

AN X-RAY PHOTOELECTRON SPECTROSCOPY STUDY ON OXIDIZED FUSION METAL PART OF WELDED 6061 AL ALLOY

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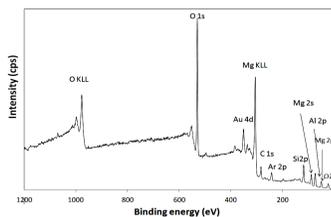
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Graphical abstract



Abstract

Surface sensitive electron spectroscopy was used to study the fundamental processes of high temperature oxidation. X-ray photoelectron spectroscopy (XPS) has been applied to determine the oxide scale growth on oxidized fusion metal part of two different types of welded 6061 Al alloy, namely AA6061 ER4043 and AA6061 ER5356. Both welded joint were prepared using different filler metal which are ER4043 (Al-5%Si) and ER5356 (Al-5%Mg) respectively. XPS were used to investigate the chemical composition of the top surface of oxide scale that had been exposed to oxidation at 600°C for 40 hours. Furthermore, SEM and XRD were applied to characterize the cross-section of oxide scale and the phase present. The presence of Mg originating from filler metal addition was found to accelerate the oxidation process. Meanwhile, Si is expected to contribute as an agent in slowing down the oxidation process. It was significant due to the nature of Si itself which is less reactive and has ceramic properties than Mg.

Keywords: XPS, SEM, XRD, welded joint, oxidation, oxide growth

Abstrak

Spektroskopi elektron untuk permukaan sensitif digunakan untuk mengkaji proses-proses asas pengoksidaan suhu tinggi. Spektroskopi Fotoelektron Sinar-X (XPS) diaplikasikan untuk menentukan pertumbuhan kerak oksida pada bahagian sambungan logam untuk dua jenis struktur terkimpal aloi Al, iaitu AA6061 ER4043 dan AA6061 ER5356. Kedua-dua jenis struktur terkimpal dikimpal menggunakan logam pengisi yang berbeza iaitu ER4043 (Al-5%Si) dan ER5356 (Al-5%Mg). XPS digunakan untuk mengkaji komposisi kimia pada bahagian atas permukaan kerak oksida yang telah dioksidakan pada suhu 600°C selama 40 jam. SEM dan XRD pula diaplikasikan untuk mencirikan keratan rentas kerak oksida dan kehadiran fasa. Kehadiran Mg yang berasal daripada tambahan logam pengisi didapati bertindak mempercepatkan proses pengoksidaan tersebut. Manakala, Si pula didapati menyumbang sebagai agen untuk memperlahankan proses pengoksidaan. Ia lebih jelas disebabkan oleh sifat Si di mana ia kurang reaktif dan mempunyai ciri-ciri seramik berbanding Mg.

Kata kunci: XPS, SEM, XRD, struktur terkimpal, pengoksidaan, pertumbuhan oksida

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1.0 INTRODUCTION

Aluminum (Al) based materials are widely used in engineering application due to their excellent

combination of mean density, high strength and good corrosion resistance [1]. In light weight constructions, for example Al alloy with Mg, Zn, Cu or Fe is commonly used since this alloy has excellent

strength but lack in corrosion resistance [2]. The natural layer developed on Al alloys which are always assigned as aluminum oxide. This thin oxide film is of great interest because it acts as a barrier layer to corrosion process [3-6].

In particular, the effect of high temperature oxidation on bare material or non-welded structure of Al 6061 is well studied. Yet, when it is involved a welded joint, the behavior and the performance due to the influence of alloying element such as Mg and Si from filler metal addition on the growth of oxide scale formation were entirely dissimilar. Furthermore, the oxidation process may be more complex for welded parts which composed of alloys with different oxide growth rates because of geometric and microstructural differences between the parent and fused parts.

XPS is a powerful technique for quantitative analysis of time-dependent chemical changes occurring at the sample surface. In this case, at high temperature oxidation, as in welding process the oxide scales formed provide interesting corrosion characteristics at fusion metal part of Al alloy [7]. The thin layer of oxide is possible to study by a special analysis such as X-ray photoelectron spectroscopy (XPS) because its signals arise from a depth of only a few nanometers [8-12]. The oxide scales which composed of multiple crystalline oxide phases that developed on the alloy surface especially on fusion metal part generally prevails catastrophic growth by the solid state diffusion of reactants [13-17].

Accordingly, the current work is to study the evolution of the chemical composition mainly the depth distribution of various chemical species within the grown oxide scales of fusion metal part of welded Al alloy as a result of the interaction with air gas environment at temperature of 600°C for 40 hours. It also covers the study of bulk and surface properties of grown oxides that were elucidated using XPS, XRD, and SEM.

2.0 METHODOLOGY

2.1 Material Selection and Welding Process

In this study, an oxide scale of two types of fusion metal part namely, AA6061 ER4043 and AA6061 ER5356 were investigated. We described the top-most surface oxide scale which had been exposed to high temperature oxidation process at a temperature of 600°C for 40 hours. Samples used for oxidation test was prepared by using gas metal arc welding (GMAW) technique with 22-25V and 185-200A, using two different types of filler metal which are ER4043 (Al-5%Si) and ER5356 (Al-5%Mg). Table 1 shows the compositions of fusion metal part of both samples. The welding parameters used to join AA6061 Al alloy is shown in Table 2.

The plate had an original dimension of 300mm (length) x 200mm (width) x 12mm (thick) with double-

V groove. The pre-joint configuration was obtained by securing the plates in position using tack welding. Following welding process, the bead contour, bead appearance, and weld quality have been inspected visually to identify the discontinuities of the fusion metal part. Then, samples of approximate dimension 58mm x 12mm x 5mm were hand cut from the plate comprising of parent and fusion metal parts. The fusion metal part samples were then mechanically ground up to 1200 mesh using silicon carbide paper and followed by polishing using diamond paste (3 and 1 μ m). Samples were then cleaned using ethanol before exposed to oxidation at high temperature. The oxidation test was carried out using a laboratory type air circulated horizontal tube furnace at 600°C in air gas for 40 hours duration. Then, the samples were cooled slowly to room temperature in the furnace.

Table 1 Element compositions in wt% of both fusion metal parts of both samples which are AA6061 ER4043 and AA6061 ER5356

| | Si | Fe | Cu | Mn | Mg | Cr | Zn | Ti | V | Al |
|---------------|-------|-------|-------|-------|-------|-------|------|-------|-------|------|
| AA6061 ER5356 | 0.134 | 0.157 | 0.024 | 0.09 | 4.37 | 0.09 | 0.01 | 0.109 | - | 94.9 |
| AA6061 ER4043 | 2.06 | 0.183 | 0.146 | 0.003 | 0.501 | 0.054 | - | 0.007 | 0.005 | 97 |

Table 2 Welding parameters used to weld both welded 6061 Al alloy samples

| Welding Parameter | Description |
|-----------------------------|--|
| Diameter filler wire ER5356 | 1.00 mm |
| Polarity | Direct current reverse polarity (DCRP) |
| Amperage | 185 A |
| Voltage | 25 V |
| Travelling speed | 400 mm/min |
| Heat input | 0.75 \pm 0.08 KJ/mm |
| Shielding Gas | Argon |

2.2 Morphology and Phase Analysis

The oxidized fusion metal part of both samples were then characterized using a scanning electron microscope (SEM) LEO 1450 model equipped with an energy dispersive X-ray spectroscopy (EDS) to obtain cross sectional images. Phase identification was carried out using X-ray diffractometer (XRD) Bruker AXS:D8 Advance model. The diffraction angle of XRD was between 20° to 80° with a count of time of 1s.

3.3 Surface Analysis

After being oxidized, the welded samples particularly at fusion metal part were cut using diamond cutter into the dimension of 5mm (length) x 5mm (width) x 5mm (thick). Then, the sample is mechanically attached to the specimen mount, and analysis is begun with the sample in the as-received

condition. Additional sample preparation is discouraged because any preparation might modify the surface composition [Moulder *et al.* [18]. The evolution of the chemical composition mainly the depth distribution of various chemical species within the grown oxide scales on fused metal were studied by using X-ray photoelectron spectroscopy (XPS) Axis Ultra model. The spectra were taken with the Al K α X-ray source operating at 400 W (15 kV – 27 mA). The fused metal samples were analyzed at an electron take-off angle of 70°, measured with respect to the surface plane. The charging effects were corrected by referencing the binding energies to that of adventitious carbon (284.8 eV). Argon ion etching was performed for 10 minutes to remove adventitious contaminants. XPS spectrum analysis was performed by peak fitting employing the respective procedures using the data system analysis. During data fitting, a Shirley background correction was applied to all spectra. In order to identify the elements present, a high resolution broad scan survey spectrum is obtained.

3.0 RESULTS AND DISCUSSION

Exposing a clean fusion metal part of welded 6061 Al alloy to high temperature oxidation environment results in growth of an oxide scale, which causes not only an attenuation of the photoelectron intensity originating from the alloy substrate, but also a shift in binding energy of the photoelectron line in the underlying metallic lattice to oxidized Al in the over layer surface. This leads to a rise in several spectral peaks of XPS spectrum on oxidized fusion metal part of both welded joint which are AA6061 ER 4043 and AA6061 ER 5356. Evidently, analyzing fusion metal part of welded joint is complicated due to the presence of multiple-metal oxide scale. It is much more challenging than the analysis of single-metal oxide layer, because more than one substrate constituent can be incorporated into the multiple-element such as spinel which is associated with compositional and microstructural changes during oxide growth [18, 19].

3.1 Cross-Section and Phase Analysis

Figures 1 (a) and (b) show a cross-sectional images of fusion metal part of 6061 Al alloy welded joint using filler metal ER 4043 and ER 5356 that has been exposed in high temperature oxidation at a temperature of 600°C for 40 hours. Both fusion metal parts show an external oxide scale formed on the top surface of the substrate. Observing the level of degradation of both samples, it shows that AA6061 ER5356 indicated higher oxidation effects compared to AA6061 ER4043. Oxide scale of AA6061 ER4043 (Figure 1 (a)) was observed to have a non-flat and brittle surface which is enriched with Si-rich oxides. Interior substrate was found enriched with Al-rich

oxide. In addition, the interior substrate of AA6061 ER5356 (Figure 1 (b)) specified the presence of oxide nodules which is enriched with Mg-rich oxide. Furthermore, the external oxide scale of AA6061 ER5356 was found to be thicker and more brittle compared to AA6061 ER4043.

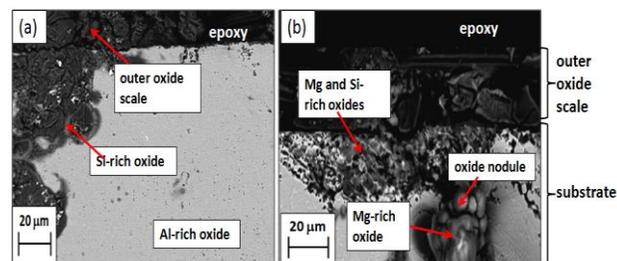


Figure 1 Cross-sectional images of oxidized fusion metal part of welded joint at 600°C for 40 hours (a) AA6061 ER 4043, and (b) AA6061 ER 5356

XRD spectrums in Figures 2 (a) and (b) confirmed the presence of oxide phases for both fusion metal parts. It shows that, both samples showed the highest intensity spectrums of γ -Al $_2$ O $_3$ phases that were recorded at 37.539°, 45.668° and 66.602°. Instead of γ -Al $_2$ O $_3$, both samples showed several peaks of δ -Al $_2$ O $_3$. Furthermore, only AA6061 ER5356 showed the presence of MgO (Figure 2(b)).

3.2 XPS Analysis

The main objective of the XPS data analysis was to determine quantitatively the relative amounts of the chemical states in each recorded spectrum in Figures 3 and 4. XPS is a widely used method in chemical shift evaluation in the binding energies of photoelectron for the determination of oxidation states of metals in their oxides [20, 21]. However, for many oxides, the XPS application is complicated. These difficulties often present for mixed oxides such as in welded alloy structure. The sensitivity and peak areas of the characteristic elements in the full scan spectrum that obtained by the argon ion sputtering method for both fusion metal parts which are AA6061 ER4043 and AA6061 ER5356 were analyzed.

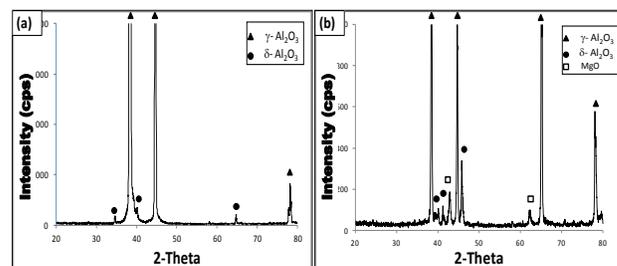


Figure 2 XRD spectrums of oxidized fusion metal part welded joint at 600°C for 40 hours, (a) AA6061 ER 4043, and (b) AA6061 ER5356

Figures 3 and 4 show the full scan analysis of fusion metal part of the welded Al alloy 6061 using ER4043 (Al-5%Si) and ER5356 (Al-5%Mg) filler metal by XPS respectively. Both figures also described the information of elements in the oxide layer and contamination adsorbed on the scale layer. The survey wide scan spectra of XPS of both fusion metal samples exposed to oxidation at 600°C for 40 hours showing the details of Al 2p, Mg 2p, Si 2p, O 1s and C 1s photoelectron lines. The XPS survey spectra showed Al, Mg, Si, O, and C to be the main elements with other elements only appearing at trace levels. The graph profile shown is corrected for sample charging effects, where the spectra were shifted to set the C-C component of the C 1s core level peak at a binding energy of 284.8 eV. In order to measure the various binding energy positions, the graph profile were determined accurately by fitting of a third degree polynomial function through the top of the respective peaks. High-resolution of O 1s, Mg 2p, Si 2p, and Al 2p of both fusion metal parts which had been oxidized at temperature of 600°C for 40 hours were shown in Figures 5 and 6.

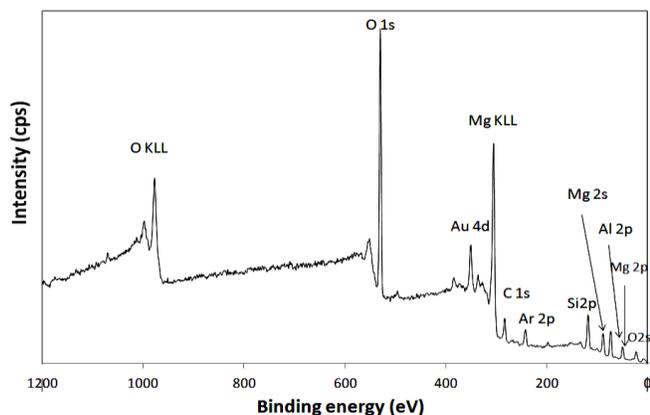


Figure 3 XPS full scan spectra of fusion metal part of AA6061 ER4043 welded joint oxidized at 600°C for 40 hours

3.3 Narrow Scan Spectra of Oxide Scale

Narrow scan analysis gives detailed information of each element selected in surface oxide scale as presented in Figures 3 and 4. The chemical composition of both oxide products of both fusion metal parts can be calculated from these spectra. The calculation is based on the integrated area under the assigned element peak and the sensitivity factor for the selected element.

The two Al peak position of Al 2p were observed on fusion metal part of AA6061 ER4043 in Figure 5 indicated a binding energy (BE) value of 72.8 eV and 74.8 eV as reported for the presence of Al and thin Al_2SiO_5 layer respectively. As recorded in Figure 6, the peak position of Al 2p on AA6061 ER5356 surface corresponds to BE value of 72.9 eV and 74.5 eV indicated the presence of Al and thin γ - Al_2O_3 films. It

is noted in previous literature that this BE value (i.e. 74.5 eV) is slightly higher than the corresponding Al 2p BE value of 74.0 eV as reported in [12] for Al cations. It has been previously reported that the BE of the Al 2p for Al_2O_3 is 74.4 – 75.8 eV [14]. It is suggested that the interfacial Al cations give rise to the Al 2p species in the grown oxide scale, are in their formal oxidation state which is Al^{3+} . Its chemical environment passes the similarity of Al cations in Al_2O_3 and/or MgAl_2O_4 as reported in [12].

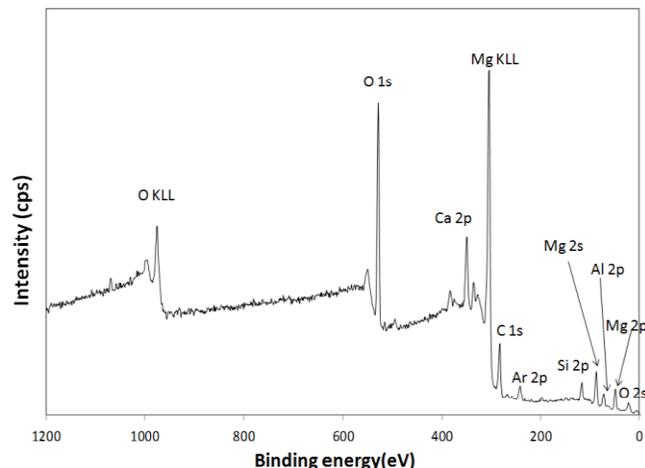


Figure 4 XPS full scan spectra of fusion metal part of AA6061 ER5356 welded joint oxidized at 600°C for 40 hours

The Mg 2p BE of 49.8 eV for the grown oxide scale in Figures 5 and 6 for both types of fusion metal parts complies well with the corresponding BE value of Mg. The second species of Mg 2p BE of 50.8 eV for both types of samples was confirmed to the compound of MgO. It is similar to those reported by Moulder *et al.* [18] indicated that the corresponding Mg 2p BE of 50.8 eV for bulk and thin film of MgO.

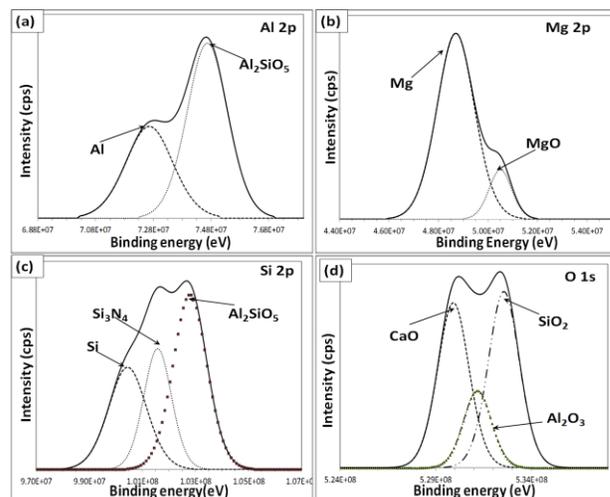


Figure 5 The profile of Al 2p, Mg 2p, Si 2p and O 1s signals of oxidized fusion metal part of AA6061 ER4043 at 600°C for 40 hours

Figures 5 (c) and 6 (c) show an XPS spectra in the Si 2p energy region for both types of oxidized fusion metal parts of AA6061 ER4043 and AA6061 ER5356 respectively. According to Figure 5 (c) indicated the peak position of Si 2p corresponds to presence of three species of Si which were expressed as Si at BE of 99.5 eV, Si₃N₄ at BE of 101.8 eV, and Al₂SiO₅ at BE of 103.0 eV. Contradict findings were observed on fusion metal part of AA6061 ER5356 in Figure 6 (c). It is observed that there were two Si 2p species that were performed using the peak convolution method. The Si 2p peaks with the BE of 102.0 eV was considered to be due to the formation of Si n-type and the other Si 2p peak with a different BE of 103.6 eV is found to be due to the presence of SiO₂. It was considered that at temperature of oxidation reaction at 600°C, the phase separation of oxide states of Si 2p is taking place. At higher temperature, possible formation mechanism involves the exchange of oxygen and silicon leading to the formation of SiO₂.

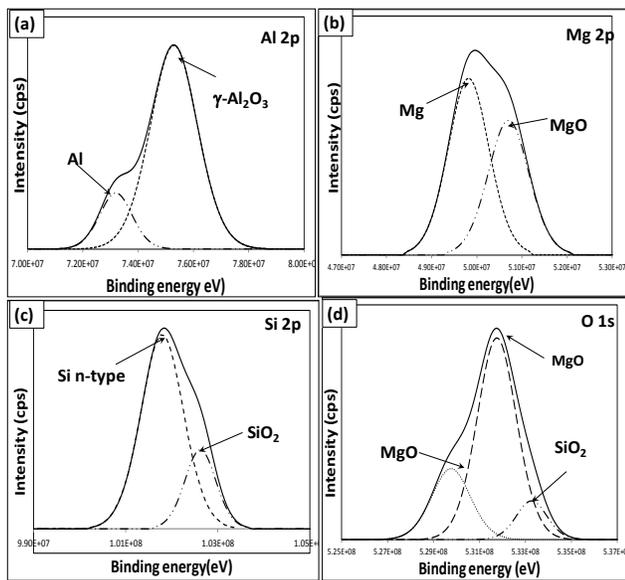


Figure 6 The profile of Al 2p, Mg 2p, Si 2p and O 1s signals of oxidized fusion metal part of AA6061 ER 5356 at 600°C for 40 hours

It is emphasized in previous literature that oxygen molecules approaching the Al surface have two possibilities in surface interaction. In that case, either they are dissociated in the vicinity of the surface by a charge transfer into the oxygen anti-bonding molecular orbital or otherwise the whole oxygen molecule is reflected from the surface as briefed by Frerichs *et al.* [2]. In Figure 5 (d), indicated the O 1s peak position of fusion metal part of AA6061 ER4043 indicated O 1s BE of 529.4 eV corresponds to the presence of CaO which was believed due to the heating contamination in the furnace. The second O 1s peak with BE of 531.3 eV and 533.0 eV indicated the presence of Al₂O₃ and SiO₂ respectively. The contradict findings were observed for AA6061 ER5356

fusion metal part in Figure 6 (d) showing the BE value of 533.03 eV and 532.10 eV, which both BE values correspond to the presence of MgO. The other peak position of O 1s with BE value of 533.2 eV corresponds to the formation of SiO₂ α-quartz.

3.4 Thermodynamic Consideration

To predict which alloy constituents namely Al, Mg, or Si will be preferentially oxidized upon oxidation of the fusion metal part of welded AA6061 Al alloy using ER 4043 and ER 5356 filler metal, the total energy gain of the reacting system can be calculated for each of the competing oxide phases. In order to provide an appropriate description for the oxidizing process of AA6061 ER4043 and AA6061 ER5356, the formation of Al₂O₃, MgO, SiO₂, and Al₂SiO₅ is considered. The possible reactions during oxidation and their corresponding standard Gibbs free energies, ΔG° in each reaction at the oxidizing temperature 600°C were calculated. The Standard Gibbs free energies ΔG in each reaction at the oxidation temperature 600°C were listed in Table 3.

Table 3 The possible chemical reaction and standard Gibbs free energies during oxidation at 600°C [8]

| Reaction | - ΔH (J/g.mole) | -ΔS (J/g.mole. °K) | ΔG° ₆₀₀ (kJ) |
|--|--------------------|--------------------------|----------------------------|
| 2 Mg + O ₂ (g) → 2MgO | 1,219,140 | 233.04 | - 1,015.68 |
| ½ Mg + Al + O ₂ (g) → ½ MgAl ₂ O ₄ | 1,164,035 | 218.84 | -972.98 |
| 4/3 Al + O ₂ (g) → 2/3 Al ₂ O ₃ | 1,121,922 | 215.47 | -931.66 |
| Si + O ₂ (g) → SiO ₂ | 901,760 | 173.38 | -750.39 |
| 2 Mg + Si → Mg ₂ Si | 155,600 | 75.0 | -90.12 |
| MgO + Al ₂ O ₃ → MgAl ₂ O ₄ | 35,600 | 2.09 | -33.77 |
| Al ₂ O ₃ + SiO ₂ → Al ₂ SiO ₅ | 8812 | 3.891 | -5.416 |

As recorded in Table 3, the possible formation of oxides was summarized as a guideline for prediction of oxide formation. The ΔG_{600°C} in the formation of MgO using 1 mol of O₂ was equal to -1,015.68 kJ which was lower than those that is observed for Mg₂Al₂O₄ (-972.98 kJ), Al₂O₃ (-931.66 kJ) and SiO₂ (-753.68 kJ). Therefore, it is suggested that the order of priority of the reactions was as follows: reaction 1: Mg was oxidized to MgO; reaction 2: Mg and Al were oxidized to MgAl₂O₄ spinel; reaction 3: Al was oxidized to Al₂O₃; reaction 4: Si was oxidized to SiO₂; reaction 5: combination of two oxides MgO and Al₂O₃ to form MgAl₂O₄ spinel; and reaction 6:

combination of two oxides SiO_2 and Al_2O_3 to form other types of oxides which is Al_2SiO_5 . Reaction 5 and 6 is different with those listed in reaction 1 to 4 since this reaction involves the combination of two oxides to form another types of different oxides.

According to Arranz and Palacio [20], there is a controversy on the mechanisms of oxygen chemisorptions and nucleation and growth of the surface oxide on single-crystal Al surfaces. They showed that the interaction of oxygen with Al works in two different ways, either the formation of surface and subsurface species during oxygen adsorption, or the simultaneous formation of two-layer oxygen islands and single-layer oxygen islands [22, 23]. The dynamic changes of the chemical state in high temperature oxidation revealed that the Al substrate containing Mg, which referring to the AA6061 ER5356 will cause the Mg distributed in the matrix and move to the surface. In the case of the role of Si in AA6061 ER4043 was significant due to the nature of Si itself which is less reactive and has ceramic properties than Mg and Al. Thus, Si is expected to contribute as an agent in slowing down the oxidation process. According to Do *et al.* [14], it is evident that the addition of Si or Mg in Al bare material will result in an increase or reduction in the number of defects in the oxide scale and therefore leads to the changes in oxidation behavior.

4.0 CONCLUSION

The structure of oxides that growth on fusion metal part of welded Al 6061 using ER 4043 (Al-5%Si) and ER5356 (Al-5%Mg) filler metal that was exposed to high temperature oxidation were examined using SEM, XRD and XPS. On exposure of both samples to oxidation at a temperature of 600°C for 40 hours, the oxidized fusion metal part samples showed the presence of spectral lines of Al 2p, Mg 2p, Si 2p and O1s. For both samples, the XPS data is consistent with the oxidation products revealed by XRD analysis showing that the oxide scale formed is constituted of $\gamma\text{-Al}_2\text{O}_3$, MgO, SiO_2 , and Al_2SiO_5 oxide phases. Thus, it can be said that, the use of ER 4043 as a filler metal to weld Al Alloy for application at 600°C shows a better performance compared to the use of filler metal ER 5356.

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