New Amorphous Alloys in Al–Si–Fe–Ni and Al–Si–Fe–Co Systems and Their Crystallization Behaviour

D. V. Louzguine, A. Takeuchi and A. Inoue

Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

An amorphous single phase was formed in wide composition ranges of rapidly solidified Al–Si–Fe–Ni and Al–Si–Fe–Co alloys. In comparison with Al–Si–Fe system, the composition range of the amorphous alloys is the widest in the Al–Si–Fe–Ni system and becomes narrower in the Al–Si–Fe–Co system in the direction of Fe concentration axis. The extension of the compositional range in the direction of the Si concentration axis leads to the formation of new amorphous alloys with high silicon concentrations: Si₄₀Al₃₀Fe₁₀Ni₁₀, Si₃₀Al₃₀Fe₁₀Ni₁₀ and Si₃₀Al₃₀Fe₁₀Co₁₀. The crystallized structure consists of fcc Al, cubic Si and some ternary compounds of AlFeSi, AlSiNi, AlFeNi and AlSiCo depending on their alloy compositions.

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I. Introduction

It has been found that a homogeneously amorphous phase is formed in wide composition ranges of Al–Si–Fe system. One of the widest composition ranges is 14 to 40 at.%Si for Al–Si–10 at.%Fe alloys and 12 to 22 at.%Fe for Al–25 at.%Si–Fe alloys. Also the lowest Si concentration for amorization in the Al–Si–Fe system has been reported to be 6 at.% at 14 at.%Fe. Besides, amorphous alloys have been formed in wide composition ranges of Al–Si–Cr, Al–Si–Ni and Al–Si–Mn systems. Quaternary Al–Si–Fe–Cr, Al–Si–Fe–Mn and Al–Si–Fe–V systems were also studied recently.

In the present study, we intend to examine the influence of 3d-transition metals Ni and Co addition on the composition range in which an amorphous phase is formed in rapidly solidified Al–Si–Fe base alloys. Crystallization behaviour of Al–Fe–Si–Ni and Al–Fe–Si–Co amorphous alloys is also another purpose of the present study. Little has been studied about the equilibrium phase diagrams of such quaternary systems.

II. Experimental Procedure

Alloy ingots of Al–Si–Fe–Ni and Al–Si–Fe–Co systems were prepared by arc melting the mixture of pure metals and Si in an argon atmosphere. From these alloys, ribbon samples of about 0.02 mm in thickness and 1 mm in width were prepared by rapid quenching the melt on a single copper roller. The amorphous structure of ribbon samples was examined by X-ray diffraction with monochromatic CuKα radiation and transmission electron microscopy. The crystallization temperature and heat of crystallization were measured by differential scanning calorimetry (DSC) at heating rates of 0.33 and 0.67 K/s.

III. Results and Discussion

An amorphous single phase was formed in wide composition ranges of the following rapidly solidified alloys: Al₁₋₅Si₁₋₅Fe₁₀Ni₁₀ and Al₁₋₅Si₁₋₅Fe₁₀Co₁₀.

Figures 1 and 2 show the composition ranges in which an amorphous phase is formed in the Al–Si–Fe–4 at.%Ni and Al–Si–Fe–4 at.%Co alloys, respectively. In comparison with Al–Si–Fe–system, the composition range of the amorphous alloys is the widest in the Al–Si–Fe–Ni system and becomes narrower in the Al–Si–Fe–Co system in the direction of the Fe concentration axis. The alloying of Fe and other transition metal does not affect an influence on the upper and lower limits of Fe content in the amorphous formation range of the Al–Si–Fe–Ni system in comparison with ternary Al–Si–Fe alloys.

The X-ray diffraction patterns of the rapidly solidified
Al$_{72.5}$Si$_{14.5}$Fe$_{10}$Co$_4$ alloys with different Si concentrations are shown in Fig. 3. It is seen that the further increase in Si content from the glass-formation range results in the precipitation of a cubic (Fd3m) Si phase. One weak unidentified peak is also seen at $2\theta = 44.4$ deg. In the X-ray diffraction pattern of the 14 at% Si-containing alloy, we can see well-defined diffraction peaks of FCC Al phase. Al crystals seem to have a preferential orientation relationship with ribbon surface due to primary heterogeneous nucleation of Al. As a result, the intensity of the (111) Al peak in the relation with the other peaks increases for the Al$_{72.5}$Si$_{14.5}$Fe$_{10}$Co$_4$ alloy.

The X-ray diffraction pattern of the amorphous alloys consists of two broad peaks at 26 and 44 degrees of double $\theta$ angle, corresponding to the scattering vectors 18.3 and 30.5 nm$^{-1}$. The split of these peaks can be seen in the electron diffraction pattern shown in Fig. 4(a). The bright-field electron micrograph reveals a featureless homogeneous contrast for all amorphous alloys of these systems (Fig. 4(b)).

In comparison with the 40 at%Si alloy of the Al–Si–Fe system, the extension of Si content to 45 at% for the formation of the amorphous phase in the Al–Si–Fe–Ni system leads to the formation of new Si-rich amorphous alloys such as Si$_{45}$Al$_{35}$Fe$_{20}$Ni$_4$, Si$_{45}$Al$_{35}$Fe$_{15}$Ni$_6$ and Si$_{45}$Al$_{35}$Fe$_{10}$Co$_4$. Thus, the addition of Ni, Co and Cr to the Al–Si–Fe system is favourable for the production of Si-based amorphous alloys.

During heat treatment of amorphous alloys at temperatures above the crystallization temperature, various crystalline phases precipitate from an amorphous matrix.
Many exothermic peaks are also seen on the DSC curve. They are attributed to the fact that the ternary Al–Fe–Si phase diagram is relatively complicated. In the equilibrium phase diagram inside the investigated region, there are many peritectic reactions and various kinds of ternary phases exist in the solid state. Crystalline structures of some ternary phases remain unknown. The data on some other phases, given by various authors, also differ significantly.

Phase distribution in the fully crystallized alloys inside the amorphous phase region is also shown in Figs. 1 to 2. The formation of a-Fe phase (FeSiAl- or FeSi2Al, with a tetragonal structure of a=0.609 nm and c=0.944 nm is observed in all systems investigated. In the aluminium- and silicon-rich alloys, FCC Al and Si (F3d3m space group) phases precipitate respectively.

Crystallization of βFe2Si2Al6(τ4) phase (FeSiAl, with a monoclinic structure of a=b=0.612 nm, c=4.15 nm and β=91° was recognized in a wide concentration region of the Al-rich alloy systems studied. In the region with higher Fe concentrations, the γFe2Al6Si12 phase with a monoclinic structure of a=1.78 nm, b=1.025 nm, c=0.89 nm and β=135° is formed in coexistence with the δ Fe2Si2Al6(τ4) or FeSiSi2Al6(τ4) phase with an orthorhombic lattice parameter of a=0.768 nm, b=1.53 nm, c=1.6 nm. A small amount of the Pm3m Al2FeNi phase with a lattice parameter a=0.2883 nm was also observed in the Alloy Al6Si12Fe20Ni4 alloy.

Fully crystallized Al–Si–Fe–4 at%Ni alloys also contain a small amount of (Al1−xSi)xNi3 phase with a cubic Im3m structure of a=0.8291 nm. Ni is thought to be dissolved into the Fe2Al6Si12(γ) and FeSi2Al6(δ) phases in the Al2Si12Fe10Ni3 alloys. In the Si20Al11Fe20Ni3 alloy an unidentified phase was found to precipitate simultaneously with the FeSi2Al6(δ) and Si phases. In the concentration region of the ternary Al–Fe–Si system the Fe2Si2Al6(τ4) phase with unknown structure was observed. It is possible that the Fe2Si2Al6 ternary phase is also formed in the Si20Al11Fe20Ni3 alloy.

In the case of amorphous Al–Si–Fe–4 at%Co alloys, both Co2AlSi2 phase with a hexagonal structure (a=0.3875 nm, c=0.4762 nm) and the cubic Im3m Co2AlSi2 phase with a lattice parameter of a=0.8091 nm were observed to precipitate.

No quaternary phases such as AlFeMnSi or AlFeCrSi were observed in fully crystallized alloys studied.

The shape of the exothermic peaks on the DSC curve is significantly different from that for the Al–Si–Fe–4 at% TM alloys with the same Fe and Si concentrations. According to the DSC analyses, the addition of 4 at%Ni or Co has the strong effect on the crystallization behaviour of the Al–Si–Fe alloys. For example, the DSC curves for the alloy Al12Si2Fe10 ternary and Al12Si2Fe10TM4 quaternary alloys are shown in Fig. 5. In spite of the slight difference in chemical composition, the shape of crystallization curves of these alloys is significantly different. In the ternary Al12Si2Fe10 alloy, only two phases of FeSiAl2(β) and FeSiSi2Al2(δ) are recognized. FeSiAl2(β), Si and Co2AlSi2 phases precipitate in the Al14Si2Fe10Co4 alloy.

The most complicated structure consisting of Si, FeSiAl2(β) and (Al, Si)2Ni3 phases is seen in the fully crystallized Al6Si12Fe20Ni4 alloy. The first exothermic peak is attributed to the primary crystallization of Si. The intensity of the first Si (111) diffraction peak was observed to be much higher than that for the other peaks on the X-ray diffraction pattern of the Al6Si12Fe20Ni4 alloy heated up to the temperature of the first exothermic reaction. In the case of fully crystallized alloy the intensities of Si peaks correspond to the intensities of powder Si. It seems that the primary crystallization of Si in the amorphous matrix initiates by the heterogeneous nucleation of Si particles on the ribbon surface rather than by the heterogeneous nucleation in the body of the specimen.

The increase in Fe concentration leads to the rise of crystallization temperature (Fig. 6(a)). This rise seems to be caused by the rise of melting temperature. In the direction parallel to the Si concentration axis, the crystallization temperature is practically invariable in the formation range of amorphous alloys. The onset temperature of the exothermic reaction due to crystallization is shown as a function of Si concentration in Fig. 6(b).

The amorphous phase formation is explained by attractive interaction of TM–Si and Al–Fe atomic pairs. The limitation of Fe and Si contents is probably due to the increase of melting temperature at the upper side and the decrease of attractive bonding nature of Al–TM and Si–TM atomic pairs at the lower side.

The amorphous single phase regions are located around FeSi2Al6(δ) phase and also near Fe2Si2Al6(β) and Fe2Si2Al6(γ) phases in the ternary Al–Fe–Si phase diagram. The complicated structures of the ternary FeSi2Al6(δ), Fe2Si2Al6(β) and Fe2Si2Al6(γ) phases can
matrix of the Al–Si–Fe–Ni and Al–Si–Fe–Co alloys and the microstructure becomes inhomogeneous. Such a change in the microstructure is consistent with the formation of amorphous + crystalline phases at 41.9 m/s. The data obtained in the present study are useful in future investigations for the fabrication of a new Si-based amorphous alloy.

IV. Conclusions

(1) An amorphous single phase was obtained over wide composition ranges in rapidly solidified Al–Si–Fe–TM (TM=Ni, Co) alloys. The alloy system with the widest composition range is the Al–Si–Fe–Ni system. The formation of the amorphous phase was interpreted as due to the attractive interaction of Al–TM and TM–Si atomic pairs and the complicated crystalline structures of intermetallic compounds in the equilibrium Al–Si–Fe system.

(2) Some new amorphous alloys with high Si concentrations: Si\textsubscript{45}Al\textsubscript{55}Fe\textsubscript{20}Ni\textsubscript{4}, Si\textsubscript{45}Al\textsubscript{55}Fe\textsubscript{15}Ni\textsubscript{4} and Si\textsubscript{45}Al\textsubscript{55}Fe\textsubscript{10}Co\textsubscript{5} were obtained.

(3) The structure of fully crystallized Al–Si–Fe–Ni and Al–Si–Fe–Co alloys was observed to be complicated mixtures consisting of Al, Si and several ternary Al–Si–Fe, (Al, Si)\textsubscript{2}Ni\textsubscript{3}, Al\textsubscript{2}FeNi and Al–Si–Co phases.

REFERENCES