EFFECT OF PRESSURE ON CRYSTALLIZATION CHARACTERISTICS AND CRYSTALLIZED MICROSTRUCTURE OF AMORPHOUS $Al_{85}Ni_{10}Y_5$ ALLOY①

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ABSTRACT The crystallization behaviour of amorphous $Al_{85}Ni_{10}Y_5$ alloy under high pressure was investigated. Results showed that the amorphous state can be preserved when the alloy is treated under high pressure at temperature below 325 ℃, the polytropic crystallization takes place when the alloy is treated at 325～520 ℃ and 3～6 GPa for 1 min; the crystallizing product is nanometer scale supersaturated *fcc* -Al solid solution particles dispersed in amorphous matrix; under 1 GPa pressure amorphous alloy crystallizes in an eutectic way, the crystallizing products are *fcc* -Al, Al_3Y, Al_3Ni, AlNiY equilibrium crystalline phases etc. High pressure appreciably changes the crystallization mode and the products, elevates the crystallizing temperature.

Key words amorphous alloy crystallization high pressure effect

1 INTRODUCTION

In recent years, it is found that some microcrystalline alloys obtained by controlling the crystallization process of amorphous alloys exhibit excellent mechanical and physical properties which are closely related to the phase constitution and the microstructure of the microcrystalline alloys. Therefore, it is academically significant to investigate the amorphous alloy crystallization characteristics. Super high pressure consolidation of amorphous alloy powder is a practical way to prepare bulk amorphous metallic materials. Under high pressure, amorphous alloys differ in behaviour from those under ambient pressure. The purpose of the present study is to investigate the crystallization characteristics of amorphous alloys under high pressure.

2 EXPERIMENTAL

The powder deposition plates were produced with a self-developed RS device. First, master $Al_{85}Ni_{10}Y_5$ alloy was melted in a crucible placed in an electrical furnace; then, the melt was put into a turdish and flew through a nozzle, where it was atomized into small droplets by high pressure nitrogen; the spray impacted to a copper disc rotating at a velocity of 3 000 r/min and cooled by liquid N_2. 0. 1～0. 5 mm thick, 1～2 cm^2 powder deposits were obtained[1].

Temperature and pressure were acted on the alloy through hexahedral apparatus usually used to synthesize diamond. Pressure was loaded at first; then, the sample was heated to the desired temperature within 10～20 s and kept for a selected period of time; next, within 10～30 s, the sample was cooled to near room temperature. The temperature was directly measureed with a NiCr/NiAl thermal couple[1].

SEM Rigaku X-Ray diffractometer, DSC and H-800 TEM were used to characterize the samples. The TEM samples were prepared by

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means of breaking bulk samples and manually selecting of small pieces. TEM observations were carried out in the thinner area of the broken piece of sample.

3 RESULTS AND DISCUSSION

3.1 *The Crystallization Characteristics Under Ambient Pressure*

X-Ray diffraction and TEM analysis indicated that the $Al_{85}Ni_{10}Y_5$ powder deposits is amorphous. Fig. 1 shows that the alloy transforms into a metastable state at 313 ℃, then an equilibrium state at about 340 ℃.

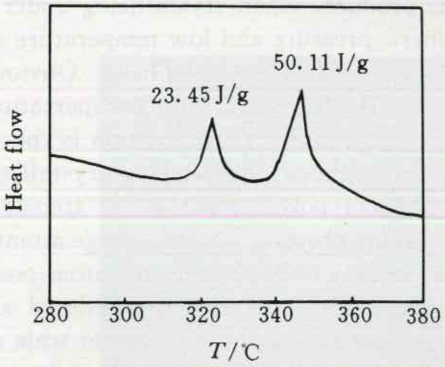

Fig. 1 DSC curve of amorphous alloy
heating rate: 30 K/min

Amorphous alloy was heat treated at 200, 250, 300 ℃ respectively for 30 min in N_2. XRD analysis reveals the phases constituents of the treated alloys as illustrated in Fig. 2.

In the XRD pattern of sample treated at 200 ℃, there are two sharp diffraction peaks in the large background; it shows that the amorphous phase still dominates the alloy; the crystalline phase is *fcc*-Al. Broadening peaks indicates that it has very fine grains. Treated at 250 ℃, the only crystalline phase is *fcc*-Al too; but in this case, the fraction of amorphous phase is much lower comparing with that in 200 ℃. At 300 ℃ the XRD pattern is composed entirely of sharp peaks with a low background; it reveals that the alloys are totally crystallized. XRD pattern analysis indicates that the alloy contains *fcc*-Al, Al_3Y, Al_3Ni, AiNiY phases etc.

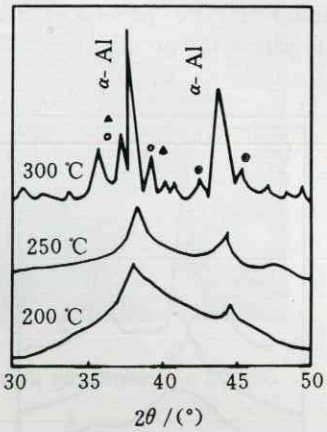

Fig. 2 XRD patterns of isothermally treated alloys
○—Al_3Y phase;
●—Al_3Ni phase;
△—AlNiY phase

3.2 *The Crystallization Characteristics of* $Al_{85}Ni_{10}Y_5$ *Alloy Under High Pressure*

Alloy samples were treated at 290, 325, 390, 450 and 520 ℃ under pressure of 1, 3, 6 GPa for 1 ~ 5 min respectively. Some XRD phase analysis results are listed in Fig. 3.

At 290 ℃, under the pressure ranging from 1 to 6 GPa, amorphous state is well preserved in the alloys. At 325 ℃, under 6 GPa pressure, kept for 5 min, amorphous state can be sustained; contrarily, under 1 or 3 GPa pressure, even if being kept for 1 min, crystallization occurs. Under 3 GPa pressure, there is a small fraction of *fcc*-Al in the alloy; under 1 GPa pressure, the alloy is totally composed of crystalline phases *fcc*-Al and other phases. In the XRD pattern, the diffraction peaks have not separated each other, which means that these phases have not fully grown yet.

At 390 ℃, even under 6 GPa pressure, the crystallization occurs; small amount *fcc*-Al formed in the amorphous matrix. With increasing temperature, crystallization accelerates. At 450, 520 ℃ under 3, 6 GPa pressure, there remains small amount of amorphous phase in the alloys coexisting with the *fcc*-Al phase; under 1 GPa pressure, there is no amorphous phase in the alloys at all.

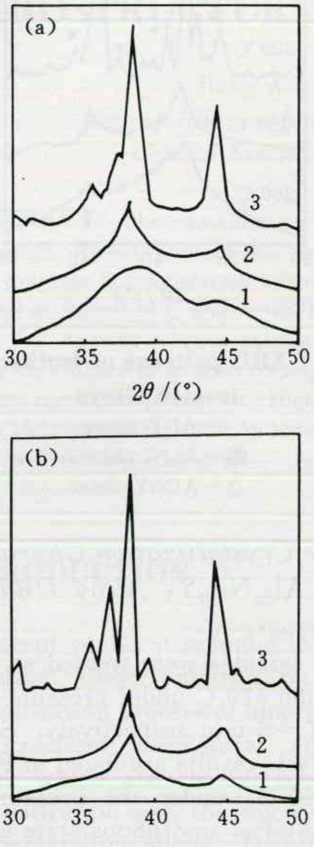

Fig. 3 XRD patterns of alloy treated under high pressure for 1 min

(a)—325 ℃; (b)—520 ℃;
1—6 GPa; 2—3 GPa; 3—1 GPa

3.3 *Microstructure of Crystallized Alloys*

Figs. 4a and 4b show the morphologies of $Al_{85}Ni_{10}Y_5$ alloy treated under 3 GPa pressure for 1 min at 450 and 520 ℃ respectively. At 450 ℃, it is difficult to find crystalline structure in the TEM image; it means that the size of the crystalline phase particle is very small and the crystalline volume fraction is very low. But at 520 ℃, 50 ~ 100 nm equiaxed crystalline grains which are dispersed in amorphous matrix can be observed. Fig. 5a demonstrates the electron diffraction pattern of the same area of the sample treated at 520 ℃ (corresponding to Fig. 4b), there is a diffraction ring and some unclear diffraction spots. This pattern provides evidence that the crystalline structure in the alloy is still not fully grown, probably imperfect and amorphous still exists. Fig. 5b, the dark field image of the corresponding area shows the distribution of the crystalline phase particles.

3.4 *Discussion*

From the results above, the only crystalline product, when crystallizing under atomospheric pressure and low temperature or 3, 6 GPa pressure is *fcc*-Al phase. Obviously, this *fcc*-Al phase is a Ni, Y supersaturated Al solid solution, its composition is the same as the amorphous phase. This crystallization reaction is a polymorphic phase transformation. In this process, no long-range atoms diffusion occurs, only short-range atom position adjustment takes places. The ordered atoms arrangement can reach a nanometer scale and a detectable volume fraction in the alloy. The crystallized tiny area in the alloy is surrounded by the amorphous structure. These are consistent with microstructure observations of partly crystallized alloy.

Under 1 GPa pressure, at 325, 390, 450 and 520 ℃, amorphous $Al_{85}Ni_{10}Y_5$ alloy transforms into crystalline alloy containing *fcc*-Al, Al_3Y, Al_3Ni, AlNiY phases etc in 1 min. It can be concluded that under lower pressure, crystallization overpasses the polymorphic transformation from amorphous state to *fcc*-Al supersaturated solid solution and the amorphous alloy directly transforms into crystalline phases in an eutectic way.

The thermodynamic and dynamic analysis of the crystallization process is useful on understanding the crystallizing behaviour of amorphous alloy demonstrated above . As illustrated in Fig. 6, the Gibbs free energy of amorphous alloy with a composition C_g is F_1; this thermodynamically unstable alloy tends to

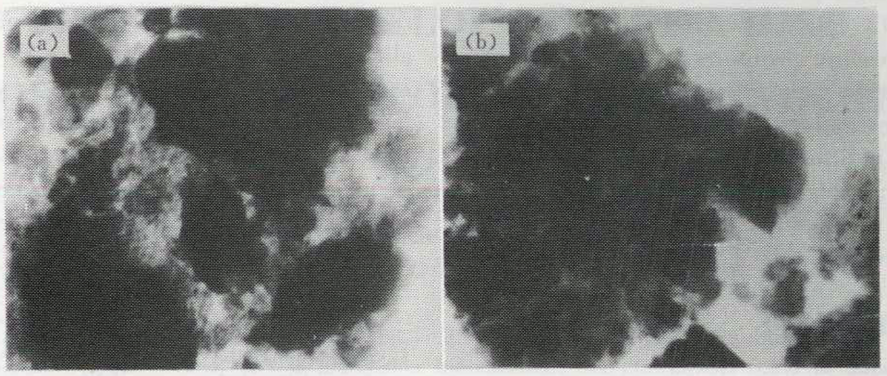

Fig. 4 Microstructure of alloys treated under high pressure, ×20 000
(a)—450 ℃, 3 GPa, 1 min;
(b)—520 ℃, 3 GPa, 1 min

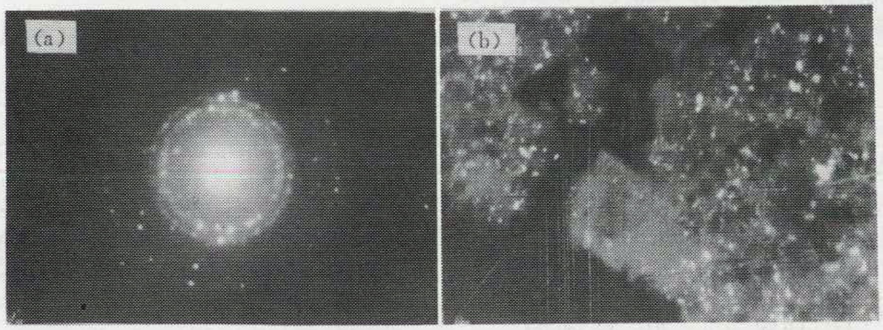

Fig. 5 Electron diffraction pattern (a) and the dark field image of alloy treated at 520 ℃, 3 GPa for 1 min (b)

crystallize automatically. Under high pressure and at low temperature, the mobility of the atoms in the alloy is largely restricted. In this case, the atom diffusion coefficient is lowered and atoms migration becomes difficult; therefore, the main mechanism of the crystallization is the diffusion free growing of the quenched crystalline nuclei. The crystallizing product is the solid solution with same composition. In this way, the free energy of the alloy is lowered to F_2. At higher temperature, the mobility of the atoms increases, diffusion-controlled phase transformation can take place[2]. In this case, the crystallized alloy is composed of solid solution $C_{s.s}$ and an intermetallic compound C_θ; the free energy of the system reaches its equilibrium value F_3.

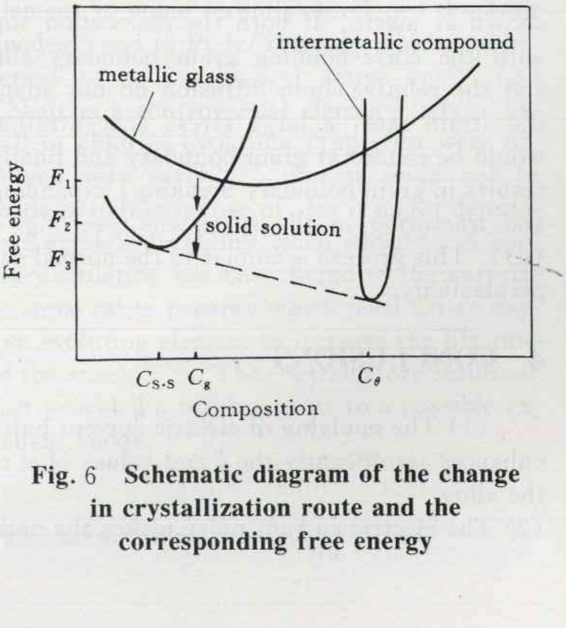

Fig. 6 Schematic diagram of the change in crystallization route and the corresponding free energy

under high pressure of 3 or 6 GPa in a nearly 200 ℃ temperature span (325 ～ 520 ℃), pressure prohibits the diffusion controlled eutectic type crystallization, only the diffusion-free polymorphic crystallization can occur. It is indicated that high pressure is very effective on restraining the mobility of the atoms. As a contrast, the action of 1 GPa is relatively weak.

4 CONCLUSIONS

(1) The amorphous state of $Al_{85}Ni_{10}Y_5$ alloy is preserved when treated at 290 ～ 325 ℃, under 6 GPa pressure for 1～5 min.

(2) Pressure can appreciably change the crystallization process. At 325 ℃, 3 GPa or 390, 450, 520 ℃ and 3, 6 GPa for 1 min condition, polymorphic crystallization occurs in the amorphous alloy; the produced phase in the crystallization is supersaturated *fcc*-Al solid solution. At the same temperature and 1 GPa pressure, eutectic crystallization takes place; equilibrium *fcc*-Al, Al_3Y, Al_3Ni and AlNiY crystalline phases etc are the main phases in the alloys.

(3) Nanocrystalline structure can be obtained by means of crystallizing of amorphous alloy under 3, 6 Gpa pressure at 450, 520 ℃ for 1 min.

(4) Under atomospheric pressure, being treated at 200, 250 ℃ for 30 min, the amorphous alloy crystallizes in a polymorphic way; at 300 ℃, it crystallizes in an eutectic way.

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specimens, so that high elongation rate and strain-stress index are shown at macro. If both the dislocation slip with the corresponding grain boundary slip and the relative atom diffusion do not adapt the strain rate, a large stress concentration would be caused at grain boundary and finally results in grain boundary breaking, expanding and fracturing in the specimens (see Fig. 4 (d)). This process is similar to the normal superplasticity.

4 CONCLUSIONS

(1) The applying of electric current pulse enhances significantly the δ and values of m of the alloy.

(2) The electric current pulse makes the optimum temperature of the superplastic deformation move to low temperature.

(3) Superplastic defomation is the results of both the dislocation slips in the grains and the grain boundary slips with the electric current pulse.

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