Novel Recycling System of Aluminum and Iron Wastes-in-situ Al-Al₃Fe Functionally Graded Material Manufactured by a Centrifugal Method-

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In this study, the concept of novel recycling system using waste Al and Fe is described. Taking advantage of the fact that due to its cyclic usage, aluminum scrap unavoidably contains iron and steel wastes, an in-situ Al-Al₃Fe functionally graded material (FGM) is planned to be fabricated. A centrifugal method is applied to a model master alloy, Al-10 mass% Fe, obtained from virgin materials, the content of which is decided from the liquidus temperature. The resulting product is a thick-walled tube having a graded distribution of second phase particles in the Al matrix. It has been established that the shape of the particles varies depending on their position along the radial direction. The second phase is confirmed to be a stable Al₁₁Fe intermetallic compound. Thin plates of Al₁₁Fe having homogeneously distributed Al₁₁Fe particles, considering both the composition gradient and the particle morphology, were machined from the thick-walled tube. The mechanical properties measured. Based on the experimental observations, the potential and the advantages of the Al-Al₃Fe alloy as a recyclable eco-FGM are discussed.

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1. Introduction

In recent years much effort is being expended in protecting the earth’s environment and one of the most desirable concepts that have been established through these developments is the recycling of waste materials. Aluminum waste must be one of the most desirable materials for recycling or re-using. This is because the energy costs involved in its production can be reduced by up to 95% by recycling Al scrap, as the production of Al from its ore, bauxite, is an energy consuming and very expensive process. ¹) However, the Al recycled from scrap is usually contaminated by many impurity elements, Fe being the most common one. Therefore, the refinement of Al alloy from such scrap wastes has high costs associated with it, because of the difficulties involved in removing Fe and other impurities from an Al alloy melt. In this case, it is desirable to be able to recycle the Al scrap into a component and/or structural material, with the minimum constituent adjustment possible, based on the ecological concept of recycling, as opposed to the prevailing disposal concept associated with dissipation of resources. In addition, in the Al matrix, Fe precipitates and/or crystallizes in the form of Al-Fe intermetallic compounds and such Al-Fe intermetallic compounds are known to exhibit extremely high resistance against corrosion and oxidation at elevated temperatures, as well as in general exhibiting high strength and hardness. The authors have produced Al-based functionally graded materials (FGMs) by a centrifugal method,²⁻⁵ where the FGM is an advanced composite that exhibits continuous changes of microstructure, composition and/or properties in specific directions. In the Al-Fe system FGM by the centrifugal method can be achieved easily using Al₁₀ mass% Fe, where the liquidus temperature is under 900°C with reference to the Al-Fe binary phase diagram shown in Fig. 1. Al-Fe alloy containing more than 10 mass% Fe has a higher melting point, which makes dissolution in the system difficult, and in addition, a temperature of over 900°C causes severe

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Fig. 1 Al-Fe binary phase diagram after Massalski.⁶
oxidation of the liquid aluminum. In the case of Al-10 mass% Fe alloy, it is expected that stable Al$_3$Fe particles are dispersed in the direction of the centrifugal force, having a graded volume fraction, although there are some metastable particles such as Al$_6$Fe and Al$_{12}$Fe$_2$. It is difficult to establish the basic mechanical properties of Al$_3$Fe, Al-Al$_3$Fe composite and Al-Al$_3$Fe FGM, because of little interest for its practical use, as known from various reports. However, it is meaningful to measure the basic mechanical properties of Al-Al$_3$Fe FGM for the development of FGM as a structural and/or component material when the recycling system is established, expecting therefore an increase in the practical interest of the Al-Al$_3$Fe composite and Al-Al$_3$Fe FGM.

Our final goal is to develop this novel recycling system of Al and Fe scrap wastes. However, in this study, a model Al-Al$_3$Fe FGM will be fabricated from virgin materials by the centrifugal method, and its mechanical properties will be measured in order to support its further development as an eco-FGM. Based on the experimental observations, the potential and the advantages of Al-Al$_3$Fe alloy as a recyclable FGM are discussed. If it is possible to utilize the Al-Fe system FGM commercially, the scrap waste-used FGM recyclable FGM are discussed. If it is possible to utilize the Al-Fe system FGM commercially, the scrap waste-used FGM must be recycled again by the centrifugal method.

2. Experimental Procedure

2.1 Material and vacuum centrifugal method

A model Al-Fe alloy containing nominally 10 mass% Fe is used in the present study. The master alloy, which was melted in a crucible furnace by mixing commercial pure Al of 0.04 Si, 0.06 Fe, 0.00 Cu, 0.01 Mn, 99.89 Al (mass%) and commercial Al-Fe alloy powder of 48.03 Al, 51.50 Fe, 0.16 Mn, 0.04 Si, 0.01 P, 0.01 S, 0.03 C (mass%), was made in our laboratory. The process of making the master alloy is as follows: A weight of 400 g pure Al was melted in a crucible furnace at 820°C under Ar gas atmosphere and then 17 g of Al-Fe alloy powder wrapped in Al foil was put into the melt and stirred for 20 ~ 30 minutes. After full dissolution, the next batch was added and the temperature of the furnace was raised at an increment of 15°C. The same procedure was repeated 6 times in order to produce one alloy ingot. Following this, the ingot was cut into 4 pieces, melted again and stirred over 6 hours at 900°C to achieve a uniform composition and finally the Al-10 mass% Fe master alloy was obtained.

The vacuum centrifugal method (centrifugal method under evacuated condition)$^{15}$ is applied to the alloy and a thick-walled tube with 90 mm diameter × 90 mm length × 15 mm thickness was manufactured. From the phase diagram of Al-Fe system, shown in Fig. 1, it is found that the Al$_3$Fe intermetallic compound, whose melting point is ~1160°C, nucleates in the present Al-10 mass% Fe melt. However, metastable phases of Al$_6$Fe, Al$_{12}$Fe$_2$, etc. were reported in the Al-Fe system.$^{9-11}$ The crystal structure of Al$_3$Fe is known to be a monoclinic system with unit cell size $a = 1.5487$ nm, $b = 0.8083$ nm, $c = 1.2476$ nm and $\beta = 107.43^{\circ}$. Thus, the density of Al$_3$Fe is obtained as $\rho_{AlFe} = 3900$ kg/m$^3$, which is greater than the densities of molten Al (2315 kg/m$^3$ at 900°C)$^{12}$ and solid Al ($\rho_{Al} = 2700$ kg/m$^3$). Owing to the density difference between Al$_3$Fe and the melt, an Al-Al$_3$Fe FGM tube, where Al$_3$Fe is rich at the outer region, must be manufactured even if metastable phases exist, since they must behave in a similar manner.

The vacuum centrifugal casting system was used in this experiment in order to avoid undesirable oxidation of the material. This system consists of an alloy melting furnace, inlet, mold, etc., which are set in a chamber of about 0.2 m$^3$ as shown in Fig. 2. A batch of about 1 kg alloy lumps, which were cut from the master alloy, was melted in the crucible furnace at 900°C under Ar gas atmosphere. After the alloy was melted, the lids of the chamber were closed and a pump evacuated the vacuum chamber. The melt was kept over 1 hour under the vacuum condition in order to remove the gas dissolved in the alloy melt. The melt was then poured into the rotating mold through the inlet. Both the inlet and the mold were pre-heated to about 620°C, guarding against solidification before the melt is fully poured into the mold. 10 minutes later, air was introduced into the chamber and the mold was subjected to forced air-cooling. Here, the effect of centrifugal force was evaluated by a parameter of $G$ number, which is the ratio of the centrifugal force to the gravity and is calculated as:

$$G = 2DN^2$$

(1)

where $D$ is the diameter of the casting tube (m) and $N$ is the rate of revolution (s$^{-1}$). In the present study, $D = 9 \times 10^{-2}$ m and $N = 34.6$ s$^{-1}$, i.e., 2070 rpm, and the molten alloy experiences about 216 times the gravity force.

2.2 Specimen and experiments

The thick walled FGM tube was initially cut into bars having a circular arc cross-section. Each bar was then subjected to slight hot working, in its thickness direction, at 620°C allowing the circular arc to be deformed into a flat portion of 10 mm width in the cross-section. Then, both the morphology of the second phase and the composition gradient in the bars were characterized by optical microscopy from metallographic samples prepared by standard metallographic polishing techniques. Microscopic observation was easily done without any etching because the colors of the precipitated second phase and the Al matrix is clearly different, and they are dark gray and whitish, respectively.
Both quantitative energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analyses were performed in order to identify the structure of the second phase. The shape of Al$_3$Fe particles was evaluated by using the circularity, $F$, which is given by the following equation:

$$F = 4\pi S/L^2$$

where $L$ is perimeter length of the particle and $S$ is the area of the cross-section of the particle. The circularity ranges between the values $F = 0$ and $F = 1$, and it is 1 for a perfect circle. The density of specimen is measured by using the suspension method.

From the flattened FGM bars, 4-point bending and tensile specimens were machined by an electric spark discharge machine, considering both the distribution and morphology of the second phase such that the thickness direction coincides with the radial direction of the original FGM tube. Both tensile and bending tests were carried out using a 5 kN screw driven tensile-compression testing machine at a cross-head speed of 0.5 mm/min. For the 4-point bending tests, plate specimens of 9 mm width $\times$ 2.5 mm thickness $\times$ 67 mm length were set as shown in Fig. 3(a). The shape of the standard tensile specimen of 1.6 mm thickness is shown in Fig. 3(b). Strains for both bending and tensile tests were monitored by strain gauges, with 2 mm grid length $\times$ 1.3 mm width, adhered on both plate planes. Fractographic observations of fractured tensile specimens were carried out using scanning electron microscopy (SEM) and the crack paths were observed by optical microscopy (OM).

### 3. Results and Discussion

#### 3.1 Morphology of second phase

The microstructure of the present FGM and the corresponding variation of volume fraction of second phase particles were evaluated by computer graphic analysis and are shown in Fig. 4. EDX spectra indicate that the second phase does not comprise of metastable phases of Al$_6$Fe and Al$_9$Fe$_2$ but judging from their relative intensity, a stable Al$_3$Fe phase. Figure 5 shows XRD patterns of the FGM measured from Al plane to a plane containing second phase, using a step by step milling operation of 0.1 mm thickness. In Fig. 5, only the Al structure is observed at the lower XRD pattern and then the Al$_3$Fe intermetallic compound gradually appears. The upper XRD pattern in Fig. 5 shows a perfect Al$_3$Fe structure. Both EDX and XRD analyses show that the whitish part is the Al matrix and dark particles are Al$_3$Fe intermetallic compound whose shapes are bar and/or block with over several hundred $\mu$m in length. This is the result of the vacuum centrifugal casting system, because the heat-retaining vacuum chamber makes the solidification rate slow and therefore the metastable phase does not exist, which is different from direct chill casting. Thus, the FGM is identified as Al-Al$_3$Fe FGM and the volume fraction of Al$_3$Fe phase in the thick walled tube is decreases gradually from 40 vol% at the outside of the tube to 0 vol% at the inside.

It is also observed from Fig. 4 that both particle shape and particle size change from place to place. Granular-like Al$_3$Fe particles are formed at the outer region of the tube and stick-like Al$_3$Fe particles are formed at the inner region. The thickness direction is divided into three regions, as shown in Fig. 4, and the circularity and area-equivalent diameter of particles in each region are evaluated from the micrographs. Table 1 summarizes the results and shows that larger value of
in a mold. It is proposed that the variation of morphology must be due to the slow cooling rate is larger than that at the inner region. It is proposed that the migration distance is greater in the case of larger particles is proportional to the square of the particle diameter, and cooling rate distribution within the FGM tube becomes uniform and as a result, the mechanism to form a graded composition resembles the case of FGM produced by the centrifugal solid-particle method. A similar result is observed in Al-12Ni FGMs fabricated using in furnace cooling, where the temperature gradient and cooling rate during solidification should be small.

Figure 4 also shows the corresponding positions of both thin plate bending and tensile specimens in a thick-walled tube. The shapes of Al$_3$Fe particles in both specimens are different because the shapes of the particles vary macroscopically, depending on the radial position within the tube. Bending and tensile specimens have granular-like and stick-like particles, respectively. Circularity and area-equivalent diameter of particles of bending specimens are 0.34 and 61\(\mu\)m, respectively and 0.30 and 34\(\mu\)m for the tensile specimens. However, it is difficult to find microscopically any composition gradient in each specimen, because the thin thickness variation of 1.6–2.5 mm must be within the gradation. The number of particles contained in 1 mm thickness is more than 10 and they appear uniformly distributed without any detectable graded distribution. As a result, each specimen is treated not as an FGM but as a composite. Based on the assumption of a composite, the volume fraction of Al$_3$Fe particles in each specimen is evaluated again macroscopically using an equation based on a rule of mixtures:

\[
v_f = \frac{\rho_{Al} - \rho}{\rho_{Al} - \rho_{AlFe}}
\]

where, \(v_f\) is volume fraction and \(\rho\) is measured density. The densities of bending and tensile specimens were measured to be \(\rho = 3156\ kg/m^3\) and \(\rho = 3030\ kg/m^3\), respectively. Therefore volumes \(v_f = 0.38\) and \(v_f = 0.28\), are obtained respectively from eq. (3), since it can be assumed that casting defects such as gas holes, internal porosity, etc., which cause density reductions, would be eliminated by the vacuum centrifugal method. There is no contradiction with the distribution curve of Fig. 4.

3.2 Measurement of Young’s modulus

Elastic modulus is a key issue in materials science and engineering and it characterizes the mechanical properties of a material. 4-point bending testing is one of the conventional methods used to measure Young’s modulus. The bending specimen is an Al-38 vol\% Al$_3$Fe composite plate which contains the granular-like Al$_3$Fe phase and is cut from the Al-Al$_3$Fe FGM thick-walled tube at the position shown in Fig. 4. The circularity of the Al$_3$Fe phase within the bending specimen is 0.34. Young’s modulus is given by the following equation:

\[
E = \frac{3PL_1 - L_2}{2bh^2\varepsilon}
\]

where, \(E\) is Young’s modulus, \(P\) is applied load, \(L_1\) is lower span distance (\(\approx 50\ mm\)), \(L_2\) is upper span distance (\(\approx 26\ mm\)), \(b\) is specimen width (\(\approx 9\ mm\)), \(h\) is specimen thickness (\(\approx 2.5\ mm\)) and \(\varepsilon\) is measured strain. In the present
study, strain of $643 \times 10^{-6}$ per 100 N applied load is obtained and by applying eq. (4) this result gives a value of $E = 99.5$ GPa. Here, Young’s modulus of a particle-distributed composite is estimated by applying Wakashima’s Equation:

$$E = (1 - v_1)E_{Al} + v_1E_{Al,Fe} = \frac{v_1(1 - v_1)(E_{Al} - E_{Al,Fe})^2}{(1/2 + v_1)E_{Al} + (1 - v_1)E_{Al,Fe}}$$

(5)

The volume fraction of Al$_3$Fe particles in the present specimen is $v_1 = 0.38$. Thus, Young’s modulus of $E_{Al,Fe}$ is calculated from eq. (5) using $v_1 = 0.38$ and $E_{Al} = 71$ GPa, and therefore $E_{Al,Fe} = 201$ GPa is estimated. The value is almost equivalent to Young’s modulus of Fe (200–210 GPa) while the density of Al$_3$Fe is half.

3.3 Stress vs strain curve

One of the basic properties of structural and/or component materials is tensile behavior, and the tensile specimen illustrated in Fig. 3(b) was cut from the Al-Al$_3$Fe FGM thick-walled tube at the position shown in Fig. 4. The tensile specimen is made of an Al-28 vol% Al$_3$Fe composite and it contains the stick-like Al$_3$Fe phase, where the circularity of the Al$_3$Fe phase is calculated to be 0.30. A typical stress vs strain curve, measured from the thin plate specimen, is shown in Fig. 6. The relation shows a smooth curve with slight undulations and abrupt rupture. The maximum tensile strength and fracture strain are obtained as 94 MPa and 0.49%, respectively. It is difficult to find any proportionally increasing zone, proportional limit and/or yield point from the stress vs strain curve in Fig. 6 even for such a small fracture strain. Moreover, there is no detectable reduction in area in any of the specimens. The reason for this is discussed later combined with fractographic observations. Young’s modulus of the Al-28 vol% Al$_3$Fe composite is estimated as $E = 90.4$ GPa from Eq. (5) using $v_1 = 0.28$, $E_{Al} = 71$ GPa and $E_{Al,Fe} = 201$ GPa and this value gives 52 MPa of 0.05% offset yield stress. 0.2% offset yield stress may be of a much higher value but it seems meaningless, as the fracture strain is very small. The small fracture strain and low strength values obtained clearly prevent any commercial use of the Al-Al$_3$Fe FGM and therefore some ideas should be put forward for improving the strength and ductility of these materials.

3.4 Fractographic features of tensile specimen

Typical fracture contours of the Al-28 vol%, Al$_3$Fe composite tensile specimen are shown in Fig. 7. The tensile direction is from the upper to the lower of the view and the fracture occurred along the Al$_3$Fe particle to form a jagged line. Many cracked Al$_3$Fe particles, small number of uncracked particles and many voids are visible in the Al matrix. An SEM micrograph of the typical fracture surface is shown in Fig. 8. In Fig. 8, the plate thickness direction is left to right. The fracture surface of Al$_3$Fe particles shows typical cleavage fracture of a smooth surface and occasionally with a river pattern as indicated by an arrow in Fig. 8. The Al matrix breaks in a ductile fracture manner, with small dimples that are surrounded by large Al$_3$Fe particles. However, the area fraction of Al$_3$Fe particles is far greater than the nominal 28 vol% of Al$_3$Fe. This is the result of coalescence of brittle cleavage fracture in Al$_3$Fe particles through the ductile Al matrix as indicated in Fig. 7. This feature indicates that the bonding strength of the interface between Al matrix and Al$_3$Fe particles is higher than the fracture strength of Al$_3$Fe particle itself, because it is difficult to find any intergranular cracking.

The fracture process is summarized as follows: At the beginning of the tensile test, cleavage fractures occur in many Al$_3$Fe particles and only the Al matrix bears the applied tensile load. This is supported by the fact that there is a small elastic portion in the stress-strain curve. As the applied load increases, the Al matrix suffers local elongation that constrains the crack opening of the transgranular crack in the Al$_3$Fe particles, and coalescence of the cleavage crack in Al$_3$Fe particles gradually proceeds through the Al matrix. The ductile fracture of the Al matrix leads to fine dimples and then the net area of cross-section of specimen gradually decreases. However, the gross cross-sectional area does not decrease apparently because fractured Al$_3$Fe particles are
compound is not understood. We are currently investigating the Al-Al$_3$Fe FGM through near-net-shape forming over the eutectic melting temperature.

3.6 Advantages of in-situ Al-Al$_3$Fe functionally graded material

It is often difficult to separate the ingredients from the metallic composite materials and the metallic composite materials are not suitable for the environment requirements of recycling or re-using. Most of the current FGMs are composite materials, and therefore it is also difficult to separate the ingredients from the FGMs. In contrast, in-situ FGMs have the possibility of recycling their component materials by using the very simple and easy method of remelting that allows them to be turned back to the original materials. Based on this concept, a recycling process for the in-situ Al-Al$_3$Fe FGM manufactured by the centrifugal method is shown in Fig. 9. As can be seen, the scrap waste-used FGM could be recycled again by the centrifugal method. As already mentioned above, the re-melting of Al requires only 5% of the energy to produce the same weight of primary Al from the ore, bauxite. Therefore, recycling and re-using of the scrap waste-used FGM are very important for minimizing the environmental load.

In this study, Al-Al$_3$Fe FGM could be successfully fabricated, not from waste Al and Fe but from virgin materials, by the centrifugal method. However, the concept also demonstrates the potential that an Al-Al$_3$Fe eco-FGM can also be fabricated from Al and Fe wastes. Fabricating an Al-Al$_3$Fe eco-FGM from Al and Fe wastes in order to evaluate its properties is currently being planned. Moreover, we are currently studying the near-net shape forming of the Al-Al$_3$Fe FGM over the eutectic melting point, in order to achieve better microstructure and mechanical properties for possible structural and/or component usage.

4. Conclusions

The ability to develop a novel recycling system of Al and Fe wastes is examined through the manufacturing of an Al-Al$_3$Fe functionally graded material (FGM) by the centrifugal method using Al-10 mass% Fe alloy. The character and mechanical properties of the Al-Al$_3$Fe material are analyzed for the development of the eco-FGM. The results of the present work are summarized below:

1. The second phase observed in a thick-walled tube is only stable Al$_3$Fe intermetallic compound; metastable phases of Al$_3$Fe, Al$_2$Fe$_2$, etc., were not found.
2. Both the gradation of Al$_3$Fe particle volume fraction and the morphology of the Al$_3$Fe particles are varied, depending on the position in the radial direction of the tube.
3. A value of 99.5 GPa for the Young’s modulus is obtained from 4-point bending test of Al-38 vol% Al$_3$Fe composite specimen and the Young’s modulus of the Al$_3$Fe is calculated as 201 GPa.
4. Values of 52 MPa of 0.05% off-set yield strength, 94 MPa of maximum tensile strength and 0.49% of fracture strain are obtained from an Al-28 vol% Al$_3$Fe composite tensile specimen.
Tensile fracture of Al-Al$_3$Fe specimen happens as a result of coalescence of brittle fracture in Al$_3$Fe particles through ductile fracture of Al matrix and therefore the fracture surface consists of cleavage plane of Al$_3$Fe and dimples of Al matrix.

For commercial usage, Al-Al$_3$Fe FGM with fine Al$_3$Fe particles is necessary that has more ductility and higher strength.

The scrap waste-used FGM can be recycled again by the centrifugal method, avoiding cascade recycling.

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