Structure factors of modified liquid Al–Si alloys

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Abstract

The structure factor and the coordination numbers of liquid Al–Si alloys with different Si content have been measured by a high temperature X-ray diffractometer. Radial distribution functions (RDFs), the nearest atomic distance and the coordination numbers of eutectic Al–Si alloys before and after being modified with Sr and Sb were studied. The RDFs of the liquid alloy were decomposed by five Gaussian peaks. The results show that a Si–Si covalent bond exists in the liquid of eutectic and hyper-eutectic alloys. Sr in the liquid Al–Si has a capability to weaken the covalent bonds of Si–Si, suppressing the nucleation of the eutectic silicon phase. On the other hand, Sb in the liquid Al–Si increases the order degree of Si atoms, decreasing the supercooling degree of the nucleation and promoting the nucleation of eutectic silicon. © 2001 Published by Elsevier Science Ltd.

Keywords: Structure factor; Liquid Al–Si alloys; Gaussian

1. Introduction

The commercial application of Al–Si alloys often depends on the successful modification of the eutectic silicon. The elements used for modification are usually divided into two kinds; one is the elements that make eutectic silicon change from a flake form to a fibre form [1,2], whilst the other is the elements that refine eutectic silicon [3,4]. Ever since the discovery of the possibility of modification of Al–Si alloys [5], the study of modification process has attracted investigators. However, no theory has attained universal acceptance or really explained the principles of the phenomenon. Edwards and Archer [1] proposed the following explanation for the suppression of the nucleation of the silicon phase during modification by sodium: (a) destruction of crystalline nuclei, (b) increased obstruction to crystal growth according to the ‘colloid’ theory and the ‘adsorption’ theory. Thull and Chalmers [6] reported the presence of a concentration of sodium around the silicon crystals. However, Plumb and Lewis [7] argued that they had not observed the selective adsorption of sodium around the silicon phase through the use of autoradiography. Najafabadi [8] studied a modification mechanism in which the Sr adsorbs at the Si growth front, poisoning growth steps operative during flake growth and creating lattice instabilities which result in multiple twinning.

Several other studies have been reported on the modification mechanism, however relatively little work has been done on the liquid structure of Al–Si. The present work studies the structure factors of liquid Al–Si melt modified by Sr and Sb in order to understand the modification mechanism at a more microscopic scale.

2. Experimental procedure

Al–Si specimens were prepared from high pure Al (99.999) and Si (99.98%) in a crucible made of SiC. The modifying elements were added into the liquid alloy in pure Sr (99.99) and Sb (99.98%). X-ray diffraction measurements were carried out in a high purity helium (99.999%) atmosphere. Specimens were placed in an alumina crucible of 30 × 24 × 8 mm in size, using Ta sheet heating elements. An X-ray tube with MoKα and counter synchronized with each other (θ-θ), graphite mosaic monochromator crystal was used in this work. The voltage of the X-ray tube was 40 kV, the current 30 mA, and the exposition time 30 s.

The X-ray scattering intensity in the experiment was measured in arbitrary units and normalized into S(Q), then converted to the RDF with a Fourier integral. The coordination number and the nearest neighbor atomic distance were calculated from RDF and S(Q) separately using the methods described in Ref. [9]. The former is the integration of RDF from zero to its first minimum.

The Gaussian functions related to the position of different atomic shells were obtained by a decomposition of five functions, y = exp[−A(x − x₀)] in the range from 0 to...
0.7 nm for the RDF of the liquid Al–Si alloys. Three peak positions were 0.28, 0.37, and 0.53 nm, respectively.

DSC analyses were carried out using a Netsch DSC 404 in Ar atmosphere at a heating rate of 20°C/min.

3. Results

Structure factors $S(Q)$ of the Al–Si alloys with different composition at 943 K is shown in Fig. 1. The main peak of the $S(Q)$ curve becomes broader with the increase of the Si content. The position of the main peak shifts towards in the direction of the increase of $Q$. The total coordination number (Al–Al, Al–Si and Si–Si) for hypoeutectic liquid Al–Si alloys was 11.5 and 10.5 for eutectic and hyper-eutectic liquid Al–Si alloy. Fig. 2 shows five Gaussian peaks decomposing RDF ($4\pi r^2 \rho(r)$) of Al–Si alloys with different Si contents at 943 K, in which the full line is experimental curves of the RDF of the liquid alloys, the dotted line the Gaussian peak obtained by a decomposition, and the circumference line the curves of a fitting function overlaid by five Gaussian peaks that coincides well with the experimental result. Fig. 3 is the five Gaussian peaks decomposing RDF ($4\pi r^2 \rho(r)$) of Al–12.5% Si added 0.1% Sr at 943 and 1043 K (Fig. 3a and b, respectively).

The area of the Si–Si peak for the addition of 0.1% Sr at 0.37 nm under the temperature of 943 K is smaller than that of the alloy without Sr (Fig. 2c). The position of the Si–Si peak shifts towards the right. The peak disappears when the temperature reaches 1043 K. The variation of area of $A_{Si-Si}$ and the location of $r_{Si-Si}$ of Si–Si with Sr concentration at 943 K is shown in Fig. 4. With the increase of Sr content, the area of the Si–Si peak decreases gradually. The position of the Si–Si peak shifts towards larger $r$-values. Fig. 5 shows the structure factor curves $S(Q)$ of liquid Al–12.5 wt% Si alloy with and without Sb at different temperatures. The position of the main peak of the liquid

Fig. 1. The structure factor $S(Q)$ of Al–Si alloys with different composition (943 K).

(a)

(b)

(c)

(d)

Fig. 2. Five Gaussian peaks decomposing RDF ($4\pi r^2 \rho(r)$) of Al–Si alloys at 943 K.
Al–12.5 wt% Si alloy is \( Q_1 \), 26.8 nm, the same as that of liquid pure aluminum [10]. Fig. 6 is an amplification of Fig. 5 in the low \( Q \) range.

Fig. 7 shows the relation between the heights of the first maximum \( H_{max} \) of \( S(Q) \) and temperature, and the heights of the prepeak \( H_1 \) of \( S(Q) \) and temperature. The existence of a prepeak in the structure factor curves \( S(Q) \) demonstrates that there is a medium range order in liquid [11]. The RDF of the liquid Al–12 wt% Si alloy with and without Sb at different temperature is shown in Fig. 8. According to the data in Fig. 4 and Ref. [9], the nearest neighbor atom distance and the coordination number \( N_{1nn} \) of the liquid Al–12.5 wt% Si alloy can be obtained (Fig. 9). Table 1 is the result of DSC analyses of the Al–12.5 wt% Si with different Sb addition.

4. Discussion

It can be seen from Fig. 1 and the variation of total coordination number that the coordination number of the eutectic and the hypereutectic Al–Si alloy is smaller than that of hypoeutectic. The Gaussian peak at \( r = 0.37 \) nm in the eutectic and the hypereutectic is called the Si–Si peak, the position of which corresponds with the second peak of the RDF of pure liquid aluminum. The area of the Gaussian peak increases with the addition of Sr. Stich [10] drew a conclusion by an ab initio molecular dynamics simulation that about 25–30% of Si atoms in pure liquid possess covalent bonds. The peak at \( r = 0.37 \) nm (Fig. 3) indicates the covalent bonds and clusters of Si–Si in liquid Al–Si alloy. The bigger is the area of the Si–Si Peak, the greater is the number of the covalent bonds in the liquid: as a result, the number of Si–Si clusters in the liquid increases.

It can be seen from Fig. 4 that the area of the Si–Si peak obtained by a decomposition of the RDF of the liquid decreases progressively with the increase of Sr content. Once the number of Si–Si clusters in the liquid decreases, the number developing into nuclei decreases. In this situation the nucleation of Si clusters during solidification is subjected to a depression. As a result, the aluminum phase separates out over the silicon phase: this is the essence of the hypoeutectic style structure obtained by modification with Sr.

The pre-peak occurs at 13 nm \(^{-1} \) on the structure factor of the Al–12.5 wt% Si alloy with added Sb. It can be seen from

![Fig. 3. Five Gaussian peaks decomposing RDF (4\( \pi r^2 \rho(r) \)) of Al–12.5% Si added 0.1% Sr at (a) 943 K and (b) 1043 K.](image)

![Fig. 4. Variation of area \( A_{Si-Si} \) and location \( r_{Si-Si} \), Si–Si peaks with Sr concentration.](image)

![Fig. 5. Structure factor curves of liquid alloy with and without Sb additions.](image)
Fig. 6. Details of the structure factor in low Q range (corresponding to the square in Fig. 5).

Figs. 5 and 6 that the pre-peak tends to disappear as the temperature increases. The height of the first maximum ($H_{\text{mm}}$) of the alloy without Sb is greater than that with Sb with the increase of temperature, the difference being greatest at 775°C. The nearest neighbor atomic distance $r_n$ and the coordination number $N_{\text{sym}}$ of the alloy with added Sb is smaller than that without Sb at the normal melting condition, less than 850°C, as shown in Figs. 8 and 9. Thus considering all of these results, it seems reasonable to conclude that because of the addition of Sb, most of the Si atoms comprise Si–Si clusters that exist in the most steady form in liquid Al–Si alloys. The medium range order structure (Fig. 7) in the alloy with added Sb has confirmed this feature. The DSC analyses (Table 1) showed that the supercooling degree of the alloy with Sb addition is lower than without Sb. The solidification latent heat increases with the addition of Sb (Table 1).

During the solidification of the alloy, Sb strengthens the distribution order of the Si atoms in the liquid alloy so that the nucleation of eutectic silicon phases is promoted. Therefore the modifying elements first change the structure of liquid Al–Si alloys and the affect the finally solidified structure.

![Graph showing relation between temperature and height of first maximum and pre-peak](image1)

![Graph showing RDF of liquid alloys with and without Sb at various temperatures](image2)

![Graph showing nearest neighbor atomic distance and coordination number](image3)

![Graph showing DSC analysis of alloys with different Sb addition](image4)

**Table 1**

| Sb content (%) | Melting point (°C) | Supercooling (°C) | Solidification latent heat (kJ kg$^{-1}$) |
|----------------|--------------------|-------------------|----------------------------------------|
| 0.0Sb          | 591.9              | 32.5              | 405.5                                  |
| 0.1Sb          | 591.6              | 28.5              | 407.2                                  |
| 0.2Sb          | 591.3              | 25.5              | 411.9                                  |
5. Conclusions

1. The total coordination number of eutectic and hyper-eutectic Al–Si alloy is smaller than that of hypoeutectic at 943 K. There are Si–Si covalent bonds in liquid eutectic and hypoeutectic Al–Si alloys.
2. Sr weakens the covalent bonds in liquid Al–Si alloys, decreases the number of Si–Si cluster and then depresses the nucleation of Si atoms.
3. Sb strengthens the order degree of the Si atoms and promotes the nucleation of eutectic Si phases.

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