Utilization of Al Scrap for Fabrication of Al(alloy)/Al₂O₃ Composite Material

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In status quo, Al scrap melt is diluted with pure Al and adjusted its composition for reuse. We studied a method to utilize Al scrap directly for fabricating composite materials, which can be used for machine elements having resistance to abrasion. The composite material is a product of displacement reaction between molten Al scrap and SiO₂. Its microstructure consists of Al₂O₃ network and Al alloy among them. In this study, Al alloy was prepared which have a composition of Al scrap due to window frame of houses. The synthesized Al scrap are melted and reacted with SiO₂ at 1473 K to obtain the composite material. The mechanical properties of this material were compared with Al/Al₂O₃ and (Al-Fe)/Al₂O₃ composite materials fabricated using pure Al, and Al-Fe alloy, respectively. It was demonstrated that the composite materials using scrap had a little higher strength and hardness than Al/Al₂O₃, and they were not broken into pieces upon fracture, as occurred in the case of (Al-10 at%Fe)/Al₂O₃. Further studies needed for application of this method was discussed. It was pointed out that the reactivity and the property change with compositional fluctuations of the scraps and reduction of the reaction temperature have to be taken into consideration.

(Received February 3, 2003; Accepted April 8, 2003)

Keywords: aluminum scrap, recycle, composite material, displacement reaction, alumina, hardness, microstructure

1. Introduction

If Al scrap is utilized, it is possible to produce aluminum (Al) at much lower electric cost than to produce new Al by electrolytic refining.¹⁾ Al scraps have different compositions depending on the collection routes²⁾ as illustrated in Table 1. It is to be noted that Fe contamination is one of the problems for their reuse, because Fe impurity deteriorates the ductility of Al. And Fe is known as one of the elements which are difficult to be removed from the alloy melt.³⁾ In status quo, in order to overcome this difficulty, pure Al is added to the scrap melt for dilution and the compositions are adjusted for reuse.⁴⁾ Considering these backgrounds, it is of importance to find a new process to use Al scrap as a raw material for fabricating some functional materials.

The authors have performed studies⁵⁾ on fabricating Al/Al₂O₃ composite materials⁶⁾ using a displacement reaction between molten Al and vitreous silica (SiO₂), as follows:

This composite material has been known as an *in-situ* composite⁷⁾ and the process has a characteristic feature that an arbitrary shaped SiO₂ body changes into the composite body without changing their shape and size. In the subse-

quent study,⁸⁾ the composite materials were fabricated using Al-Fe alloy melt to improve the high temperature strength and to provide variations in their mechanical properties. The composite material of (Al-Fe)/Al₂O₃ contains only Al, Fe and O (and small amount of Si), thus they can be disposed by charging into a converter in the steel making process, for example. SiO₂ is abundant and the reaction by-product (Al melt containing Si) can be reused for casting.⁹⁾ Series of studies on these composite materials led us to an idea that this reaction process can be applied to utilization of Al scrap.

In this study, it is aimed to investigate the possibility of the displacement reaction of SiO₂ with molten Al scrap, then to investigate their microstructures and the mechanical properties for the practical use. Synthetic Al alloy having composition of the scrap was prepared and the composite materials are fabricated for this purpose. The studies are intended to be performed in comparison with that on the (Al-Fe)/Al₂O₃ systems.

2. Experimental

SiO₂ used in this study is a commercial vitreous silica rods (Toshiba Ceramics Ltd. T3010). Diameter of the rods is 5–15 mm and the length is 100 mm. The Al lumps have three

Table 1 Composition of Al scrap from different routes²⁾ and the synthetic Al scrap alloy used for this study.

	content/mass%						
	Si	Mn	Fe	Cu	Zn	Mg	Al
Scrap from heat exchanger	1	1	0.6	0.2	0.8	—	bal.
Scrap from car	7.8	0.6	0.5	3.1	0.6	0.4	bal.
Scrap from window frame	0.7	—	0.8	0.4	0.4	0.2	bal.
Scrap from Al can	0.24	0.89	0.43	0.02(Ti)	—	1.35	bal.
Synthetic Al scrap alloy (measured by means of ICP)	0.51	—	0.8	0.19	1	0.35	bal.

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nines in purity (Kojyundo Kagaku Ltd.).

In this study, Al scrap alloy having composition due to window frame of house was selected (Table 1). Al-Fe alloy and the synthetic Al scrap were prepared as the following methods: Electrolytically refined Fe lump (Toho-Aen, Atomiron LX-30, 99.99%) was melted together with Al. Si was added by immersing SiO₂ rod into Al melt (by eq. 1). Immersion time period was determined by try and error. Mg and Zn were wrapped with Al foils and thrown into the melt. The alloy composition was determined by means of ICP. The measured composition of the synthetic scrap alloy is also listed in Table 1.

The alloys were melted in Ar atmosphere either in an electric resistance furnace (SiC heating element) or in an induction furnace. SiO₂ rods were immersed into the melt and they were reacted for the given time period. After the reaction, specimens for the rate measurements were quenched into water, and specimens for the strength measurements were cooled in air.

Microstructures of the obtained composite body specimens were observed by means of an optical microscope (OM, Olympus, BX60). X-ray diffraction (XRD, Rad-B, Rigaku) was taken to identify the existing phase in the composite materials. The local compositional distributions were measured by means of energy dispersive X-ray spectroscopy (EDX) attached with SEM (Hitachi, S-6501).

Compressive strength of the composites was measured at room temperature. Specimens for the compression test were rods of 5 mm in diameter and 7 mm in length. The displacement speed was $8.3 \times 10^{-6} \text{ ms}^{-1}$ (0.5 mm/min). Vickers hardness of the composite materials was measured with imposing a load of 49 N.

3. Results and Discussion

3.1 Reactivity

In order to estimate the reaction rate with Al alloy having the scrap composition, it is appropriate to compare the rates between SiO₂ and Al-Fe alloy (in the previous study⁸⁾). Changes of the reaction layer thickness were measured for the alloy melts having different Fe contents at 1473 K. This reaction temperature was selected because of high reaction rate and giving rise fairly good mechanical properties. And the range of liquid phase is broad in Al-Fe phase diagram above 1473 K. The relationships between the reaction time and the reacted layer thickness are shown in Fig. 1. Linear dependence was obtained in the pure Al case, however, the curves deviate from the linear behavior as an increase of Fe content. Reaction halted after formation of the initial reaction layer at composition of 30 at%Fe.

The synthetic Al scrap was melted at 1473 K and reacted with SiO₂ rod for 4 h. The rod of 5 mm in diameter was possible to be converted into the composite body within this time period, by observation of their cross section. The time period was enough for completion of the reaction, considering the Al-Fe case (Fig. 1). The detailed reaction rate and its dependence on the impurity concentration will be investigated in the future study.

According to these results, Fe content in the scrap is not considered to hinder the rate very much. Here, it is of

Fig. 1 Dependence of reaction layer thickness (d) on reaction time (t) between SiO₂ and molten Al-Fe alloy having various Fe contents.

importance to consider the effects of other impurities in the scrap on the reaction rate. As discussed before,⁸⁾ Fe is an element having an interaction with Si, such as to form silicides. Si is present in the Al-Fe melt as the by-product of the reaction, and interacts with Fe. Elements of Zn and Cu are the same kinds, thus, they are expected to retard the reaction kinetics, as the Fe case. On the other hand, Mg has stronger affinity with oxygen than Al, and it is expected that Mg is contained in the ceramic (Al₂O₃) parts. The effect of Mg addition is not clarified so far, completely, because there are controversial reports, such as to be drastically inhibitive to the reaction¹⁰⁾ or to improve the wettability of SiO₂ and molten Al.¹¹⁾ Effect of Si on the reaction kinetics might be different from them. Although there is no aluminum silicide, solute Si affects the properties of liquid Al. Microscopic mechanisms to retard the kinetics of by Si generated at the reaction interface are proposed.¹²⁾ It is necessary to perform the detailed study on the relationship between addition of various elements and the reaction kinetics. We are preparing for the further study from this point of view.

3.2 Microstructure

Al/Al₂O₃ composite materials obtained by the displacement reaction (1) has a microstructure consisting of mutually connecting Al₂O₃ networks and Al, which exists among them. Si is contained in Al parts with the content of a few atomic percent. The volume fraction of Al is usually less than 35%. The composite body using molten Al scrap has similar but a little coarse microstructures. The photographs are shown in Fig. 2, where dark and bright areas are seen. They correspond to Al₂O₃ and Al parts, respectively. The coarsened microstructure by addition of Mg is consistent with the previous report.¹¹⁾

Existing phases in the composite material using Al scrap were determined by XRD and the profile is shown in Fig. 3. Al and α -Al₂O₃ phases were detected, similar to the Al/Al₂O₃ cases.⁵⁾ It was shown that compounds of MgSiO and MgAlSiO phases existed but no MgO phase was detected,

Fig. 2 Optical micrographs of composite materials fabricated using (a) pure Al and (b) synthetic Al scrap alloy.

Fig. 3 XRD profile from composite material fabricated using synthetic Al scrap alloy.

indicating that Mg was incorporated into the ceramic phase together with Al. Si is also incorporated in this case. There are other unidentified peaks due to intermetallic compounds which might exist in the metal parts. Major peaks of those phases (if existed) are overlapped with the other main peaks in the profile, and they are not identified.

The compositional distribution in the transverse cross section of the rods was relatively homogeneous. Namely, content of each element was mostly similar between the edge area and the central area of the specimens. The microscopic distribution of the composition was observed by means of SEM/EDX. It was shown in Fig. 4 that Mg is higher in the ceramic phase and the profile is complementary to that of Fe, thus Mg existed in ceramic phase and the other elements (Fe, Cu and Zn) are accumulated in the metal phase. This phenomenon is consistent with the prediction based on the thermodynamics.¹³⁾

3.3 Mechanical properties of the composite materials

Compressive fracture stress of Al/Al₂O₃ and (Al-Fe)/Al₂O₃ is plotted in Fig. 5. In (Al-5 at%Fe)/Al₂O₃ specimens, compressive fracture stress is higher and the data are less scattered than Al/Al₂O₃. However, the strength decreased at 10 at%Fe case. All the tested composite materials fractured in a brittle manner. Among them, the (Al-10 at%Fe)/Al₂O₃ composite material was especially brittle as the specimens were fragmented into pieces upon fracture.

Fig. 4 SEM photograph and EDX profile from the area indicated by arrows. The bright areas in the microstructure correspond to ceramics.

The strength data of the composite materials using Al scrap is shown in the right side of Fig. 5. The strength was between Al/Al₂O₃ and (Al-5 at%Fe)/Al₂O₃, and consistent with the results of the Al-Fe cases. The materials using Al scrap were not very brittle as the (Al-10 at%Fe)/Al₂O₃, and the fracture surface was inclined 45 degree with respect to the longitudinal axis.

Fig. 5 Relationship between Fe content (c) and compressive fracture stress (σ_f) of (Al-Fe)/Al₂O₃ composite materials (left) and compressive fracture stress of composite materials using synthetic Al scrap alloy (right).

Fig. 6 Vickers hardness (H_v) of (Al-Fe)/Al₂O₃ composite material as a function of Fe content of alloy melt (c) (left) and the hardness of composite material fabricated using scrap alloy (right).

In Fig. 6, dependence of the hardness of (Al-Fe)/Al₂O₃ composite materials on the Fe content is plotted. It is shown that the hardness increased as an increase of Fe content up to about 20 at%, then the values are saturated. Hardness increased due to strengthening of the metal parts in the composites by alloying with Fe. The composite body using a synthetic Al scrap alloy had hardness value of about 400 GPa, which is a little higher or mostly same as that of Al/Al₂O₃. Other elements in the scrap are in the metal parts either in the solid solution or in the precipitates (intermetallic compounds). They hinder the plastic deformation of the metal part and the hardness is increased.

3.4 Consideration of the composite material using Al scrap in practical use

In this study, it was shown that the composite material fabricated using synthetic Al scrap alloy had a little higher strength and hardness than the Al/Al₂O₃ materials. The material was not too brittle as the (Al-10 at%Fe)/Al₂O₃. The

mechanical properties of the composite material seem to be even better than Al/Al₂O₃.

The Al/Al₂O₃ composite material has originally high hardness and its near-net shape process is attractive. Thus, this material is expected to be applicable to some machine elements used under abrasive conditions. The hard machine elements having complicated shapes, which are difficult to be formed by grinding can be fabricated by this method. The composite materials obtained using Al scrap can be applied for the same purpose.

However, in order to design the actual fabrication processes by using Al scrap, we have to perform further studies on the changes in reactivity and mechanical properties with fluctuation of the scrap compositions, though an approximate prediction can be made using the Al-Fe data.

In this study, the reaction temperature was set to 1473 K, which is higher than the melting temperature of the Al scrap (<1000 K) in industry. Raising the melting temperature of Al scrap is not cost-effective. Therefore, reduction of the reaction temperature should be taken into consideration. The actual scrap can be melted at lower temperature, because the contents of the impurity elements are not so high as to raise the liquidus very much. However, if the temperature is below 1373 K, the displacement reaction rate becomes low⁸⁾ and the materials are very brittle due to existence of different Al₂O₃ phases.¹⁴⁾ Therefore, reaction temperature about 1350 K might be the optimum.

4. Conclusion

Synthesized Al scrap alloy was melted and reacted with SiO₂ and (Al-Scrap)/Al₂O₃ composite material was fabricated. The following results were obtained:

- (1) SiO₂ reacted with synthetic Al scrap alloy melt (scrap composition due to window frame) at 1473 K. Microstructure of the composite materials was not altered very much from Al/Al₂O₃ essentially, if Al scrap was utilized as the raw materials. There was no large macroscopic segregation of the elements, but the elements were distributed separately in both phases, microscopically. The composite materials had a little higher strength and hardness than Al/Al₂O₃, and it was not fractured into pieces as the case of (Al-10 at%Fe)/Al₂O₃.
- (2) Aspects to be considered for utilization of Al scrap were discussed, and it was pointed out that the further studies are needed to clarify their reactivity and the property dependence on the compositional fluctuation in the scrap, and that reduction in the reaction temperature must be taken into consideration.

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