Fig. 3.16 and can be described by Bragg's law in Eq. 3.9 [42] i.e.

$$2d \sin \theta = n\lambda \quad (3.9)$$

where d is the lattice spacing, θ the incident angle to specimen surface, n an integer (1, 2, 3,...) and λ the wavelength of X-ray.

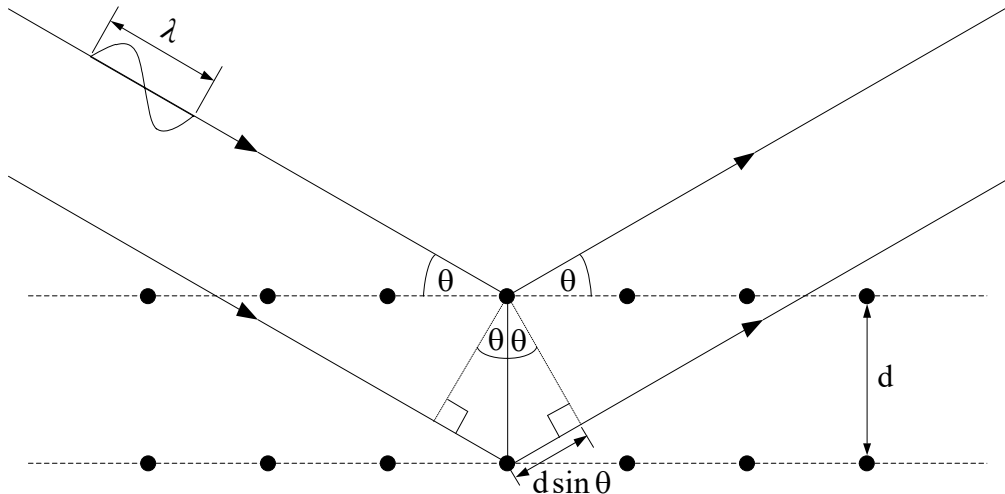


Fig. 3.16. Diffraction of X-ray in crystalline structure at different incident angles. Redrawn and adapted from R. Abbaschian et al., *Physical Metallurgy Principles*, fourth ed., Cengage Learning Press, UK, 2009 [42].

Due to the characteristics of crystal structure and lattice spacing of each compound, X-ray diffraction pattern is unique and can be analysed by scanning X-ray with various incident angles and observing the intensity of the diffracted X-ray at each angle. The data attained from XRD are the crystal structure of the unit cell and the orientation of the lattice plane. In the crystalline solid, the atoms are arranged periodically.

The crystal types can be classified through the lattice parameters. Table 3.3 shows the crystal systems in the unit cell.

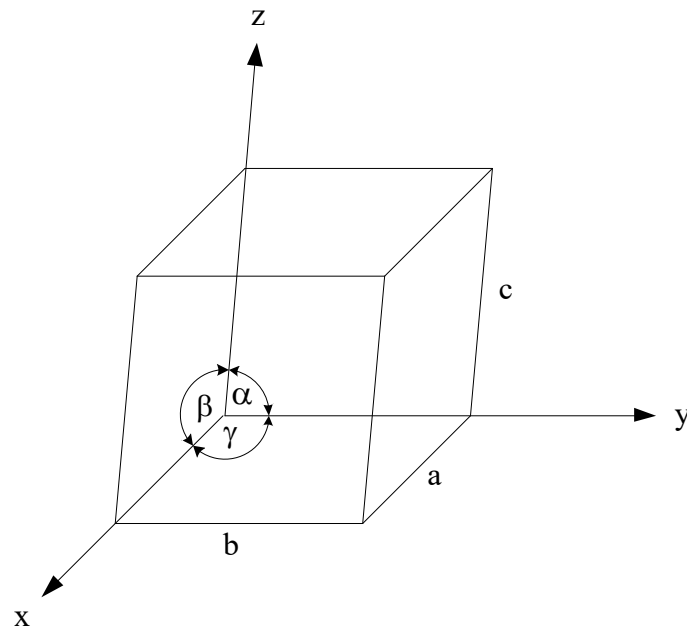
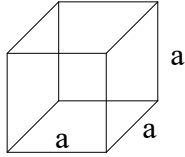
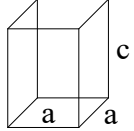
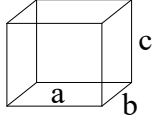
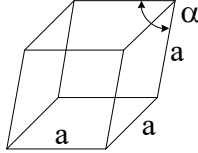
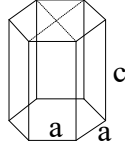
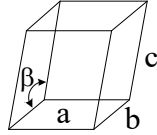
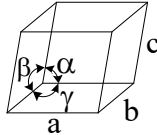


Fig. 3.17. Unit cell with axial lengths (a, b, c) and interaxial angles (α , β , γ). Redrawn and adapted from W.D. Callister, D.G. Rethwisch, *Materials Science and Engineering*, eighth ed., John Wiley & Sons, USA, 2011 [43].

Table 3.3 Classification of crystal systems. Redrawn and adapted from W.D. Callister, D.G. Rethwisch, Materials Science and Engineering, eighth ed., John Wiley & Sons, USA, 2011 [43].

Crystal system	Axial relationships	Interaxial angle	Unit cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

For the lattice plane in the cubic structure, three integers called Miller indices (h, k, l) are used to represent the planes and the directions in the crystal lattices. The examples of the lattice planes in cubic structure and their Miller indices are shown in Fig. 3.18.

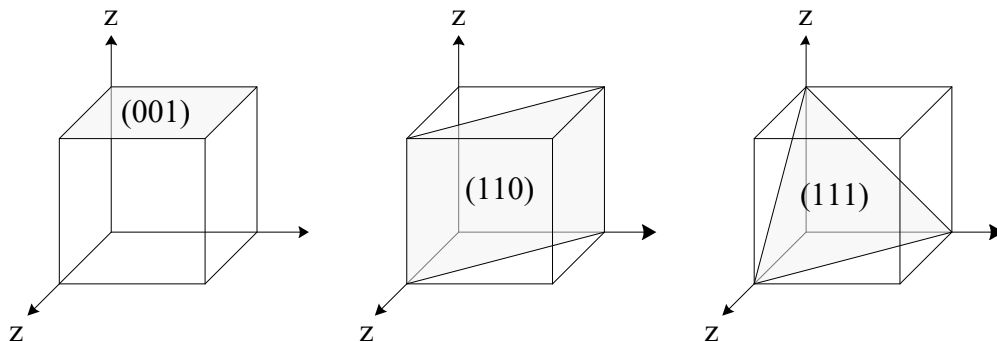


Fig. 3.18. The lattice planes in cubic structure and their Miller indices. Redrawn and adapted from R. Abbaschian et al., Physical Metallurgy Principles, fourth ed., Cengage Learning Press, UK, 2009 [42].

After analysis, the peaks can be observed at different incident angles. These results can be interpreted by comparing the patterns obtained from the experiment with the standard database called “Joint Committee of Power Diffraction Standards (JCPDS)”, currently renamed to be “International Centre for Diffraction Data (ICDD)”. The example of XRD patterns obtained from the oxidised AISI 441 specimen is presented in Fig. 3.19. This figure shows the effect of oxidising gas, time, and temperature on thermal oxide phase where x and y is chromium mole fraction in $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ and $\text{Mn}_{3-y}\text{Cr}_y\text{O}_4$ respectively.

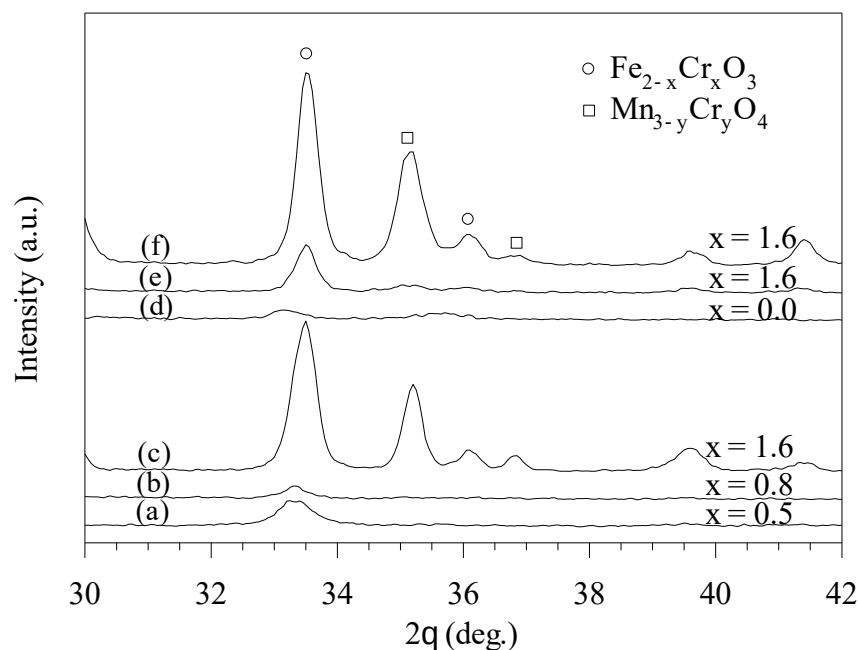


Fig. 3.19. XRD patterns of AISI 441 specimens oxidised in air: (a) 650 °C, 5 min; (b) 850 °C, 5 min; (c) 850 °C, 60 min; in water vapour: (d) 650 °C, 5 min; (e) 850 °C, 5 min; (f) 850 °C, 60 min. Redrawn from A. Srisrual et al., Corros. Sci. 51 (2009) 562–568 [44].

3.4.6 Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique based on inelastic scattering or the frequency change of monochromatic light typically delivered by laser. The incident monochromatic light interacts with sample and then a spontaneous scattering of incident light is re-emitted. Frequency of the re-emitted photons is usually shifted up or down compared with original frequency, which is named the *Raman scattering* or *Raman effect*, following the name of the first observer, C.V. Raman, an Indian physicist. The intensity of Raman scattering for each frequency shift is recorded and plotted. The shift provides information about vibrational and rotational transitions in molecules that can indicate the structure, orientation, and chemical composition of the interested molecule.

The incident light or photon can excite molecule of matter from ground state in a rotational or vibrational energy state to virtual energy state, and then it emits or scatters a photon and returns to a rotational or vibrational state when the molecule relaxes. From the phenomena, the light scattering can be categorised in three types as presented in Fig. 3.20. *Rayleigh scattering* is an elastic scattering that the scattering light has the same frequency as the exciting light. *Stokes scattering* and *anti-Stokes scattering* are an inelastic scattering. In the case of the *Stokes scattering*, the final energy state is higher than the initial energy state. Hence, the scattering light shifts to the lower frequency comparing with the exciting light. In the case of the *anti-Stokes scattering*, the final energy state is lower than the initial energy state. Thus the scattered light shifts to the higher frequency comparing with the exciting light. In general, the total amount of inelastic Stokes and anti-Stokes radiation is small comparing with the elastic Rayleigh radiation. However, only inelastic radiation, typically Stokes radiation, is used in Raman spectroscopy.

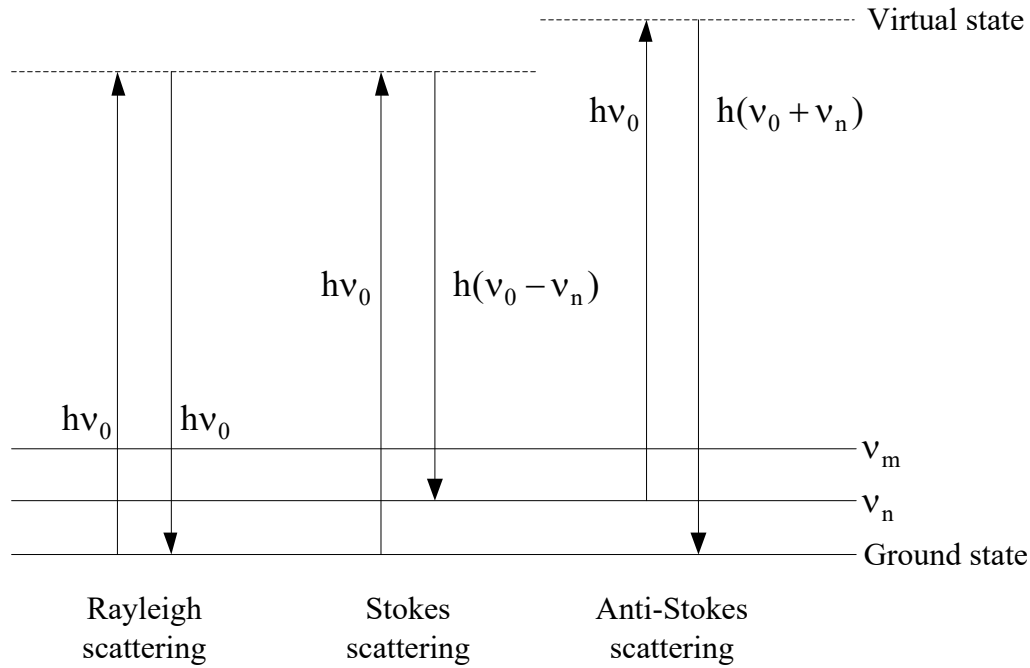


Fig. 3.20. Rayleigh, Stokes and anti-Stokes scattering phenomena. Redrawn and adapted from J.E. Pemberton, A.L. Guy, Raman spectroscopy, in: ASM Handbook Committee (Ed.), ASM Handbook Vol. 10, ninth ed., ASM International, USA, 1986, pp. 261–286 [45].

Raman shift is generally presented in wavenumber or in the unit of reciprocal length (cm^{-1}). The correlation between spectral wavelength and Raman shift is as the following equation:

$$\Delta w = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \quad (3.10)$$

where Δw is the Raman shift, λ_0 and λ_1 are the exciting wavelength and the Raman scattering wavelength respectively.

Raman spectroscopy is widely used for material identification because the technique is easy to use and sample preparation is not required. The related technique is infrared spectroscopy that is less sensitive to surface species and difficult to analyse an aqueous system, comparing to Raman spectroscopy. Fig. 3.21 presents Raman spectra recorded from the AISI 441 ferritic stainless steel oxidised in air and in water vapour. The spectra reveal the identical peaks of haematite (Fe_2O_3), chromia (Cr_2O_3), corundum solid solution ($\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$), and spinel solid solution ($\text{Mn}_{3-y}\text{Cr}_y\text{O}_4$) [44]. Peaks of chromia grown under water vapour are always higher and sharper than those of films grown in air. Haematite decreases while solid solution and chromia increase when temperature increases both in air and in oxidising conditions containing water vapour.

In addition, Raman spectroscopy can be performed at microscopic scale as called micro-Raman spectroscopy. Fig. 3.22 shows Raman spectra recorded from austenite and ferrite phases of the oxidised 2205 duplex stainless steel. Both spectra show the characteristic peaks of haematite, chromia and corundum solid solution. The peak of corundum solid solution is shifted from 668 cm^{-1} (austenitic grains) to 674 cm^{-1} (ferritic grains) indicating that the solid solution oxide with a lower x-value is formed on austenite [46].

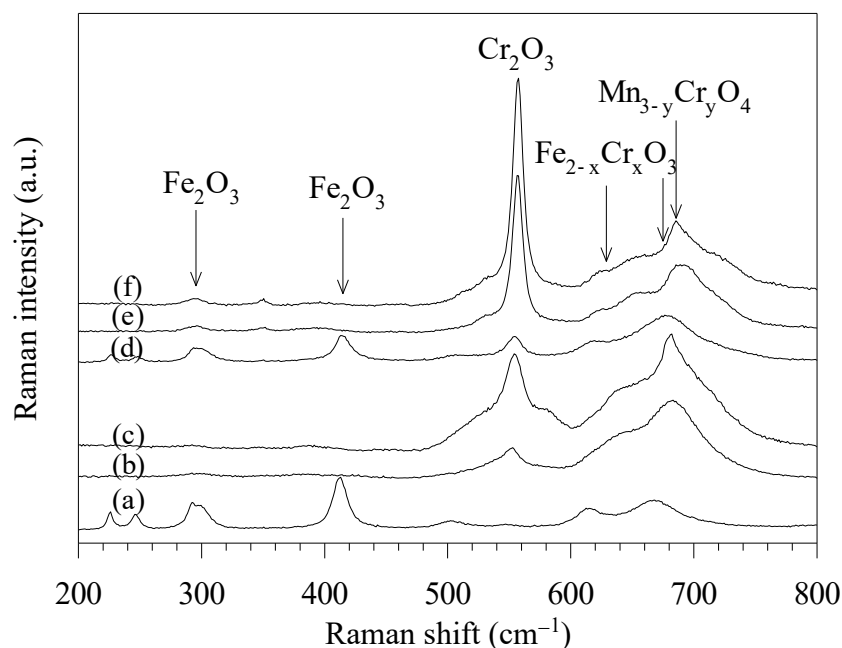


Fig. 3.21. Raman spectra of AISI 441 ferritic stainless steel oxidised in air: (a) 650 °C, 5 min; (b) 850 °C, 5 min; (c) 850 °C, 60 min; in water vapour: (d) 650 °C, 5 min; (e) 850 °C, 5 min; (f) 850 °C, 60 min. Redrawn and adapted from A. Srisrual et al., *Corros. Sci.* 51 (2009) 562–568 [44].

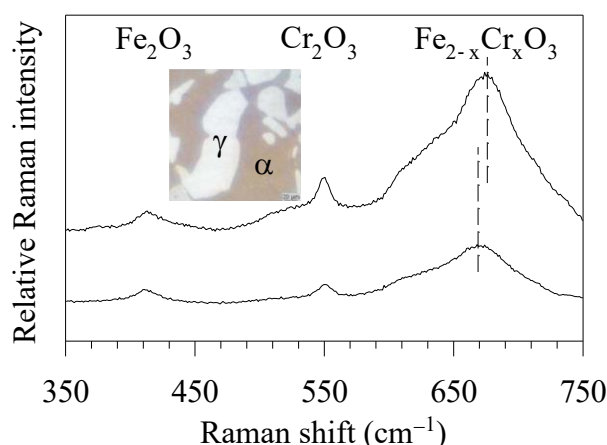


Fig. 3.22. Raman spectra recorded from individual austenitic (lower curve) and ferritic (upper curve) grains of the 2205 duplex stainless steel oxidised at 650 °C in water vapour atmosphere for 5 min. Redrawn and adapted from A. Srisrual et al., *Mater. High Temp.* 28 (2011) 349–354 [46].

As the micro-Raman spectroscopy can be locally performed on individual area [47], Fig. 3.23(a) reports Raman spectra collected from different areas of the oxidised Inconel 690 alloy. Both of Cr_2O_3 and NiFe_2O_4 identical shifts are found on grain and grain boundary. Cr_2O_3 is a main oxide at grain boundary, whereas the presence of NiFe_2O_4 is more evident at grain area and nodules. Fig. 3.23(b) illustrates Raman mapping of Cr_2O_3 and NiFe_2O_4 . The Cr_2O_3 covers the whole surface but the oxide intensely presents at grain boundary. NiFe_2O_4 clearly presents at the grain area. Moreover, the different oxide distribution over the grain between black and white areas should be affected from the different orientation, causing by twin defect in the alloy.

Even though the Raman spectroscopy is very useful in high temperature oxidation area, the characterisation should be carefully performed with a suitable laser power to avoid sample deterioration especially with a dark sample. Moreover, fluorescence effect can be occurred and can affect the interpretation of the results.

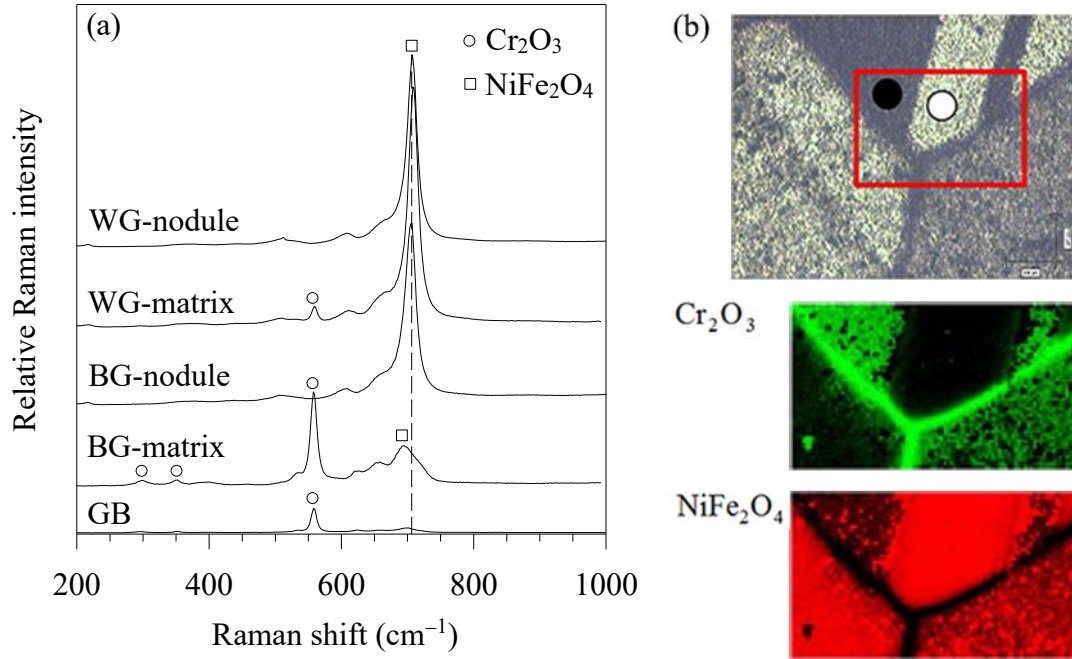


Fig. 3.23. (a) Raman shift at white grain (WG), black grain (BG) and grain boundary (GB), and (b) Raman mapping obtained from selected area of Inconel 690 oxidised at 900 °C in air for 21 h. Redrawn and adapted from A. Srisrual, PhD Thesis, University of Grenoble, France, 2013 [47].

3.4.7 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), which is sometimes known as Electron Spectroscopy for Chemical Analysis (ESCA), is used for observing the element composition, chemical stoichiometry, chemical state and electronic state of the elements existing in the materials [41]. The advantage of XPS is the characterisation of the near surface about 10 nm depth which is much thinner than other techniques. Fig. 3.24 shows the principle of XPS. A high energy photon (X-ray) strikes the inner-shell electron in the atom of material at the surface, and then the escaped inner-shell electron becomes photoelectron meanwhile the hole is created as shown in Figs. 3.24 (a) and (b) respectively. To stabilise the atom, electron from the other shell drops into the inner-shell hole. In the meantime, the excess energy is emitted as photon or characteristic X-ray. If the photon is absorbed by electron and electron has enough energy, the characteristic electron will escape from atom in the name of Auger electron as in Fig. 3.24(c).

Since the binding energy is characteristics of any element, it is used to identify the element. The binding energy (B.E.) can be evaluated from photon energy ($h\nu$) and kinetic energy of photoelectron (K.E.) following Eq. 3.11 when a work function of sample is ignored. Kinetic energy of photoelectron is generally measured by cylindrical mirror analyser or concentric hemispherical analyser. The result of XPS is reported as a spectrum line. The example of XPS spectrum is shown in Fig. 3.25. The quantitative analysis can be achieved by calculating the ratio of the curve area divided by the sensibility factor of that element as shown in Eq. 3.12 [40]. In this equation, S_A and S_B are respectively the curve areas of A and B, while α_A and α_B are the sensitivity factors of A and B respectively.

$$\text{B.E.} = h\nu - \text{K.E.} \quad (3.11)$$

$$\text{Ratio of A to B} = \frac{(S_A/\alpha_A)}{(S_B/\alpha_B)} \quad (3.12)$$

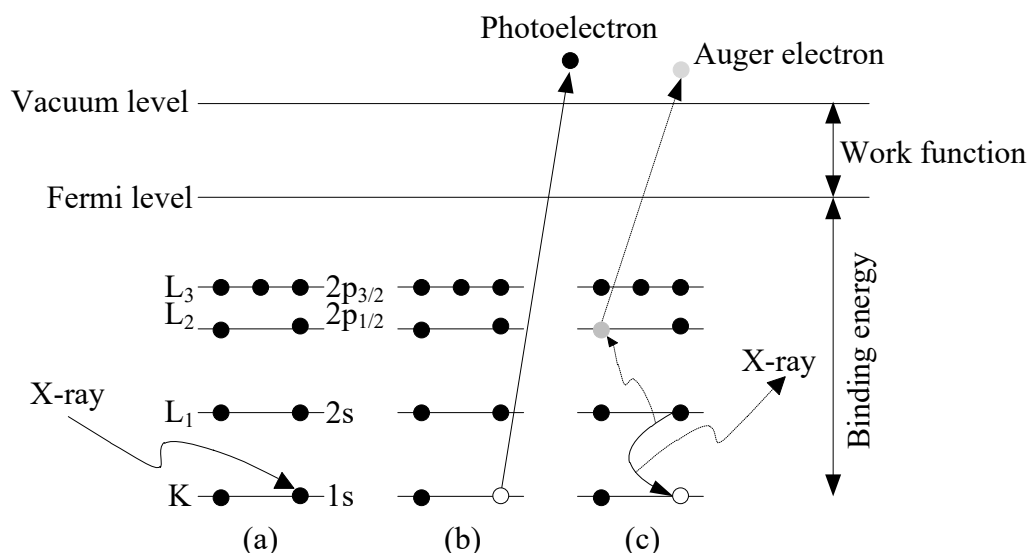


Fig. 3.24. Principle of XPS. Redrawn and adapted from J.B. Lumsden, X-ray photoelectron spectroscopy, in: ASM Handbook Committee (Ed.), ASM Handbook Vol. 10, ninth ed., ASM International, USA, 1986, pp. 1025–1056. [48].

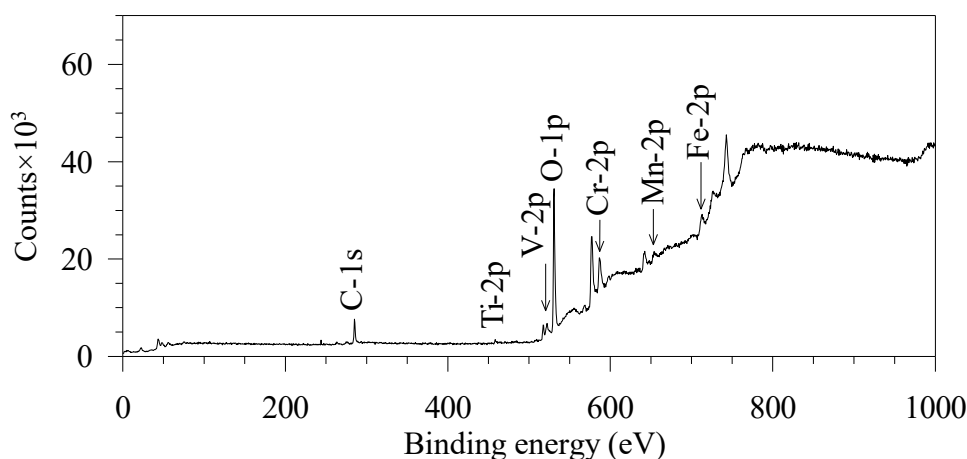


Fig. 3.25. XPS spectrum of AISI 441 oxidised in water vapour at 850 °C for 5 min [36].

3.5 Photoelectrochemical Characterisation

Photoelectrochemistry or PEC is the technique for measuring and interpreting electrical currents generated by illuminating a semiconductor material in an electrolyte. In the last decades, photoelectrochemistry has been used in thin solid film applications such as photovoltaic cell and corrosion studies. This technique could provide the information on electronic structure and indirectly (through the optical band gap values) chemical composition of passive films *in situ* and under controlled potential in long-lasting experiments. It could also provide information on mechanisms of generation (recombination effect) and transport of photocarrier in amorphous material. These informations are utilised to find the physico-chemical property of oxide film. The PEC could also give information on kinetics of growth under illumination of photoconducting films and interference effect in absorbing material at constant growth rate.

The main components of typical photoelectrochemical set-up compose of lamp, monochromator, chopper, electrochemical cell, potentiostat, lock-in amplifier, and computer. The lamp-monochromator system provides a variable wavelength in a wide range of photon energy and photocurrents will be recorded according to photon energies as called photocurrent energy spectra. However, the system may include a laser source at constant wavelength when the imaging study is preferred.

The *Science et Ingénierie des Matériaux et Procédés* (SIMaP) laboratory, Université Grenoble Alpes, France, has developed the photoelectrochemical set-up that has evolved from macroscopic, microscopic, and mesoscopic scale of characterisation, as named macroscopic PEC, microscopic PEC, and mesoscopic PEC, respectively. Both macroscopic and microscopic PEC are typical modes of photoelectrochemical technique that are performed to obtain photocurrent energy and potential spectra and the photocurrent image, respectively. Mesoscopic PEC is the unique mode that is firstly developed and proved for the local photocurrent energy spectra with 30 μm spatial resolution [46]. Generally, the technique is used to find the band energy gap and semiconducting type of thermal oxides. On the other hand, the thermal oxide phases can be identified when the band energy gap of thermal oxide is known. However, each mode of PEC is utilised for the different objectives as will be presented in the following.

In the three operating modes of the photoelectrochemical set-up, some components are shared such as the photoelectrochemical cell, the potentiostat, the lock-in amplifier, and the mechanical light modulator (chopper and optical path device). The electrochemical cell consists of three electrodes equipped with a flat quartz optical window, which allows light illuminated on sample surface. The oxidised sample should be used as a working electrode and the oxide at the back side must be removed to provide the electrical contact. A platinum foil is used as a counter electrode. An Hg/Hg₂SO₄ mercury sulphate electrode (MSE) is used as a reference electrode (+0.650 V/SHE). A sodium sulphate solution with 0.1 M at pH 8.0 ± 0.1 is typically used as the electrolyte in the cell. Potentiostat is used to control the electrochemical cell where the voltage is proportional to overall electrochemical current issued from the matter interface. The electrochemical current is collected by a lock-in amplifier. Chopper and lock-in amplifier are necessary components for extracting a weak photocurrent signal in dark current (modulus and phase shift) from the collected electrochemical current.

3.5.1 Macroscopic Photoelectrochemical Characterisation

Macroscopic photoelectrochemistry characterisation is generally performed with a white light and monochromator system [20, 21]. The technique provides information about semiconducting type and bandgap energy, evaluating from photovoltammograms and photocurrent energy spectra. Fig. 3.26 presents the schematic diagram of macroscopic PEC set-up at SIMaP laboratory [47]. A xenon arc bulb connected to a monochromator is used as a light source to provide variable wavelength photons with a minimum spectral width of ± 1 nm. The characterised area is around 0.8 cm² while the whole sample surface is illuminated.

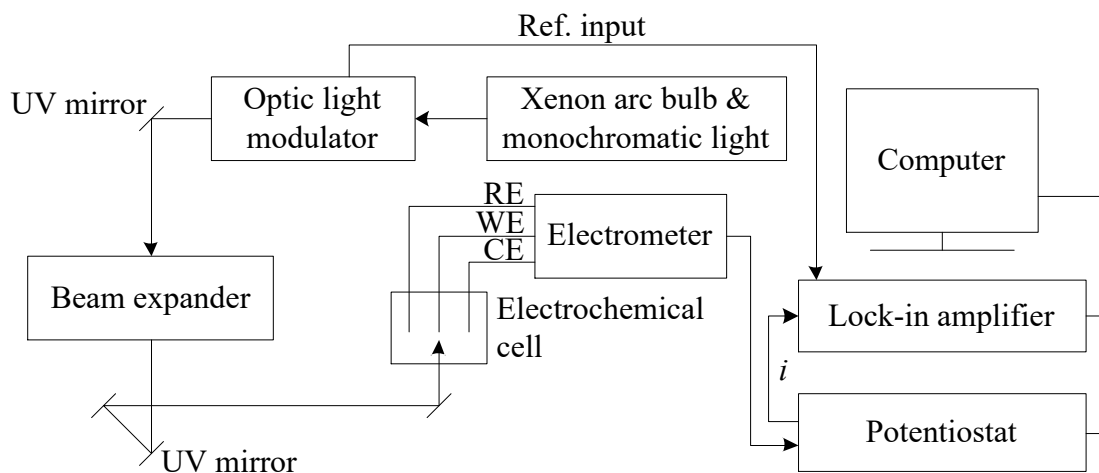


Fig. 3.26. Schematic diagram of the macroscopic photoelectrochemical set-up at SIMaP laboratory. Redrawn from A. Srisrual, PhD Thesis, University of Grenoble, France, 2013 [47].

Photovoltammogram is the curve between photocurrent and applied potential. It is usually plotted at the different selected constant photon energy provided by monochromator. Applied potential is varied and controlled by potentiostat. The as-measured photocurrent, I_{PH} , is recorded according to the applied potential. Semiconducting type can be evaluated from the change of the curve. If the modulus of the photocurrent increases when the applied potential is increased, the oxide exhibits an n-type semiconducting behaviour, as demonstrated in Fig. 3.27(a). On the other hand, if the modulus of the photocurrent decreases when the applied potential is increased, the sample exhibits a p-type semiconducting behaviour, as demonstrated in Fig. 3.27(c). In addition, Fig. 3.27(b) indicates the presence of at least two components in the thermal scale that one being n-type as the curve is recorded at 2.41 eV whereas another one being more or less insulating as the V-shaped part is recorded at 3.53 eV.

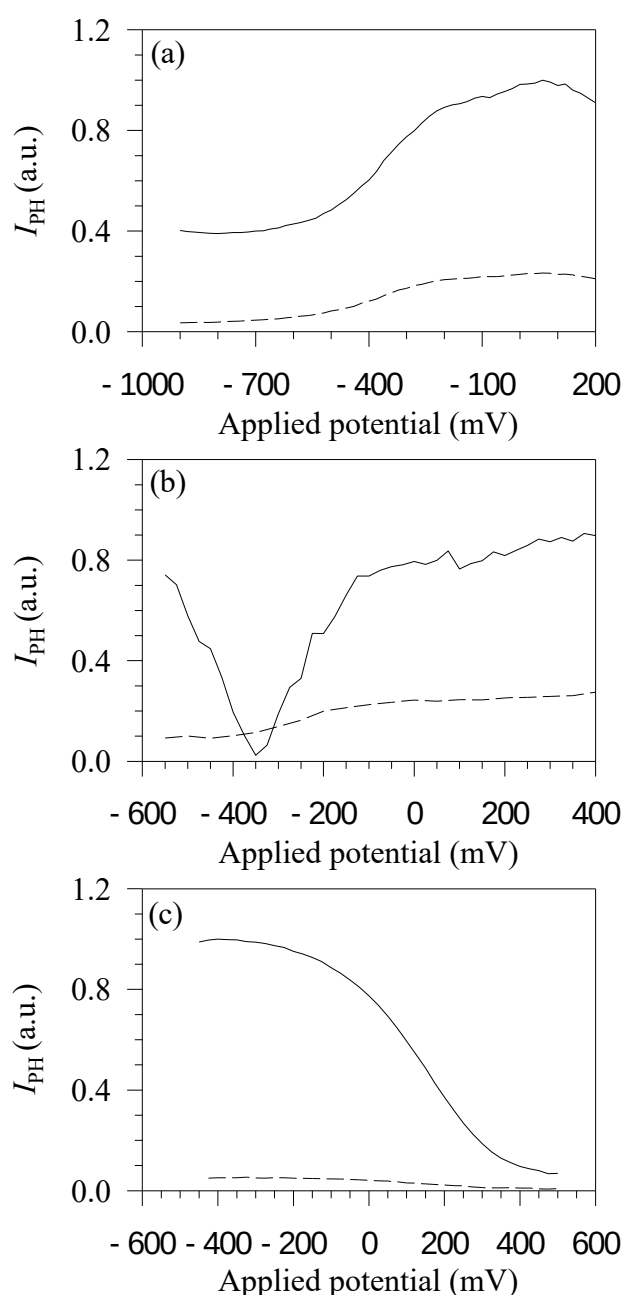


Fig. 3.27. Plots of the typically measured photocurrent amplitude as a function of the applied potential obtained at $h\nu = 2.41$ eV (dashed line) and 3.53 eV (solid line) on the whole surface of the 2205 duplex stainless steel oxidised in water vapour (a) at 650 °C for 5 min, (b) at 850 °C for 60 min, and in oxygen (c) at 850 °C for 60 min. Redrawn from A. Srisrual et al., *Oxid. Met.* 79 (2013) 337–347 [49].

Photocurrent energy spectrum or the curve plotting the photocurrent *versus* energy is performed at variable wavelength provided by monochromator. The spectrum is typically plotted at different applied potentials depending on the presence of oxides, as illustrated in Figs. 3.28 and 3.29. Since the photon flux from the light source is different and depends on the wavelength, the as-measured photocurrent must be corrected to the calculated photocurrent, J_{PH} , by

$$J_{PH} = \frac{I_{PH}}{\Phi_N(h\nu)} \quad (3.13)$$

where $\Phi_N(h\nu)$ is the normalised photon flux at each wavelength. Fig. 3.29 illustrates the photocurrent energy spectra obtained from the same sample in Fig. 3.27. Each energy spectrum reveals the combination of the photocurrent contributions, implying the presence of different oxide types with different bandgap energies. Bandgap energy of semiconductor, E_g , can be determined by the simple equation of Gärtner-Butler model in Eq. 3.14, i.e. for each sample

$$(\eta \times E)^{1/2} = C \times (E - E_g) \quad (3.14)$$

where η is the quantum yield of the photocurrent that equals J_{PH} , E is the photon energy, and C is a constant. Fig. 3.30 shows the linear transformed photocurrent energy spectra of the curves in Fig. 3.28 performed at -250 mV/MSE and at -700 mV/MSE. The transforms in Figs. 3.30 (a) and (b) indicate the bandgap energy of the first contribution at around 2.0 eV corresponding to the bandgap energy of haematite [50, 51], and the bandgap energy of the second contribution at around 2.6 eV which corresponds to the bandgap energy of the rhombohedral solid solution [51].

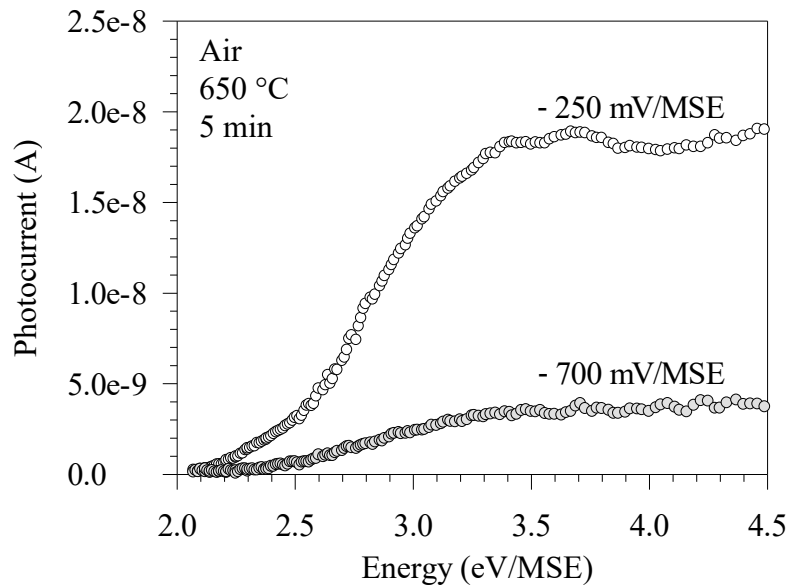


Fig. 3.28. Photocurrent energy spectra at two potentials for AISI 441 ferritic stainless steel oxidised at 650 °C in air for 5 min. Redrawn from A. Srisrual et al., Corros. Sci. 51 (2009) 562–568 [44].

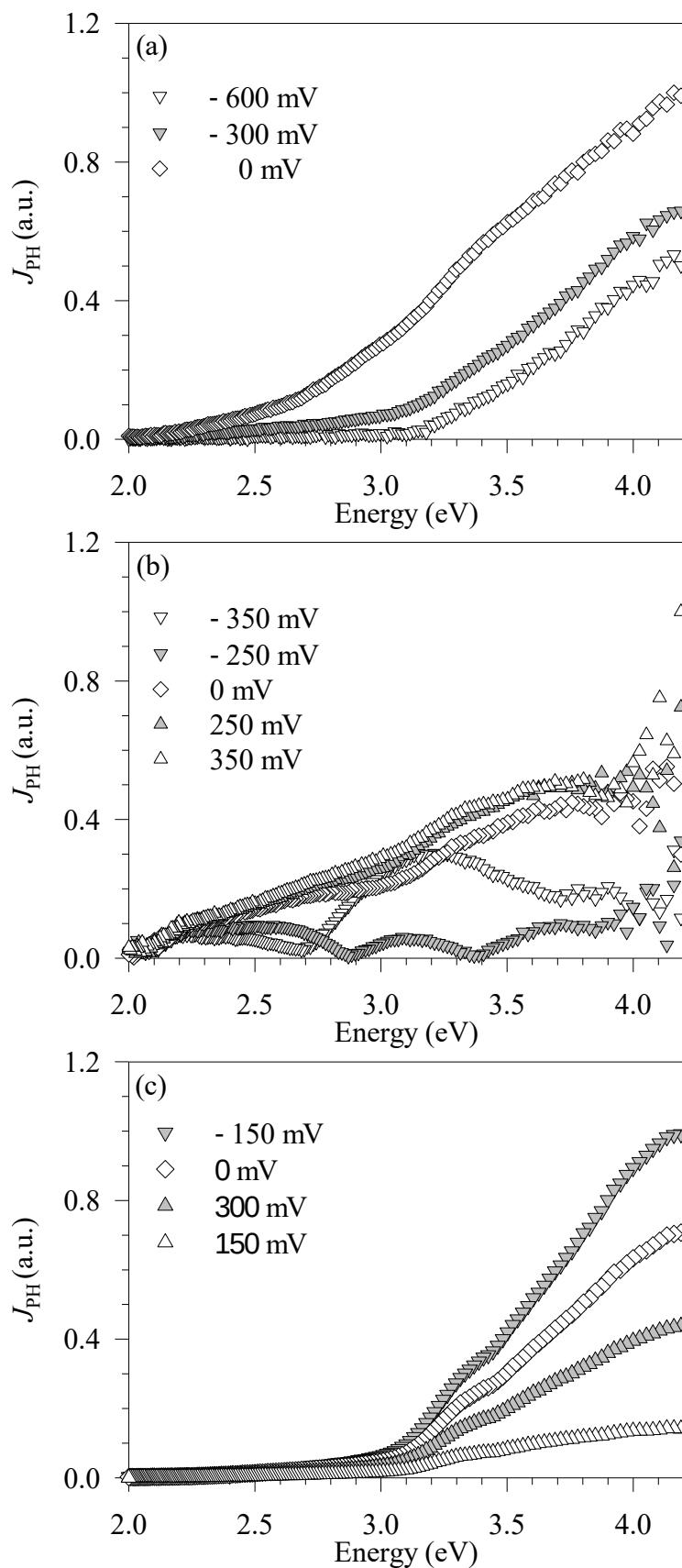


Fig. 3.29. Photocurrent energy spectra at several applied potentials obtained from the whole surface of the 2205 duplex stainless steel oxidised (a) at 650 °C in water vapour for 5 min, (b) at 850 °C in water vapour for 60 min, and (c) at 850 °C in oxygen for 60 min. Redrawn from A. Srisrual et al., *Oxid. Met.* 79 (2013) 337–347 [49].

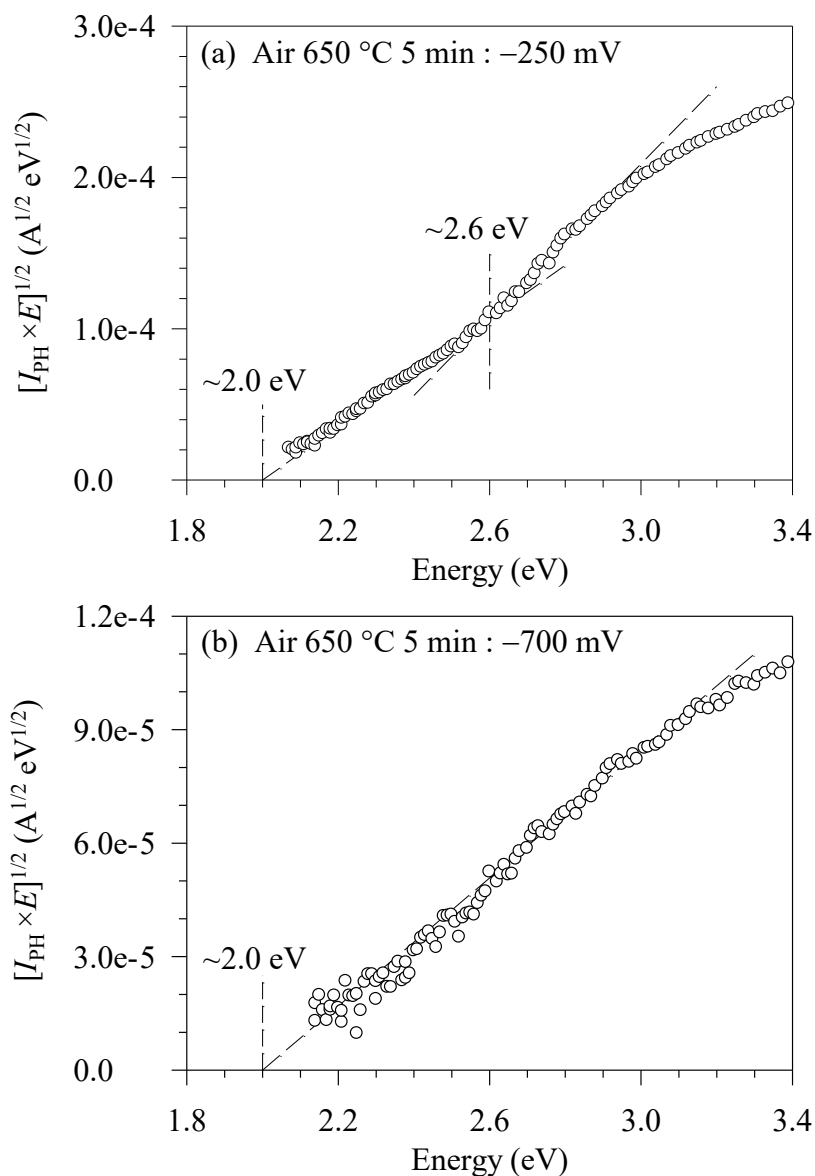


Fig. 3.30. Linear transforms of curves in Fig. 3.28; (a) -250 mV/MSE , (b) -700 mV/MSE . Redrawn from A. Srisrual et al., *Corros. Sci.* 51 (2009) 562–568 [44].

3.5.2 Microscopic Photoelectrochemical Characterisation

Microscopic photoelectrochemical is generally performed with the laser source to obtain a photoelectrochemical image that provides the information about the spatial distribution of oxide. Fig. 3.31 presents the schematic diagram of the microscopic PEC set-up at SIMaP laboratory [47]. A monochromatic light from argon laser is used instead of a xenon lamp in macroscopic PEC. An inverted microscope is modified by the 50/50 beam splitter to allow the positioning of the focused beam on the area selected on the optical image provided by CCD camera. A positioning system with a high resolution in XY axes motorised microscope stage is mounted. The laser is used for raster scanning and photocurrent (modulus and phase shift) is collected to perform the image. Spatial resolution of the image can be achieved $1 \mu\text{m}$ by this set-up.

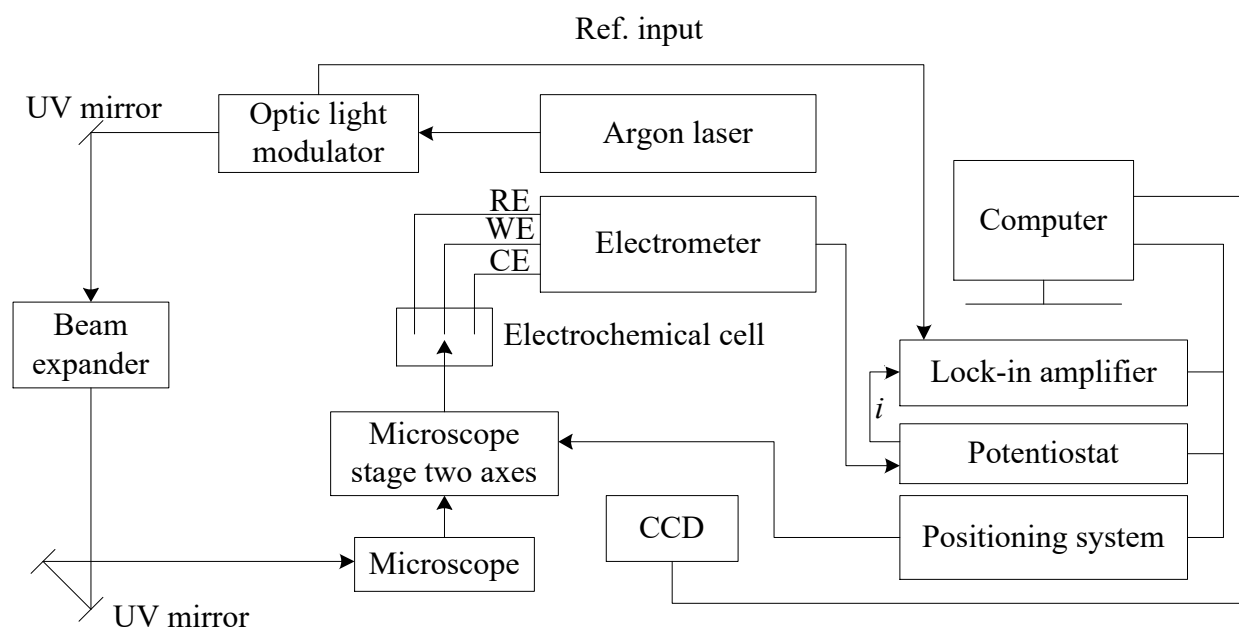


Fig. 3.31. Schematic diagram of the microscopic photoelectrochemical set-up at SIMaP laboratory. Redrawn from A. Srisrual, PhD Thesis, University of Grenoble, France, 2013 [47].

Fig. 3.32 shows a set of images obtained from the 2205 duplex stainless steel oxidised in water vapour and in oxygen at 850 °C for 60 min. The characterisation was performed at the same applied potential. The 2.60 eV photon energy contributes Fe_2O_3 and iron-rich $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$, whereas the 3.53 eV photon energy contributes Fe_2O_3 , $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$, and Cr_2O_3 .

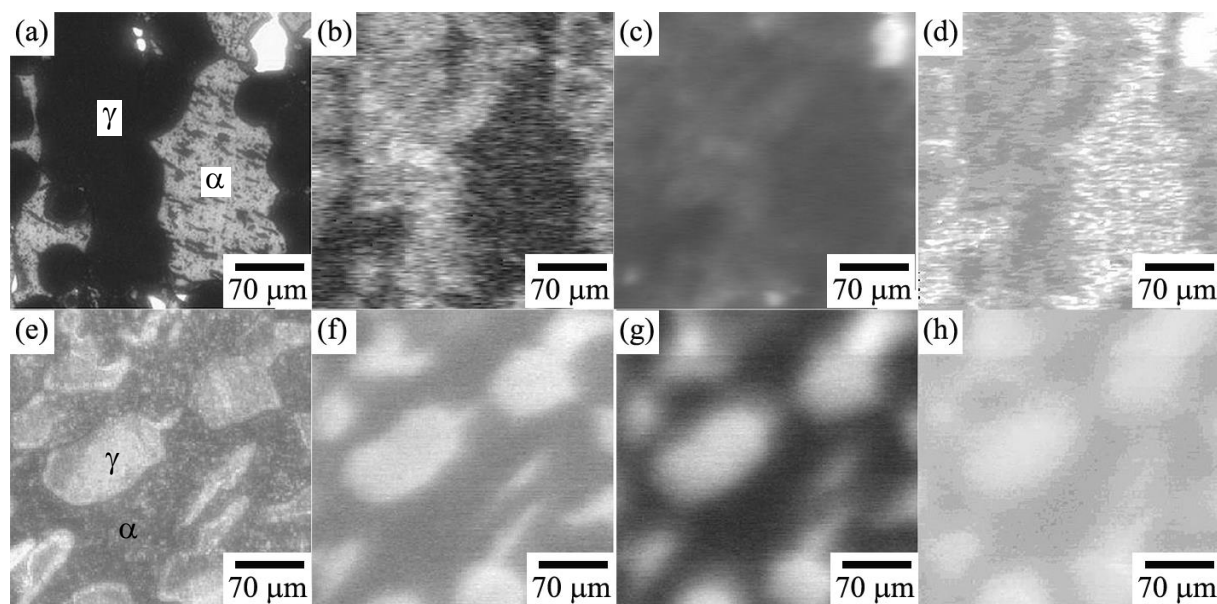


Fig. 3.32. Image set of the 2205 duplex stainless steel oxidised at 850 °C for 60 min in water vapour (top images) and in oxygen (bottom images): (a) and (e) optical image; (b) and (f) PEC image at $h\nu = 2.60$ eV; (c) and (g) PEC image at $h\nu = 3.53$ eV; and (d) and (h) processed image. Reproduced and adapted from A. Srisrual et al., *Oxid. Met.* 79 (2013) 337–347 [49].

Both in Figs. 3.32 (b) and (f), the ferrite area is darker than the austenite area, indicating the higher Fe_2O_3 and $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ on the austenite. To see Cr_2O_3 fraction in the scale, the processed images in Figs. 3.32 (d) and (h) are constructed by dividing, point by point, the photocurrent measured at 2.60 eV by that measured at 3.53 eV for each sample. In the case of water vapour oxidation giving the image shown in Fig. 3.32(d), the Cr_2O_3 fraction is higher on ferrite which

should be from the higher chromium content in ferritic phase and the faster chromium diffusion rate in ferritic phase [49]. In the austenite phase, iron content is high, inducing higher iron diffusion in the corundum oxide and therefore reducing the chromia fraction [49]. In the case of the oxidation in oxygen giving the image shown in Fig. 3.32(h), the higher oxygen partial pressure plays a negative role and opposite results are observed as the higher Cr_2O_3 fraction occurred on the austenitic phase.

3.5.3 Mesoscopic Photoelectrochemical Characterisation

Mesoscopic photoelectrochemical is developed for recording the photovoltammograms and photocurrent energy spectra on a specific microscopic area, thus promoting the superior performance of photoelectrochemical technique. Fig. 3.33 presents the schematic diagram of the mesoscopic photoelectrochemical set-up. It is similar to the microscopic photoelectrochemical set-up in Fig. 3.31, except the part of the light source unit that xenon arc bulb and monochromator system as in macroscopic PEC are used instead of argon laser. Moreover, the optical path is specially designed to obtain a good alignment and to allow an intense micro-focusing light on the interesting area. Spatial resolution of the technique can achieve $30\text{ }\mu\text{m}$ according to the spot size of the focussed light.

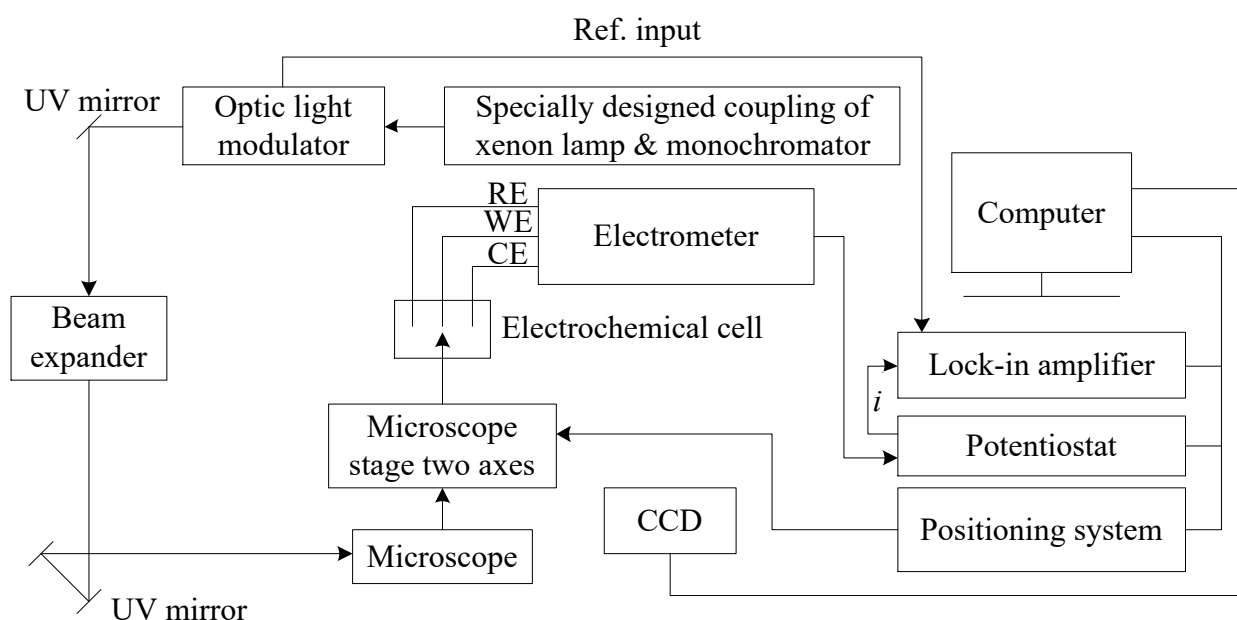


Fig. 3.33. Schematic diagram of the mesoscopic photoelectrochemical set-up at SIMaP laboratory. Redrawn from A. Srisrual, PhD Thesis, University of Grenoble, France, 2013 [47].

Fig. 3.34 shows the typical photovoltammograms obtained at 3.53 eV photon energy on the whole surface of the oxidised 2205 duplex stainless steel sample and grains of austenite and ferrite oxidised at 850 °C for 60 min in water vapour and in oxygen. Photon energy at 3.53 eV is higher than the bandgap energies of Fe_2O_3 , $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$, and Cr_2O_3 . As a result, the recorded photocurrents can be obtained from all of these oxides. The photovoltammograms in Figs. 3.34 (a) and (b) report the effect of oxygen activity on semiconducting type of thermal oxide. It is seen that the oxides act as insulator and p-type behaviour in water vapour and in oxygen atmosphere respectively. Moreover, Fig. 3.34(a) shows the flatband potential of the macroscopic spectra located at around -350 mV that is an intermediate value between the ones of individual ferritic and austenitic grains, indicating that the macroscopic response averages the ones of the different grains.

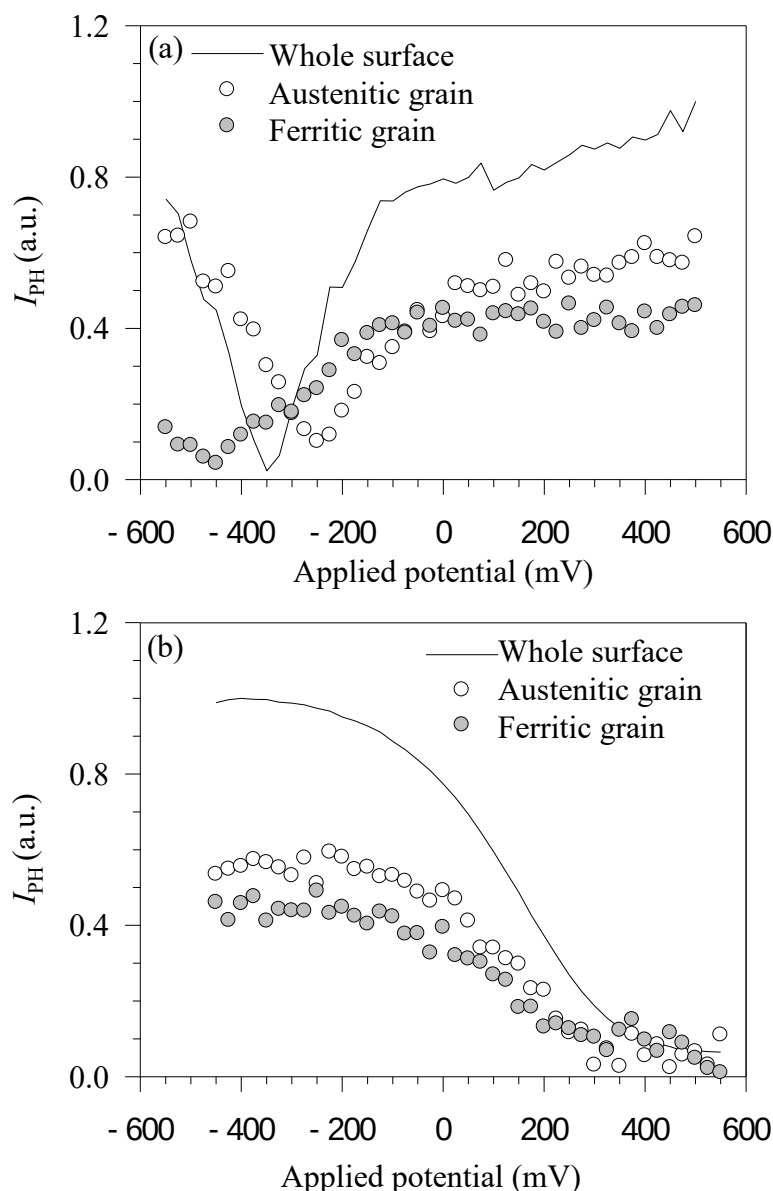


Fig. 3.34. Typical photovoltammograms obtained at $h\nu = 3.53$ eV on the whole surface of the 2205 duplex stainless steel and the individual grain of austenitic and ferritic phases oxidised at 850 °C for 60 min (a) in water vapour and (b) in oxygen. Redrawn from A. Srisrual et al., *Oxid. Met.* 79 (2013) 337–347 [49].

Fig. 3.35 presents the photocurrent energy spectra obtained from individual austenitic and ferritic grains of the 2205 duplex stainless steel oxidised at 850 °C in water vapour for 60 min. The characterisation was performed at the applied potential of -350 mV. Both amplitude and dephasing angle of photocurrent are reported. Dephasing angle that shifts might correlate with either semiconducting behaviour or oxide type. The amplitude and dephasing angle coincidentally report the lower bandgap energy of $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ solid solution obtained from austenite comparing to ferrite, indicating a lower x value in oxide grown on austenitic grain.

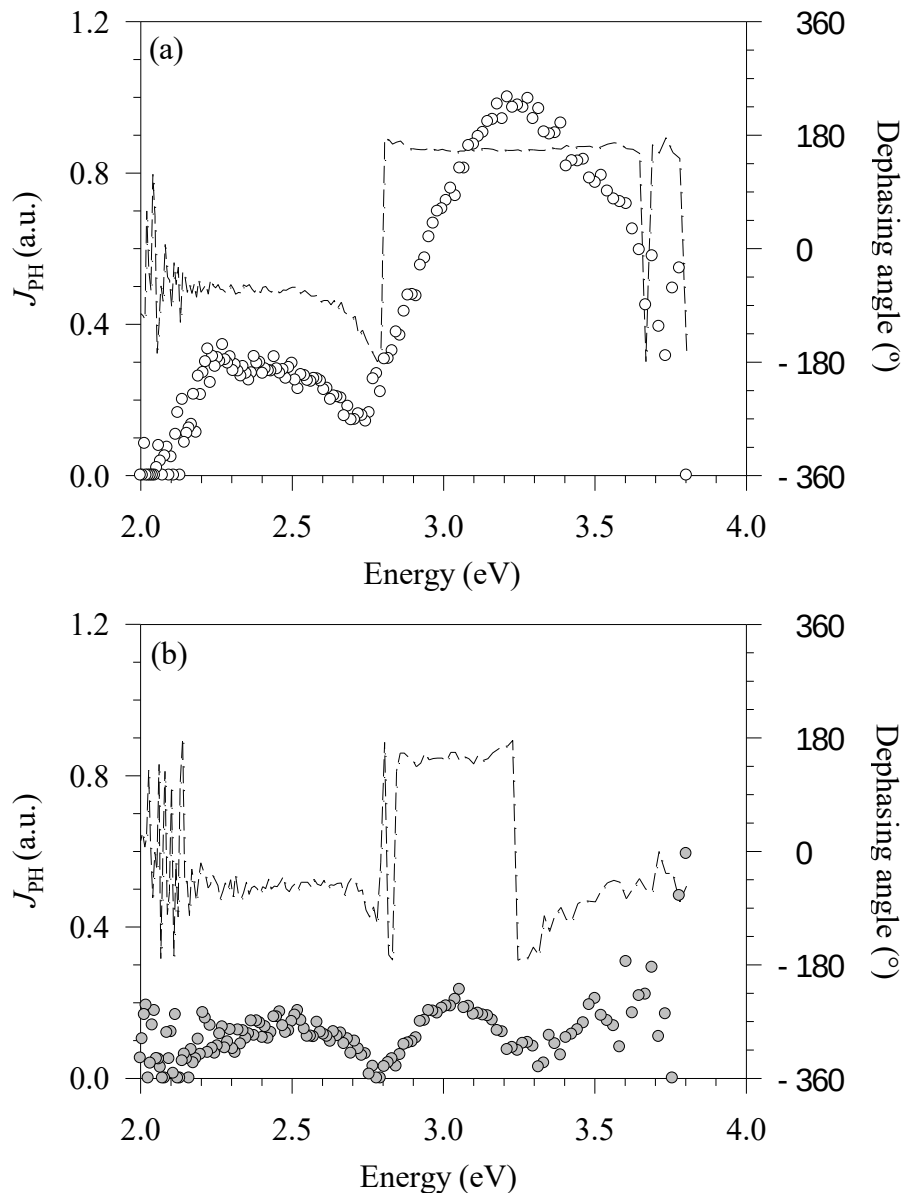


Fig. 3.35. Photocurrent amplitude (white or gray circle) and dephasing angle (dashed line) *versus* energy spectra obtained on individual (a) austenitic and (b) ferritic grains at the applied potential of -350 mV of the 2205 duplex stainless steel oxidised at 850 °C in water vapour for 60 min. Redrawn from A. Srisrual et al., *Oxid. Met.* 79 (2013) 337–347 [49].

Fig. 3.36 shows the photocurrent energy spectra of the sample from Fig. 3.35. In this case the characterisation was performed at the applied potentials of 350 and 0 mV for the sample oxidised in water vapour and in oxygen respectively. For the results of the oxidation in water vapour (low oxygen activity) shown in Fig. 3.36(a), the differences in photocurrent of ferritic and austenitic oxidised grains are mainly located in the low photon energy range with higher photocurrent issued from the iron rich oxide on the austenitic grain. On the contrary, for the results of the oxidation in oxygen (high oxygen activity) shown in Fig. 3.36(b), the difference in the photocurrent of the ferritic and austenitic oxidised grains is mainly located in the high photon energy range with higher photocurrent issued from the chromium rich oxide on the austenitic grain.

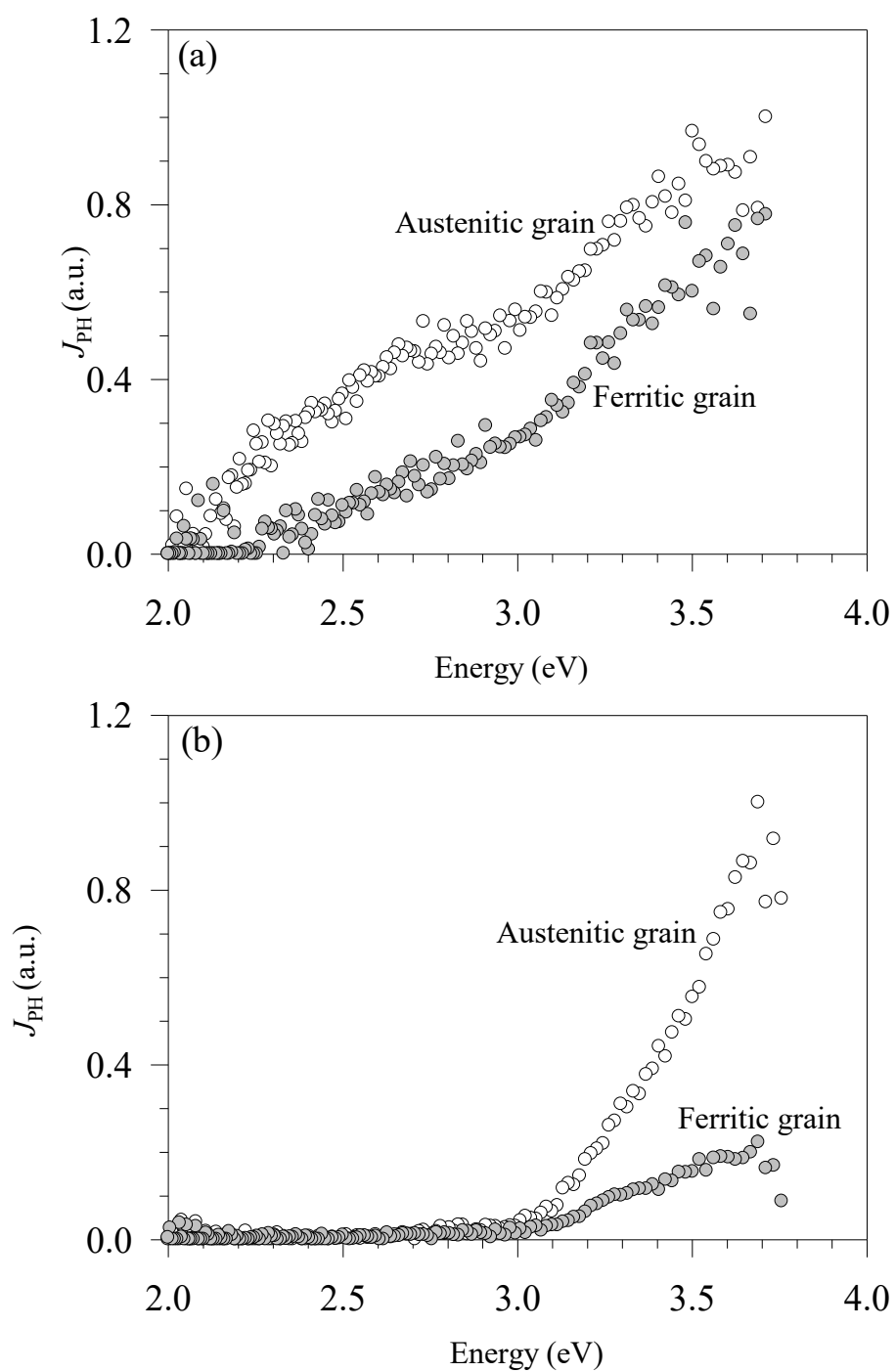


Fig. 3.36. Photocurrent energy spectra obtained on individual austenitic (open circle) and ferritic (closed circle) grains of the 2205 duplex stainless steel oxidised at 850 °C for 60 min (a) in water vapour at 350 mV, (b) in oxygen at 0 mV. Redrawn from A. Srisrual et al., *Oxid. Met.* 79 (2013) 337–347 [49].

3.6 Summary

This chapter firstly reviews the thermogravimetric method and the analysis of gas composition in the atmosphere emphasising the one with water vapour. The experimental set-up for chromium volatilisation measurement is further addressed. The characterisation techniques for finding physico-chemical properties and semiconducting characteristics of thermal oxide scale are later reviewed. OM and SEM can reveal surface morphology. In addition, the elemental composition can be analysed and mapped by EDS that is typically integrated with SEM. FIB-SEM allows the *in-situ* milling during SEM performing and can lead to study the oxide in cross-section, to make a thin lamella, and to reconstruct the phases of interest. XPS provides the element composition and chemical state of material which can help identify the oxide species. XRD, Raman spectroscopy, and PEC technique are generally performed to identify the oxide phases. Moreover, PEC is also used to find the semiconducting behaviour of the oxide.

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