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Article *in* International Journal of Minerals Metallurgy and Materials · January 2012

DOI: 10.1007/s12613-012-0518-1

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International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 1, Jan 2012, Page 77
DOI: 10.1007/s12613-012-0518-1

Effect of magnesium and nickel coatings on the wetting behavior of alumina toughened zirconia by molten Al-Mg alloy

H. Sharifi[1)], *A.R. Khavandi*[1)], *M. Divandari*[1)], *and M.I. Hasbullah*[2)]

1) School of Materials and Metallurgical Engineering, Iran University of Science and Technology, Tehran 16844, Iran
2) Department of Material Engineering, Faculty of Mechanical Engineering, University Teknologi Malaysia, Skudai 81310, Malaysia

(Received: 7 March 2011; revised: 10 April 2011; accepted: 19 April 2011)

Abstract: The wettability of alumina toughened zirconia (ZTA) by Al-Mg alloy was investigated using the sessile drop technique. The effects of nickel coating, magnesium content, nitrogen atmosphere, and processing temperature on the contact angle between the molten alloy and the substrate were determined. Likewise, the effect of these factors on the wetting properties was studied. The results showed that the nickel coating on the ceramic substrate caused a significant reduction in solid/liquid surface energy and the contact angle decreased obviously. The presence of magnesium in the molten aluminum alloy in nitrogen atmosphere reduced the contact angle effectively. The presence of magnesium in the alloy must be at a minimum amount of 2wt%-3wt%. Moreover, it was suggested that some chemical reactions in the Al-Mg-N system led to the production of Mg_3N_2 and AlN compositions. These compositions improved the wetting properties of the systems by reducing the surface energy of the molten. It was shown that increasing the temperature is also an effective factor for the enhancement of wetting properties.

Keywords: wetting; coatings; alumina; zirconia; ceramic materials; composite materials

1. Introduction

The wetting of ceramic materials by molten metals has attracted much attention in numerous techniques, such as metal refinement, fabrication of metal/ceramic composites, soldering, and welding. One of the most important problems in the fabrication of metal matrix composites (MMC) by the pressureless infiltration technique is the non-wettability of ceramic portions by molten metals [1-5]. According to previous investigations, the formation of an inevitable oxide layer on the surface of molten metals leads to an indirect interface between the metal and the ceramic. Hence, metals do not tend to wet ceramics [5]. In the absence of this metal oxide layer, metal reacts with the ceramic and then will wet the surface easily in most systems [6-7].

The wetting term can be studied by the contact between the molten metal and the ceramic portion [3, 8]. Methods such as sessile drop, transferred drop, dispensed drop, dip coverage, immersion-emersion, pressure infiltration, and micro-droplet are used for this purpose [9]. The sessile drop is one of the most applied laboratory methods for the investigation of the wetting of metal/ceramic. In this method, the contact angle between a molten metal droplet and the ceramic substrate (θ) could be calculated in the condition of constant temperature and pressure [3, 10]. The ceramic/metal wetting behavior can be categorized into two groups: reactive and non-reactive [9]. According to Young's theory, in the non-reactive group, the contact angle (θ) in equilibrium only depends on the solid-liquid (γ_{sl}), solid-vapor (γ_{sv}), and liquid-vapor (γ_{lv}) interfaces and can be represented by the following equation:

$$\cos\theta = \frac{\gamma_{sl} - \gamma_{sv}}{\gamma_{lv}} \tag{1}$$

According to Eq. (1), the wetting of the ceramic substrate by molten metal will happen at $\theta<90°$. Otherwise, wetting will not occur [3, 8-11].

The mechanism of wetting, in the reactive group, could

Corresponding author: A.R. Khavandi E-mail: khavandi@iust.ac.ir be studied by the thermodynamics of reactions, which occur in the interface of molten metal and the ceramic substrate. Basically, these reactions lead to the formation of new products on the surface of the ceramic phase where it is in contact with the molten metal and reduces the wetting angle. Therefore, the calculated θ in this case indicates the contact angle between the molten metal and reaction products [10, 12-14].

Several investigations have been conducted to ameliorate the wetting of ceramic substrates by molten metal. In most of these case studies, the reduction of contact angle is accompanied by reactions between solid and molten phases. Some of the most useful methods are listed as the following.

(1) Increasing temperature. For example, under 1200 K, the Al-Al_2O_3 system is almost inactive; over this temperature, the wetting angle less than 90° is obtained [7].

(2) Using active elements, such as Ti, Cr, and V, which lead to the formation of a complex layer on the surface of the ceramic and alleviate the wetting property, such as Ti in Al-SiC [11], steel-ZrO_2 [15], and Al-B_4C [16] systems and Cr in the Cu-ZrO_2 [1] system.

(3) Coating the ceramic portion, such as coating SiC with Cu, Ni, Mo, and W [11] and coating Al_2O_3 with Y_2O_3 [2].

(4) Reaction between alloying elements in the metal portion and the ceramic substrate with the atmosphere, for instance, reaction between magnesium and the ceramic part in the Al-Al_2O_3 system [12].

(5) Chemical reaction between elements in the matrix and the atmosphere. Aghajanian *et al.*, in this regard, for the first time reported the reaction between the magnesium present in the aluminum matrix and the nitrogen atmosphere [17].

In this paper, some of the basic parameters dominated on the wetting of the aluminum/alumina system toughened by zirconia have been investigated. In the first step, the best method for coating the ceramic part was selected. Then, the effect of nickel coating on the wettability of the ceramic part by molten aluminum with different portions of magnesium was investigated at different temperatures and time. For this purpose, the sessile drop method was used.

2. Experimental

2.1. Materials

Al-Mg alloys were produced with approximately 2wt%, 4wt%, 6wt%, 8wt%, and 10wt% Mg by pure commercial aluminum and magnesium. First, aluminum was melted with an induction furnace in a graphite crucible under air atmosphere. Then, magnesium along with sulfur powder was added to the melt. After the melting of magnesium and the stirring of the melt the furnace was switched off and the slag was removed. At last the molten was poured into a steel mould. The chemical analysis of Al-Mg alloy is shown in Table 1. Alloys with 2wt%, 4wt%, and 6wt% magnesium contained a microstructure of course columnar grains. Alloys with 8wt% and 10wt% magnesium contained a microstructure of dendritic columnar grains. Also, an intermetallic phase of Al_3Mg_2 was seen in these alloys.

Table 1. Chemical composition of Al alloys **wt%**

Sample	Al	Mg	Si	Cu	Zn	Fe	Mn	Sn
1	97.4	2.16	0.125	0.023	0.045	0.157	≤0.018	≤0.01
2	95.2	4.18	0.153	0.038	0.076	0.180	≤0.033	≤0.02
3	93.0	6.27	0.195	0.051	0.105	0.186	≤0.042	≤0.01
4	91.1	8.07	0.200	0.053	0.122	0.191	≤0.067	≤0.04
5	88.6	10.5	0.245	0.075	0.153	0.196	≤0.069	≤0.01

The ceramic substrate was produced from alumina powder (MR70, Martoxid Albemarle Co., Germany), yttria partially stabilized zirconia (Y-PSZ) (ZR-5Y, Nikkato Co. Ltd., Japan), bentonite (Supplied by Touse Co., Iran), and a commercial silica sol, as characterized in Ref. [18]. A compound of 24wt% silica sol (8wt% SiO_2), 52wt% Al_2O_3, 23wt% ZrO_2, and 1wt% bentonite was selected. To obtain a well-dispersed slurry, the selected compound was milled for 3 h. Then, the optimum was moisture controlled by heating the slurry in an oven of 100°C for 45 min. The powder mixture was pressed into discs of 20 mm in diameter and 1.2 mm in thickness to produce the substrate. The samples were then sintered at 1400°C for 1 h. Finally, the surface of substrates was polished to the roughness of 5 to 6 μm.

2.2. Ceramic substrate coating

The coating process consists of four steps: cleaning, sensitization, activation, and metallization. Table 2 summarizes the solutions used for coating the alumina toughened zirconia (ZTA) ceramic substrates.

Table 2. Applied solutions for electroless nickel coating

Stage	Solution
Cleaning	Acetone
Sensitization	10 g $SnCl_2 \cdot 2H_2O$ 35 mL HCl
Activation	0.25 g $PdCl_2$ 3 mL HCl
Metallization	28 g $NiSO_4 \cdot 6H_2O$ 17 g $CH_3COONa \cdot 3H_2O$ 24 g $NaPH_2O_2 \cdot 2H_2O$ 0.0015 g CH_4N_2S NH_3 to control pH values

After cleaning with acetone, the samples were stirred continuously for 15 min. Then, the samples were activated in an ultrasonic bath. Finally, they were metalized in a water medium with a pH value of 8 at 80°C for 20 min. As the final step, the samples were washed with distilled water and dried.

2.3. Sessile drop test

The wettability of the nickel-coated ZTA ceramic substrate with Al-Mg alloy was determined by the sessile drop method. For this purpose, cubic pellets of 5±1 g were cut from aluminum alloy bars and their surfaces were polished by emery paper of grade 800. Exactly before testing, the samples were washed in a solution of 5vol% NaOH for 5 min at 30°C and consequently washed in a solution of 2vol% HF for 3 min. Both the substrate and alloy samples were cleaned ultrasonically in acetone.

A cubic sample of the aluminum alloy was put on the ZTA substrate and heated at a rate of 10°C/min under nitrogen atmosphere in a tube aluminum furnace. Pictures of the droplet were taken with a camera automatically and the contact angle was calculated from the pictures. The test was performed in the temperature range of 750 to 1050°C and the time to reach a stable state in the wetting of the Al-Mg/ZTA system was investigated at different temperatures.

2.4. Measurements

The phase evaluations of samples were studied by X-ray diffraction (XRD, D5000, Siemens, Germany). Field-emission scanning electron microscopy (FESM, Ziss, Supra, 35VP) provided with energy-dispersive X-ray analysis (EDAX) and optical microscopy were applied to study and analyze the microstructures of the coating.

3. Results and discussion

XRD patterns of the ceramic substrate are illustrated in Fig. 1(a). It can be seen that the structure of the ceramic substrate after sintering consists of crystalline alumina, mullite, and zirconia phases with cubic and tetragonal structures. According to the investigations, amorphous silica in ceramic composition transfers to cristobalite phase above 950°C. Increasing the sintering temperature to 1200-1400°C provides the thermodynamic and kinetic conditions for the phase transformation to mullite. Thus, according to the reaction, cristobalite and alumina phases transfer to mullite as follows:

$$SiO_2+\alpha\text{-}Al_2O_3 \rightarrow SiO_2 \cdot xAl_2O_3+(1-x)\alpha\text{-}Al_2O_3,\ \Delta G_{1670^\circ C}<0 \quad (2)$$

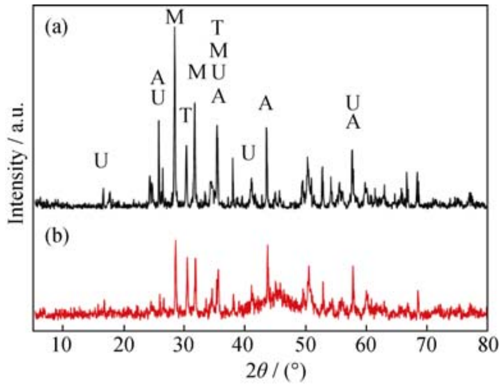

Fig. 1. XRD patterns of ZTA: (a) before coating; (b) after coating (A—alumina, T—tetragonal zirconia, M—monoclinic zirconia, U—mullite).

According to the Al_2O_3-ZrO_2 phase diagram, there is no solubility between alumina and zirconia under 1710±10°C, and sintering and surface melting are the only ways for the toughening between these two phases.

Moreover, Fig. 1 shows the XRD patterns of the ceramic substrate before and after coating. It can be seen that the geometrical locus of peaks in Fig. 1(b) is similar to that in Fig. 1(a) and new peaks are not observed. The only difference between these two patterns is the appearance of a background region. This shows that the coating of nickel and phosphorus atoms was created on the surface of the ceramic substrate as an amorphous phase.

Fig. 2(a) demonstrates the electron micrograph of the coating after 20-min metallization. Considering the coating rate of 8 to 10 μm/h and the coating time, the thickness of coating on the ceramic substrate is 4 to 5 μm. Furthermore, the figure indicates that a continuous and condensed coating has formed on the surface. Fig. 2(b) shows the elemental analysis of the coating by EDS. Elements such as nickel (95.8wt%) and phosphorus (4.2wt%) were detected from the Ni coating.

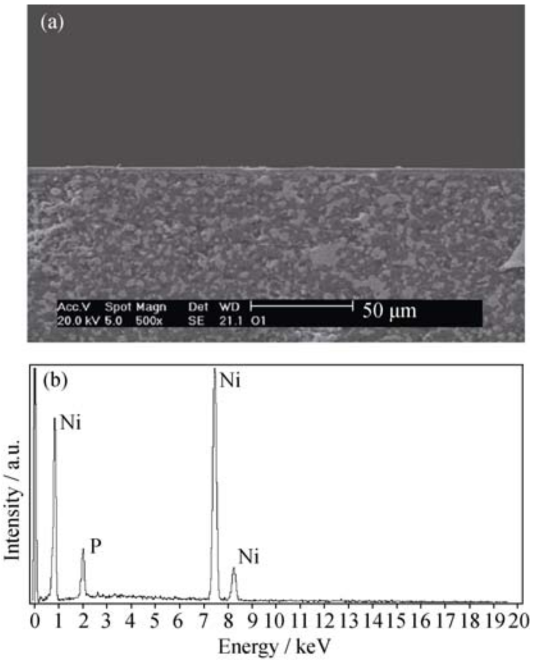

Fig. 2. SEM image (a) and EDS spectrum (b) of nickel coating on the ZTA ceramic substrate.

The changes in contact angle with temperature were calculated for Al-Mg/ZTA and Al-Mg/coated ZTA systems after the stabilization of the system as shown in Figs. 3(a) and 3(b), respectively. Fig. 3 shows that increasing the temperature leads to a decrease in contact angle. The system is non-wettability in all compositions, with and without coating, in the temperature range of 750 to 800°C. At 800-900°C, the contact angle decreases dramatically. Transferring from non-wettability to wettability, indeed, happens in this temperature range. In all systems, at temperatures above 900°C, especially the ones without coating, changes in contact angle are not significant. In Fig. 3, the effect of magnesium on the wetting of the substrate, with and without coating, is obvious. An increase in the magnesium content of the melt leads to a decrease in contact angle at all tested temperatures. As an example, the contact angles for non-coating alloys with 2wt% and 10wt% magnesium are 85° and 59°, while for the same alloys with coatings they are 80° and 47°, respectively. This fact shows the importance of the presence of magnesium in the melt. According to Eq. (1), the presence of magnesium element in nitrogen atmosphere reduces the surface energy of the molten alloy; consequently, the contact angle decreases and the wettability of the system is improved.

As seen in Fig. 3, the alloy with 2wt% magnesium does not have a suitable wettability in the desired temperature range in comparison with the other tested alloys. Moreover, by increasing the temperature, the difference between the contact angles of this alloy and those of other alloys increases significantly. Nevertheless, a minimum amount of magnesium is necessary in the aluminum molten to improve the wettability. The threshold amount of magnesium in the other studies is reported to be 2wt% to 3wt% in the presence of ambient nitrogen [19].

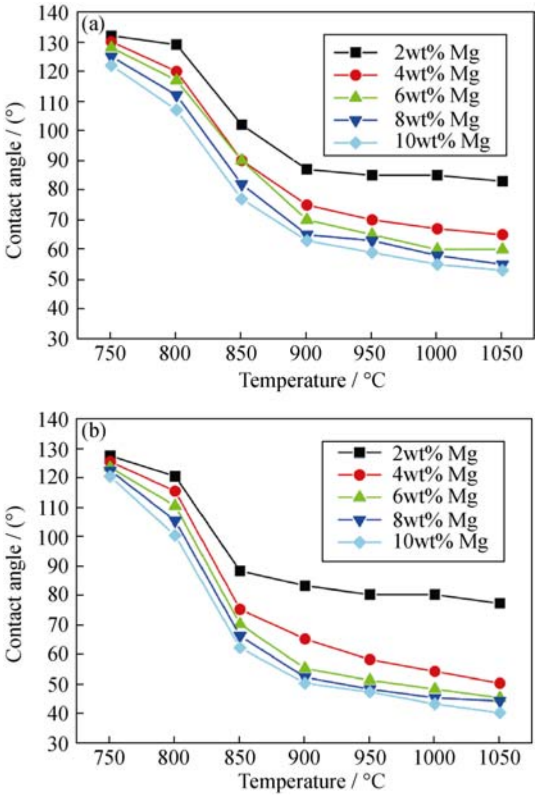

Fig. 3. Changes of contact angle with temperature in the presence of different amounts of magnesium on the substrate: (a) without nickel coatings; (b) with nickel coatings.

Comparing Figs. 3(a) and 3(b) shows that, in the temperature range of 750 to 1050°C, contact angles in coated ZTA are less than those of uncoated ZTA. This fact shows that the wettability of the substrate coated by Ni-P with Al-xMg is improved significantly in comparison with the uncoated substrate. According to Eq. (1), increasing the solid surface energy, decreasing the solid/liquid surface energy, or decreasing the molten surface energy could improve the contact angle. The presence of Ni-P on the substrate surface in the ZAT system brings about a decrease in solid/liquid surface energy and consequently improves the wettability.

The investigations showed that the wetting angle between the melt and the substrate depends on the time at all tested temperatures. For instance, the changes in contact angle with time at 850°C are shown in Figs. 4(a) and 4(b) for systems of 2wt% and 6wt% magnesium with and without coating. The contact angles decreased with time at 850°C and after 30 min reached a constant amount. The calculated amounts for 2wt% magnesium, with and without coating, were 102° and 88°, while they were 90° and 73° for 6wt% magnesium, respectively.

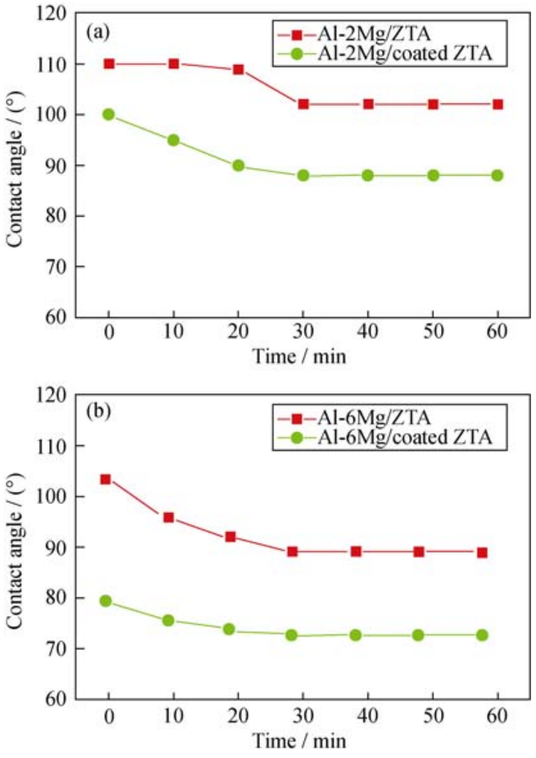

Fig. 4. Relationship between time and temperature at 850°C for Al-2Mg (a) and Al-6Mg (b) alloys.

The furnace atmosphere has a deep effect on the contact angle. First, the sessile drop was tested on pure molten aluminum in nitrogen and argon atmosphere separately. The obtained contact angle was approximately equal in the condition of the same time and temperature. It is known that the surface oxide on molten pure Al or Al alloys at higher temperatures can be broken by gaseous Al_2O formed by a reaction between Al and the surface oxide (Al_2O_3), which causes bare contact between the molten alloys and the substrate [20]. Then the sessile drop was tested on molten aluminum-magnesium in nitrogen and argon atmosphere separately. The investigations depicted that, in the same experiment conditions, the calculated contact angle in pure argon was much larger than that in nitrogen atmosphere.

According to our studies, the reaction of molten magnesium and nitrogen led to the increase in wettability of the molten. The presence of magnesium in the aluminum melt reduces the surface energy of the melt. However, nitrogen atmosphere reduces the contact angle more than magnesium does and improves the wettability. Magnesium has a low steam pressure, and it evaporates at the experiment temperature according to the following equation:

$$Al(Mg)=Al+Mg(g) \tag{3}$$

During sessile drop tests under the optimum conditions, a yellow green powder was observed on the wall of the furnace and the surface of samples. This powder was collected during several experiments for XRD analysis because the amount of the powder was low. The XRD pattern of the obtained powder was confirmed to be Mg_3N_2, as illustrated in Fig. 5. The magnesium steam, which is produced from Eq. (3), reacts with nitrogen and produces Mg_3N_2 (Eq. (4)). This powder covers the surface of molten and the substrate and leads to the enhancement of wettability by changing the surface energies.

$$3Mg(g)+N_2(g)=Mg_3N_2(S) \tag{4}$$

Furthermore, by adding this powder to water, ammonia could be smelt which could be a product of Eq. (5):

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3 \tag{5}$$

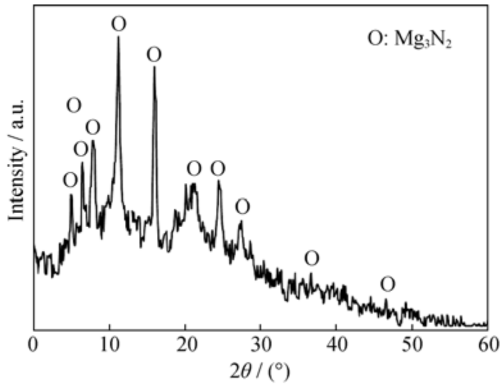

Fig. 5. XRD pattern of the yellow green Mg_3N_2 powder.

Our observations also showed that the samples tested over 1000°C had a different surface in comparison with other samples. After each sessile drop experiment was completed and the droplet had cooled down to room temperature, the skin of the droplet was removed with a clean sharp piece of CVD SiC and collected as powder. The XRD pattern of this powder is shown in Fig. 6. It shows that the presence of AlN at 1000°C on the surface of these samples is thermodynamically inevitable.

The investigations show that AlN is more stable than Mg_3N_2 at temperatures over 1000°C. Taking Eq. (6) into consideration, it can be said that Al diffuses into Mg_3N_2 powder and AlN is the product of an *in situ* reaction.

$$2Al(l)+Mg_3N_2=2AlN(s)+3Mg(g) \tag{6}$$

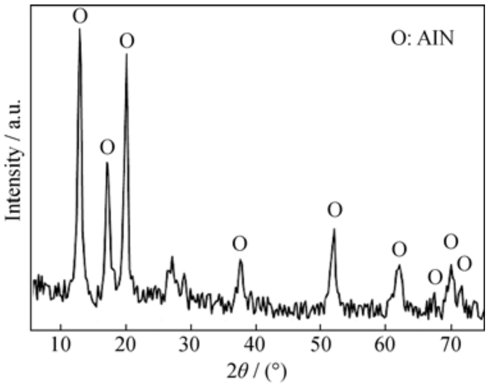

Fig. 6. XRD pattern of AlN.

In this condition, it should be assumed that part of magnesium in the system exits from the melt and re-enters it again.

4. Conclusion

By means of nickel electroless processing, a homogeneous metal coating of Ni-P was applied on the surface of ZTA. The effects of the substrate coating, magnesium addition into the melt, and the nitrogen gas atmosphere of the furnace on the wettability of ZTA by molten aluminum were investigated by sessile drop technique. In comparison with uncoated ZTA, the wettability of aluminum-coated ZTA is improved significantly in the temperature range of 750 to 1050°C. A minimum amount of about 2wt%-3wt% magnesium in the aluminum alloy is required to enhance the wettability of the substrate. Magnesium in the aluminum alloy alongside the nitrogen ambient leads to the formation of Mg_3N_2 and AlN phases. Consequently, the molten surface energy and the solid/liquid surface energy are decreased, while the wettability is improved significantly.

Acknowledgements

The authors are thankful to the Ceramic Division of Materials and Energy Research Center (MERC) for providing the necessary facilities and Mr. Dalali for his useful comments.

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