Precipitation of Nanogranular Ge Particles in Rapidly Solidified Al-Si-Fe-Cr-Ge Alloys

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The effect of Ge addition on the microstructure and some properties of rapidly solidified Al-Si-Fe-Cr alloys was examined. In particular, the addition of 9 to 15 at% Ge to $\text{Al}_{56}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4$ alloy causes a change from an amorphous phase in the Ge content below about 9 at% to a mixed structure consisting of homogeneous dispersion of fine Ge solid solution particles in an amorphous matrix in the Ge content range of 9 to 15 at%. The size, volume fraction and composition of the Ge particle depend on Ge concentration in the alloys. The Ge particle in the $\text{Al}_{44}\text{Si}_{30}\text{Ge}_{12}\text{Fe}_{10}\text{Cr}_4$ alloy has a size of about 10 nm and homogeneously distributes in the amorphous matrix. The Al-Si-Fe-Cr-Ge alloys are characterized by high hardness numbers H_v of 680 to 910. The crystallization process and phase composition of the above-mentioned alloys in the crystallized state change with Ge content. The primary precipitation of Ge from the amorphous phase is thought to result from the complicated interaction among the constituent elements.

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I. Introduction

An amorphous single phase is formed in rapidly solidified Al-Si-TM and Al-Ge-TM (TM-transition metals) alloys and there is in common in the composition ranges of the amorphous phase formation between Al-Ge-TM and Al-Si-TM ternary systems⁽¹⁾⁻⁽⁷⁾. Vickers hardness (H_v) and electrical resistivity of the amorphous alloys in the above-mentioned systems lie in the wide range from about 200 to 1000 H_v and from 2.2 to 18.4 $\mu\Omega\text{m}$, respectively, depending on the TM, Si and Ge contents which allow to produce an alloys with greatly different properties⁽³⁾. Quaternary Al-Si-Fe-TM (TM=3d transition metals) systems were studied recently⁽⁸⁾⁽⁹⁾. One of the widest composition ranges in the direction of Si concentration axis for $\text{Al}_{86-x}\text{Si}_x\text{Fe}_{10}\text{Cr}_4$ alloys is from 16 to 45 at% Si.

The microstructure and properties of metalloid-based Si-Ge-Al-TM alloys obtained by melt spinning have been studied recently⁽¹⁰⁾. The changes in the properties and microstructure from amorphous to amorphous + c-Ge (c-Ge-crystalline Ge) for the Si-based alloys by the addition of Ge were found and the mechanism for their changes was discussed. This paper intends to present the changes in the structure and crystallization behavior of the Al-Si-Fe-Cr alloys by the addition of Ge.

II. Experimental Procedure

Alloy ingots of Al-Si-Fe-Cr-Ge system were prepared by arc melting the mixture of pure metals and Si in an argon atmosphere. From these alloys, ribbon samples of

about 0.015–0.02 mm in thickness and 0.9 mm in width were prepared by rapid solidification of the melt on a single copper roller at the wheel surface velocity of 41.9 m/s. The structure of ribbon samples was examined by X-ray diffraction with monochromatic CuK_α radiation. Transmission electron microscopic (TEM) observation was carried out using a JEM 2010 microscope operating at 200 kV. Samples for TEM were polished electrolytically in a solution of 10 vol% perchloric acid and 90 vol% methanol at 208–213 K. Hardness was measured by a Vickers microhardness tester with a 0.098 N load. Crystallization temperature and heat of crystallization were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s.

III. Results

The influence of Ge addition on the structure of the Al-Si-Fe-Cr rapidly solidified alloys was studied in the present work. The microstructure of the different Al-Si-Fe-TM (TM transition metals) alloys obtained by rapid solidification changes from homogeneously amorphous to heterogeneous-amorphous + c-Ge (c-Ge-crystalline Ge solid solution) by the Ge addition. The Al-Si-Fe-Cr system was chosen from Al-Si-Fe-TM systems because the Cr containing system has the widest composition range for formation of an amorphous phase. The detailed study on the influence of Ge addition has been carried out for rapidly solidified $\text{Al}_{66-56}\text{Si}_{20-30}\text{Fe}_{10}\text{Cr}_4$ alloys having an amorphous phase. Crystalline peaks corresponding to the c-Ge are seen in the X-ray diffraction pattern of the $\text{Al}_{66-x}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ and $\text{Al}_{56-x}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ alloys containing more than 9 and 17 at% Ge, respectively, as shown in Figs. 1 and 2. The intensity of the Ge diffraction peaks increases with increasing Ge content. The

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Fig. 1 X-ray diffraction patterns of rapidly solidified $\text{Al}_{66-x}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ alloys.

Fig. 2 X-ray diffraction patterns of rapidly solidified $\text{Al}_{56-x}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ alloys.

volume fraction of the c-Ge phase embedded in the amorphous matrix changes in a similar way. The size and volume fraction of Ge particles in the amorphous matrix are controlled by Ge concentration in the alloy. The Ge diffraction peaks slightly shift into the direction of higher 2θ angle and lower d_{hkl} by the dissolution of Si. The Si concentration in Ge particles embedded into the amorphous matrix is estimated to be 19 at% for $\text{Al}_{44}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{12}$ and 12 at% for $\text{Al}_{46}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{20}$ alloy.

The microstructure and selected-area electron diffraction patterns of the fully amorphous $\text{Al}_{49}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_7$ and partially crystalline $\text{Al}_{45}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{12}$ alloys are shown in Fig. 3. The split of the first halo peak seen in Fig. 3(a) is interpreted as an overlapping diffraction phenomenon resulting from two separate amorphous

phases, indicating that the $\text{Al}_{49}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_7$ alloy is composed of two separated aluminum-rich and silicon-rich amorphous phases on a short range scale. The mixture of the Al- and Si-rich amorphous phases has been discussed for rapidly solidified Al-Si-TM and Al-Ge-TM ternary alloys in a previous work⁽²⁾. Fine and homogeneous distribution of nanoscale c-Ge particles with a size of about 10 nm embedded into the amorphous matrix are recognized in Fig. 3(e) and (f). The sharp ring on the diffraction pattern of the $\text{Al}_{45}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{12}$ alloy is attributed to the c-Ge particles and corresponds to (111) Ge. The Al-Si-Fe-Cr-Ge alloys with a fully amorphous structure were found to be formed in the range up to 9 at% Ge at 30 at% Si and up to 17 at% Ge at 20 at% Si, respectively.

The addition of Ge to the rapidly solidified Al-Si-Fe-Cr alloys causes an increase in Vickers hardness (Fig. 4(a)) and the highest value is 908 for $\text{Al}_{46}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{20}$. The crystallization temperature of the fully amorphous Al-Si-Fe-Cr-Ge alloys changes insignificantly with Ge content (Fig. 4(b)), but in the case of the mixed amorphous+c-Ge alloys the increase of crystallization temperature takes place by the change in matrix composition. The DSC curves of rapidly solidified Al-Si-Fe-Cr-Ge alloys are shown in (Fig. 5). The addition of Ge causes the decrease in the heat of crystallization of $\text{Al}_{56-x}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ alloys at more than 9 at% Ge in accordance with the decrease in the volume fraction of the amorphous phase. Phase compositions in a crystallized state are follows. The formation of $(\text{Fe}, \text{Cr})_4\text{Si}_4\text{Al}_{13}$ with a cubic structure of $a=1.260 \text{ nm}^{(11)}$ and Fd3m Si phases upon crystallization was observed in the Ge-free Al-Si-Fe-Cr alloys in the range from 20 to 30 at% Si. The addition of 7 at% Ge to the $\text{Al}_{66}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4$ alloy does not change its phase composition in a fully crystalline state. Ge is dissolved in Si phase. The Ge dissolution causes a shift of Si diffraction peaks to a lower 2θ side as shown in Fig. 6. In the alloys with higher Ge contents, the formation of Fe_6Ge_5 phase with a monoclinic structure of $a=0.9965 \text{ nm}$, $b=0.7826 \text{ nm}$, $c=0.7801 \text{ nm}$ and $\beta=109.67^\circ^{(12)}$ was observed. In the $\text{Al}_{44}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{12}$ alloy, a Fe_2SiAl_8 phase with a hexagonal structure of $a=1.24056 \text{ nm}$ and $c=2.6236 \text{ nm}^{(12)}$ is formed. The precipitation of the above-mentioned $(\text{Fe}, \text{Cr})_4\text{Si}_4\text{Al}_{13}$ phase has been also recognized in all alloys studied up to 12 at% Ge.

IV. Discussion

Ge has the same crystal structure (Fd3m space group) as Si and an unlimited mutual solubility in the solid state is observed between Si and Ge⁽¹³⁾. Furthermore, nearly the same compositional ranges in which an amorphous single phase is formed by melt spinning have been observed in the Al-Si-TM and Al-Ge-TM systems⁽²⁾. However, the microstructure of the Al-Si-Fe-Cr-Ge alloys was found to change from homogeneously amorphous to amorphous+c-Ge by the addition of Ge. This result seems to reflect the complicate interaction among Ge, Al, Si and TM atoms in Al-Si-Fe-TM-Ge alloys. Si

Fig. 3 Selected-area electron diffraction patterns, bright- and dark-field electron micrographs of rapidly solidified $\text{Al}_{49}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_7$ ((a), (b) and (c)) and $\text{Al}_{45}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_{12}$ ((d), (e) and (f)) alloys.

produces a number of ternary compound phases with Al and Fe, indicating that the heats of mixing among Al, Si and Fe elements are large and negative⁽¹⁴⁾⁽¹⁵⁾. On the contrary, in the Al-Ge-Fe system no ternary compound phase is formed⁽¹⁴⁾, indicate of either low negative heats of mixing for ternary alloy formation or even positive one. That is one of the reasons why Ge is excluded from the amorphous matrix and precipitates as the Ge-Si solid solution. It follows that in the case of rapid solidification a relatively weak attractive interaction in Ge-Si atomic pair is obscured by the strong bonding nature among Si, Al and TM atoms. The results obtained were found to be in good correlation with earlier reported data for Si-Al-TM-Ge alloys⁽¹⁰⁾.

The addition of Ge causes the increase in hardness due to the dissolution of Ge in the amorphous matrix in the case of fully amorphous alloys and due to the precipitation of Ge particles embedded in the amorphous matrix in alloys with a mixed amorphous + c-Ge structure. The crystallization temperature of the amorphous Al-Si-Fe-

Cr-Ge alloys with up to 12 at% Ge changes insignificantly due to the primary precipitation of Si or Si-Ge solid solution in all these alloys. In the case of the mixed amorphous + c-Ge alloys, the increase of crystallization temperature takes place due to the change in the composition of the amorphous matrix (Fig. 4(b)). Because of the strongly attractive interaction among Si, Al and TM atoms, the $(\text{Fe}, \text{Cr})_4\text{Si}_4\text{Al}_{13}$ and Fe_2SiAl_8 compound phases are formed as main phases, though only a small amount of Fe_6Ge_5 phase is observed. The Fe_6Ge_5 phase is formed because of the attractive interaction between Fe and Ge atoms and the negative heat of mixing in Fe-Ge system⁽¹⁵⁾. As mentioned above, some amount of Ge is also dissolved in the Fd3m Si.

The dissolution amount of Ge in the amorphous phase increases with decreasing Si concentration by the decrease in the number of the bonding between Si and other constituent elements. Similar results can be obtained in other Al-Si-Fe-TM (TM-transition metals) systems.

Fig. 4 Vickers microhardness (H_v) (a) and crystallization temperature (T_x) (b) as a function of Ge content for rapidly solidified $\text{Al}_{66-x}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ ($\blacktriangle$) and $\text{Al}_{56-x}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ ($\bullet$) alloys.

Fig. 5 DSC curves of rapidly solidified $\text{Al}_{66-x}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ (a) and $\text{Al}_{56-x}\text{Si}_{30}\text{Fe}_{10}\text{Cr}_4\text{Ge}_x$ (b) alloys taken at a heating rate of 0.67 K/s.

V. Conclusions

The addition of Ge to the Al-Si-Fe-Cr alloys obtained by rapid solidification causes the change of microstruc-

Fig. 6 X-ray diffraction pattern of a fully crystallized $\text{Al}_{59}\text{Si}_{20}\text{Fe}_{10}\text{Cr}_4\text{Ge}_7$ alloy.

ture from homogeneously amorphous to heterogeneous-amorphous + c-Ge. The Ge is excluded from the Al-Si-Fe-Cr amorphous matrix and precipitates as the Ge-Si solid solution. The amount of Ge addition that is necessary for such a change increases with decreasing Si content. In the case of rapid solidification the relatively weak attractive interaction in Ge-Si atomic pair is obscured by the strong bonding nature among Si, Al and TM atoms. The structure of the fully crystallized Al-Si-Fe-Cr-Ge alloys consists of Si, $(\text{Fe,Cr})_4\text{Si}_4\text{Al}_{13}$ and Fe_2SiAl_8 phases, depending on alloy composition. Ge is dissolved in Si forming a solid solution. The formation of Fe_6Ge_5 phase was observed in the alloys containing 12 at% Ge.

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