Composition and microhardness of Si–Ge solid solution precipitates in Al–Si–Ge alloys solidified during centrifugation


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Abstract

The chemical composition of precipitates, the Knoop microhardness of the precipitates and of the matrix of Al–Si–Ge alloys solidified during centrifugation at 7 × g were investigated. The initial content of (Si + Ge) was (10 + 10), (20 + 20) or (25 + 25) at.%. The Knoop microhardness of the ingots varied with height in the ingot. This variation is attributed to sedimentation of Si–Ge during solidification. Chemical analysis showed that the maximum Si:Ge ratio in the precipitates for Al–10 at.% Si–10 at.% Ge alloy was about 92:8, and decreased with increasing Si and Ge content in ingots. The Si:Ge ratio and Knoop microhardness also varied throughout each precipitate. The composition was constant along precipitates of alloy solidified without centrifugation. A variation in Knoop microhardness along the precipitates was attributed to this composition variation. The variation of the maximum Si:Ge ratio in the precipitates in ingots of different composition solidified with centrifugation is attributed to nonequilibrium conditions of solidification induced by decreased mass transport in the melt adjacent to the growing precipitates. The variation of Si and Ge along the Si–Ge precipitates is created by convection of the melt during solidification with centrifugation.

Keywords: Silicon; Germanium; Aluminum; Precipitates; Alloys; Composition; Microhardness

1. Introduction

Al–Ge–Si alloys with low concentrations of silicon and germanium have very fine and densely-distributed precipitates of Si–Ge solid solution [1,2]. These precipitates induce a large increase in the mechanical strength that makes these alloys very promising for many applications. Unlike most commercial aluminum alloys, the Al–Ge–Si alloys yield no metastable phases during precipitation. The only (and stable) phase that precipitates is the Si–Ge solid solution, whose crystal structure and composition are fixed during aging and annealing [3,4]. These alloys show hardness comparable to many commercially available aluminum alloys [5–8]. For better understanding of precipitation hardening in these alloys, the effect of different solidification conditions on the structure and composition of the Si–Ge precipitates should be investigated. There has been no previous investigation of the precipitates’ composition and of the properties of ternary alloys solidified under various conditions, particularly during centrifugation. There have been a few investigations of Al and Mg alloys solidified during centrifugation [9–12], although there are no data on the composition distribution in the precipitates of those alloys.

We present here the results of a study of the influence of centrifugation preceding and during solidification of Al–Si–Ge alloys on the microhardness of the resulting ingots, and the composition and microhardness of Si–Ge solid solution precipitates. The first results of this study were presented in [13]. Here, measurements of microhardness are presented, along with possible explanations for the concentration distribution along the Si–Ge precipitates.

2. Experimental

Al–(Si–Ge) ingots for the centrifugation experiments were produced by pouring a melt electromagnetically levitated in a He atmosphere into a massive copper mold. The starting Al and Ge were 99.99 and 99.9 wt.% purity, respectively. The Si was n-type with a resistivity of 20 Ωm. The initial atomic Si:Ge ratio was always 1:1. The content of (Si + Ge) was (10 + 10),

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(20 + 20) or (25 + 25) at.%. The resulting ingots were 6-mm diameter, and from 8 to 9-cm long. One ingot of every composition was selected for centrifuge experiments. These ingots were placed in 6-mm internal diameter alumina tubes closed at one end and 10–16-cm long. These tubes were inserted into quartz tubes, which were evacuated and sealed. Three alumina tubes with ingots of three compositions were stacked in every quartz tube. A quartz tube was tightly inserted into the gradient-freeze furnace of the centrifuge at Clarkson University, Potsdam, NY, USA. This centrifuge had an arm length of 1.5 m, and a furnace that swung outward as the rotation rate was increased, so that the acceleration vector was always along the axis of the tube. The power was turned on to the furnace. When its temperature reached about 450 °C, centrifuge rotation was begun and increased until the acceleration at the furnace was about 7 × g. The temperature in the furnace reached about 1050 °C in 1.5–2 h and was maintained constant for 4 h. Then the power to the furnace was turned off. Centrifuge rotation was stopped in about 70 min, when the furnace temperature had decreased to approximately 420 °C. Approximately another 15 h was required for the furnace to cool to room temperature.

A control experiment was carried out under the same conditions, but without turning on the centrifuge rotation, for a Al–10 at.% Si–10 at.% Ge alloy.

Three experiments with centrifugation were performed, yielding 3 ingots of each of the 3 compositions. Three of
these were selected for investigation of precipitate composition.

The resulting ingots were 8–10-cm long and weighed 5–10 g. Each was cut into two sections. The top section was 5–7 mm from the end of the ingot nearest the centrifuge axis. The bottom section was 5–7 mm from the end most distant from the axis of the centrifuge. The cross sections of the ingots were polished for optical microscope examination and for measurement of Knoop microhardness $H_K$. Single crystal precipitates of Si–Ge solid solution in Al were observed in these cross sections and were analyzed with a Cameca Camebax electron microprobe analyzer operating in the EDS mode. The Si and Ge contents were determined over 10-μm intervals along one direction of several Si–Ge precipitates beginning and finishing at their interfaces with the Al matrix. The Si and Ge contents of some precipitates also were determined along two perpendicular directions.

3. Results and discussion

An optical micrograph of a cross section of the Al–10% Si–10% Ge ingot solidified without centrifugation is shown in Fig. 1a. Fig. 1b shows the Si and Ge contents roughly along the crystal’s longest dimension and shortest dimension for one of the precipitates seen in Fig. 1a. The Si:Ge ratio remained constant at about 7:1. A sharp increase of the Ge content (and corresponding decrease in Si content) was observed near the borders of the Si–Ge precipitate. Thus, it appears that the precipitate was covered by a $\sim 40$-μm Ge layer with a small Si content (up to $\sim 5$ at.%). It is emphasized that chemical analysis was made only for two elements—Si and Ge. According to the Al–Ge phase diagram, Ge would include a maximum of 2.8 at.% Al [14]. Jumps of the concentration at about 40 μm near the interface can be connected with boundary defects formed by grinding and polishing two materials with different hardness.

Fig. 2 shows photomicrographs of the cross sections of the top and bottom parts of the Al–10% Si–10% Ge ingot solidified during centrifugation. Fig. 2c shows corresponding Si and Ge profiles in the precipitates, enclosed by the white rectangles. The Si:Ge ratio inside the precipitates varied from approximately 92:8 to 85:15, again with a Ge-rich layer at the interfaces with the matrix.

Fig. 3 shows similar results for the Al–20% Si–20% Ge ingot. The Si:Ge ratio varied from approximately 88:12 to 64:36. Fig. 4c presents similar results for the Al–25% Si–25% Ge ingot,
Fig. 4. Cross-sections of the Al–25Si–25Ge (at.%) ingot solidified during centrifugation. (a and b) Photomicrographs at 15× showing black precipitates in the top (a) and bottom (b) parts of the ingot. The white lines in the rectangles show the paths of two EDS scans across precipitates. (c) Ge and Si concentrations from the EDS scans.

showing less variation in the Si:Ge. Thus, Figs. 2c–4c show that the maximum Si:Ge ratio decreased when the initial Si + Ge concentration was increased from (10 + 10) to (25 + 25) at.%. For all alloys, the surfaces of the Si–Ge precipitates were covered almost entirely by a Ge-rich layer, as had been reported by others [12,15].

The Knoop microhardness, $H_K$, was measured along precipitates in ingots with different Si + Ge contents. Fig. 5 shows the variation in $H_K$ along sections of precipitates for all samples. Data are presented only for one precipitate in the top and bottom pieces of each ingot because of the difficulty of measuring microhardness on narrow cross sections. Fig. 6 shows the average $H_K$ of the mixture of the α solid solution matrix (Si and Ge in Al) and the β solid solution (Al in Si–Ge) among precipitates of the top and bottom pieces of all ingots. (The solid mixture is gray, among dark precipitates on the micrographs of Figs. 2a and b and 4a and b.) It can be seen that $H_K$ of the upper parts of the ingots is higher than of the lower ones. The difference increases with increasing Si + Ge content.

The main results can be explained in the following way. The growth of Si–Ge solid solution precipitates takes place in the field of the primary solidification of Al–Si–Ge melt. The Si:Ge ratio is determined by the Ge distribution coefficient between

Fig. 5. The Knoop microhardness $H_K$ measured along precipitates in ingots solidified during centrifugation. Curves 1 and 2 correspond to top and bottom parts of the (10 + 10) at.% ingot, 3 and 4 for top and bottom parts of the (20 + 20) at.% ingot, 5 and 6 for the (25 + 25) at.% ingot.
the precipitates and the melt. According to the binary phase diagrams, the maximum Si:Ge ratio in solid solution in equilibrium with melt with Si:Ge = 1:1 is about 80:20 [14]. This ratio can be higher when the growth occurs under nonequilibrium conditions, which is expected in our experiments. In addition, when the Si:Ge ratio equals 1:1, the Si + Ge solid solution crystals form at a lower temperature in this ternary system than in the binary Si–Ge system. As can be seen in Fig. 3 in [13] 1:1 crystals form at about 600–700 °C in the ternary system and at about 1270 °C in the binary system. Finally the growth of Si + Ge crystals requires Ge transport to Si crystallization centers in a (10 + 10) at.% Si + Ge solution in an Al melt as opposed to crystallization from a binary Si–Ge melt. The requirement for Ge transport results in an average Si:Ge ratio equal to about 90:10. When the (Si + Ge) content in the Al melt is increased, the mass transport is increased and the Si:Ge ratio decreases. The increasing mass transport with increasing total (Si + Ge) content in the melt is connected also with the solidification temperature. The solidification temperature of the ternary system increases when the total Si + Ge content increases, as can be seen from Fig. 7.

Fig. 7. Schematic composition triangle of the Al–Si–Ge system. The initial compositions (Si + Ge = 10 + 10, 20 + 20 and 25 + 25 at.%) of the alloys studied are indicated for an initial Si:Ge ratio of 1:1. The Si:Ge ratio of Si–Ge solid solution for equilibrium conditions is given along the Si–Ge side. The experimental Si:Ge ratio for precipitates is shown in brackets. The line connecting eutectic concentrations in the binary Al–Si and Al–Ge systems is shown, along with the melting temperatures of the pure components and the eutectics.

Si–Ge precipitates is connected with the gradient of the concentration in the liquid phase created by centrifugation. In Al–10% Si–10% Ge alloy solidified without centrifugation there was no concentration gradient.

4. Conclusions

(1) The Knoop microhardness of the Al matrix increased along the direction opposite of centrifugal acceleration. This can be explained by centrifugation causing a higher concentration of Ge in the ingot end most distant from the axis of the centrifuge.

(2) The Si:Ge ratio varied along precipitates formed during centrifugation. Thus all samples show a change of Si:Ge ratio along precipitates (all Si:Ge curves are inclined and almost every one has a nonlinear character), except for the non-centrifuged control sample. Moreover, the surface of the precipitates was covered by a thin Ge-rich layer.

(3) The variation in $H_K$ is attributed to the variation in Si:Ge ratio.

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References