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Effect of dopants on the phase formation in microwave processed Al–Al_2O_3 composites

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ABSTRACT

Microwave processing of undoped and doped Al powder compacts was performed for the preparation of Al–Al_2O_3 composites. Mg, Mg–Si and Al_2O_3 were used as dopants to study their effects on the oxidation of Al powder and resultant Al–Al_2O_3 composites. The microwave heated undoped and doped Al powder compacts were characterized by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. XRD and EDX data of the microwave treated powder compacts confirmed the formation of Al–Al_2O_3 composites. Mg and Mg–Si doped Al powder compacts exhibited bulk composite growth. On the contrary, composite formation was restricted to the surface and near surface only in the undoped and Al_2O_3 doped Al powder compacts. SEM showed the microstructures of the microwave processed undoped and doped Al powder compacts.

1. Introduction

Metal–ceramic composites are important classes of materials with high potential for structural applications requiring high specific modulus, strength and toughness [1]. Al–Al_2O_3 is one of the metal–ceramic composite materials, which is now increasingly used for potential applications in the aerospace, defense and automotive industries [2]. Al–Al_2O_3 composites have been prepared from aluminium and its alloys by various routes, e.g. high temperature (~900–1400 °C) oxidation of liquid Al–Mg and Al–Mg–Si alloys [3–5], directed metal oxidation [6], microwave heating [7], reactive melt infiltration [8], squeeze casting [9–10], in situ method [11], friction stir processing [12], powder metallurgy [13–14] etc.

During high temperature oxidation of liquid Al–Mg and Al–Mg–Si alloys in the temperature range of 1100–1300 °C initial oxidation followed by an incubation period of limited oxide growth and then bulk Al–Al_2O_3 composite formation was observed [3–5]. A duplex oxide layer in which MgO was the upper layer and $MgAl_2O_4$ containing metal microchannels was the lower layer, was formed at the surface and got continuously thickened during incubation. The bulk oxide growth was preceded by the decrease in MgO layer thickness. Continuous formation of MgO at the surface, reaction of some of the MgO with the melt to form $MgAl_2O_4$, dissolution of the MgO and $MgAl_2O_4$ in the Al-rich alloy, diffusion of dissolved oxygen through the metal layer and epitaxial growth of Al_2O_3 resulted in bulk oxide growth [3–5]. Growth of Al–Al_2O_3 composites by directed metal oxidation technique occurred by continuous infiltration of a preform (reinforcement of filler) consisted of Al_2O_3 powder through outward oxidation of Mg, MgO and Si doped molten Al metal [6]. Al–Al_2O_3 composite was prepared by microwave processing using thermally oxidized Al metal. Porous aluminium oxide coating was developed on Al by thermal oxidation, which was essential for further processing in microwave radiation. When this oxidized Al was given a microwave exposure, the oxide coating absorbed microwave energy and became volumetrically heated. Consequently, the metallic layer adjacent to the coating got heated by the conduction method. At higher temperatures, the aluminium oxide coating absorbed microwave energy at an enhanced rate because of large value of the loss tangent and the relative dielectric constant. Thus, metal is heated to a high temperature during long microwave exposure, which led to activated diffusion resulting in high rate of oxidation. Oxygen atoms diffused through the pores of the oxide coating to the aluminium metal. Depending upon provision for the diffusion of oxygen atoms towards the inner side, aluminium metal was oxidized and formed Al–Al_2O_3 composite [7]. Al_2O_3–Al co-continuous composite was synthesized through the reactive melt infiltration technique by infiltration of molten aluminium into the SiO_2 preform. Chemical reaction of molten aluminium with SiO_2 at the infiltration front generates a transition zone having a new type of continuous porosity. Further infiltration of molten aluminium into this porosity and reaction with residual SiO_2 leads to transformation of all the SiO_2 into Al_2O_3 [8]. Chou et al. fabricated Al_2O_3–Al composite by infiltration of aluminium alloy into the porous Al_2O_3 preform by squeeze

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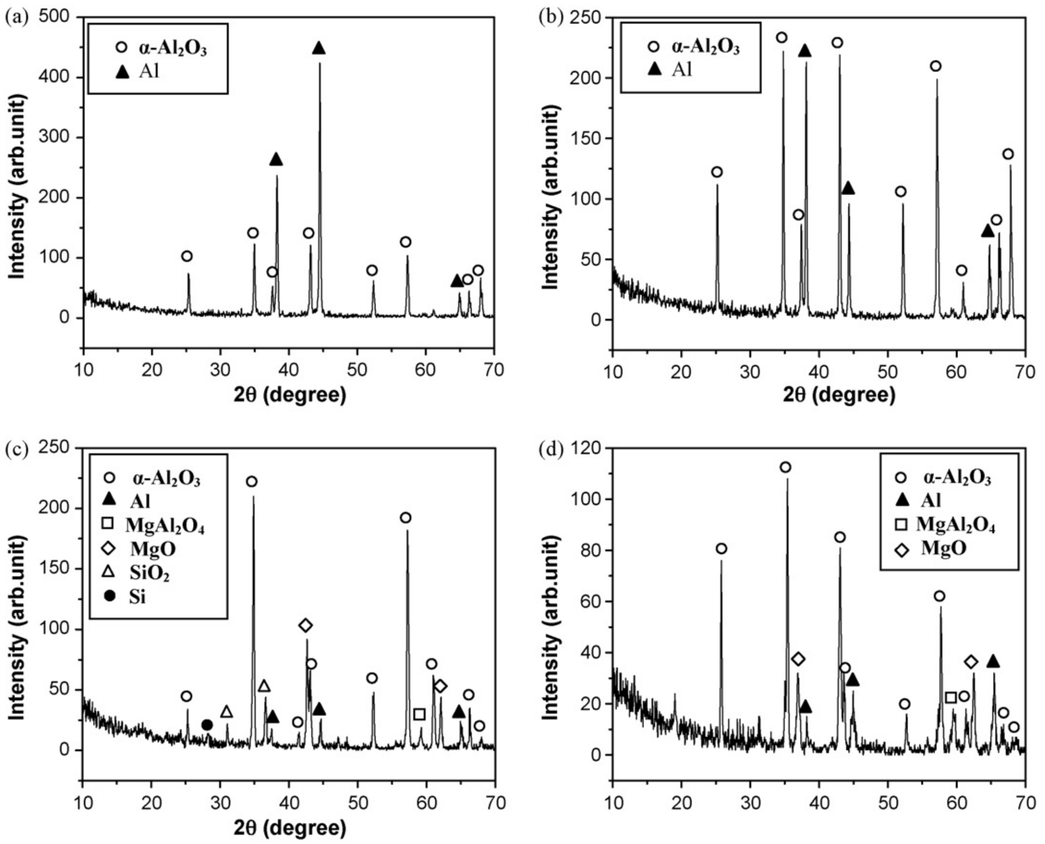

Fig. 1. XRD patterns of undoped and doped Al powder compacts microwave heated for 1 h at 1200 °C: (a) undoped Al powder compact, (b) Al–5Al_2O_3 powder compact, (c) Al–3Mg–2Si powder compact and (d) Al–5Mg powder compact.

casting [10]. Aluminium matrix composites have been produced by the in situ method, which involves reaction between a metal oxide and aluminium to produce alumina particles or whisker reinforcements [11]. A new processing technique e.g. friction stir processing (FSP) was utilized to incorporate nano-sized Al_2O_3 into aluminium alloy to form particulate composite surface layer. In this technique, aluminium alloy samples were subjected to various numbers of FSP passes with and without Al_2O_3 powder [12]. Al_2O_3 reinforced Al matrix composite was fabricated using powder metallurgy method in which the Al, Al_2O_3 powders were mixed, consolidated and finally sintered [13,14].

Microwave energy is being utilized as an alternative energy source for the processing of materials to ensure rapid, volumetric heating, finer microstructure and better properties [15,16]. We have already reported on the development of oxide coating on Al and Al–Al_2O_3 composite by microwave heating [7,17,18]. Researchers have established that metal powder can be efficiently heated by microwave energy [19,20] wherein the dielectric loss and eddy current loss have important roles. In addition, multiple scattering in the powdered sample also leads to the absorption of the microwave energy [19]. The objective of the present work was to prepare Al–Al_2O_3 composites by microwave induced oxidation of the undoped and doped Al powder compacts and to study the effects of various dopants on the process and the products.

2. Experimental

Commercially available powders such as Al (average particle size: 25–30 μm, purity: 99.7%), Mg (average particle size: 22–26 μm, purity: 99.7%), Si (average particle size: 20–25 μm, purity: 98.5%) and Al_2O_3 (average particle size: 18–22 μm, purity: 99.7%) were used as such without any further processing. Al powder was mixed with Mg, Mg–Si and Al_2O_3 powders in 19:1, 95:3:2, 19:1 weight ratios and then milled in a planetary mill for 2 h. Al, Al–5 wt.% Al_2O_3, Al–3 wt.% Mg–2 wt.% Si and Al–5 wt.% Mg powder compacts were prepared by uniaxial pressing with 100 MPa pressure. The size of all the powder compacts was 15 mm × 15 mm × 2 mm. Green density of the powder compacts was ∼35% of theoretical density. Subsequently, the undoped and doped Al powder compacts were heated inside a microwave furnace (Linn High Therm, 2.45 GHz, 2 kW, GmbH, Germany) equipped with an applicator having in-built insulation of alumina fibre boards at a temperature in the range of 800–1200 °C for 1 h in air to form the Al–Al_2O_3 composites. The samples were kept in a silicon carbide crucible (susceptor), which was placed inside the insulation arrangement. Temperature of the sample was measured using an optical pyrometer (accuracy ±1 °C).

The phase composition of the microwave heated undoped and doped Al powder compacts was examined by X-ray diffractometry (PW 1710, Philips Research Laboratory, Eindhoven, The Netherlands) using Cu Kα radiation (45 kV, 35 mA). The percent weight gain was calculated as: $(W_f - W_i)/W_i \times 100$, where W_i and W_f are the initial and final weights of the powder compact, respectively before and after microwave heating for 1 h in air at 800–1200 °C. The microstructural characterization of the microwave treated powder compacts was conducted by scanning electron microcopy (SEM, LEO S430i, LEO, UK). Elemental composition of the same samples was determined by energy dispersive X-ray analysis (EDX, LEO S430i, LEO, UK, SiLi detector).

3. Results and discussion

3.1. XRD and oxidative weight gain

XRD data from the surfaces of the undoped and doped Al powder compacts microwave treated at 1200 °C for 1 h are shown in Fig. 1a–d. Al and α-Al_2O_3 phases were identified in the microwave exposed undoped and Al_2O_3 doped Al powder compacts (Fig. 1a and b). In the case of microwave heated Mg–Si doped Al powder compact, different phases such as Al, α-Al_2O_3, MgO, $MgAl_2O_4$, Si and SiO_2 were detected (Fig. 1c) while Al, α-Al_2O_3, MgO and $MgAl_2O_4$ phases were present in the microwave treated Mg doped Al powder compact (Fig. 1d). Therefore, the XRD data of the microwave processed Al powder compacts with or without dopants confirmed the formation of Al–Al_2O_3 composites in all the cases.

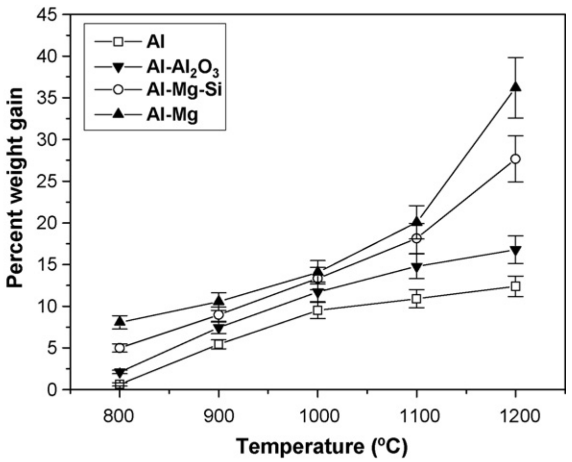

Fig. 2. Percent weight gain as a function of microwave processing temperature for undoped and doped Al powder compacts.

Fig. 2 shows the percent weight gain data of the undoped and doped Al powder compacts during heating in the microwave furnace in the temperature range of 800–1200 °C for 1 h in air. The weight gain increased with increasing temperature in the case of all the microwave processed powder compacts. After 1 h microwave heating at 1200 °C, undoped Al powder compact, Al_2O_3 doped Al powder compact, Mg–Si doped Al powder compact and Mg doped Al powder compact showed the oxidative weight gain of ~13%, ~17%, ~28% and ~31%, respectively. It is evident that the highest weight gain occurred in the Mg doped Al powder compacts at 800–1200 °C temperature range due to oxidation while the undoped Al powder compacts showed the lowest oxidative weight gain at all the processing temperatures.

During microwave heating protective Al_2O_3 layer was formed at the surface of the undoped Al powder compact, which restricted the diffusion of oxygen towards the bulk side [4]. Therefore, Al–Al_2O_3 composite growth rate was very slow. As a result, the undoped Al powder compacts showed lowest weight gain values after microwave heating for 1 h in the temperature range of 800–1200 °C (Fig. 2). The role of Al_2O_3 as dopant in Al powder compact during microwave processing is yet to be understood. However, it seems that Al_2O_3 dopant acting as seed material accelerated the oxidation of Al powder to a certain extent and thereby, facilitated the formation of Al_2O_3 [21]. On account of this fact, Al–5Al_2O_3 powder compacts showed higher weight gain values as compared to those obtained in the undoped Al powder compacts under identical microwave heat treatments (Fig. 2). The relative XRD peak intensity of α-Al_2O_3 to Al was greater for Al_2O_3 doped Al powder compact than that of undoped Al powder compact (Fig. 1a and b). This indicated that α-Al_2O_3 was present as minor phase and major phase in the surfaces of the undoped Al powder compact and Al_2O_3 doped Al powder compact, respectively.

As mentioned above, Mg–Si doped Al powder compact and Mg doped Al powder compact showed oxidative weight gain of ~28% and ~37%, respectively after 1 h microwave heating at 1200 °C (Fig. 2). This data confirmed further the possibility of bulk composite growth in the Mg–Si and Mg doped Al powder compacts microwave treated at 1200 °C for 1 h.

During microwave heating, dopant addition of Mg in the Al powder compact possibly helped in the formation of non-protective oxides such as MgO (top) and $MgAl_2O_4$ (bottom) at the surface [3].

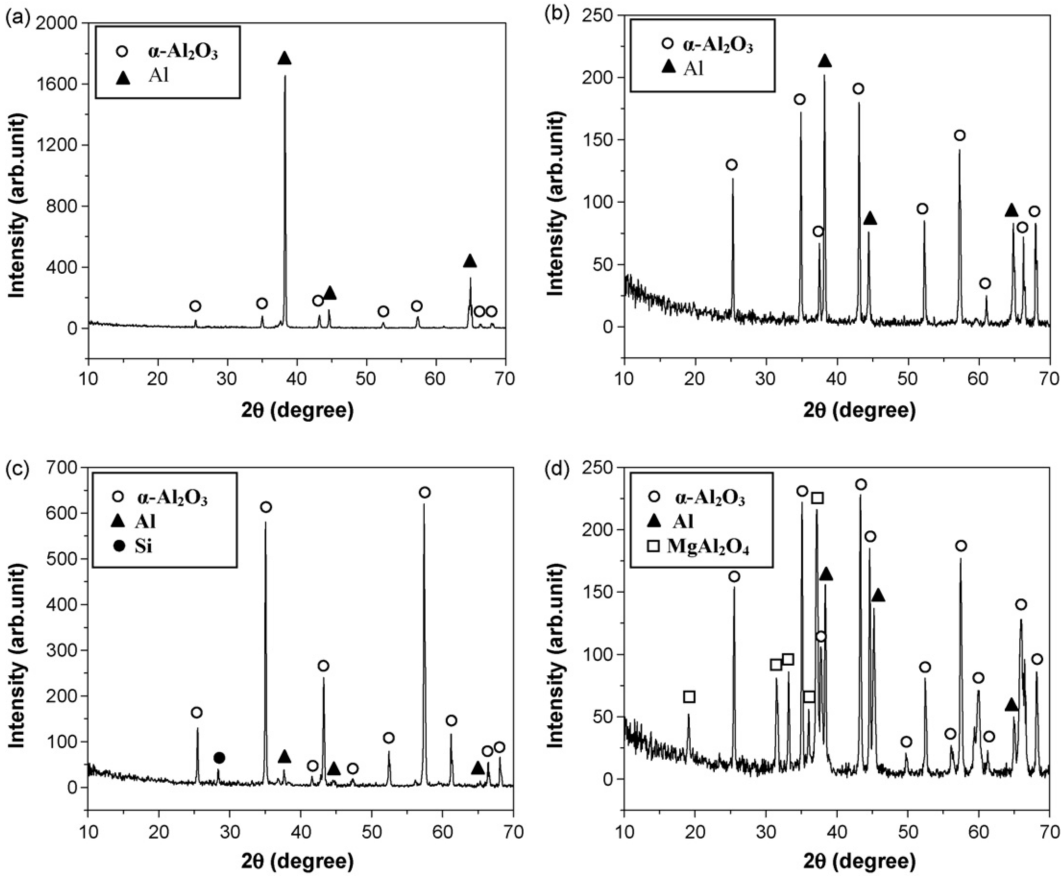

Fig. 3. XRD patterns of undoped and doped Al powder compacts microwave heated for 1 h at 1200 °C at a depth of about 200 μm: (a) undoped Al powder compact, (b) Al–5Al_2O_3 powder compact, (c) Al–3Mg–2Si powder compact and (d) Al–5Mg powder compact.

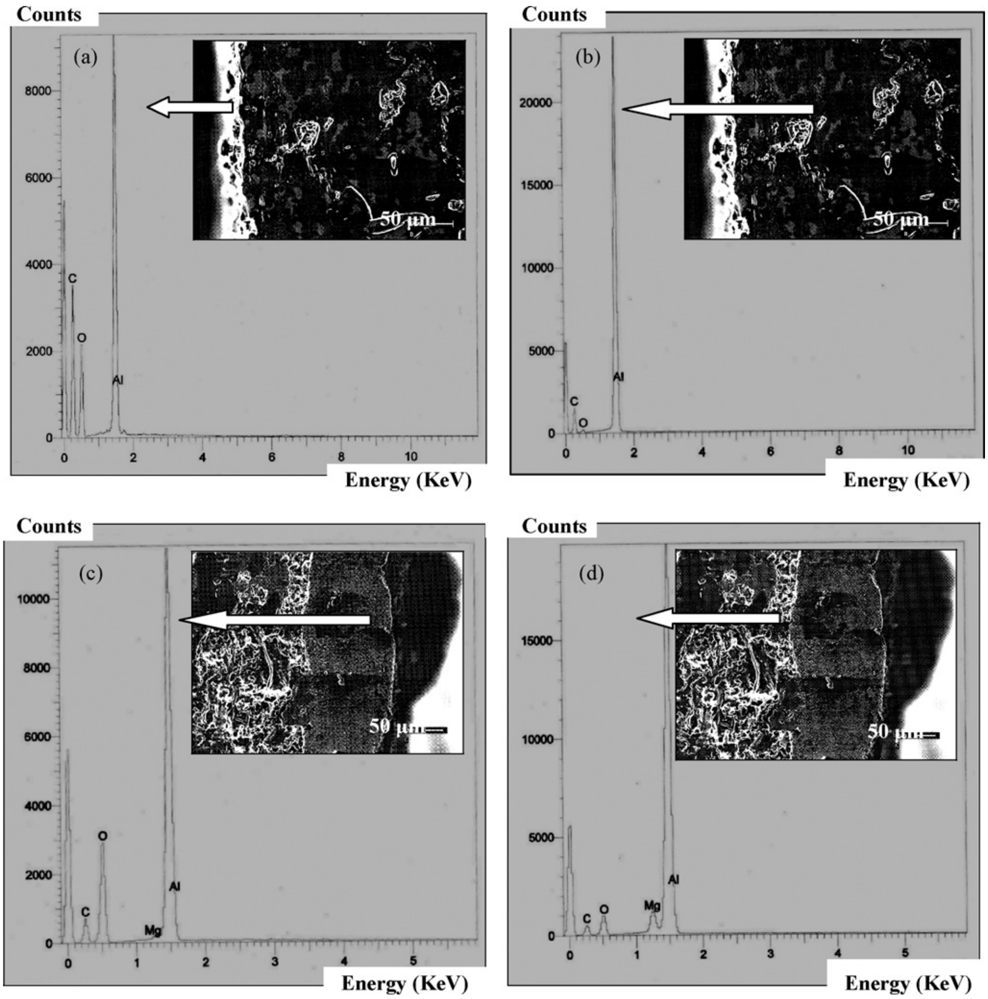

Fig. 4. EDX spectra of undoped and Mg doped Al powder compacts microwave heat treated at 1200 °C for 1 h: undoped Al powder compact from positions at (a) near surface and (b) bulk; Al–5Mg powder compact from positions at (c) near surface and (d) bulk.

This was ascribed to the faster outward diffusion of Mg relative to Al toward the high O_2 potential at the surface [3] because the free energy of formation of MgO is more negative than that of Al_2O_3 in presence of oxygen in the temperature range of 800–1200 °C [22].

The oxygen needed for the oxidation of Al was supplied by the continuous dissolution of one or both of the Mg-rich surface oxides into the Mg-lean alloy than by direct dissolution of oxygen from air [3,4]. MgO was thermodynamically less stable than $MgAl_2O_4$ in the Mg-lean alloy (<7.24% Mg). Hence, its dissolution was more favorable than that of the spinel [3]. The reaction of metastable MgO with Al could result in the formation of Al_2O_3 or spinel [3].

Following suggestions of earlier researchers [3,4], it is proposed that Mg formed due to dissolution of MgO and $MgAl_2O_4$ had first evaporated and then migrated to the surface due to its high mobility toward the higher O_2 potential at the gas-oxide interface and finally got oxidized in the presence of air to re-form the MgO layer. Mg got vaporized because of its high vapour pressure. As such, the vapour pressure of Mg increases from ~3 kPa at 1100 °C to ~25 kPa at 1400 °C [4]. Therefore, with increase in temperature enhancement in vaporization rate of Mg occurred. The more such vaporization would occur, the more continuous disruption of the pre-existing native oxide film on Al would follow. Such a process would allow direct contact with the MgO and formation of spinel or Al_2O_3, as suggested by others [4].

In the present experiments, it is proposed further that the rapid mobility of Mg facilitated the dissolution and re-oxidation processes, which provided continuous supply of oxygen to the reaction interface [3]. In this manner, Mg promoted the oxidation of Al in the Al–5Mg powder compact. With the increase in temperature, the rate of MgO and/or $MgAl_2O_4$ dissolution was accelerated, which in turn enhanced the rate of oxygen supply and Al_2O_3 formation in the Mg doped Al powder compact [4]. Such a picture explains the observation that Mg doped Al powder compact had highest oxidative weight gain among all the powder compacts studied in the present work (Fig. 2).

In the case of 3Mg–2Si doped Al powder compact, Mg promoted the formation of non-protective oxides (MgO and $MgAl_2O_4$) at the surface, which was required for the bulk composite growth. The role of Si in this mixed dopant was not clearly understood. There are two possibilities as suggested by other researchers [4]. One is that Si might shorten the incubation period. The other is that Si might accelerate the growth process by reducing the activity of Mg in the near-surface alloy and thereby promoting the dissolution of the surface oxides so as to provide further supply of oxygen to the growth interface. As the amount of Mg was low in the 3Mg–2Si doped Al powder compacts, these powder compacts showed lower oxidative weight gain values than those of the Al–5Mg powder compacts under identical microwave processing conditions (Fig. 2) [3].

Non-protective thin MgO layer needed for $A1_2O_3$ growth remained on the surfaces of Mg–Si and Mg doped Al powder compacts in spite of its continuous dissolution by the Al-rich alloy [3]. Thus, oxidation of Al was faster in the Mg and Mg–Si doped Al powder compacts than that of the undoped Al powder compacts

(Figs. 1 and 2). The presence of both Si and SiO_2 in the Mg–Si doped Al powder compact (Fig. 1c) confirmed that Si was oxidized to certain extent. The XRD result (Fig. 1c) further indicated that during microwave heating of Mg–Si doped Al powder compact MgO and $MgAl_2O_4$ supplied oxygen to the alloy and Si or SiO_2 accelerated the composite growth process [4]. In the case of Mg doped Al powder compact (Fig. 1d), presence of $MgAl_2O_4$ and MgO phases indicated that the Al–Al_2O_3 composite growth took place as a consequence of a continuous process consisting of dissolution of MgO and $MgAl_2O_4$ in the alloy and oxidation of Mg to form these non-protective surface oxides again [3].

In the Mg–Si doped Al powder compact (Fig. 1c), the difference of relative peak intensities for α-Al_2O_3 and Al phases was slightly more compared to that for the same phases in the Mg doped Al powder compact (Fig. 1d) as Si or SiO_2 in the Mg–Si doped Al powder compact accelerated the formation of α-Al_2O_3 [4]. The relative peak intensity of MgO to $MgAl_2O_4$ was greater for the Mg–Si doped Al powder compact (Fig. 1c) than that of the Mg doped Al powder compact (Fig. 1d). This was happened due to high rate of conversion of MgO to $MgAl_2O_4$ in the case of Mg doped Al powder compact [3]. Based on the XRD results (Fig. 1), it can be said that $Al_2O_{3,}$ Mg–Si and Mg dopants promoted the surface oxidation of Al.

However, a confirmatory proof of bulk composite formation demands XRD of all the powder compacts from certain depth after removal of the surface layer. Therefore, XRD of all the powder compacts was conducted from a depth of about 200 μm. Fig. 3a–d shows the XRD patterns of undoped and doped Al powder compacts microwave treated at 1200 °C for 1 h at a depth of ~200 μm. Al and α-Al_2O_3 phases were identified in the undoped and Al_2O_3 doped Al powder compacts (Fig. 3a and b). Al, α-Al_2O_3 and Si were present in the microwave heated Mg–Si doped Al powder compact (Fig. 3c) whereas Al, α-Al_2O_3 and $MgAl_2O_4$ phases were detected in the microwave treated Mg doped Al powder compact (Fig. 3d). XRD results confirmed the presence of α-Al_2O_3 in all the powder compacts at a depth of ~200 μm.

$MgAl_2O_4$ was formed in the Mg doped Al powder compact (Fig. 3d) due to presence of both oxygen and Mg at ~200 μm away from the surface. Bulk depletion of Mg at this depth led to conversion of all the MgO to $MgAl_2O_4$ [3]. On the contrary, $MgAl_2O_4$ phase was not observed in the Mg–Si doped Al powder compact (Fig. 3c) on account of trace amount of Mg at ~200 μm depth of the powder compact, which favored alumina formation rather than spinel formation [3].

The relative peak intensity of Al to α-Al_2O_3 was significantly greater for undoped Al powder compact (Fig. 3a) than that of the Al_2O_3 doped Al powder compact (Fig. 3b), indicating that α-Al_2O_3 was present as minor phase and major phase at ~200 μm depth of the undoped and Al_2O_3 doped Al powder compacts, respectively. The relative peak intensity of α-Al_2O_3 to Al was larger in the case of Mg–Si doped Al powder compact (Fig. 3c) than that of the Mg doped Al powder compact (Fig. 3d). It is therefore suggested that the presence of Si at this depth of the Mg–Si doped Al powder compact accelerated the α-Al_2O_3 growth. Hence, the amount of unreacted Al metal was lower than that in the Mg doped Al powder compact (Fig. 3c and d).

3.2. SEM and EDX analysis

The cross-sectional EDX analysis was carried out from the surface to the interior of the undoped and Mg doped Al powder compacts microwave heated for 1 h at 1200 °C, Fig. 4a–d. The arrows on the SEM micrographs indicate the positions from where the data were taken. Presence of Al and O elements in the microwave treated undoped Al powder compact is shown by their respective EDX spectra (Fig. 4a and b). In turn, Al element along with O and Mg elements were detected in the Mg doped Al powder compact after microwave heat treatment (Fig. 4c and d).

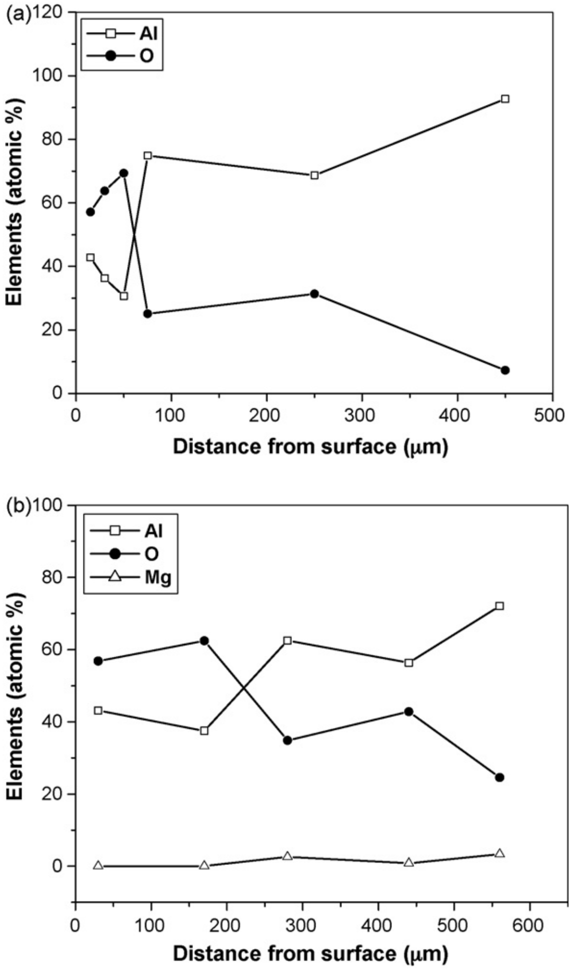

Fig. 5. EDX data based composition analysis for (a) undoped Al powder compact and (b) Al–5Mg powder compact heat treated at 1200 °C for 1 h in microwave.

EDX analysis data of the microwave oxidized undoped Al powder compact showed that oxygen diffused up to ~290 μm towards the interior with a concentration of about 25 atomic % (Fig. 5a). Fig. 5b depicts that oxygen penetration occurred up to ~550 μm with about 25 atomic % concentration in the case of microwave oxidized Mg doped Al powder compact. It can be further noticed that the concentration of Mg was very low in the near surface region while it was slightly higher at the larger depth of the powder compact (Figs. 4c and d and 5b). Formation of MgO and $MgAl_2O_4$ phases at the surface of the Mg doped Al powder compact caused the depletion of Mg in the near surface region. The EDX data of Mg doped Al powder compact (Fig. 5b) confirmed the XRD result (Fig. 3d). It is quite clear from EDX data (Fig. 5a and b) that better oxygen diffusion occurred in the Al–5Mg powder compact as compared to that in the undoped Al powder compact with identical processing conditions. This is a strong evidence of the fact that Mg promoted the oxidation of Al that led to bulk Al–Al_2O_3 composite growth [3–6].

4. Conclusions

Al–Al_2O_3 composites were formed by the microwave heating of the undoped and doped Al powder compacts. Oxidation of Al was enhanced by the addition of certain dopants such as $Al_2O_{3,}$ Mg–Si and Mg. Mg dopant promoted the bulk Al–Al_2O_3 composite growth while Si dopant accelerated the growth process. Al_2O_3 dopant was not effective for bulk Al–Al_2O_3 composite growth. Significant bulk Al–Al_2O_3 composite growth occurred in the case of Mg and Mg–Si doped Al powder compacts. The experimental results showed that the microwave heating and the use of suitable dopants can tailor the nature of the resultant Al–Al_2O_3 composite.

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