Fabrication of *In-Situ* Intermetallic Compound Dispersed Aluminum Matrix Composites by Addition of Metal Powders*

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A new process was proposed to fabricate intermetallic compound reinforced Al matrix composites by the reaction between metal powders and molten Al. The Ni powders were added gradually onto the surface of the molten pure Al by stirring. The Al_3Ni particles, which are smaller than the added Ni powder, were *in situ* formed and homogeneously dispersed in the Al. The processing temperature was lower and the stirring time was shorter than those of the conventional vortex method for fabricating non-metal (Al_2O_3 , SiC etc) reinforced Al matrix composites. The effects of the processing variables, such as processing temperature, size of the Ni powder, and stirring time, on the formation and dispersion behavior of Al_3Ni were investigated. It was found that the size of the Al_3Ni decreased with the decreasing processing temperature and stirring time. The process was also applied to Ti, Zr, Cr, Mo, W and Fe powders. Al_3Ti , Al_3Zr , Al_7Cr and Al_{12}Mo were formed and homogeneously dispersed, but the others failed. The size of the intermetallic compounds significantly depended on the specific elemental metal powder. The dispersion of the intermetallic compounds was affected by the oxidation of the metal powders. This process was applicable to the JIS AC8A alloy for forming the AC8A- Al_3Ni composite. [doi:10.2320/matertrans.47.2972]

(Received March 17, 2006; Accepted October 5, 2006; Published December 15, 2006)

Keywords: metal matrix composite, aluminum, nickel, powder, Al_3Ni , intermetallic compounds, solidification, microstructure

1. Introduction

The requirement for lighter-weight materials in recent years has led to the adoption of aluminum as a substitute for steel or cast iron in material processing. To facilitate these efforts, material designers need to create Al alloys with advanced functions. A method to accomplish this is to apply ceramic-particulate-reinforced Al matrix composites. Composites of this type have been used in materials for disk break rotors now in practical use.^{1,2)}

Ceramic-particulate-reinforced Al matrix composites are generally produced by powder metallurgy or casting. Both methods have drawbacks. Powder metallurgy is costly. Casting is a good deal simpler than powder metallurgy, but the poor wettability of ceramics by molten Al makes it difficult to incorporate ceramics into molten Al and then homogeneously disperse them. The best ways to overcome these difficulties are to use metal-coated ceramics,³⁾ to add surface-active elements to the Al matrix,^{4,5)} and to apply the method known as compocasting.⁶⁾ In these processes, however, brittle reaction products tend to be generated at the reinforcement-matrix interface,⁷⁾ and it is difficult to incorporate fine particles into molten Al.⁸⁾

Another approach is to apply *in-situ* processes for the synthesis of the reinforcements. For example, TiC can be dispersed by adding SiC or Al_4C_3 to the molten Al-Ti alloy,^{9,10)} and Al_2O_3 can be dispersed by adding oxides to a molten Al alloy.^{11,12)} In both processes, the reinforcements formed *in situ* are thermodynamically stable and can be homogeneously dispersed. Better still, the underlying mechanism in these processes, particle formation, is expected to assure a clean reinforcement-matrix interface entirely free from inclusions (*e.g.*, oxides). Yet both processes also have drawbacks; they can only succeed when high temperatures are maintained, and the reaction by-products remain in the Al

matrix as impurities.

In this study we sought to fabricate Al matrix composites *in situ* by adding particles in a vortex process. Specifically, we used transition metal powders with a relatively high wettability by molten Al. By adding these metal powders to the molten Al, we induced a reaction to form intermetallic compounds via the vortex process. Our intention was to synthesize intermetallic compounds in the molten Al and homogeneously disperse them.

Many investigations have focused on the synthesis of composites through the reaction between a metal powder and Al. Those includes the reactive infiltration process,¹³⁾ a method involving the combustion synthesis of TiC and spontaneous infiltration, and the methods in which Al_3Ti can be formed and dispersed by infiltrating molten Al into a Ti powder or an Al-Ti mixed powder.^{14,15)} The reaction temperatures of these processes reach high levels, as both process make the most of the reaction heat to promote the formation of reinforcements and the infiltration of the molten Al. The latter process also requires a complex apparatus as a controlled atmosphere is essential.

The process we applied in this study has advantages, as the intermetallic compounds formed *in situ* have a granular shape and can be dispersed at lower temperatures—and thus more economically—than the compounds dispersed via the previously described vortex process. In this study, we investigated how various processing variables affected the morphology of the intermetallic compounds.

2. Experimental Procedure

The experimental apparatus is schematically shown in Fig. 1. Molten Al (50 g, purity: 99.99% or JIS AC8A (Al-12.1 mass%Si-1.0 mass%Cu-1.0 mas%Mg-1.2 mass%Ni) in a AISI304 stainless steel container (30 mm inner diameter) was set in an electric furnace and kept at the desired temperatures. Various powders (mass% from 10 to 25) were added onto the surface of the molten Al by a powder feeder

*This Paper was Originally Published in Japanese in J. JFS 77 (2005) 731–737.

Fig. 1 Schematic illustration of experimental apparatus.

Table 1 Size and purity of powders.

Type	Size (μm)	Purity (mass%)
Ni	3 ~ 5	99.9
	<53	99
	<150	99
Ti	<150	99
	63 ~ 90	99.9
Zr	<150	98
Cr	63 ~ 90	99.9
Mo	44 ~ 88	99.8
W	<150	99.9
Fe	<150	99

using ultrasonic vibration and then stirred into the melt. Table 1 lists the sizes and purities of the powders used. All of the powders were added in air, while the Zr powder was also added in an Ar atmosphere. The rate of introduction was a few grams per minute. The stirrer was an Al₂O₃ plate fixed at the end of an AISI304 bar (8 mm diameter) and set at the center of the molten Al. The stirrer revolved at 2000 rpm in the main experiments, and at 1000 or 3000 rpm in separate experiments for comparison. After the powders were added and then constantly stirred for 5 to 30 min, the AISI304 container was taken out of the furnace, gradually cooled in air for 1 min, and quenched in water. The temperature of the molten Al was measured by a K-type thermocouple immersed in the molten Al. This thermocouple was also used to control the temperature of the electric furnace, and the set temperature was that of the molten Al when the addition of the powder commenced. The microstructures were examined by optical microscopy of the longitudinal cross sections of the columnar samples. Energy dispersive X-ray spectroscopy (EDX) and an X-ray diffraction analysis (XRD) were used to determine the phase compositions.

Fig. 2 Phase diagram for Al-rich side of Al-Ni binary system.

3. Results and Discussion

3.1 Al-Ni system

3.1.1 Microstructure

The phase diagram of the Al-rich side of the Al-Ni system¹⁶⁾ is shown in Fig. 2. When the Al-20 mass%Ni alloy was gradually cooled from 1123 K in a furnace and quenched in water at 1003 K, a coarse and needle-like Al₃Ni intermetallic compound precipitated as the primary phase, as shown in Fig. 3(a). Figure 3(b) shows the solidification microstructure obtained under the same condition used to obtain the microstructure shown in Fig. 3(a), but with stirring of the molten Al at 1000 rpm. The microstructure in Fig. 3(b) is clearly similar to the needle-like Al₃Ni microstructure observed in Fig. 3(a), but with fragmentation due to stirring and a somewhat coarser grade. The shear force of the stirring probably prevented the Al₃Ni from growing into the needle-like form exhibited in Fig. 3(a). For reference, the cooling rates of the samples shown in Figs. 3(a) and (b) before water-quenching were 4.84 and 4.89 K/min, respectively. Figure 3(c) shows the solidification microstructure of the molten pure Al mixed with 20 mass% Ni powder (under 53 μm) and stirred at 2000 rpm for 30 min. The fine Al₃Ni compounds were homogeneously dispersed. This morphology is typical of this process and is expected to improve the mechanical properties.

There has been some apprehension that the AISI304 container and molten Al may react in this type of process. Though we have yet to discount this possibility, we found no Fe compounds in the solidification microstructures of the samples fabricated at the lower temperature and low stirring rate used in the present experiments.

3.1.2 Change in temperature

Figure 4 shows the temperature change in the molten Al induced by the addition of Ni powder. The Ni powder (under 53 μm) was added to the molten pure Al at 973 K, hence the heat of reaction (1) (standard enthalpy of formation at 973 K) increased the temperature of the melt up to the first peak.

After the first peak, the temperature dipped, rose to a second peak near the end of the addition, and gradually dropped back to the set temperature of 973 K. We attributed these temperature changes to the following series of events. As the stable

Fig. 3 Optical micrographs of Al-20 mass%Ni alloy for various processes: (a) no stirring, (b) stirring, (c) Ni powder addition and stirring.

Fig. 4 Temperature change of molten Al with Ni addition.

phase is a single phase of liquid when the powder is first added, the molten Al and the Ni powder rapidly react. Within seconds, all of the added Ni powder is therefore changed to Al_3Ni and it dissolves in the melt. Next, when the Ni concentration saturates, the reaction between the molten Al and the Ni powder gradually slows down until it involves only the surface of the Ni powder. As the amount of Ni contributing to the reaction thus decreases, the temperature of the melt decreases along with it. The subsequent increase in the temperature, the second peak, results from the increase in the amount of reacting Ni powder due to its successive addition.

In the case of Fig. 4, the rate of addition was 1.9 g/min. As the rate of addition increased, the temperature increase of the melt tended to accelerate in parallel. This rate must be carefully controlled, as the intermetallic compounds will grow dendritic (see Fig. 3) if the temperature finally rises above liquidus.

3.1.3 Reaction between powder and melt

Figure 5 shows the solidification microstructure of molten pure Al mixed with 20 mass% Ni powder (under $53\mu\text{m}$) at 943 K and quenched in water seconds after the powder addition. A spot EDX analysis confirmed an Al_3Ni phase (darkened areas in Fig. 5), an un-reacted Ni phase at the center of the powder, and an intermediate Al_3Ni_2 phase between the Al_3Ni and un-reacted Ni. No other intermetallic compounds were detected. These observations were consistent with a report by Hibino on the rate of formation of Ni-Al

Fig. 5 Reaction between molten Al and Ni powder.

intermetallic compounds.¹⁸⁾ As seen in Fig. 5, the Ni powder does not instantly react and change to Al_3Ni as soon as it is added. On the contrary, the reaction with the molten Al gradually proceeds, working inward towards the center of the Ni powder from the outer surface, and the Al_3Ni particles smaller than the added Ni powder are dispersed into the matrix as a result of the stirring.

In light of the densities of the Ni, Al_3Ni_2 , and Al_3Ni , *i.e.*, 8.9×10^3 , 4.8×10^3 , and $4.0 \times 10^3 \text{ kg/m}^3$,¹⁹⁾ respectively, the Ni powder is thought to undergo an expansion reaction with the molten Al. The stress induced by the expansion probably works together with the shear force to refine the Al_3Ni .

3.2 Effects of processing variables on the microstructure

3.2.1 The effect of the revolution rate

Figure 6 shows the solidification microstructures of the molten pure Al mixed with 20 mass% Ni powder (under $53\mu\text{m}$) and stirred at various revolution rates for 10 min after the powder addition. The microstructures formed under the faster stirring conditions tended to consist of the finer Al_3Ni . We presume, in this case, that the increased shear force induced by the higher revolution separated the Al_3Ni from the Ni powder before it could grow large on the surface of the

Fig. 6 Influence of revolution rate on microstructure: (a) 1000 rpm, (b) 2000 rpm, (c) 3000 rpm.

Fig. 7 Influence of the size of the Ni powder on microstructure: (a) 3 ~ 5 μm, (b) < 53 μm, (c) < 150 μm.

Ni powder. In another test conducted at a revolution rate of 500 rpm, the stirring was too slow to generate a vortex or to pull any of the Ni powder down into the melt from the surface. The microstructure formed under the rapid stirring condition of 3000 rpm also included needle-like Fe compounds (Fig. 6(c)), presumably from the reaction between the AISI304 container and molten Al.

3.2.2 The effect of the size of the Ni powder

Figure 7 shows the solidification microstructures of the molten pure Al mixed with 20 mass% Ni powders of various sizes at 943 K and continuously stirred for 5 min after the powder addition. The microstructure formed from the relatively fine powder contained coarse compounds generated from the reaction between the segregated powder and molten Al (Fig. 7(a)). We attribute this to the method used to add the powder. Unable to automatically feed the powder using the powder feeder described in section 2, we had to manually introduce it little by little. When introduced in this discontinuous manner, the powder was likely to agglomerate. In the microstructures prepared using the relatively coarse powder, on the other hand, much of the Ni powder apparently settled due to the specific gravity difference at the lower part of the specimen with the un-reacted Ni phase (Fig. 7(c)). The microstructure prepared with the medium-grade powder exhibited a homogenous dispersion of fine Al_3Ni and no visible traces of Ni powder with an un-reacted Ni phase (Fig. 7(b)).

According to Stoke's law, the sedimentation velocity of a

Fig. 8 Sedimentation time for Ni and Al_3Ni particles as a function of diameter.

spherical particle through a motionless fluid is given by equation (2).

$$v = \frac{g \cdot D^2 \cdot (\rho_p - \rho_f)}{18 \cdot \mu} \quad (2)$$

where g is the acceleration due to gravity, D is the particle diameter, ρ_p is the particle density, ρ_f is the density of the fluid, and μ is the viscosity of the fluid. This equation can be used to estimate the time it takes for a compound to sediment to a height of 50 mm, the sedimentation height of molten Al. Figure 8 plots the sedimentation time when the ρ_p values are

Fig. 9 Influence of the temperature of molten Al alloy and the stirring time on the microstructure.

defined as the densities of Al_3Ni ($4.0 \times 10^3 \text{ kg/m}^3$) and Ni ($8.9 \times 10^3 \text{ kg/m}^3$), ρ_f is defined as the density of the molten Al at 973 K ($2.4 \times 10^3 \text{ kg/m}^{320}$), and the viscosity of the molten Al is assumed to be that of water ($0.001 \text{ Pa}\cdot\text{s}$). As we clearly see, the sedimentation time significantly decreases when the size of the compound increases and when a powder with an un-reacted Ni phase is applied.

Under our experimental conditions, it took 1 min from the completion of the stirring before the melt was quenched. In the microstructure formed with the coarsest powder ($150 \mu\text{m}$), the powder settled to the lower part of the specimen in accordance with the previous result, as shown in Fig. 7(c). We attribute this to the relatively large particle size of the added Ni powder and the un-reacted large Ni phase in the powder. Given that the viscosity of the molten Al increases as the solid fraction increases, the sedimentation time in Fig. 8 could conceivably shift to a longer-time profile.

When we compare the diameters of the Al_3Ni particles dispersed in the matrix, the microstructure in Fig. 7(a) has the finest morphology. In other words, the finer Ni powder generated a finer grade of Al_3Ni . If we had been able to continuously introduce the fine powder, presumably we would have obtained a dispersion of exclusively fine Al_3Ni . In addition, the use of a fine Ni powder can shorten the processing time (the time required for the complete reaction of all the Ni with the molten Al).

3.2.3 Effects of the stirring time and molten Al temperature

Figure 9 shows the solidification microstructures of molten pure Al mixed with 20 mass% Ni powder (under $53 \mu\text{m}$) at various temperatures and continuously stirred for various times after the powder addition. In the batch stirred for 5 min, all of the Ni powder reacted to form Al_3Ni . The

morphology of Al_3Ni was granular at 943 and 973 K, but mostly needle-like at 1023 K, as shown in Fig. 3. The addition of the Ni powder at 1023 K increased the temperature of the molten Al to 1073 K. Thus, the temperature did not rise to liquidus; *i.e.*, 1087 K for the Al-20 mass%Ni, the target composition. The temperature of the molten Al probably increased above the liquidus locally, however, and the generation of Al_3Ni with a needle-like and coarse morphology probably took place during cooling. Figure 9 also shows the increase in the size of the Al_3Ni in parallel with the increasing stirring time. This change is probably attributable to Ostwald ripening and the combinations formed by pairs of colliding particles.

3.2.4 The effect of the amount of added Ni powder

Figure 10 shows the solidification microstructures of molten pure Al mixed with various amounts of Ni powder (under $53 \mu\text{m}$) at 943 K and continuously stirred for 10 min after the powder addition. An increase in the amount of Ni powder led to an increase in the amount of Al_3Ni , as expected from Fig. 2. The coarseness of the Al_3Ni also tended to increase as more Ni was added. This enhanced coarsening of the Al_3Ni can be attributed to two factors: first, the longer addition times and stirring times required for the additions of progressively larger amounts of Ni powder; and second, the increase in the temperature of the molten Al induced by the increase in the total heat of formation. Taken together, these results suggest that we can produce materials with dispersed Al_3Ni of a proper size and fraction by appropriately controlling the process variables.

3.3 Al-Ti system

Figure 11 shows the solidification microstructures of the molten pure Al mixed with Ti powder (under $150 \mu\text{m}$) at 943 or 973 K and continuously stirred for 5 or 30 min after the

Fig. 10 Influence of the amount of Ni addition on the microstructure: (a) 5.6 g, (b) 8.8 g, (c) 12.5 g, (d) 16.7 g.

Fig. 11 Optical micrographs of Al-10 mass%Ti alloy under various conditions: (a) Temp.: 943 K, Stirring time: 5 min. (b) Temp.: 973 K, Stirring time: 30 min.

powder addition. In the microstructure formed under the 943 K mixture and the 5 min stirring condition (Fig. 11(a)), most of the powder exhibited an un-reacted Ti phase, although the surface of the Ti powder and molten Al reacted. In an effort to enhance the reaction between the Ti powder and molten Al, we repeated the experiment with an increased temperature of 973 K and stirring time of 30 min (Fig. 11(b)). No traces of any un-reacted Ti phase were found in the microstructure, and Al_3Ti was finely and homogeneously dispersed. However the latter condition apparently led to a

partial dissolution of the AISI304 container and an Fe-enriched zone was found in the microstructure (see the arrow in Fig. 11(b)). These results indicate that the process in this study can be applied to the Al-Ti system as well as the Al-Ni system. The main difference between the two systems is reactivity; the Ti powder is less reactive to Al than the Ni powder. The heat of formation (standard enthalpy of formation at 973 K), 181 kJ/mol,²⁰⁾ is comparable to that of Al_3Ni , 190 kJ/mol. In our experiments, however, the temperature increase induced by the addition of the Ni powder

Fig. 12 Optical micrographs of intermetallic compounds dispersed aluminum alloys: (a) Al_3Zr , (b) Al_7Cr , (c) Al_{12}Mo .

(under 150 μm) was 38 K. On the other hand, the addition of a Ti powder of the same grade as the Ni powder above did not induce any apparent increase in the temperature of the molten Al. In separate experiments using a relatively fine Ti powder (63 to 90 μm), however, we observed no apparent increase in the temperature of the molten Al, and most of the powder exhibited an un-reacted Ti phase. These findings might have been due to the effects of the powder oxidation. Such details will be discussed in the next section.

3.4 Other systems

Figure 12 shows the solidification microstructures of molten pure Al mixed with 10 mass% Zr, Cr, or Mo powder at 943 K and continuously stirred for 5 to 10 min after the powder addition. Granular intermetallic compounds were well dispersed in the Al matrix in all cases. Moreover, the intermetallic compounds were confirmed to be in equilibrium with the α -Al phase in the phase diagrams by X-ray diffraction. Fig. 13 shows the X-ray diffraction pattern of the specimen with Zr powder as an example. The Zr powder was added under Ar. In an earlier attempt to add the Zr powder in air, the powder addition induced a rapid oxidation reaction which prevented the production and homogenous dispersion of Al_3Zr after only 10 min of stirring. On the other hand, attempts to add W or Fe powder to the molten Al resulted in a segregation of the powder at the surface and bottom of the melt, a condition which prevented dispersion of the intermetallic compounds.

The result of the Zr powder addition suggests that the oxidation of the metal powder influenced the difference in the dispersion behavior of the intermetallic compounds. Metal powders must be wetted with molten Al if intermetallic compounds are to be formed. However, when a powder is

Fig. 13 X-ray diffraction pattern of Al-Zr alloy.

oxidized by air before it enters molten Al, its wettability in the molten Al declines and the oxidized powder segregates without reacting at the surface and bottom of the melt. As reported in a previous section, the Ti powder is less reactive to Al than the Ni powder. The lower reactivity of the former is probably attributable to the barrier effect of the Ti powder oxide layer. Even if the powder is oxidized, it can be deoxidized by the thermite reaction with the molten Al. Table 2 shows the standard free energy of formation of representative oxides at 943 K.¹⁷⁾ Given that all of the oxides except ZrO_2 have lower values than Al_2O_3 , we know that thermite reactions are possible. However, sufficient contact between the powder and molten Al is a necessary condition. In the experiment with the W powder, the powder settled to the bottom of the melt due to the high density of W relative to that of the molten Al. Thus, the absence of the thermite

Table 2 Gibbs standard free energy of oxide formation at 943 K.

(kJ/mol O ₂)			
NiO	−308	MoO ₂	−415
TiO ₂	−772	WO ₂	−411
ZrO ₂	−921	Fe ₃ O ₄	−402
Cr ₂ O ₃	−589	Al ₂ O ₃	−921

Fig. 14 Optical micrograph of AC8A-Al₃Ni composite.

reaction may have been partly due to the poor contact between the powder and molten Al.

In summary, the dispersion behavior of intermetallic compounds is influenced by the oxidation rate, the rate of the thermite reaction, and the density difference between the powder and melt, as well as the rate of formation of intermetallic compounds induced by the direct reaction between the metal powder and melt.

There were considerable differences in the sizes of the intermetallic compounds which were homogeneously dispersed. The Al₃Zr particles, the smallest, were only a few micrometers in diameter. Thus, the particles sizes of the produced intermetallic compounds were clearly very dependent on the specific elemental metal powder added. Further investigations into the finer details of the reaction processes will elucidate the reasons for this.

3.5 Application to an alloy in service

In the previous sections, we described the properties of the microstructures of pure Al with various added metal powders. In pursuit of practical applications, we applied the same process to JIS AC8A, an alloy with an excellent heat resistance and wear resistance among the various JIS Al alloys currently in use. Figure 14 shows the solidification microstructure of the molten AC8A alloy mixed with Ni powder (under 53 μm) at 853 K. The amount of the Ni powder was 20 mass% and the stirring was continued for 10 min after the powder addition. Though coarse Si was observed in some portions of the microstructure (indicated by

the arrow in Fig. 14), the dark gray areas indicating granularly-shaped Al₃Ni were homogeneously dispersed. On the basis of this result, we believe that the process is probably applicable to various Al alloys. By optimizing the composition of the Al matrix, we expect to produce new Al-based composites with a high hardness and other attractive properties typically seen in intermetallic compounds.

4. Conclusion

We have tried to produce new materials reinforced with homogenous dispersions of fine intermetallic compounds by adding metal powder to molten Al and stirring the melt to induce the formation of intermetallic compounds *in situ*. The important results are listed below.

- (1) The intermetallic compounds produced by the process applied in our experiments tend to be fine and granular, though they exhibit a coarse and needle-like morphology in conventional castings.
- (2) The sizes of the intermetallic compounds formed *in situ* decrease as the size of added metal powder decreases.
- (3) Lower process temperatures and reduced stirring times refine the intermetallic compounds.
- (4) The sizes of the intermetallic compounds formed *in situ* are highly dependent on the types of added metal powders.
- (5) The process investigated in this study can be applied to various transition metals and molten Al alloys.

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