

Alumina/Aluminum Composites Prepared by Directed Oxidation of Aluminum Alloy

— Short Review —

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Introduction

The brittleness of monolithic ceramics limits the widespread uses in mechanical applications. Metal phase incorporated into a ceramic matrix makes it possible to increase the toughness of ceramics. There are many popular methods to make ceramics/metal composites, such as squeeze casting, pressure casting and powder metallurgy [1]. Recently, a new fabrication method called the "directed metal oxidation process (DIMOX^{TM*})" has been developed. This remarkable process has the following benefits; (1) ease of making composites, (2) low cost and (3) near-net shape capability [2]. Among many kinds of ceramics/metal composites fabricated by the DIMOXTM process [3,4,5], this paper describes Al₂O₃/Al composites and filler-reinforced Al₂O₃/Al composites.

DIMOXTM process

The illustrative figure corresponding to a typical DIMOXTM process is shown in Fig.1(a) [6]. The molten aluminum alloy is oxidized by a vapor-phase oxidant to form Al₂O₃/Al composite. Usually, the oxidant is air and the alloying metals are Mg, Si,

*)DIMOX is a registered trademark of Lanxide Co., Newark, DE.

Sn, etc. The apparatus is very simple and the process temperature is moderate (1400K or less). These factors result in the benefits mentioned above.

DIMOXTM process is much different from the usual oxidation of metals. This is to say, in DIMOXTM process, the molten Al alloy goes up to the surface of the resulting composite through many channels in it and then reacts with the oxidant. Consequently, the composite grows outward from the original metal surface and keeps growing as long as the supply of the molten metal continues [6]. Therefore, Al₂O₃/Al composites containing fillers can be obtained by oxidizing Al alloy with filler materials (e.g. Al₂O₃, SiC, BaTiO₃) on it as shown in Fig.1(b) [2]. Al₂O₃/Al grows through the interstices in the filler bed resulting in the fillers embedded Al₂O₃/Al matrix.

Next, the important process parameters are discussed.

Alloying metals The growth of Al₂O₃/Al composite was seriously affected by alloying metals as listed in Table 1. In the case of pure Al and some Al alloys, continuous oxidation does not occur owing to the protective oxide film formed on their surfaces. How-

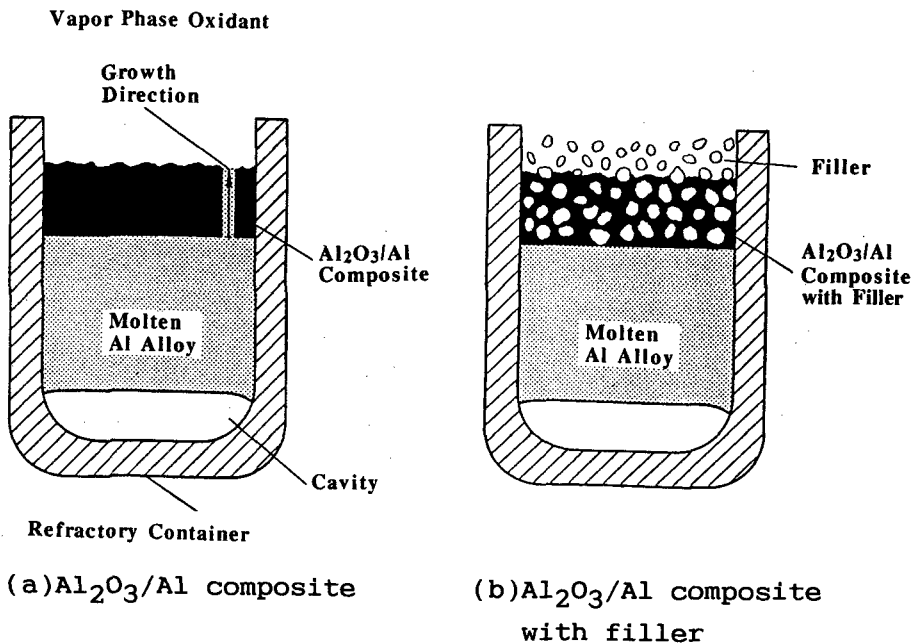


Fig.1. Scheme of DIMOXTM process.

Table 1. Effect of alloying metals on Al₂O₃/Al composite growth.

Composition (wt%)				Growing	Note	References
Mg	Si	Zn	Sn			
0	0	0	0	No	pure aluminum	
0	3	0	0	No		
2	0	0	0	No		
1~10	1~10	0	0	Yes	Group IVB elements also accelerated Al ₂ O ₃ /Al growth instead of silicon	[6]
0.001	4.5	12.5	0	No		
0.001	4.5	12.5	0	Yes	Alloy was in contact with MgAl ₂ O ₄	[7]
0	0	0	3	No		
0	0	0	3	Yes	Alloy was coated with MgO powder before oxidation	[8]

ever, Al₂O₃/Al composites grew by continuous oxidation of Al-Mg- (IVB group elements) alloys [6], Al-Si-Zn alloy (in contact with MgAl₂O₄) [7] and Al-Sn (in contact with MgO powder) [8]. These results indicate that Mg plays an important role in this process. It is known that the oxidation of Al was promoted by the addition of Mg [9,10]. Then, MgAl₂O₄ was formed on the metal surface and this reaction caused continuous oxidation [10]. However, it is not clear whether this concept can apply the DIMOXTM process or not. The growth mechanism is discussed later. Though the systematic research about the effect of the concentration of alloying metals on the growth rate was not undertaken, a few percent of alloying metals is enough to proceed the composite formation [6].

Temperature & Oxygen partial pressure The growth rate (R_g) changed with alloy components, process temperature (T), and oxygen partial pressure (P_{O_x}) [11,12]. The effect of T and P_{O_x} on R_g is generally given by

$$R_g \propto P_{O_x}^n \cdot \exp(-\Delta E/RT)$$

where n is a constant, ΔE the activation energy, R the gas constant, and T the absolute temperature. Figure 2 shows the

relations between $\log R_g$ and $1/T$ on Al-Si(10wt%)-Mg(3wt%) (Alloy A) and Al-Si(9wt%)-Zn(3wt%)-Cu(3wt%)-Fe(1wt%)-Mg(0.2wt%) (Alloy B) [11]. The activation energy obtained from the slope of the line of Alloy A was 370 kJ/mol and that of Alloy B was 89 kJ/mol. The n value from Alloy A was $1/4$, though the growth rate in Alloy B was independent of P_{O_x} [11].

There are few data about the relation between process parameters and mechanical properties. We can only see the effect of process temperature on the strength and toughness of Al_2O_3/Al composite with 500-mesh SiC particles [2]. The strength increased with increasing process temperature; 350MPa(1173K), 390MPa(1273K) and 525MPa(1423K). However, the fracture toughness decreased with increasing process temperature; $7.8MPa \cdot m^{1/2}$ (1173K), $5.4MPa \cdot m^{1/2}$ (1273K) and $4.7MPa \cdot m^{1/2}$ (1423K).

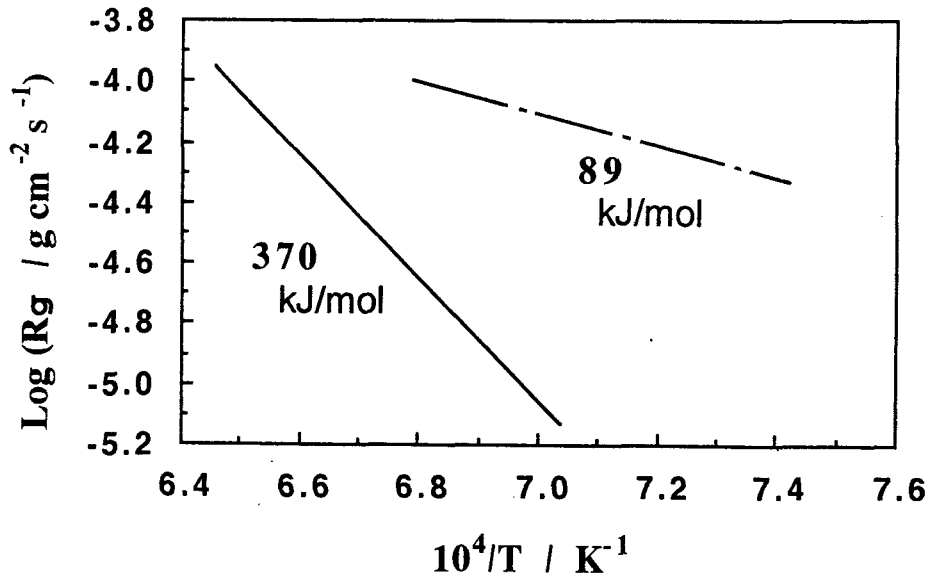


Fig.2. Relations between $\log R_g$ and $1/T$.

— Alloy A, --- Alloy B

According to Nagelberg [11,12], on oxidizing Alloy A, the surface of the growing composite consisted of two layers; the lower layer was molten Al alloy and the upper layer was Al_2O_3 -doped MgO. Oxygen diffuses through MgO layer from its surface to

the MgO-(Al alloy) interface and dissolves in the alloy. Then, the dissolved oxygen diffuses to the real composite surface to form additional Al_2O_3 by reacting with Al. He concluded that the electronic transport within the external Al_2O_3 -doped MgO layer controlled the growth process. In the case of Alloy B, the external ZnO layer controlled the growth process just as Alloy A [12].

Effect of fillers On making $\text{Al}_2\text{O}_3/\text{Al}$ composites with a filler phase, the fillers affected the growth rate of the composite in a complicated manner. For example, on fabricating Al_2O_3 particles embedded $\text{Al}_2\text{O}_3/\text{Al}$ composite using Al-Si-Mg alloy, the growth rate had a maximum value at the initial oxidation stage in pure O_2 atmosphere but, in low oxygen partial pressure, increased with oxidation time. The growth mechanism in this system is the same as that of non-filler system. The details are given in ref. [11].

DIMOX™ composite

On oxidizing Al-Si-Mg alloy, MgO and/or MgAl_2O_4 are first formed even though the content of Mg is very low. This is because Mg is more easily oxidized than Al. Therefore, the as-grown composite consists of two layers. The bottom layer (initially formed) contains MgAl_2O_4 , Al_2O_3 , and Al phases and the bulk layer (formed on the bottom layer) contains Al_2O_3 and Al phases. Preval et al. [13] examined the components of the bottom and bulk layers of the composite fabricated at 1400K with Al alloy 5052 (Al-Mg(2.5wt%)) that was externally coated with SiO_2 particles. The results are shown in Table 2. The main crystal in the bottom layer was MgAl_2O_4 , whereas that in the bulk layer was Al_2O_3 , and both regions contained an Al phase.

Table 2. Composition of $\text{Al}_2\text{O}_3/\text{Al}$ composite.

	Chemical analysis (wt%)		
	Al	Al_2O_3	MgAl_2O_4
Bulk	19 ± 1	75 ± 2	1 ± 1
Bottom	13 ± 1	19 ± 1	68 ± 1

The $\text{Al}_2\text{O}_3/\text{Al}$ composite consisted of a three-dimensionally interconnected Al_2O_3 and both interconnected and isolated Al alloy [13]. Figure 3 shows one example of the optical photograph of DIMOXTM $\text{Al}_2\text{O}_3/\text{Al}$ composite. The dark area corresponds to Al_2O_3 and the light area to metal phase. Tiny metal disperses homogeneously in Al_2O_3 . The volume fraction of Al alloy changes from 5 to 30vol% by controlling the process parameters [2].

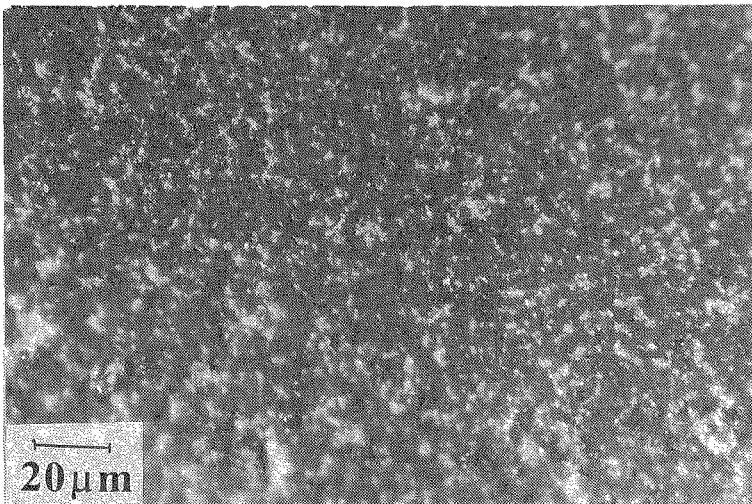


Fig.3. Microstructure of $\text{Al}_2\text{O}_3/\text{Al}$ composite.

Aghajanian et al. [14] examined the physical and mechanical properties of $\text{Al}_2\text{O}_3/\text{Al}$ composites in detail. Figure 4 shows one example of the relation between the bend strength and fracture toughness of $\text{Al}_2\text{O}_3/\text{Al}$ composite and temperature. The composite was grown by oxidizing Al alloy in air at 1400K. The volume fraction of Al and pore are 22 and 4vol%, respectively. The bend strength and the fracture toughness at room temperature are 340MPa and $9.5\text{MPa}\cdot\text{m}^{1/2}$, respectively. Although the bend strength decreased significantly with increasing temperature, the fracture toughness slightly decreased till 600K. The toughening mechanism is discussed in refs. [15,16].

In the case of $\text{Al}_2\text{O}_3/\text{Al}$ composite containing fillers, the composite showed three-dimensionally interconnected microstructure like non-filler composite although the fillers disrupted

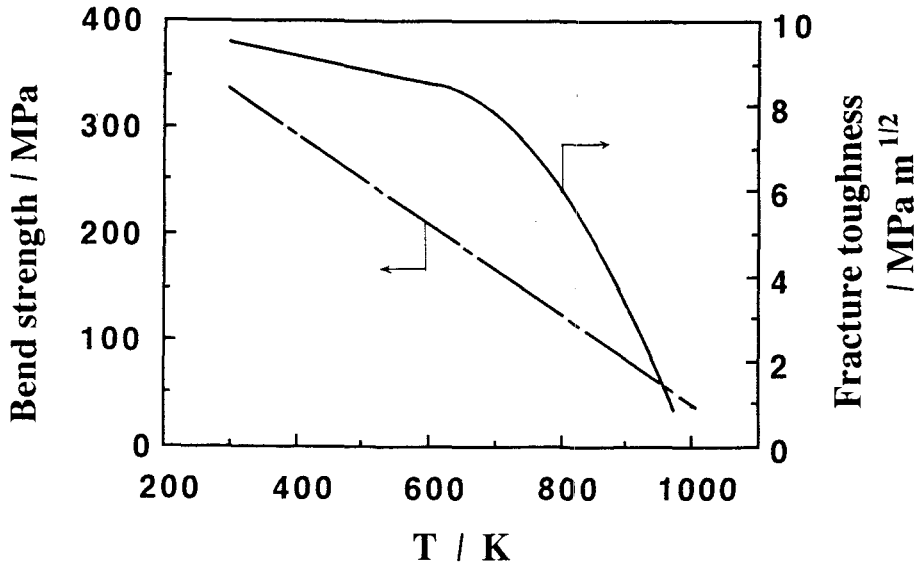


Fig.4. Bend strength and fracture toughness vs. temperature.

Al_2O_3 large columns which were seen in non-filler composite [6,14] and increased the tortuosity of the metal channels[11,17]. The mechanical properties of fiber-reinforced $\text{Al}_2\text{O}_3/\text{Al}$ composites are superior to $\text{Al}_2\text{O}_3/\text{Al}$ composite without fillers [18,19]. Barron-Antolin et al. [18] reported the mechanical properties of SiC-fiber reinforced alumina^{*}) composite prepared by DIMOXTM process. The composite showed bend strength up to 997MPa and fracture toughness up to 29MPa·m^{1/2}. Furthermore, the composite had ~1.5mm deflection when the load was ~1200N. These materials are expected as wear parts, heat exchangers, piston and gas turbine engine components.

Acknowledgment

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^{*})The composition of this composite was not commented and the matrix phase was called "alumina".

References

1. M. Taya and R.J. Arsenault, *Metal Matrix Composites*, Pergamon Press, Oxford (1989).
2. M.S. Newkirk, H.D. Lesher, D.R. White, C.R. Kennedy, A.W. Urquhart, and T.D. Claar, "Preparation of LanxideTM Ceramic Matrix Composites: Matrix Formation by the Directed Oxidation of Molten Metals," *Ceram. Eng. Sci. Proc.*, **8**[7-8], 879-85(1987).
3. S.B. Lasday, "Tailoring Properties of Platelet Reinforced Ceramics by Liquid Metal Oxidation Process," *Industrial Heating*, August, 14-16(1989).
4. J.J. Mecholsky, Jr., "Engineering Research Needs of Advanced Ceramics and Ceramic-Matrix Composites," *Ceram. Bull.*, **68**[2], 367-75(1989).
5. Y. Chiang, J.S. Haggerty, R.P. Messner, and C. Demetry, "Reaction-Based Processing Methods for Ceramic-Matrix Composites," *Ceram. Bull.*, **68**[2], 420-28(1989).
6. M.S. Newkirk, A.W. Urquhart, H.R. Zwicker, and E. Breval, "Formation of LanxideTM Ceramic Composite Materials," *J. Mater. Res.*, **1**[1], 81-89(1986).
7. M. Sindel, N.A. Travitzky, and N. Claussen, "Influence of Magnesium-Aluminum Spinel on the Directed Oxidation of Molten Aluminum Alloys," *J. Am. Ceram. Soc.*, **73**[9], 2615-18(1990).
8. T. Watari, K. Ohta, T. Torikai and O. Matsuda, to be published.
9. I. Haginoya, "On Oxidation of Molten Al-Mg Alloys in Air," *Keikinzoku*, **24**[8], 364-71(1974).
10. C.N. Cochran, D.L. Belitskus, and D.L. Kinosz, "Oxidation of Aluminum-Magnesium Melts in Air, Oxygen, Flue Gas, and Carbon Dioxide," *Metall. Trans.*, **8B**, 323-32(1977).
11. A.S. Nagelberg, "The Effect of Processing Parameters on the Growth Rate and Microstructure of Al₂O₃/Metal Matrix Composites," *Mater. Res. Soc. Symp. Proc.*, **155**, 275-82(1989).
12. A.S. Nagelberg, "Growth Kinetics of Al₂O₃/Metal Composites from a Complex Aluminum Alloy," *Solid State Ionics*, **32/33**, 783-88(1989).

13. E. Breval, M.K. Aghajanian, and S.J. Luszcz, "Microstructure and Composition of Alumina/Aluminum Composites Made by Directed Oxidation of Aluminum, " *J. Am. Ceram. Soc.*, **73**[9], 2610-14(1990).
14. M.K. Aghajanian, N.H. Macmillan, C.R. Kennedy, S.J. Luszcz, and R. Roy, "Properties and Microstructures of Lanxide[®] Al₂O₃-Al Ceramic Composite Materials, " *J. Mater. Sci.*, **24**, 658-70(1989).
15. C.A. Andersson and M.K. Aghajanian, "The Fracture Toughening Mechanism of Ceramic Composites Containing Adherent Ductile Metal Phases," *Ceram. Eng. Sci. Proc.*, **9**[7-8], 621-26(1988).
16. L.S. Sigl, P.A. Mataga, B.J. Dalgleish, R.M. McMeeking and A.G. Evans, "On the Toughness of Brittle Materials Reinforced with a Ductile Phase," *Acta Metall.*, **36**[4], 945-53(1988).
17. E. Breval and A.S. Nagelberg, "Microstructure of an Al₂O₃/Metal Composite Containing an Al₂O₃ Filler Material," *Mater. Res. Soc. Symp. Proc.*, **132**, 93-98(1989).
18. P. Barron-Antolin, G.H. Schiroky, and C.A. Andersson, "Properties of Fiber-Reinforced Alumina Matrix Composites," *Ceram. Eng. Sci. Proc.*, **9**[7-8], 759-66(1988).
19. A.S. Fareed, B. Sonuparlak, C.T. Lee, A.J. Fortini, and G.H. Schiroky, "Mechanical Properties of 2-D Nicalon[™] Fiber-Reinforced LANXIDE[™] Aluminum Oxide and Aluminum Nitride Matrix Composites," *Ceram. Eng. Sci. Proc.*, **11**[7-8], 782-94(1990).