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Mechanism for phase boundary sliding and its relevance to diffusion-solution zone in SPD①

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[Abstract] The diffusion behavior of Zn/Al interfaces in their powders sintering was investigated with SEM. The results show that Zn-Al eutectoid microstructure can be achieved through their powders sintering, and the diffusion characteristic between Zn and Al is just a demonstration of Kirkendall effect, by which Zn can dissolve into Al and contrarily Al cannot dissolve into Zn. During sintering, a diffusion-solution zone α' has formed and subsequently transforms into eutectoid microstructure in cooling process. The superplastic deformation mechanism of Zn-Al eutectic alloy is phase boundary sliding which is controlled by diffusion-solution zone α'. If diffusion-solution zone α' is unsaturated, it will have much more crystal defects and the combination between α' and β phase is weak, thus the process of phase boundary sliding becomes easily; on the contrary, if the diffusion-solution zone α' becomes thick and saturated, the sliding will be difficult.

[Key words] Zn-Al alloy; superplasticity; phase boundary sliding; diffusion-solution zone(DSZ)
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1 INTRODUCTION

Since the discovery of superplasticity, people have investigated hundreds of superplastic materials including polycrystal ceramics, and lots of super-plastic deformation (SPD) mechanisms have been advanced, such as dissolution-deposition theory[1], metastable state theory[2], diffusion-flowage theory[3], dislocation creep theory[4], grain transposition model[5], grain transfer model[6], etc. Equiaxed grain has been accepted as one fundamental condition of structural superplasticity. Due to the complication of superplasticity, one of the above theory can generally explain part of phenomena in SPD. Nowadays SPD theory mainly focuses on GBS, which can be divided into Ball-Hutchison model[7] accommodated by dislocation and Ashby-Verall model[8] accommodated by diffusion according to different accommodation mechanisms.

Zn-22Al eutectoid alloy has been studied as a typical superplastic alloy more than fifty years, and investigations are still carrying on till now[1, 9~13]. While works on the superplastisity of Zn-5Al eutectic alloy are much less. Experiment results show that when superplastically deformed at 350 ℃, Zn-5Al eutectic alloy can reach a ultra-high elongation of 5 000%[14], so researches on its SPD mechanism would help to clarify microscopic characteristics of SPD. In this paper, the diffusion behavior of Zn/Al interfaces in their powders sintering has been investigated with SEM, and the effect of holding time on superplastic characteristic of Zn-5Al eutectic alloy is also studied. According to the experiment results, a superplastic deformation model of phase boundary sliding controlled by diffusion-solution zone for Zn-5Al eutectic alloy is proposed in the end.

2 EXPERIMENTAL

Chemical pure powders of Zn and Al were used in dissolution sintering test. In order to make metallographic specimens, aluminium powder and zinc powder were mixed together and pressed into shape under 1 700 MPa at 300 ℃ and subsequently carried on diffusion processing at 350 ℃. A special chemical etchant was used to give the bi-phase Zn-Al alloy a selective eroding, so that the microstructure of Zn-Al alloy specimen with a good contrast was attained and could be observed under SEM clearly. The composition of chemical etchant was: water, 100 mL; nitric acid, 5 mL; sodium sulfate, 1.5 g; chromic acid, 30 g.

Superplastic tensile specimens were cut from Zn-5Al as-rolled sheet. The alloy was made from industrial pure materials by intermediate-frequency induction fur-nace. After melting the liquid alloy was cast into an iron mold with the size of 300 mm × 400 mm × 24 mm at the temperature of 450~ 500 ℃ by water cooling, then followed by homogeneous annealing

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at 350 ℃ for 8h. The cast plate was hot rolled several times with the total distortion amount of 70%. After 310 ℃×4 h homogeneous annealing, the rolled plate was rolled again and finally a plate with 2 mm in thickness was obtained. Tensile specimens were cut from the as-rolled sheet parallel to the rolling direction, and then machined to a gauge-length of 10 mm and a width of 4 mm. All of the superplastic tensile tests were finished with a constant velocity tensile machine made by ourselves. The temperature controlling precision of the test machine was ±1 ℃ and up to 15 different velocities(from 10^{-5} mm/s to 10^{-1} mm/s) can be chosen in the test.

3 RESULT AND DISCUSSION

3.1 Diffusion-solution formation mechanism on α/β interfaces

According to Al-Zn phase diagram[15], Zn-5Al alloy is an eutectic alloy whose microstructure is composed of phase α and phase β. α and β are two kinds of solid solutions, α is abound in Al and β is abound in Zn. Grain boundaries in Zn-5Al are almost α/β phase boundaries. As shown in Al-Zn phase diagram, the maximum solvency of Zn in Al is 4% (mass fraction), and that of Al in Zn is less than 0.1%, so α/β interfaces can be approximately regarded as Al/Zn interfaces. Investigations on changes of Al/Zn interfaces during heating can help to reveal sliding mechanism in α/β interfaces.

5% (mass fraction) Al powder and 95% Zn powder are mixed together and pressed into shape. After diffusion at 350 ℃ for quite a long time, Zn/Al eutectoid forms, as shown in Fig. 1. Fig. 1(a) illustrates the appearance of pure Al powder, and Figs. 1(b) and (c) show the metallographic morphologies of Zn and Al powder mixture after pressure shaping under 1 700 MPa at 300 ℃ and subsequent diffusion processing at 350 ℃ for different time. Experiments indicate that eutectoid occurs where original Al powder granules exist and no eutectoid appears at the position of original Zn powder granules. If keep temperature constant for quite a long time at 350 ℃, Zn will dissolve into Al and α′ solid solution forms. During subsequent cooling process, self-eutectic reaction takes place in α′ solid solution and eutectoid (α+β) forms, and the scope that eutectoid occurs is restrained by the size of Al powder granules.

Eutectoid formed by diffusion sintering of Zn powder and Al powder is actually an application of Kirkendall effect. Ref.[16] introduced Kirkendall effect for Ni/Cu diffusion couple. Although Ni and Cu can form infinitive solid solution, Cu can dissolve into Ni and Ni cannot dissolve into Cu in solid diffusion. A similar case occurs in the process of powder sintering of Zn and Al, in which Zn can dissolve into Al and contrarily Al can not dissolve into Zn. Comparison of parameters of Kirkendall effect between Al/Zn and Ni/Cu is listed in Table 1.

Fig. 2 illustrates the formation of eutectoid for Al powder and Zn powder after sintering. During sintering, DSZ forms on Al/Zn interface (as shown in Fig. 2(a)). In fact, the so called DSZ is inhomogeneous solid solution α′ formed by solvency of Zn in Al, whose structure is the same as that of Al. α′ contains more Zn than α in Zn-5Al. Furthermore, the contents of α′ is uneven and its Zn amount is 0 at the end next to Al and 65%(mole fraction) at the end next to Zn. During subsequent cooling process, eutectoid reaction occurs in α′ and (α+β) forms, as shown in Fig. 2(b).

3.2 Controlling mechanism of DSZ on α/β interface sliding

As demonstrated in the experiments, Al is more

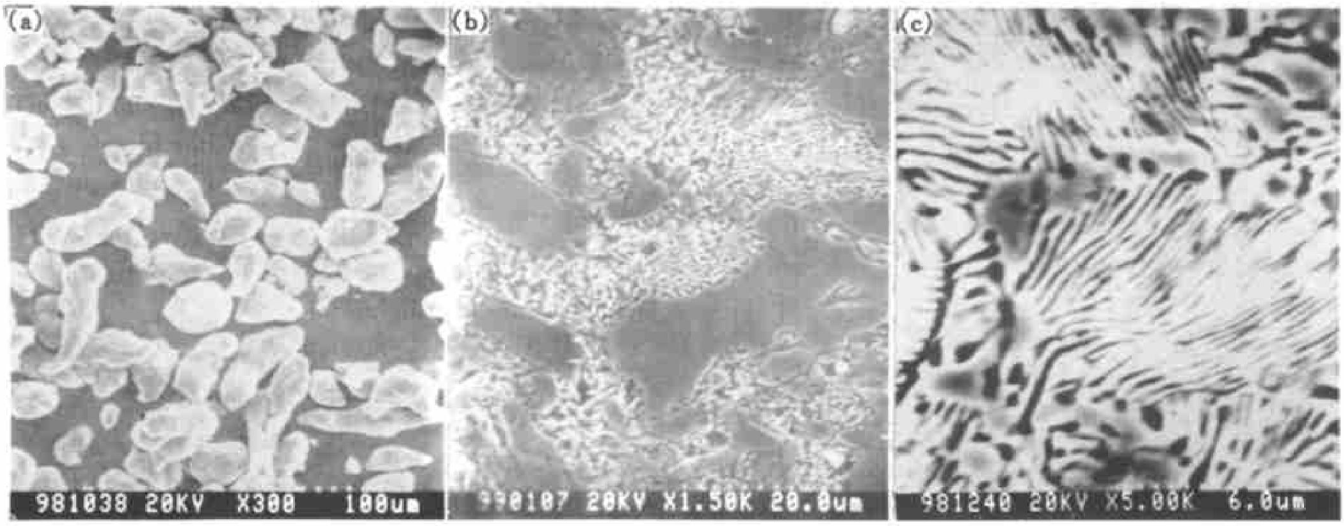

Fig. 1 Eutectoid microstructures of Zn(95%) and Al(5%) mixed powder after sintering (SEM)
(a) —Al powder; (b) —Sintering at 350 ℃ for 75 h; (c) —Sintering at 350 ℃ for 100 h

Table 1 Comparison of Kirkendall effect between Ni/Cu and Al/Zn

Parameter	Al/Zn	Ni/Cu
Diffusion coefficient	$D_{Al} < D_{Zn}$	$D_{Ni} < D_{Cu}$
Binding energy	$E_{Al} > E_{Zn}$	$E_{Ni} > E_{Cu}$
Diffusion direction	Zn into Al	Cu into Ni
Atomic radius	$R_{Al} > R_{Zn}$	$R_{Ni} < R_{Cu}$

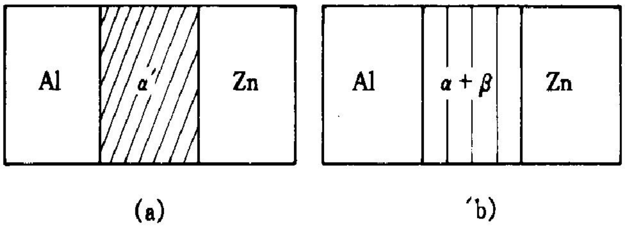

Fig. 2 Diffusion-solution zone on Zn/Al interface

stable than Zn at 350 ℃. Zn can dissolve into Al and Al cannot dissolve into Zn, which also proves that Zn atoms keeping contact with Al on Zn/Al interface have weaker binding with original Zn crystal. For Zn-5Al, at 350 ℃, there exists one layer of "freer" Zn atoms on the interface, which combine weakly with β and also weakly with α before dissolving into α, so α/β is easy to slide under the action of external force.

For rolled alloy, its high density of defects contributes to diffusion of atoms, so DSZ, viz, α′ solid solution with more defects easily forms on the interface, whose Zn content is 1.7% (mole fraction) at the end close to α and x % at the end close to β (assume that x is less than 64.5, and 64.5% is the maximum solvency of Zn in Al at 350 ℃). The unsaturated DSZ with defects would combine weakly with β and easily slide.

Experiments show that Zn-5Al in rolled state has the largest elongation. After temporary recrystallization (such as 350 ℃, 10~20 min), the flow stress increases steeply and the elongation decreases dramatically, as illustrated in Fig. 3. Structure analysis demonstrates that, no pronounced differences exist between the structures after recrystallization at 350 ℃ for 10~20 min and those in rolled state, so the heat treatment at 350 ℃ for 10~20 min only equals to recovery process. Prolonging holding time before SPD helps thicken DSZ, as shown in Fig. 4(b). Assume that α′ solid solution reaches dynamic saturation at certain time, viz, Zn content of α′ is 1.7% (mole fraction) at the end adjacent to α and 64.5% (mole fraction) at the end adjacent to β, then the time corresponding to the dynamic saturation is the critical time, as shown in Fig. 4(f). After that, the interfaces at two ends of DSZ no longer change, so prolonging holding time exceeding the critical point cannot remarkably influence superplasticity.

Precipitation of β from α′ satisfies the following

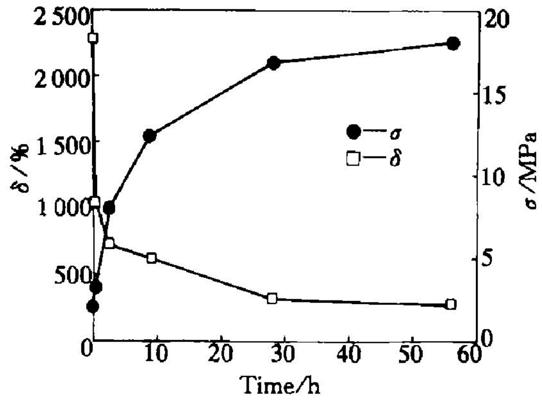

Fig. 3 Influence of holding time on stress and elongation for Zn-5Al alloy

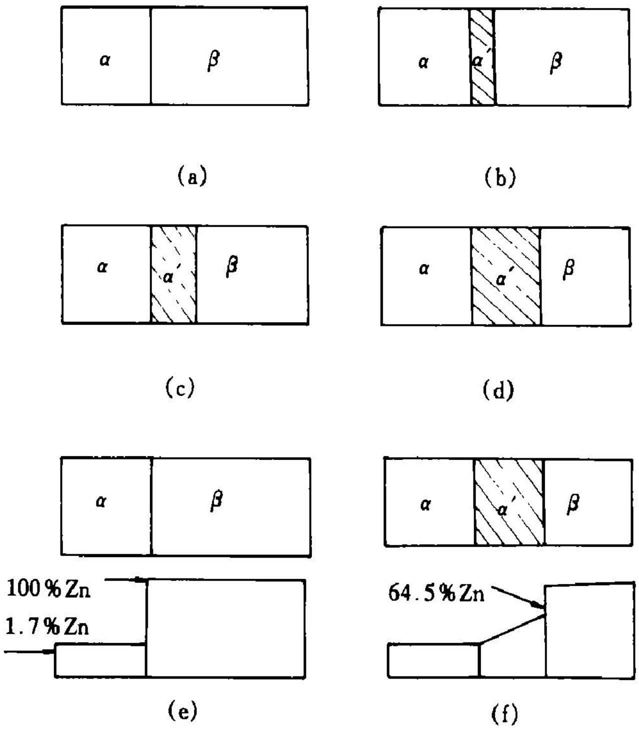

Fig. 4 Sketch of formation of α/β diffusion-solution zone

(a) —Before diffusion; (b) —350 ℃, 20 min; (c) —350 ℃, 2.5 h; (d) —350 ℃, 29 h; (e) —Interface before diffusion and dissolution; (f) —Interface after diffusion and dissolution

relation[17]: (111) α′ // (001) β, among which α′ has the same face-centred (fcc) structure as α and β is hexagonal closely-packed (hcp) structure. α′ crystal is the extension of α crystal, but α′ contains more Zn atoms, so α′/α interface is difficult to slide. (0001) plane of β parallels to (111) plane of α′, so (0001) plane in β can be regarded as the extension of (111) plane in α′. The stacking sequence of (111) plane in face-centred α′ is ABCABC and that of (0001) plane in β is ABAB. At β end of α′, the maximum Zn content can reach 64.5% (mole fraction), so Zn can construct fcc structure for the particular situation. Obviously, the transition from fcc structure to hcp structure is just the transition of stacking sequence from

ABCABC to ABAB, so α'/β interface is not easy to slide either.

For Zn-5Al, prolonging holding time before SPD can thicken DSZ on α'/β interfaces until it reaches saturation, which disadvantages the sliding of α'/β. DSZ in dynamic saturation state will impose maximum influence on superplasticity and prolonging holding time no longer influences stress and elongation remarkably.

4 CONCLUSIONS

1) Zn-Al eutectoid microstructure can be achieved through their powders sintering, and the diffusion characteristic between Zn and Al is a demonstration of Kirkendall effect, with which Zn can dissolve into Al and Al can't dissolve into Zn. During sintering, a diffusion-solution zone α' has formed and subsequently transforms into eutectoid microstructure in cooling process.

2) At SPD temperature, Zn-5Al in rolled state has the characteristics of higher density of defects, larger atom migration rate and lower activation energy, so inhomogeneous DSZ(i.e., solid solution α') is easy to form on its α/β interfaces. Moreover, Zn content of the solid solution α' at β end is unsaturated (less than 64.5% (mole fraction)), which advantages the sliding of α/β interfaces.

3) With the increasing of holding time prior to SPD, DSZ on α/β interfaces tends to reach dynamic saturation state, in which Zn content of DSZ is 1.7% at α end and 64.5% at β end. The crystal structure of DSZ at α end is the extension of α crystal, so α binds strong with DSZ and is not easy to slide. In spite of fcc structure, β end of DSZ is composed of 64.5% Zn atoms. Consequently, the transition from DSZ to β phase is the transition of stacking sequence from ABCABC to ABAB, so the interface between saturated DSZ and β phase is also not easy to slide.

4) There exists a critical point for effect of holding time on stress and elongation. Prolonging holding time exceeding critical point would no longer influence superplasticity remarkably, because when DSZ reaches saturation, prolonging holding time only thicken it and the interfaces at its two ends change little.

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