Thermal Stability, Microstructure and Mechanical Properties of Nanostructured Al-Ni-Mm-X (X = Cu and Fe) Alloys
Hot-Extruded from Gas-Atomized Powders

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The effects of Cu and Fe additions on the thermal stability, microstructure and mechanical properties of Al₈₄,Ni₈₄,Mm₆₅, Al₈₄,Ni₈₄,Mm₆₅,Mm₆₅(Cu₁, Mm₆₅,Ni₈₄,Mm₆₅(Fe) alloys, manufactured by gas atomization, degassing and hot-extrusion were investigated. All hot-extruded alloys consisted of homogeneously-distributed fine-grained fcc-Al matrix and intermetallic compounds. A substitution of 1 at% Al by Cu increased the thermal stability of the amorphous phase and produced alloy microstructure with smaller fcc-Al grains. On the other hand, the same substitution of 1 at% Al by Fe decreased the stability of the amorphous phase and produced larger fcc-Al grains. The formation of intermetallic compounds such as Al₆(Fe, Ni) and Al₃(Ce) was suppressed by the addition of Cu or Fe. Among the three alloys examined, the highest Vickers hardness and compressive strength were obtained for Al₈₄,Ni₈₄,Mm₆₅(Cu₁ alloy, and related to the lowest fcc-Al grain size attained from increased thermal stability with Cu addition. [doi:10.2320/matertrans.MRA2007631]

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1. Introduction

Increasing demand for high performance engineering components continuously drives the development of new and advanced materials. Amorphous and nanocrystalline Al alloys with transition and rare-earth metals have attracted considerable attention as possible high-strength and lightweight materials. For example Al-based amorphous alloys¹,² have been reported to exhibit tensile strengths in excess of 1000 MPa; about two times higher than the highest value for conventional crystalline Al-based alloys. Similarly nanocrystalline alloys fabricated by primary crystallization of an amorphous phase have been reported to exhibit useful mechanical properties that cannot be obtained from amorphous and conventional crystalline alloys.³,⁴ Also the hardening in these nanocrystalline alloys has been quantitatively explained using a rule of mixture model based on the volume fraction of the amorphous matrix and the Al-rich particles.⁵ However, most studies on Al-based amorphous alloys were fabricated by melt spinning processing, in spite of difficulties in mass production. For practical manufacturing of rapidly solidified amorphous and nanostructured alloy powders the gas atomization process is a promising processing method, because it is suitable for mass production. To prepare these alloys in bulk form, hot extrusion process is a good consolidation process of powders because severe plastic deformation occurs during consolidation. In previous study, the extrusion behavior of fully crystallized and partially devitrified nanostructured Al-Ni-Mm alloy was examined as a function of powder size, all prepared by gas atomization followed by degassing and hot extrusion.⁶ This paper reports a successful mass production of powders and consolidation of amorphous and nanostructured Al-Ni-Mm alloys with the addition of Cu and Fe. The effects of Cu and Fe additions on the thermal stability, microstructural development and mechanical properties of these alloys are presented.

2. Experimental

Master alloys of Al₈₄,Ni₈₄,Mm₆₅, Al₈₄,Ni₈₄,Mm₆₅,Cu₁, Al₈₄,Ni₈₄,Mm₆₅,Fe₁ were prepared by a high frequency induction melting of commercial pure metals in graphite crucibles in air. The Mn consists of 51 mass% Ce, 26 mass% La, 14.25 mass% Nd, 5.33 mass% Pr, 1.43 mass% Fe and 0.12 mass% Ba. Gas atomization process was carried out with confined N₂ gas atomizer, operating at a pressure of 1.4 MPa. The size and distribution of the powders was measured by conventional mechanical sieving, and sieved powders smaller than 26 μm were selected for consolidation by hot-extrusion. Powders of each alloy were first cold-pressed in an Al can to a packing density of 70%, and degassed for 1 hour at 400°C down to 10⁻³ Torr. Hot-extrusion was carried out at a ram speed of 2.5 mm/s, using an extrusion ratio of 25:1, and at temperature of 400 °C. The extruded alloy bars had a diameter of 10 mm, and did not exhibit any blistering or cracking on the surface.

Microstructural analysis of both as-solidified powders and extruded bars was carried out using scanning electron microscope (SEM) and transmission electron microscope (TEM), both equipped with X-ray Energy Dispersive Spectrometers (XEDS). The phase constituents in as-atomized powders and extruded bars were investigated by X-ray diffraction (XRD) using monochromatic Cu Kα1 radiation (λ = 0.1542 nm) at 30 kV and 40 mA settings. The crystallization behavior of rapidly solidified powders was investigated by differential scanning calorimetry (DSC) during heating at a rate of 20°C/min. Alloy bars were machined (5.5 mm in diameter and 9.35 mm in length) and compressive
strength was measured for each alloy using Instron 4206 with a cross head speed of 0.001 mm/min. The hardness of extruded alloys was measured using a Shimadzu Vickers hardness indenter with a 1 kg load.

3. Results and Discussion

3.1 Microstructure and phase constituents of gas-atomized powders

Figure 1 shows the cross-sectional secondary electron micrographs of as-atomized (a) Al$_{85}$Ni$_{8.5}$-Mm$_{6.5}$, (b) Al$_{84}$Ni$_{8.5}$-Mm$_{6.5}$Cu$_1$, and (c) Al$_{84}$Ni$_{8.5}$-Mm$_{6.5}$Fe$_1$ powders, respectively. Figs. 1(a) and 1(b) show featureless microstructure (at least by secondary electron) indicating a uniform response for etching. According to a previous study by Jones, two distinct microstructural zones, A and B, developed for Al-8 mass% Fe produced by splat quenching depending on the solidification rate. Zone A did not show any response to etching by Keller’s reagent (i.e., featureless) and was observed with a higher solidification rate near the chill substrate. Zone B, which is the region far from the chill substrate, on the other hand, was darkened by etching with the same Keller’s reagent, and constituted region that solidified with slower cooling rates. Since an increase in solidification rate leads to microstructural refinement, the nanocrystalline features or amorphous phase in fine powder cannot be resolved by secondary electron micrograph after etching. Figure 1(c) shows some response to etching, indicating less amorphousness of this alloy.

In order to examine the thermal stability and phase transformations during heat treatment, as-atomized powders were analyzed by differential scanning calorimetry (DSC). Figure 2 shows DSC traces for gas-atomized (a) Al$_{85}$Ni$_{8.5}$-Mm$_{6.5}$, (b) Al$_{84}$Ni$_{8.5}$-Mm$_{6.5}$Cu$_1$, and (c) Al$_{84}$Ni$_{8.5}$-Mm$_{6.5}$Fe$_1$ powders using continuous heating at 20°C/min. Each exothermic peak temperature of Al-Ni-Mm-x alloy is reported in the Table 1. As seen in Fig. 2, Al$_{85}$Ni$_{8.5}$-Mm$_{6.5}$ powders show a sharp first peak at 281°C, and second, third, and forth peaks at temperatures of 316, 355 and 367°C, respectively.
respectively. $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Cu}_1$ powders show a sharp first peak at $284^\circ\text{C}$, which was the highest temperature observed among the three alloys, followed by peaks at $328$ and $345^\circ\text{C}$ as presented in Fig. 2(b). $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Fe}_1$ powders exhibit a first peak at $274^\circ\text{C}$, followed by peaks at $341$ and $367^\circ\text{C}$ as shown in Fig. 2(c). The first reaction, observed between $250$ and $300^\circ\text{C}$, corresponds to the precipitation of the fcc-Al particles from the amorphous matrix, and the two other exothermic peaks are associated with the formation of intermetallic phases and completion of crystallization according to previous results. 

Comparison of the temperatures for the first peak suggests that the substitution of $1$ at\% $\text{Al}$ by $\text{Cu}$ increases the stability of the amorphous phase, whereas the same substitution by $\text{Fe}$ decreases the stability. The first exothermic peak for $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Cu}_1$ alloy has a larger intensity than that of $\text{Al}_{55}-\text{Ni}_{8.5}-\text{Mm}_{6.5}$, indicating that the substitution of $\text{Al}$ by $\text{Cu}$ prevents the crystallization of $\alpha\text{-Al}$ from the amorphous matrix during gas atomization. On the other hand, the first exothermic peak of $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Fe}_1$ has a smaller intensity than that of $\text{Al-Ni-Mm}$, however exhibits larger second and third peaks. This suggests that the substitution of $\text{Al}$ by $\text{Fe}$ prevents the crystallization of intermetallic compounds from amorphous matrix during gas atomization.

Figure 3 presents XRD patterns obtained from as-atomized (a) $\text{Al}_{55}-\text{Ni}_{8.5}-\text{Mm}_{6.5}$, (b) $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Cu}_1$, and (c) $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Fe}_1$ powders. All three patterns exhibit weak and broad peaks near $2\theta = 32 \sim 42^\circ$ corresponding to the presence of amorphous phases. The XRD pattern in Fig. 3(a) from $\text{Al}_{55}-\text{Ni}_{8.5}-\text{Mm}_{6.5}$ powders consists of fcc-$\text{Al}$, orthorhombic $\text{Al}_{11}\text{Ce}_3$ ($a = 0.4389$, $b = 1.305$, $c = 1.009\text{nm}$), orthorhombic $\text{Al}_{11}\text{Ni}$ ($a = 0.6598$, $b = 0.7332$, $c = 0.4862\text{nm}$). The XRD pattern in Fig. 3(b) from $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Cu}_1$ powders also corresponds to $\text{Al}$, $\text{Al}_3\text{Ni}$, and $\text{Al}_3\text{Ce}_3$ phases, however the intensity of $\text{Al}$ peaks is weaker than those observed for $\text{Al}_{55}-\text{Ni}_{8.5}-\text{Mm}_{6.5}$ powders. This XRD result, along with DSC data, indicates that the crystallization of fcc-$\text{Al}$ was suppressed by the addition of $\text{Cu}$ during gas atomization. Furthermore, formation of intermetallic phases such as $\text{Al}_3\text{Ni}$ and $\text{Al}_3\text{Ce}_3$ is also suppressed by an addition of $\text{Cu}$ based on XRD intensities shown in Fig. 3. The XRD pattern of $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Fe}_1$ alloy powders also indicates a presence of fcc-$\text{Al}$, $\text{Al}_3\text{Ni}$, $\text{Al}_3\text{Ce}_3$, and $\text{Al}_3\text{La}_3$ phase. The intensity of diffraction from fcc-$\text{Al}$ phase is quite strong, whereas that of intermetallic compounds is weak when compared to other compositions. The XRD result of $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Fe}_1$ alloy powders corresponds with the result of DSC data that had smaller intensity for first exothermic peak and larger intensity for the second and third exothermic peaks. Thus the substitution of $1$ at\% $\text{Al}$ by $\text{Fe}$ promotes the nucleation of $\alpha\text{-Al}$, and suppresses the nucleation of intermetallic compounds during gas atomization.

3.2 Microstructure and phase constituents of hot-extruded alloys

Figure 4 shows SEM micrographs of hot-extruded $\text{Al}_{55}-\text{Ni}_{8.5}-\text{Mm}_{6.5}$, $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Cu}_1$, and $\text{Al}_{54}-\text{Ni}_{8.5}-\text{Mm}_{6.5}\text{Fe}_1$ alloys after deep etching. It should be noted that the small
dark areas in Fig. 4 are due to deep etching, since optical microscopy carried out prior to etching did not reveal any porosity. The microstructure of Al<sub>65</sub>-Ni<sub>8</sub>-Mn<sub>6</sub> alloy in Fig. 4(a) shows featureless microstructure with some etched-out regions. Figure 4(b) shows the featureless microstructure from homogeneous etching response of a very fine microstructure for Al<sub>83</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Cu<sub>1</sub> alloy. Deeply etched microstructure of Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloy is presented in Fig. 4(c). These micrographs of alloys indicate that the microstructures of all hot-extruded bars remain very fine although the extrusion was carried out above the crystallization temperature.

Figure 5 presents XRD patterns obtained from hot-extruded (a) Al<sub>65</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>, (b) Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Cu<sub>1</sub>, and (c) Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloys. After extrusion at 400 °C, Al<sub>65</sub>-Ni<sub>8</sub>-Mn<sub>6</sub> alloy became fully crystalline, and consisted of fcc-Al, orthorhombic Al<sub>11</sub>Ni, Al<sub>11</sub>Ce<sub>3</sub> and Al<sub>11</sub>La<sub>3</sub> phases as shown in Fig. 5(a). XRD peaks corresponding to these crystalline phases are sharper with higher intensity than those observed for gas-atomized powders. The XRD patterns from Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Cu<sub>1</sub> and Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloys are similar to that of Al<sub>65</sub>-Ni<sub>8</sub>-Mn<sub>6</sub> alloy. In addition a few unidentified peaks were observed in all extruded bars. During degassing and hot-extrusion process, all powders (nanostructured and partially amorphous phase) crystallized into a mixture of several crystalline phases, as expected from the DSC of gas-atomized powders. The degassing and extrusion temperatures were apparently too high to retain the amorphous phase. Due to the limit in maximum extrusion load, extrusion temperature could not be reduced below 400 °C. The lattice constant of fcc-Al in extruded bars was determined to be about 0.4055 nm (similar to pure Al), and suggests precipitation from supersaturated Al phase.

Figure 6 shows bright field TEM images from hot-extruded Al<sub>65</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>, Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Cu<sub>1</sub>, and Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloys. The microstructure generally consisted of a randomly distributed fcc-Al and embedded intermetallic compounds. Based on TEM-XEDS, many of the small spherical particles were determined to be intermetallic compounds such as Al<sub>5</sub>Ni, Al<sub>13</sub>Ce<sub>3</sub> and Al<sub>11</sub>La<sub>3</sub>. Distribution in grain size for fcc-Al and intermetallic phases, determined within an area of 1,200 nm x 1,800 nm, are presented in Fig. 7, respectively for all three alloys. Despite the wide range of distribution, the average grain size for fcc-Al was 130, 111, and 145 nm for Al<sub>65</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>, Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Cu<sub>1</sub>, and Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloys, respectively. A large number of grains smaller than 120 nm were observed for Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Cu<sub>1</sub> alloy as clearly reported in Fig. 7(b). Coarser grains in the Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloy are observed due to the growth of already crystallized grains during hot working process. Clearly, Cu plays a significant role in the refinement of the microstructure.

The particle size of intermetallic phases in Al<sub>84</sub>-Ni<sub>8</sub>-Mn<sub>6</sub>Fe<sub>1</sub> alloy is the smallest among the three extruded alloys as presented in Fig. 7(f). This indicates that these particles nucleated from the amorphous matrix during hot working process. However, the same intermetallic phases in other two alloys had a slightly larger size presumably due to
the growth of already crystallized particles aforementioned with DSC. In this work clearly Cu and Fe play a significant role in the refinement of the microstructure. Although the small Cu additions can further refine the nanometer scale α-Al nanoparticles in Al-Ni-Fe and Al-Ni-Y alloys, few studies had been reported to understanding the mechanism of this effect. It is suggested that the reduction of grain size of α-Al particles by the substitution of Cu for Ni arises from a reduction of the nucleation barrier. This proposed mechanism is more consistent with observations of particle size and number density in the current investigation. In this research the effect of Cu in refinement of the grain size was attributed to enhanced nucleation increasing the number density of the grains, rather than diffusion limited or interface limited growth. It is also possible that the nucleation of the α-Al is being affected by chemical decomposition of discrete α-Al particle. Further study of this behavior requires nanometer scale chemical analysis of the local partitioning behavior of the Cu and Fe during crystallization.

3.3 Mechanical properties of hot-extruded alloys

Vickers hardness and compressive strength of the extruded bars are presented in Table 2 as a function of composition. The higher Vickers hardness and compressive strength obtained for Al84-Ni8.5-Mm6.5Cu1 alloys can be rationalized on the basis of the refinement of Al grains with Cu addition. The Al84-Ni8.5-Mm6.5Fe1 alloy with larger Al grain size has lower compressive strength than Al85-Ni8.5-Mm6.5 with
smaller Al grain size, even though the size of intermetallic compound is smaller for Al$_{85}$-Ni$_{8}$-Mm$_{6.5}$-Fe$_1$ alloy. Therefore, in this study, the grain size of Al-matrix is more important for compressive strength than the size of the intermetallic compounds.

4. Conclusions

Gas atomization was employed to produce amorphous and nanostructured Al-Ni-Mm and Al-Ni-Mm-X powders that were subsequently consolidated by hot-extrusion. The powders less than 26 μm in diameter consisted of nanocrystalline fcc-Al grains and intermetallic compounds embedded in an amorphous matrix. All hot-extruded alloys consisted of homogeneously-distributed fine-grained fcc-Al matrix and embedded intermetallic compounds. Substitution of 1 at% Al by Cu increased the stability of the amorphous phase, whereas the same substitution by Fe decreased the stability of the amorphous phase. A fine microstructure of fcc-Al and intermetallic compounds in the Al$_{84}$-Ni$_{8.5}$-Mm$_{6.5}$Cu$_1$ was attributed to the nucleation and growth from the amorphous phase. On the other hand, the larger grain size observed in the Al$_{84}$-Ni$_{8.5}$-Mm$_{6.5}$Fe$_1$ alloy was attributed to the growth of existing particles during hot working process. The refined microstructure of Al$_{84}$-Ni$_{8.5}$-Mm$_{6.5}$Cu$_1$ alloy, in particular the refined fcc-Al grains, gave rise to the highest Vickers hardness (319 Hv) and compressive strength of 1152 MPa.

### REFERENCES