JOURNAL OF MATERIALS SCIENCE **34** (1999) 4149–4152

Non-equilibrium microstructure of hyper-eutectic Al-Si alloy solidified under superhigh pressure

X. F. YU, G. Z. ZHANG, X. Y. WANG, Y. Y. GAO, G. L. JIA
Department of Materials Science and Engineering, Northeastern University, Shenyang 110006, People's Republic of China

Z. Y. HAO
State Key Laboratory for Super Hard Materials, Jilin University, Changchun 130023, People's Republic of China

The non-equilibrium microstructures of hyper-eutectic Al-26.6wt%Si solidified under superhigh pressure (5.5 GPa) have been investigated. The results show that there exists a great deal of primary α phase in hyper-eutectic Al-Si alloy. The non-equilibrium microstructure for hyper-eutectic Al-Si alloy is composed of primary α phase, β phase and $(\alpha+\beta)$ eutectic phase. The solid solubility of Si in α phase and the solid solubility of Al in β phase increase significantly. The effects of high pressure on the solidification structures of Al-Si alloy are discussed. © *1999 Kluwer Academic Publishers*

1. Introduction

Non-equilibrium microstructures have significant effects on the properties of materials [1, 2]. When the non-equilibrium degree is very great, qualitative changes for the properties of materials can take place. There is not absolute equilibrium microstructure, but the general increase of cooling rate of liquid alloy during solidification only changes the crystal grain size. As to the non-equilibrium microstructures formed from rapidly quenching technology [3], large undercooling technology [4] and high pressure solidification, in addition to refining crystal grains, significant changes happen in solid solubility of alloy elements, solid-liquid interface feature and formation of new phases. For example, graphite can turn into diamond at high temperature and high pressure [5]; some alloys can form amorphous and microcrystalline microstructures at high pressure [6]. Some investigations for the effects of pressure on the nucleation process and solidification microstructure have been carried out and good results have been obtained [7]. In this paper, we choose hyper-eutectic Al-26.6wt%Si alloy. The effects of high pressure on the alloy microstructures with eutectic phase are studied.

2. Experimental

Pure Al (99.999%) and single crystal Si (99.999%) were used to compound a master alloy of Al-26.6wt%Si hyper-eutectic. Round rod test sample was poured in metal mould. The round rod was made up into high pressure test sample whose diameter is 14 mm and height is 12 mm. High pressure solidification was carried out on a DC-29C type six-anvil high pressure apparatus. Pyrophyllite was used to be sealing material. The assembly schematic of high pressure solidification is shown in Fig. 1. The pre-pressure for sealing is 3.0 GPa. The maximum pressure applied is about 5.5 GPa. The melting temperature is about 1200 °C.

3. Experimental results and discussion

The typical microstructure of hyper-eutectic Al-Si alloy solidified at normal pressure consists of primary β phase and $(\alpha+\beta)$ eutectic phase. When the cooling rate is slow, the primary β phase is bulky platelet. When the solidification of alloy is carried out in metal mould, the primary β phase is refined, as shown in Fig. 2. Fig. 3 shows the microstructure of hyper-eutectic Al-Si alloy solidified at 5.5 GPa high pressure. It can be seen from Fig. 3 that the microstructure of hyper-eutectic Al-Si alloy is different from that solidified at normal pressure, there exist a number of primary α dendrites and a few concentrated lumpy β stapes. Fig. 4 shows the X-ray scanning and secondary electron image, from which we can see the fine microstructure of $(\alpha+\beta)$ eutectic. The microstructure of hyper-eutectic Al-Si alloy solidified at high pressure is composed of primary α phase, β phase and $(\alpha+\beta)$ eutectic phase. The primary α phase and β phase exist simultaneously, which has never appeared in the microstructure solidifed at normal pressure. Table I shows the results of micro-area composition analysis, from which we can observe that the solid solubility of Si in α phase is 22.44%, and that of Al in β phase is 37.62%. The results are also shown in Fig. 4. As to Al-Si alloy solidified at normal pressure, the maximum solid solubility of Si in primary α phase is only 0.05%, and the solid solubility of Al in β phase is so small that we can think β phase as pure Si. Therefore, it is obvious that the solid solubility of Al-Si alloy solidifed at high pressure greatly extends. The solidification microstructures of alloy at high pressure are non-equilibrium metastable phases.

0022–2461

TABLE I Analysis of compositions in the microstructure of Al-26.6wt%Si solidified at 5.5 GPa high pressure

Phase	α	β	$(\alpha+\beta)$
Si content (wt %)	22.44	62.38	39.57
Al content (wt %)	77.56	37.62	60.43

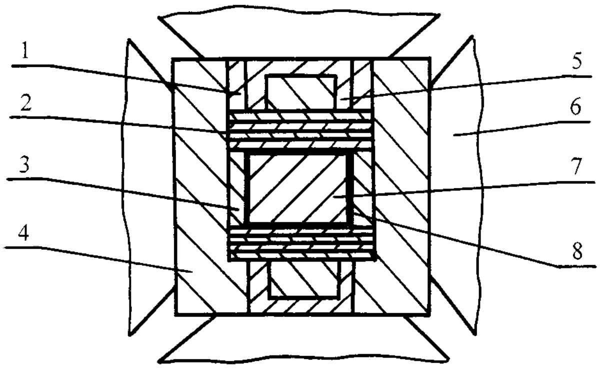

Figure 1 Assembly schematic of high pressure solidification: (1) sealing ring; (2) graphite plate; (3) graphite sleeve; (4) pyrophyllite; (5) electric conduction ring; (6) six-anvil; (7) alloy sample; and (8) insulating layer.

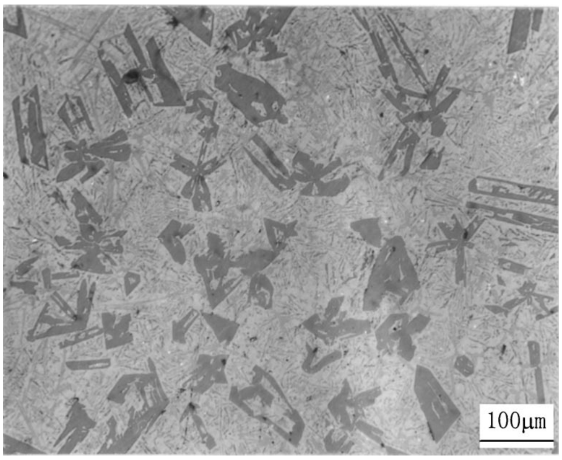

Figure 2 Microstructure of hyper-eutectic Al-Si alloy solidified at normal pressure.

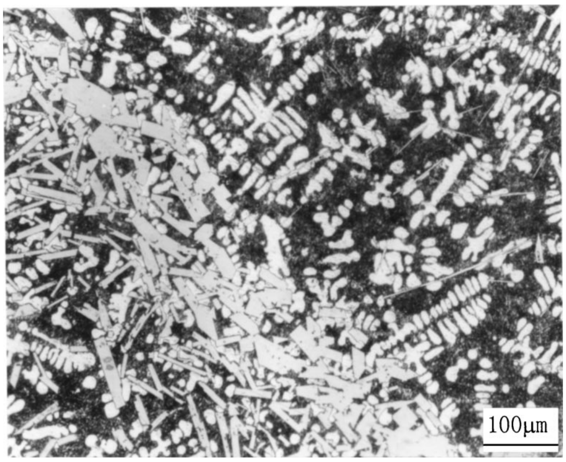

Figure 3 Microstructure of hyper-eutectic Al-Si alloy solidified at high pressure.

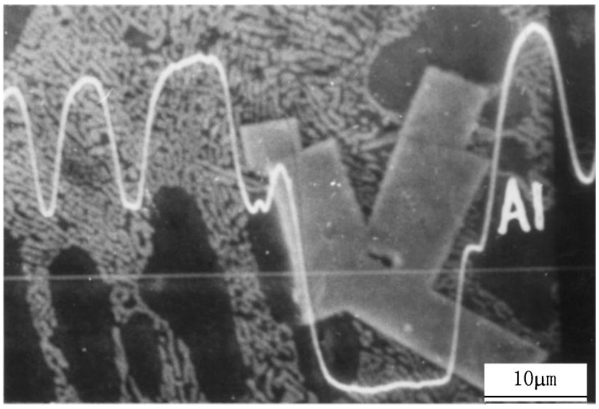

Figure 4 Alk_α X-ray scanning and secondary electron image.

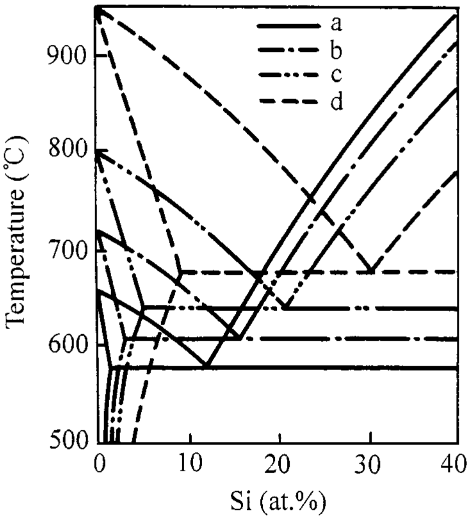

Figure 5 The effects of pressure on variation of Al-Si alloy phase diagram: (a) 0.0001 (b) 1 (c) 2.5 and (d) 5 GPa.

The primary α phase appears in hyper-eutectic Al-Si alloy solidified at high pressure, whose principal reason is that the melting point for Al heightens at high pressure. It is measured that the melting point for Al increases 6.4 °C when the pressure enhances 100 MPa [8]. According to Clapeyron equation:

$$dT = \frac{T_m(V_2 - V_1)}{\Delta H_m} dP \tag{1}$$

Where dP is the pressure change, dT the change of melting point with dP, T_m the melting point, V_1 the volume of 1 kg solid alloy, V_2 the volume of 1 kg liquid alloy, ΔH_m the melting latent heat. It can be calculated from the formula (1) that melting point for Al increases up to 1063 °C when the pressure reaches 5.5 GPa. Because the volume for Si contracts when it melts, the melting point for Si decreases with an increase in pressure. Thus, at 5.5 GPa pressure, the melting point for β phase is below that for α phase, which make α phase become primary phase in hyper-eutectic Al-Si alloy. Fig. 5 shows the effects of pressure on variation of Al-Si alloy phase diagram [9]. It can be seen from Fig. 5 that eutectic point obtained moves to the Si direction significantly with an increase of pressure and the solidification temperature also present ascendant tendency. When the pressure increases up to 5.0 GPa, the Si content in the eutectic point is about 30 at %, i.e., 31 wt %, therefore, the hyper-eutectic Al-26.6wt%Si alloy at normal pressure becomes hypoeutectic Al-Si alloy when it solidifies at 5.5 GPa high pressure, and the eutectic point temperature for Al-Si alloy increases from 577 °C to about 700 °C or so, which further explains that α phase is the primary phase when Al-26.6wt%Si alloy solidifies at 5.5 GPa high pressure.

According to the normal thermodynamics, it is difficult to explain that the primary α phase and β phase exist simultaneously. We originally thought that the primary β phase in master alloy did not completely dissolve and remained. At high pressure, these lumpy β crystals were moved by the primary α dendrites and became the concentrated lumpy β phase stapes. But the micro-area composition analysis, as shown in Table I, states clearly that the solid solubility of Al in β phase formed at high pressure is very high, and the Si content in the eutectic phase is also higher than that in the eutectic phase formed at normal pressure, which elucidates that the β phase obtained at high pressure solidification is not the β phase in master alloy and is a new β phase which separates out during the high pressure solidification. When the master alloy melts at high temperature and high pressure, although the bulky β phase in the master alloy melts, because of the slow diffuse velocity (elaborated in the ensuing paragraph), there exists local high Si concentration district in the original β phase district. When the eutectic transformation carries out, because the difference of Si contents between β phase and $(\alpha + \beta)$ eutectic phase at high pressure solidification is not as big as that at normal pressure solidification, a crystalline condition for β phase to form in the high Si district emerges when $(\alpha + \beta)$ eutectic phase forms. Therefore, the primary α phase and β phase exist simultaneously in the microstructure of hyper-eutectic Al-Si alloy solidifed at high pressure.

The crystalline process of liquid alloy consists of two stages: nucleation and crystal growth. The degree of thickness for crystalline microstructure is related closely to the two stages. With the beginning of the crystalline process, crystals nucleate and then grow. Two parameters which evaluate phase dynamics are the nucleation number, n, formed per unit time and per unit volume and the linear velocity, v, of crystal growth. The faster the velocity for nucleation, and the slower the velocity for crystal growth, the finer the crystalline grain obtained. The crystalline grain number, N, is related to the crystalline parameters, which can be given by:

$$N = a^4 \sqrt{(n^3/v^3)V_0} \tag{2}$$

Where a is the proportion coefficient, V_0 the original volume of liquid alloy. The formation of critical size nucleation must consume the energy which is equal to one third of the surface free energy for crystallization:

$$\Delta G^* = \frac{1}{3} S\sigma \tag{3}$$

Where ΔG^* is the critical formation energy for the nucleation, S the interface area for crystallization of nucleation, σ the surface tension of liquid alloy in the interface. If the equilibrium form for liquid alloy to crystallize is face-centered cube, the critical formation energy for the nucleation can be given by:

$$\Delta G^* = 8\sigma (r^*)^2 \tag{4}$$

Where r^* is the size of critical nucleation. It can be calculated by:

$$r^* = \frac{2\sigma T_{\mathrm{m}}}{\rho \Delta H_{\mathrm{m}} \Delta T} \tag{5}$$

Where ρ is the density of liquid alloy, ΔT the undercooling degree of liquid alloy. Introducing the T_{m} value of the formula (1) in the formula (5), we obtain the following formula:

$$r^* = \frac{2\sigma dT}{\rho \Delta T (V_2 - V_1) dP} \tag{6}$$

We introduce the r^* value of the formula (6) in the formula (4), and then obtain the following formula:

$$\Delta G^* = 32\sigma^3 \left[\frac{dT}{\rho \Delta T (V_2 - V_1) dP} \right]^2 \tag{7}$$

As to the formation energy ΔF^* for the equal-axial crystal on the surface of mixture, the similar relationship can be obtained:

$$\Delta F^* = 16 \left[\frac{\sigma_{1,2} dT}{\rho \Delta T (V_2 - V_1) dP} \right]^2 (\sigma_{1,2} - \sigma_{1,3} + \sigma_{2,3}) \tag{8}$$

Where $\sigma_{1,2}$ is the surface tension of the interface between undercooled liquid alloy and crystals, $\sigma_{1,3}$ the surface tension of the interface between undercooled liquid alloy and impurities, $\sigma_{2,3}$ the surface tension of the interface between crystals and impurities. It can be seen from the formula (8) that the increase of the nucleation number can depend on the decrease of the surface tension of the interface between the liquid alloy and the crystals and the increase of the undercooling degree and the applied pressure. In this experiment, because of the enhancement for the pressure, the nucleation number increases and its growth velocity reduces, which result in the refinement of microstructures obtained at high pressure solidification.

The solid solubility for Al-Si alloy significantly increases. There may be two reasons. One reason is that, under high pressure solidification condition, the velocity of atomic diffusion decreases. The relationship between the diffusivity and the viscosity of the liquid alloy is given by [10]:

$$D = \frac{RT}{\delta \eta} \tag{9}$$

Where D is the diffusivity of the liquid alloy, δ the length of atomic free travel, η the viscosity of the liquid alloy, T the temperature of the liquid alloy, R the gas constant. The relationship between the pressure, P, and the viscosity of the liquid alloy is given by [10]:

$$\eta = \eta_0 e^{PV_0/RT} \tag{10}$$

Where η_0 is the viscosity of the liquid alloy at the atmospheric pressure and the same temperature, P the applied pressure. Introducing the η value of the formula (10) in the formula (9), we can obtain the following formula:

$$D = \frac{RT}{\delta \eta_0 e^{PV_0/RT}} \tag{11}$$

It can be seen from the formula (11) that the atomic diffusivity decreases with an increase in the pressure, which will result in the reduce of the diffuse velocity for alloy elements to separate in the process of crystallization and thus make the segregation degree of alloy elements reduce. The decrease of the uneven parts for the alloy elements can give rise to the supersaturation of the solid solutions. The other reason is that, as shown in the formula (1), the undercooling degree of the liquid alloy enhances with an increase for the pressure, which increases the solidification velocity of liquid alloy. There is not enough time for the solute atoms to diffuse, and the solute atoms dissolve in the solid-phase lattice during crystal growth, therefore, the supersaturated solid solutions form.

The non-equilibrium microstructures of alloy solidifed at high pressure will be investigated deeply.

4. Conclusions

1. Under superhigh pressure condition, solidification microstructures of alloys are the non-equilibrium microstructures. The non-equilibrium microstructure of the hyper-eutectic Al-26.6wt%Si alloy consists of α phase, β phase and ($\alpha + \beta$) eutectic phase, and the α phase is the primary phase.

2. During the high pressure solidification, the undercooling degree of the liquid alloy increases, and the diffusivity of the liquid alloy reduces, therefore, the fine solidification microstructures are obtained, and the solid solubility in every phase increases greatly. The solid solubility of Si in α phase is up to about 22.44% and that of Al in β phase is up to about 37.62% at 5.5 GPa pressure.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China and Liaoning Province.

References

1. D. J. SKINNER, R. L. BYE and D. RAYHOULD, *Scr. Metall.* **20** (1986) 435.
2. R. E. FRANK and J. A. HAWK, *ibid.* **23** (1989) 113.
3. A. CZIRAKI, B. FOGARASSY, G. V. TENDELOO, P. LAMPARTER, M. TEGZE and I. BAKONYI, *J. Alloys Comp.* **210** (1994) 135.
4. J. H. PEREPEZKO and J. S. SMITH, *J. Noncryst. Solids* **44** (1981) 65.
5. Z. Y. HAO, Y. F. CHEN and L. Z. CHEN, *J. Cryst. Growth* **135** (1994) 370.
6. D. J. LI, J. T. WANG and B. Z. DING, *Scr. Metall.* **26** (1992) 621.
7. K. M. KULKARNI, *Poundry* **102** (1974) 76.
8. P. X. QI, "Extrusion Casting" (Guofang Industry Publisher, Beijing, 1984) p. 8 (Chinese).
9. A. E. BATASHEF, "Crystallization of Metals and Alloys at Pressure" (Moscow Metallurgy Publisher, Moscow, 1977) p. 16 (Russian).
10. G. S. FRENKEL, *Science* (1972) 424 (Russian).

Received 9 November 1998
and accepted 15 March 1999