Journal of Minerals and Materials Characterization and Engineering, **2012, 11, 1063-1068**
Published Online November 2012 (http://www.SciRP.org/journal/jmmce)

Identification of Growth Promoter to Fabrication SiC_p/Al_2O_3 Ceramic Matrix Composites Prepared by Directed Metal Oxidation of an Al Alloy

Malkapuram Devaiah[1,2], Thodeti Srihari[3], Thankappan Pillai Rajasekharan[1]
[1]Ceramics & Composites Group, Defence Metallurgical Research Laboratory, Hyderabad, India.
[2]Department of Mechanical Engineering, Geethanjali College of Engineering & Technology, Hyderabad, India
[3]Department of Mechanical Engineering, Shadan College of Engineering & Technology, Hyderabad, India
Email: devaiah.malkapuram@gmail.com,

Received July 3, 2012; revised August 7, 2012; accepted August 14, 2012

ABSTRACT

SiC particulates reinforced alumina matrix composites were fabricated using Directed Metal Oxidation (DIMOX) process. Continuous oxidation of an Al-Si-Mg-Zn alloy with different interlayers (dopents) as growth promoters, will encompasses the early heating of the alloy ingot, melting and continued heating to temperature in the narrow range of 950˚C to 980˚C in an atmosphere of oxygen. Varying interlayers (dopents) are incorporated to examine the growth conditions of the composite materials and to identification of suitable growth promoter. The process is extremely difficult because molten aluminum does not oxidize after prolonged duration at high temperatures due to the formation of a passivating oxide layer. It is known that the Lanxide Corporation had used a combination of dopents to cause the growth of alumina from molten metal. This growth was directed, *i.e.* the growth is allowed only in the required direction and restricted in the other directions. The react nature of the dopants was a trade secret. Though it is roughly known that Mg and Si in the Al melt can aid growth, additional dopents used, the temperatures at which the process was carried out, the experimental configurations that aided directed growth were not precisely known. In this paper we have evaluated the conditions in which composites can be grown in large enough sizes for evaluation application and have arrived at a procedure that enables the fabrication of large composite samples by determining the suitable growth promoter (dopant). Scanning electron microscopic, EDS analysis of the composite was found to contain a continuous network of Al_2O_3, which was predominantly free of grain-boundary phases, a continuous network of Al alloy. Fabrication of large enough samples was done only by the inventor company and the property measurements by the company were confirmed to those needed to enable immediate applications. Since there are a large number of variable affecting robust growth of the composite, fabrication large sized samples for measurements is a difficult task. In the present work, to identify a suitable window of parameters that enables robust growth of the composite has been attempted.

Keywords: Ceramic-Matrix Composites; Scanning Electron Microscopy; Liquid Metal Infiltration; Al_2O_3, SiC

1. Introduction

The directed oxidation of molten metal has been utilized to produce ceramic composites. This process offers the ability to produce unreinforced [1], particulate-reinforced [2] and fiber-reinforced [3,4] composites with a wide range of composition and microstructures. The composite formation process involves the rapid reaction of a molten metal with a gaseous oxidant: for example, the reactions of a molten aluminum alloy containing a growth dopant such as a few wt% of Mg and a group IVA elements (Si, Ge, Sn, or Pb) with air to form alpha aluminum oxide [2]. The reaction is sustained by the wicking of liquid metal—along interconnected microscope channels in the reaction product.

Numerous studies now exist of the oxidative growth of Al_2O_3/Al composites from Al alloys into free space [5-7], experiments on the infiltration of preforms, which are fewer, including the work of Manor *et al*. [8] into SiC and of Nagelberg [9] into Al_2O_3. As an example, the reaction of an aluminum alloy with oxygen produces an Al_2O_3/metal composite containing both ceramic and metal as three dimensionally interconnected networks [4]. The directed oxidation produced composite materials is quite flexible and offers the ability to make near-net-shape low-porosity *in situ* composites with a wide range of composition and microstructures [10]. These composites can, in principle, be designated to have good tough-

ness and thermal shock resistances, as well as high stiffness, wear resistance, and high temperature stability. The reaction product may be formed by itself as a ceramic/metal composite or as the matrix of a reinforced composite. In either case, the composite formation reaction is sustained by the wicking of liquid metal along interconnected microscopic channels within the alumina structure.

The microstructure of the α-Al_2O_3/metal composite in the absence of a reinforcing preform has been described by Breval *et al.* [11]. The composite in the absence of preform was characterized by preferred orientation of interconnected Al_2O_3 perpendicular to the plane of the original alloy surface and a bond of $MgAl_2O_4$ at the interface between the composite and original alloy surface. In a previous paper, the microstructure development of Al_2O_3/metal ceramic bodies grown from an Al-10 wt% Si-3 wt% Mg alloy was discussed in detail [12]. Nagelberg *et al.* found the growth rate of Al-10 wt% Si-3 wt% Mg alloy to exhibit activation energy of ~400 kj/mol. Growth rates varied as the oxygen partial pressure to the one quarter power. These authors proposed that the overall composite growth process involves the transport of oxygen through the external MgO layer to the molten Al alloy interface where it dissolves in the molten metal. The dissolved oxygen diffuses through the molten metal and then reacts with Al at the metal/Al_2O_3 interface to form additional Al_2O_3. It was proposed that the growth rate was controlled by the electronic conductivity of the external MgO layer [13].

Characterizing the initial fabrication of the composite microstructure in the absence of a reinforcing preform is an essential component for the fabrication of a detailed understanding of the growth dopants or promoter. This paper describes the conversion of molten Al alloy into Al_2O_3 by using different growth dopants with help of the microstructure morphology (scanning electron microscopy) and fabrication of large enough sizes of ceramic matrix composites with SiC particulates as reinforcing preform.

2. Experimental Procedure

For growth of molten Al-9Zn-8.5Si-1.5Mg alloy in O_2 atmosphere was studied by two experiments such as: 1) The alloy is exposed in O_2 atmosphere with different dopants to know exact growth promoter (dopant) without preform. 2) Further experiments were carried with SiC particulates as reinforcement (preform) to fabricate large enough sizes SiC/Al_2O_3 ceramic matrix composite materials.

In initial experiments to know growth promoter studies, a rectangular Al alloy ingot was machined into 15 mm × 15 mm × 15 mm size piece (Total 9 Nos). The surface of the Al alloy piece was evenly coated with a thin interlayer (dopants), namely SnO_2, Bi_2O_3, $CaCO_3$, MgO, ZnO, TiO_2, Y_2O_3, (SnO_2 + Bi_2O_3), and (MgO + ZnO) and other sides are coated with gypsum to prevent growth. The coated Al alloy piece was preheated in an oven for 4 hrs. The preheated alloy pieces are then placed in zircon sand mold as shown in **Figure 1**. Then the samples were heated to a temperature in the narrow range of 950˚C to 980˚C in an atmosphere of oxygen for a dwell time of 62 hours followed by furnace cooling to room temperature.

Grown sample bodies were sectioned and metallographically polished. Microscopic observations were made to determine the formation of Al_2O_3 at the top surface of the sample with different interlayer (dopant) and growth condition. Where appropriate, SEM and EDS analysis was performed. Energy Dispersive Spectroscopy (EDS) was especially helpful in identifying the chemical composition and sequence of layers in the surface oxide at the interface between the growing composite and the air atmosphere. In the case of second experiment, to fabricate large enough size of SiC_p/Al_2O_3 composites with different volume fractions were prepared by directed metal oxidation process. This was comprised of two steps namely preparation of SiC preforms with different volume fraction and appropriate heat treatment schedule to aid formation of Al_2O_3 matrix. The volume fraction of SiC was carried by using SiC particulates of different grit sizes namely #100, #120 and #220. The corresponding particle size, tapped packing density and volume fraction, as calculated using density of α-SiC (3197 Kg/m^3) are displayed in **Table 1**. SiC powders were subjected to artificial oxidation by heat treatment in air at 1100˚C for 4 hours. This would ensure that an adherent coating of SiO_2 would develop on the surface of SiC particles. Subsequently, loose powder preforms (measuring 70 × 70 × 20, in mm) of oxidized SiC with corresponding tapped packing densities were contained in refractory crucibles. Al alloy (Al-9Zn-8.5Si-1.5Mg) blocks were used as source for formation of Al_2O_3. The Al alloy block was ground and polished to good surface finish and cleaned

Figure 1. Zircon sand mold used to grow Al alloy pieces with different interlayer in O_2 atmosphere.

Table 1. Details of volume fractions of composites studied in this work.

Label	Grit size	Average particle size (μm)	Tapped packing density (Kg/m^3)	Volume Fraction
B1	#100	125	1118	0.35
B2	#120	106	1286	0.40
B3	#220	53	1382	0.43

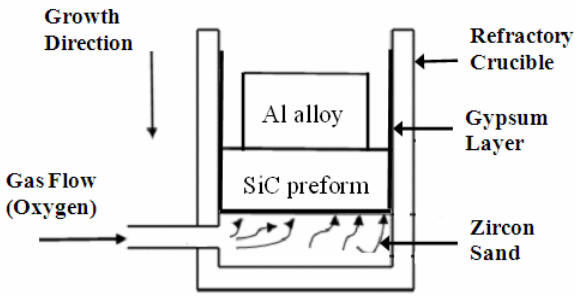


Figure 2. Schematic view of set-up used in DIMOX process for fabrication of SiCp/Al_2O_3.

with acetone. Gypsum was coated on five sides of the block to prevent growth into sides and the top, the bottom side of the Al block is coated with growth at the interface. A schematic of the experimental set-up is shown in **Figure 2**. The samples were heated to a temperature in the narrow range of 950˚C to 980˚C in an atmosphere of oxygen for a dwell time of 62 hours followed by furnace cooling to room temperature. Subsequent to cooling, the composite block shall be subjected to machining in order to obtain specimens with required dimensions necessary for various measurements.

3. Results and Discussion

Experiments are performed by Al-9Zn-8.5Si-1.5Mg alloy with different interlayer (dopants), namely SnO_2, Bi_2O_3, $CaCO_3$, MgO, ZnO, TiO_2, Y_2O_3, SnO_2^+ Bi_2O_3, and MgO^+ ZnO to know the Al_2O_3 formation on the top surface [1]. Al alloy ingot without filler material was exposed into oxygen; the exposed surface of the alloy ingot was evenly coated with a thin layer of the selected dopant (SnO_2, Bi_2O_3, $CaCO_3$, MgO, ZnO, TiO_2, Y_2O_3, (SnO_2^+ Bi_2O_3), and (MgO^+ ZnO) to promote uniform growth initiation at temperatures varying from 950˚C to 980˚C in O_2 atmosphere. The details results of the as grown samples are shown in **Table 2**. As grown samples in oxygen atmosphere are taken out from home made zircon sand mold for examination. A small piece is cut from each sample by low speed diamond saw and metallographically polished for scanning electron microscopy observations. **Figure 3(a)** shows the experimental sample of Al alloy without filler material and exposed surface of the alloy ingot was evenly coated with a thin layer of (SnO_2 + Bi_2O_3) interlayer (dopant) into air.

From the **Figure 3(a)** we can observe that the length of the alloy as been changed and increase longitudinally. The longitudinal cross section is shown in **Figure 3(b)**. It can be observed from **Figure 3(a)** the growth of the alloy at the top surface of the sample and a hollow shape at the top in cross section view (**Figure 3(b)**). Visual examination of the (SnO_2^+ Bi_2O_3) specimens showed that oxide growth occurred exclusively on the exposed surface of the metal, the microstructural features if the reaction product were used to guide the selection of a growth promoter. **Figure 4** shows the macroscopic features of reaction products grown from Al alloy at a process temperature

Table 2. Details of grown and non grown samples.

Label	Interlayer	Results
B1	SnO_2	No growth
B2	Bi_2O_3	No growth
B3	$CaCO_3$	No growth
B4	MgO	No growth
B5	ZnO	No growth
B6	TiO_2	No growth
B7	Y_2O_3	No growth
B8	(SnO_2 + Bi_2O_3)	Composite grows Vigorously
B9	(MgO + ZnO)	No growth

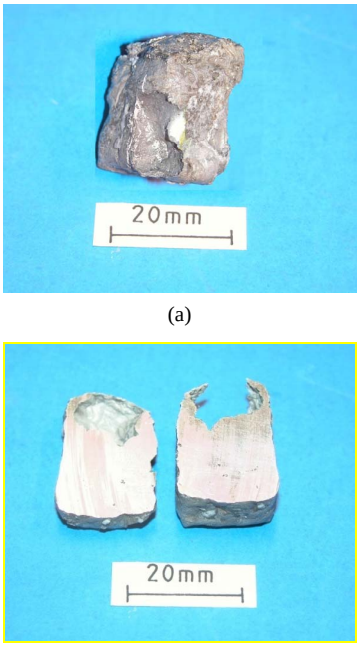


Figure 3. A schematic representation of as grown Al alloy SnO_2 + Bi_2O_3 as interlayer (a) Experimental sample (b) cross section.

of 950˚C to 980˚C in O_2 atmosphere using (SnO_2^+ Bi_2O_3) as interlayer (growth promoter) system. Differences in surface reflectivity reveal that the material is of columnar character, consistent with the directed nature of the growth process. Results from SEM observations show a Al_2O_3 layer, below MgO and Al_2O_3 layer is formed and followed by a metal. The Al_2O_3 columns in material processed at 950˚C to 980˚C contain interpenetrant but fully interconnected networks of Al_2O_3 and Al.

Typically; they are several millimeters wide and have indistinct boundaries. **Figure 5** shows the EDS line mapping observation shows the some microns of O and other elements available in the parent metal and the dopants (SnO_2+ Bi_2O_3) also. Similar experiments were conducted with different interlayer (dopants) which are listed in **Table 2**. **Figure 6** shows experimental sample and longitudinal cross section using $CaCO_3$ as interlayer under similar conditions. From the Figure the experiment sample clearly show that there in no change in the dimensions of the sample and it retained its original dimensions of the sample. The microscopic observations with $CaCO_3$ as interlayer is not found any oxidation layer on the top surface and any Al_2O_3 content at the top surface of the grown sample as shown in **Figure 7** and **8**. Similarly results are found in other experiments which are done by other interlayer (dopants) which are listed in **Table 2**.

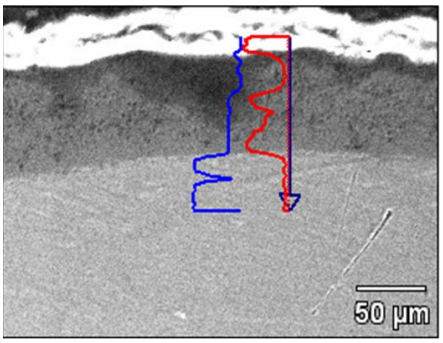


Figure 4. Representative grain boundaries between Al_2O_3 crystallites for as Al alloy with SnO_2 + Bi_2O_3 as interlayer.

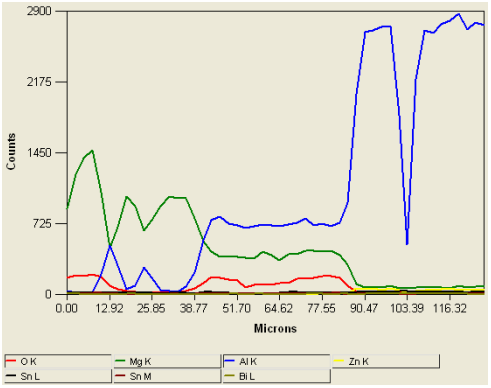


Figure 5. EDS line mapping representation of as grown Al alloy SnO_2 + Bi_2O_3 as interlayer.

Figure 9 shows as grown sample and longitudinal cross section using Bi_2O_3 as interlayer under similar conditions. The **Figure 10** shows the scanning electron microscopic observations will not found any Al_2O_3 content in the case Bi_2O_3 as interlayer same results can be observed in EDS reorientation in **Figure 11**. The above experiments reveal that the vigorous growth was found in the case of (SnO_2 + Bi_2O_3) as interlayer. Other dopents which are listed in **Table 2** will not found any growth. From the observed results to fabricated SiC/Al_2O_3 ceramic matrix composites (SnO_2 + Bi_2O_3) can be used as interlayer or growth promoter for the fabrication of the large size SiC/Al_2O_3 ceramic matrix composites. Then the experiments are done under similar conditions as a function of SiC particulates as reinforcement with volume fractions in the range of 0.35 to 0.43 are used to prepare the preforms to infiltrate into Al alloy to fabriccate

(a)

(b)

Figure 6. A schematic representation of as grown Al alloy $CaCO_3$ as interlayer (a) Experimental sample (b) cross section.

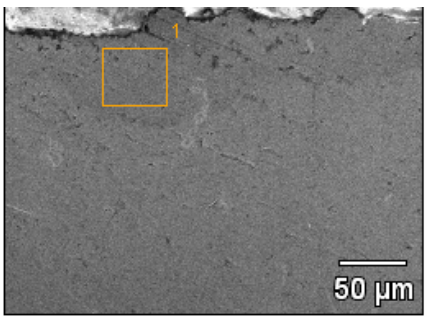


Figure 7. SEM representation of as grown Al alloy $CaCO_3$ as interlayer.

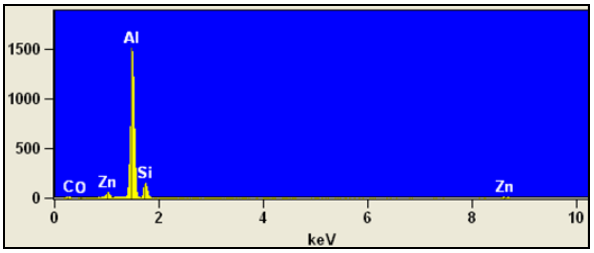
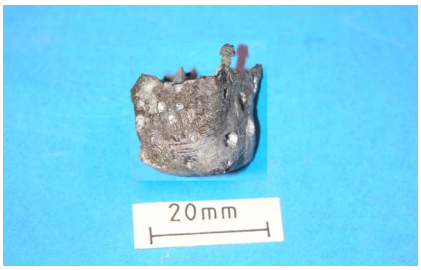
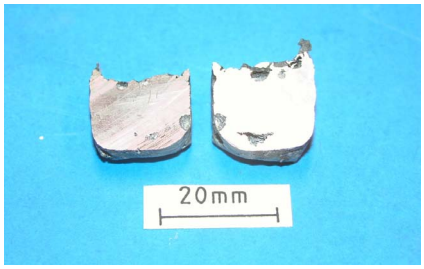


Figure 8. EDS of as grown Al alloy with $CaCO_3$ as Interlayer.



(a)



(b)

Figure 9. A schematic representation of as grown Al alloy Bi_2O_3 as interlayer (a) Experimental sample (b) cross section.

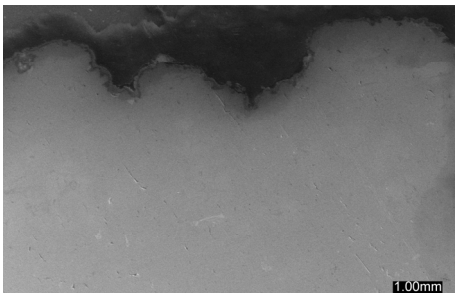


Figure 10. SEM representation of as grown Al alloy with Bi2O3 as interlayer.

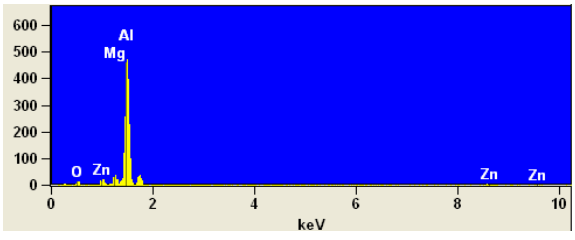
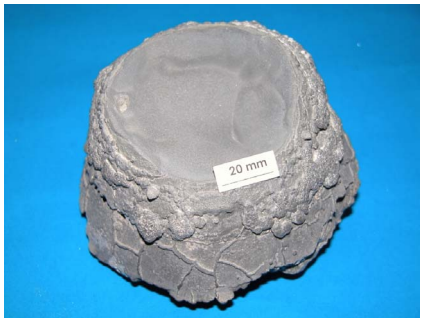


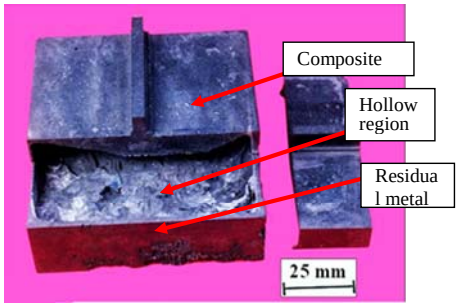
Figure 11. EDS representation of as grown Al alloy with Bi_2O_3 as interlayer.

large size SiC_p/Al_2O_3 ceramic matrix composites. **Figure 12** shows the different dimension of SiC_p/Al_2O_3 ceramic matrix composites are fabricated in the present work with dimensions. **Figure 12(b)** with dimensions measuring 70 × 70 × 20, in mm.



(a)

(b)



(c)

Figure 12. Examples of composite growth obtained in the present work (a) the aluminum alloy is allowed to oxidize and grow into SiC particulate preform in a conical refractory mold. We note that the shape of the mould could be replicated in the composite. (b) We also note the large size (70 mm × 70 mm × 20 mm) of the composite samples. An example of growth of composite from a rectangular mold. (c) a example showing the way the composite grows-the growth process was stopped midway, the outer surface was cleaned and suitably machined to reveal the salient features. The aluminum left after the process can be seen at the bottom. The hollow region is the region from where the Al was used up in the oxidation growth. The top is the composite that grow. The composite is machined to reveal the absence of macroscopic porosity. The edges of the alloy retain a box shape because of the suppression of melting due to the presence of gypsum coating.

4. Conclusion

The process details are reported for the specific example of oxidation of molten Al in oxygen atmosphere to form Al_2O_3. In the present work, the experiments are performed with and without reinforcement to fabricate large size SiC_p/Al_2O_3 ceramic matrix composites. (SnO_2 + Bi_2O_3) was identified as suitable growth promoter for fabrication SiC_p/Al_2O_3 ceramic matrix composites. The scanning electron observations revealed that the conversion of metal to oxide was possible only with (SnO_2+ Bi_2O_3) dopant as growth promoter. Other did not cause any growth of oxide from molten metal. So, the (SnO_2+ Bi_2O_3) dopant was used as growth promoter for the fabrication of SiC_p/ Al_2O_3 ceramic matrix composites. SiC_p/Al_2O_3 ceramic matrix composites are successfully fabricated with SiC particulates as reinforcement with volume fractions in the range of 0.35 to 0.43 with dimensions measuring 70 × 70 × 20, in mm. the sample are used for different mechanical and physical property measurements.

REFERENCES

[1] M. S. Newkirk, A. W. Urquhart and H. R. Zwicker, "Formation of Lanxide Ceramic Composite," *Journal of Materials Research*, Vol. 1, No. 1, 1986, pp. 81-89. doi:10.1557/JMR.1986.0081

[2] M. S. Newkirk, H. D. Lesher and D. R. White, "Formation of Lanxide Ceramic Matrix Composites: Matrix Formation by the Directed Oxidation of Molten Metals," *Ceramic Engineering & Science Proceedings*, Vol. 8, No. 7-8, 1987, pp. 879-885. doi:10.1002/9780470320402.ch46

[3] P. Barron-Antolin, G. H. Schiroky, and C. A. Anderson, "Properties of Fiber-Reinforced Alumina Matrix Composites," *Ceramic Engineering & Science Proceedings*, Vol. 9, No. 7-8, 1988, pp. 759-766. doi:10.1002/9780470310496.ch27

[4] K. Aghajanian, N. H. MacMillan, C. R. Kennedy, S. J. Luszcz and R. Roy, "Properties and Microstructures of Lanxide Al_2O_3-Al Ceramic Composite Materials," *Journal of Materials Science*, Vol. 24, No. 2, 1989, pp. 658-670. doi:10.1007/BF01107457

[5] A. S. Nagelberg, "Growth Kinetics of Al_2O_3/Metal Composites from a Complex Aluminum Alloy," *Solid State Ionics*, Vol. 32-33, 1989, pp. 783-788. doi:10.1016/0167-2738(89)90358-5

[6] A. S. Nagelberg, S. Antolin and A. W. Urquhart, "Formation of Al_2O_3/Metal Composites by the Directed Oxidation of Molten Aluminum-Magnesium-Silicon Alloys: Part II, Growth Kinetics," *Journal of the American Ceramic Society*, Vol. 75, No. 2, 1992, pp. 455-462. doi:10.1111/j.1151-2916.1992.tb08201.x

[7] O. Salas, H. Ni, V. Jayaram, K.C. Vlach, C.Q. Levi and R. Mehrabian, "Nucleation and Growth of Al_2O_3/Metal Composites by Oxidation of Aluminum Alloys," *Journal of Materials Research*, Vol. 6, No. 9, 1991, pp. 1964-1981. doi:10.1557/JMR.1991.1964

[8] E. Monar, H. Ni, C.G. Levi. and R. Meharabin, "Formation of Al_2O_3/Metal Composites by the Directed Oxidation of Molten Aluminum-Magnesium-Silicon Alloys: Part II, Growth Kinetics," *Journal of the American Ceramic Society*, Vol. 75, No. 2, 1992, pp. 455-462. doi:10.1111/j.1151-2916.1992.tb08201.x

[9] A. S. Nagelberg, "The Effect of Processing Parameters on the Growth Rate and Microstructure of Al_2O_3/Metal Matrix Composites," *Materials Research Society Symposium Proceedings*, Vol. 155, 1989, pp. 155-275.

[10] A. W. Urquhart. "Molten Metals Sire MMC's, CMC's," *Advanced Materials and Processes*, Vol. 140, No. 1, 1991, pp. 25-29.

[11] E. Breval, M. Aghajanian and S. Luszcz, "Microstructure and Composition of Alumina/Aluminum Composites Made by Directed Oxidation of Aluminum," *Journal of the American Ceramic Society*, Vol. 73, No. 9, 1990, pp. 2610-2614. doi:10.1111/j.1151-2916.1990.tb06735.x

[12] S. Antolin and A. S. Nagelberg, "Formation of Al_2O_3/ Metal Composites by the Directed Oxidation of Molten Aluminum-Magnesium-Silicon Alloy: Part I, Microstructural Development," *Journal of the American Ceramic Society*, Vol. 75, No. 2, 1992, pp. 447-454. doi:10.1111/j.1151-2916.1992.tb08200.x

[13] A. S. Nagelberg and S. Antolin, "Formation of Al_2O_3/ Metal Composites by the Directed Oxidation of Molten Aluminum-Magnesium-Silicon Alloy: Part II, Growth Kinetics," *Journal of the American Ceramic Society*, Vol. 75, No. 2, 1992, pp. 455-462. doi:10.1111/j.1151-2916.1992.tb08201.x

