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Fabrication of Al/AlN composites by in situ reaction

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Abstract The tensile properties and microstructures of various Al alloys fabricated by the pressureless infiltration method under a nitrogen atmosphere were examined. The spontaneous infiltration of molten metal into the powder bed occurred at 800 °C for 1 h under a nitrogen atmosphere. As a result, it was possible to fabricate Al alloys reinforced with AlN particles formed by in situ reaction. A significant strengthening even in the control alloy occurred due to the formation of in situ AlN particle even without an addition of artificial reinforcement. Strength values of the control alloy were increased with decreasing Al powders in bottom powders bed. In addition, tensile strength in Al–Mg alloys was increased with Mg content.

Introduction

AlN has attractive properties that include relatively high thermal conductivity, the coefficient of thermal expansion that matches that of silicon, fairly high electrical resistivity and low dielectric constant, and high dielectric strength. As a result, AlN has been recognized as one of the promising materials for electronic and structural applications [1–3]. AlN is synthesized by various methods including carbothermal reduction, direct nitridation, floating nitridation, chemical vapor deposition, etc. [1].

In recent years, AlN thus received considerable attention as a significant reinforcement in Al MMC. Furthermore, there has been a growing interest in the development of technologies for the in situ production of MMCs, such as Lanxide's PRIMEX^{TM} process, Martin Marietta's XD^{TM} process, self-propagating high-temperature synthesis (SHS) and reactive-gas injection [4–14].

The PRIMEX process is an innovative technique for fabricating MMCs by the spontaneous infiltration of molten Al alloy containing Mg into a ceramic filler or preform under a nitrogen atmosphere without the aid of vacuum or externally applied pressure [5–14]. The PRIMEX process has many advantages relative to conventional MMC fabrication techniques. One of them is the formation of AlN particles as a result of the in situ reaction during fabrication of MMC by PRIMEX process. Moreover the amount of the AlN in the metal matrix can be controlled by varying the processing conditions: temperature, time, alloying, and nitrogen concentration.

Although there were many reports on Al/AlN composites fabricated by in situ reaction, few publications on the PRIMEX process have appeared. Therefore, in this study, the characteristics of the Al alloys (refer to control alloys) without an artificial reinforcement fabricated by pressureless infiltration method were analyzed.

Experimental procedure

Figure 1 shows the schematic arrangement employed for the 6061 control alloy fabrication in this study. This method is the same for composite fabrication by pressureless infiltration technique, with the exception that a powder mixture without the reinforcement is used. The lower part of the assembly was filled with a

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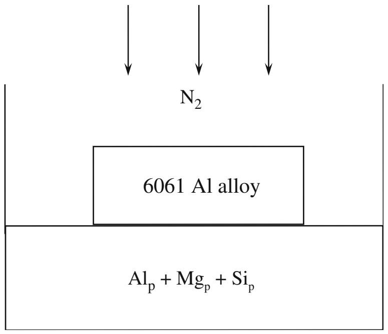


Fig. 1 Schematic arrangement employed for the fabrication of 6061 control alloy

(Al–1.2 wt% Mg–0.8 wt% Si) powder mixture which was prepared by roll mixing in an alumina jar for 10 h and then a 6061 Al ingot was placed on this powder bed. The average size of the Al, Mg and Si particles was about 50, 13, and 20 μm, respectively. The assembly was heated to 800 °C and held for 1 h under a flowing nitrogen atmosphere in the retort furnace (5,000 cc/min). The fabricated ingot whose size was about 100 × 100 × 80 mm were extruded into a bar 16 mm in diameter at 450 °C (extrusion ratio 22:1). Also, control alloys of 5052, 5083 and 7075 were fabricated by the same route. Tensile specimens having a gage length of 25 mm and a thickness of 2 mm were machined from extruded bars, parallel to the extrusion direction. Control alloys of 5052 and 5083 were solution treated at 560 °C. Control alloys of 6061 and 7075 were T6 treated. Tensile testing was performed at room temperature, using a crosshead speed of 1 mm/min. Average tensile data were obtained from testing at least five times for both the solution treated and the T6 conditions.

The resulting microstructures and reaction products were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Auger electron spectroscopy (AES). For SEM observation, specimens were prepared by dissolving away the metal matrix in a solution of methanol bromine. Thin foils for TEM analysis were ground mechanically to a thickness of about 60 μm and then punched to 3 mm diameter discs. Finally, the discs were thinned by the dimpling and ion milling.

Results and discussion

Tensile properties

Since the spontaneous infiltration of molten metal occurred at temperature of 800 °C for 1 h under a nitrogen atmosphere, it was possible to fabricate control alloys by the pressureless infiltration method, similarly in the case of the MMC fabrication. The spontaneous infiltration behavior was explained in detail in previous papers [11–14].

Figure 2 shows the variation of tensile strength in commercial Al, control Al and composites reinforced with SiC particles in solution treated (5052 and 5083 Al) and T6 treated conditions (6061 and 7075 Al). The tensile strength in the control alloys were higher than those of the commercial alloys depending on alloy composition. This strengthening in the control alloys is related to the in situ formation of AlN particles during the pressureless infiltration processing used in this study. Namely, when the MMCs were fabricated by pressureless infiltration technique, AlN is formed as a result of the in situ reaction ($Mg_3N_2 + 2Al = 2AlN + 3Mg$) [8–14]. In addition, composites reinforced with SiC particles exhibited higher strength values than that of the control alloy in all alloy composition (Fig. 3).

This result is different from many other studies reported in literature, which showed a decrease in the strength of Al–Zn–Mg–Cu alloy matrix composites with the addition of SiC reinforcement [15–21]. Figure 4 shows tensile strength in 7xxx matrix composites fabricated by various methods. It is seen that tensile properties depend on fabrication method. As mentioned above, it should be noted that tensile strengths in composites fabricated by both P/M and casting methods were nearly the same or lower than that of unreinforced materials while composite fabricated by pressureless infiltration method used in this study showed higher strength than the unreinforced material. In addition,

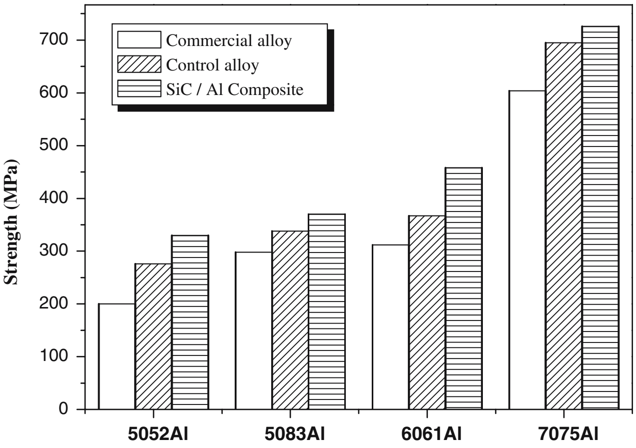


Fig. 2 Tensile strength in commercial Al, control Al and composites reinforced with SiC particles in solution treated (5052 and 5083 Al) and T6 treated conditions (6061 and 7075 Al)

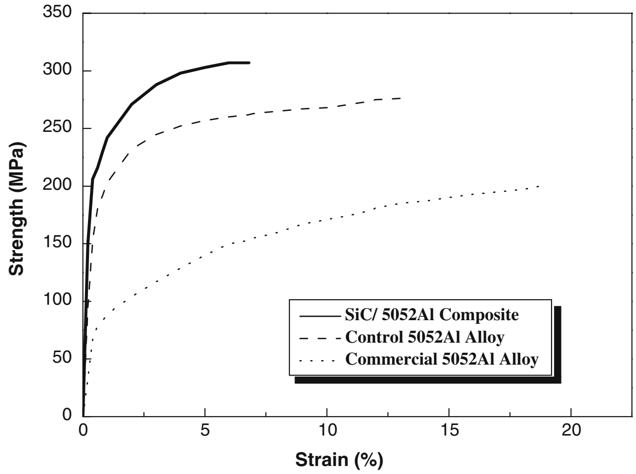


Fig. 3 Stress–strain curves of the commercial 5052 Al, control 5052 Al and SiC/5052 Al

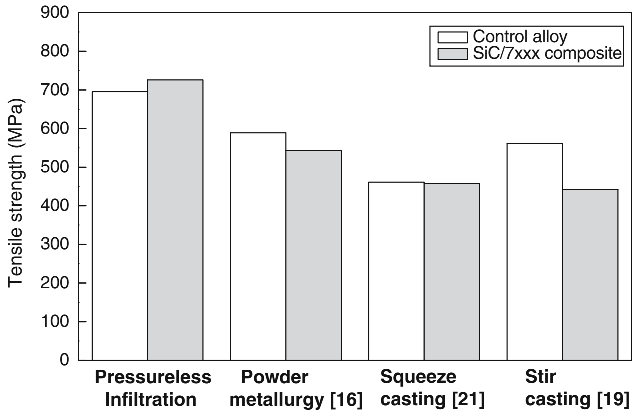


Fig. 4 Tensile strength in 7xxx matrix composites fabricated by various methods

strength values in materials fabricated by pressureless infiltration method (control alloy and composite) were higher than that of materials fabricated by other methods. It is believed that this result is mainly caused by difference in fabrication method. In general, since wetting between molten metal and reinforcements is often poor, mechanical stirring or pressure infiltration has been applied in order to obtain improved wetting between the matrix and reinforcements during fabrication of composites. However, the fact that the spontaneous infiltration of molten metal in this study occurred means that the problem of wetting between the ceramic reinforcement and molten metal is solved. Therefore, it is believed that this enhancement of wettability may result in better interfacial bonding and as a result tensile properties are improved.

However, when 7075Al/Al_2O_3 composite was fabricated by pressureless infiltration method, its strength was nearly the same or lower than that of unreinforced materials [13]. Namely, it seemed that there has been limitation in strength increase of the composites through addition of artificial reinforcement. Therefore, it is desirable that MMC is fabricated by in situ process.

Table 1 show the variation of tensile properties in AA5083 and AA7075 that were fabricated using different size of Al powders. Strength values in the case of smaller size of Al powders were higher than those of large Al powders. Aghajanian et al. [8] suggested that in the pressureless infiltration process, where wetting is preferred (i.e. the infiltration occurs spontaneously), dominant factor with respect to particle size is surface area. Smaller particles provide a greater area of wettable surface, thus enhancing infiltration [8].

Figure 5 shows the variation of tensile strength with Mg content in commercial and control Al–Mg Alloy. Tensile strength was increased with Mg content in both alloys. For the pressureless infiltration of molten metal, both nitrogen and Mg should be needed. Previous studies have investigated that the spontaneous infiltration of molten Al alloy to provide the matrix of Al composites in this process is influenced by Mg content, additional alloying elements, nitrogen concentration in the gas atmosphere, infiltration temperature and time, etc [4–14]. Mg vapor (serving as an infiltration enhancer precursor) reacts with nitrogen to form

Table 1 Tensile properties of commercial and control alloys

Alloy designations	UTS (MPa)		YS (MPa)		El (%)	
	ST	T6	ST	T6	ST	T6
Commercial 5083 Al	306 ± 2	–	134 ± 4	–	23.0 ± 1	–
Control 5083 Al (Al powder size: 50 μm)	343 ± 3	–	173 ± 5	–	17.0 ± 2	–
Control 5083 Al (Al powder size: 5 μm)	370 ± 3	–	185 ± 5	–	11.0 ± 2	–
Commercial 7075 Al	417 ± 4	604 ± 5	217 ± 6	550 ± 5	20.4 ± 1	10.6 ± 2
Control 7075 Al (Al powder size: 50 μm)	459 ± 3	695 ± 5	302 ± 5	611 ± 5	13.8 ± 1	3.8 ± 1
Control 7075 Al (Al powder size: 5 μm)	484 ± 4	710 ± 4	277 ± 5	653 ± 5	6.0 ± 1	2.8 ± 1

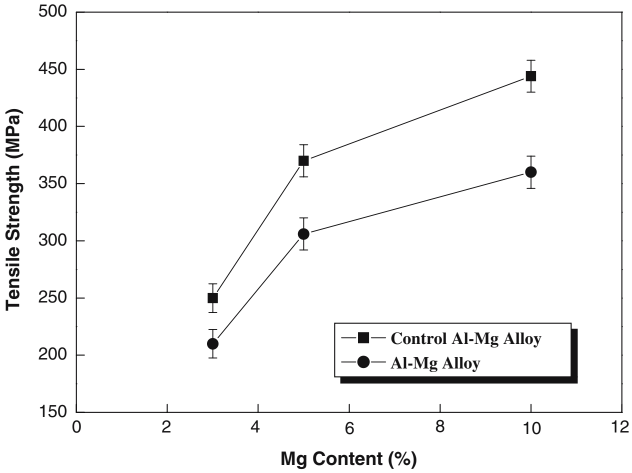


Fig. 5 Variation of tensile strength with Mg content in commercial and control Al–Mg alloy

Mg_3N_2 coatings (which serve as an infiltration enhancer) around the particles in the preform or filler. This Mg_3N_2 may lead to a spontaneous infiltration of molten Al alloy via an enhancement of wetting between molten alloy and reinforcement. Therefore, it is believed that spontaneous infiltration behavior of molten metal is enhanced with increase Mg content. In addition, fine AlN particles content in situ formed was increased and thus led to a significant enhancement of strength in the control alloy.

Microstructural analysis

Figure 6 shows the XRD spectra of the commercial and Al–Mg control alloys. As expected, the commercial alloy presented the peaks corresponding to only Al. By contrast, the control alloy exhibited the additional small peaks of AlN. This means that the AlN was formed via in situ reaction within the system during the fabrication of the control alloy. In addition, the peak of AlN becomes higher with increasing Mg content. This results means that AlN content in situ formed was increased with Mg content. Such an increasing in AlN content contributed to enhancement of strength in the control alloy (Fig. 5).

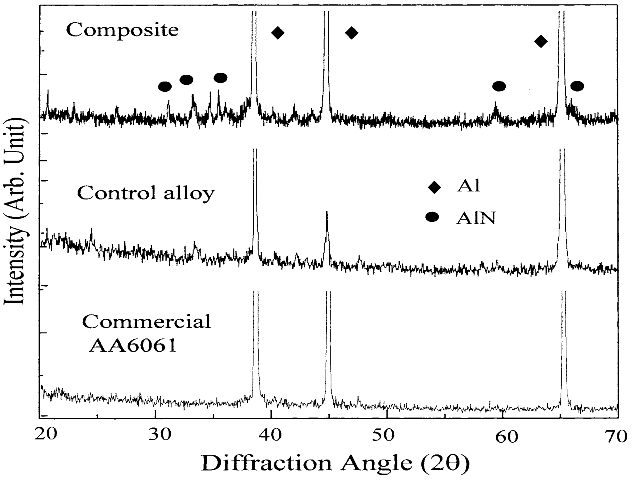


Fig. 6 XRD spectra of the commercial and control Al–Mg alloys

Figure 7 shows secondary electron images, EDS and AES spectra of the reaction product obtained in various control alloys after Al alloy matrix was dissolved away with a solution of methanol bromine. A great amount of reaction product (the size of which about 1.0 μm) was originally formed on the surface of the old Al particles that had comprised the powder bed prior to infiltration. AES and EDS analyses revealed only Al and N, and the atomic ratio of Al–N was around one, coincident with the stoichiometry of AlN.

Figure 8 shows bright field and dark field images, and selected area diffraction patterns (SADP) of the reaction product observed by TEM in control 5083 Al alloy. This reaction product was identified as the AlN of hexagonal structure with the measured lattice parameter, $a = 3.093$ nm and $c = 4.950$ nm in the composite (theoretical value $a = 3.1114$ nm and $c = 4.9792$ nm, space group: *P63mc*) [22]. This phase has been observed in all the control alloys fabricated, using the present pressureless infiltration technique in the presence of Mg and nitrogen [11–14].

Conclusions

The tensile properties and microstructures of several Al alloy fabricated by the pressureless infiltration method under a nitrogen atmosphere were examined. Since the spontaneous infiltration of molten metal into the powder bed occurred at 800 °C for 1 h under a nitrogen atmosphere, it was possible to fabricate Al alloys reinforced with AlN particles formed by in situ reaction. A significant strengthening even in the control alloy occurred due to the formation of in situ AlN particle even without an addition of artificial reinforcement. Strength values of the control alloy were increased with decreasing Al powders in bottom powders bed. In addition, tensile strengths were increased with Mg content in Al–Mg alloys.

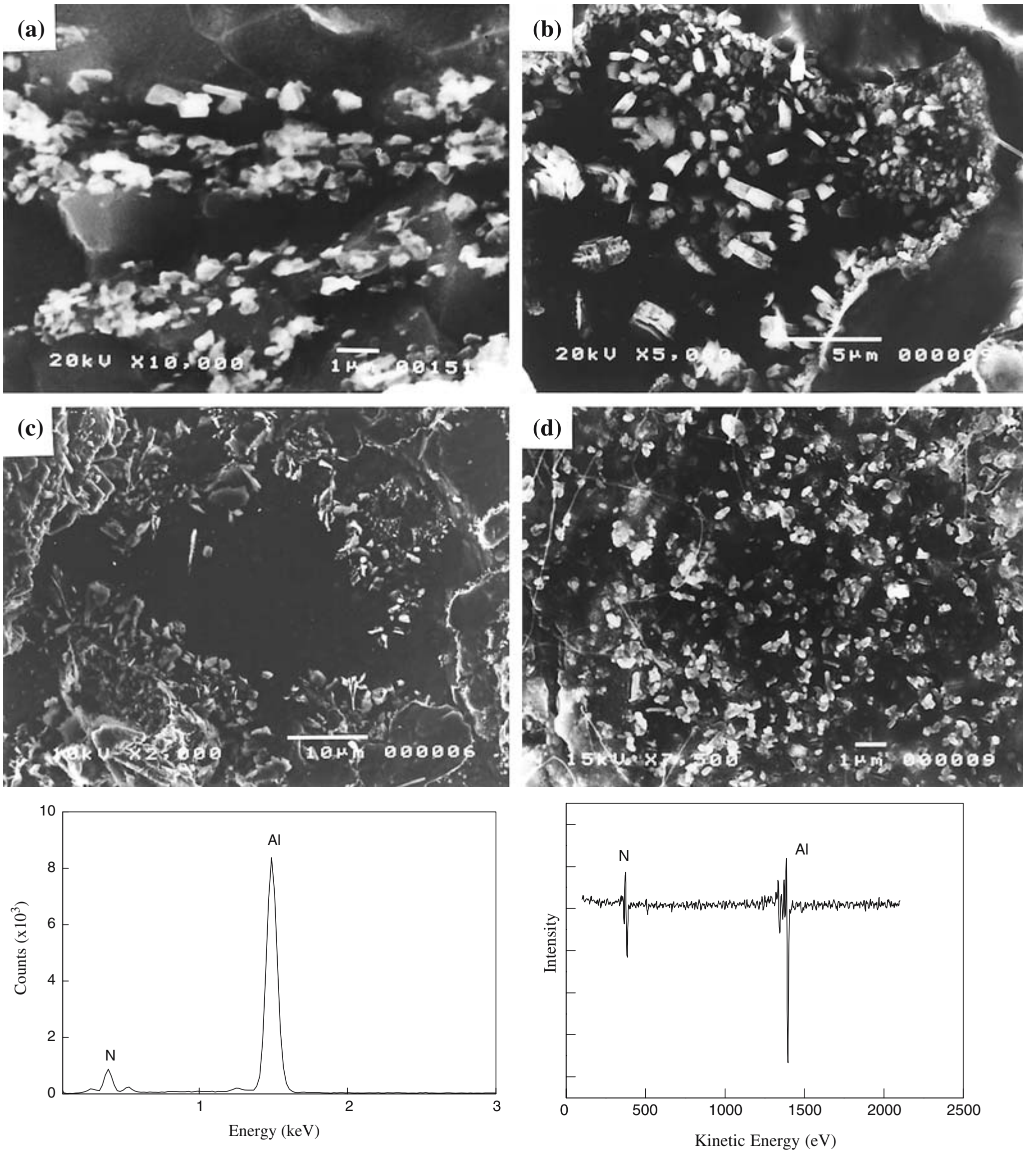
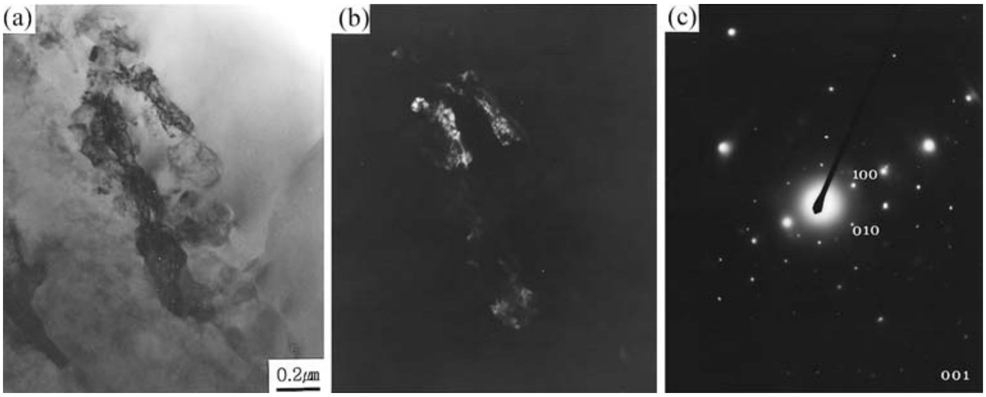


Fig. 7 SEM micrographs, EDS and AES spectra showing reaction products, AlN, after dissolving away the Al alloy matrix: (**a**) 5052 Al, (**b**) 5083 Al, (**c**) 6061 Al, and (**d**) 7075Al, respectively

Fig. 8 TEM micrographs showing reaction products, AlN: (**a**) BF, (**b**) DF, and (**c**) SADP in control 5083 Al alloy



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