Effects of Zn Content on Microstructures and Hardness of Ag925CuZn Alloys

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Abstract: The effects of Zn content on the microstructures and hardness of Ag925CuZn alloys were systematically investigated. The experimental results show that alloying element Zn significantly reduced the porosity of the as-cast microstructure of Ag925CuZn alloys and induced their grains coarsening during intermediate annealing and led convex microstructure forming during aging, which possesses face center cubic solid solution *α*-Ag. Moreover, high Zn content led to the decrease of solution-annealed hardness and aged hardness of Ag925CuZn alloys. For Ag925CuZn alloys with low Zn content, their proper aging temperatures are between 200 ℃ and 250 ℃ after solution-annealing, and their proper aging temperatures are between 150 ℃ and 200 ℃ after cold rolling.

Key words: Ag925CuZn alloys; Zn content; microstructure; hardness

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Ag925Cu75 alloy, namely, sterling silver, has been used as a standard graded alloy in coin and silverware in England for more than 800 years, because of its high strength and hardness[1]. However, it has less melt fluidity and less discoloration resistance compared to pure silver, and often oxidizes to form fire scale[1]. In order to obtain good comprehensive properties, some alloying elements, such as Zn and Sn, are usually added into the alloy[2~7].

Little information is available on the effects of alloying elements on microstructure and mechanical properties of Ag925Cu alloy in published documentations. This paper discusses the effect of Zn content on microstructure and hardness of Ag925CuZn alloys by means of hardness tests, X-Ray diffraction analysis (XRD), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

1 Experimental

The purities of the constituent elements Ag, Cu and Zn used in the present experiment were 99.9% at least. Four experimental alloys with nominal compositions listed in table 1 were arc-melted with a non-consumable electrode and water-cooled copper crucible in a 0.05 MPa argon atmosphere to produce button-like ingots. All these alloys were melted five times to get ingots with uniform composition. These button-like ingots were diffusion-annealed at 720 ℃ for 4 h, and then punched, annealed at 600 ℃ for 4 h, cold rolled into plates with thickness 2.0 mm, solution-annealed at 700 ℃ for 0.5 h and cold rolled into plates with thickness 1.4, 1.0 and 0.6 mm.

Table 1 Nominal composition of four alloys (wt%)

Alloy	Ag	Cu	Zn
A	92.5	7.5	0
B	92.5	5.0	2.5
C	92.5	4.0	3.5
D	92.5	3.0	4.5

For solution-annealing and aging, specimens were cut from the solution-annealed plates with thickness 1.4 mm, followed by solution annealing at 700 ℃ for 0.5 h and aging at the temperature between 150 ℃ and 350 ℃ for various time from 1 h to 4 h, and air cooling. For cold rolling and aging, specimens were cut from the plates with thickness 1.0 mm and 0.6 mm (namely, plates cold rolled with 50% reduction and 70% reduction in thickness), followed by aging at the temperature between 150 ℃ and 300 ℃ for various time from 1 h to 4 h, and air cooling. Specimens for hardness test were ground to

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remove surface scale with $2000^{\#}$ SiC waterproof abrasive paper. Those for OM and SEM observation and EDS analysis were ground with $2000^{\#}$ and $2400^{\#}$ SiC waterproof abrasive papers and polished with W1.0 diamond abrasive paste, and then etched in etching reagent composed 25% H_2O_2 and 75% $NH_3{\cdot}H_2O$ by volume fraction.

Hardness tests were performed by an HXS-1000AK semiautomatic microindenter with a 200 g load for 20 s, whose results provided should be considered with 3.5% scatter. XRD analysis was carried out by an X'Pert PRO X-ray diffractometer, by continuous scanning in the 2θ between 30° and 150° with 0.0167° steps at room temperature. OM observations were carried out by a PMG3 optical microscope. SEM observations and EDS analysis were carried out with a Quanta 400 scanning electron microscope and Oxford INCA energy dispersive spectrometer, respectively.

2 Results and Discussion

2.1 Effect of Zn content on microstructure

As shown in Fig.1, almost no macropores appeared in as-cast microstructure of alloy C, while lots of macropores appeared in as-cast microstructure of alloy A. This shows that Zn increases melt fluidity improving castability and mould filling of Ag925Cu alloys[4].

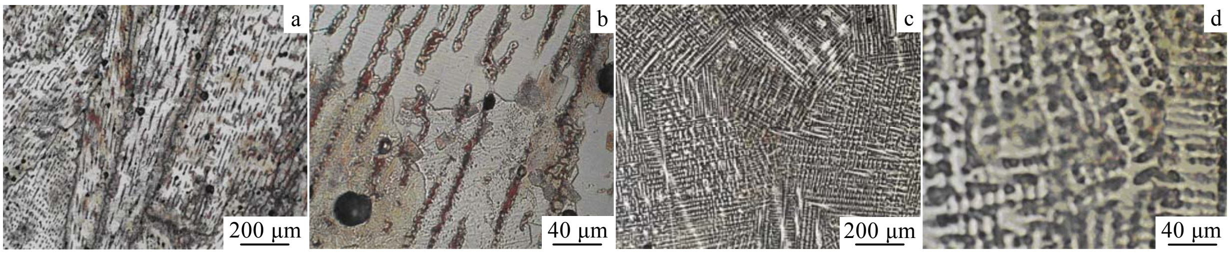

Fig.1 OM images of as-cast microstructure: (a), (b) Alloy A; (c), (d) Alloy C

After solution-annealing at 700 ℃ for 0.5 h, there were a lot of annealed twins in four solution annealed alloys, as shown in Fig.2. This shows that Cu and Zn additions did not drastically increase the stacking fault energy of silver[8]. In addition, compared with alloy A, the grains of the other three alloys are coarser. This shows that Zn induces grain coarsening of Ag925CuZn alloys during annealing-in-process.

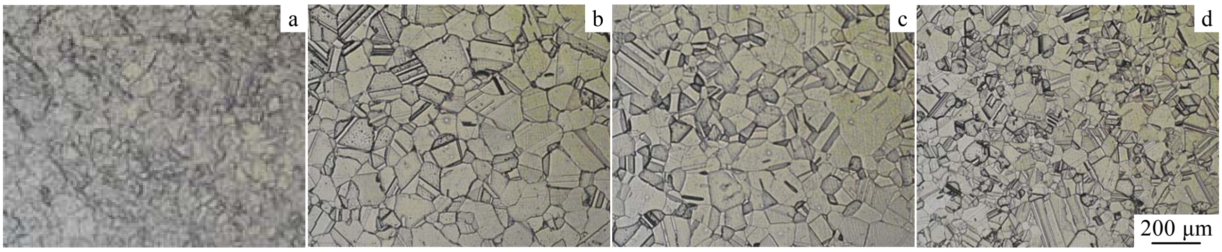

Fig.2 OM images of four alloys solution annealed at 700 ℃ for 0.5 h: (a) alloy A, (b) alloy B, (c) alloy C, and (d) alloy D

For solution-annealed alloy A, β-Cu phase precipitated during aging, as shown in Fig.3a. For the other three solution-annealed alloys, when aged at 200 ℃, a convex microstructure appeared along grain boundary

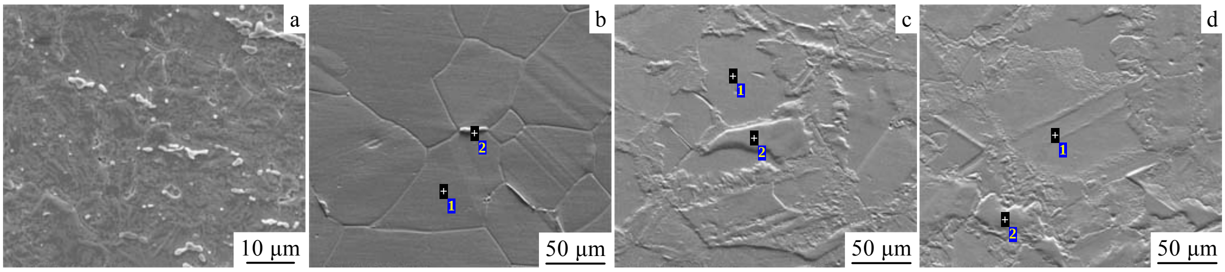

Fig.3 Typical SEM images of solution annealed alloys aged at the different temperatures for 4 h: (a) alloy A, 250 ℃; (b) alloy C, 200 ℃; (c) alloy C, 250 ℃; (d) alloy C, 350 ℃

after 4 h, as shown in Fig.3b, and lots of the convex microstructure appeared after aging at the temperatures between 250 ℃ and 350 ℃ for 4 h, as shown in Fig.3c and Fig.3d. According to EDS analysis listed in table 2, the composition of the convex microstructure is almost the same to that of the matrix microstructure. XRD spectrums of alloy C in three heat treatment states are shown in Fig.4. After aging at 250 ℃ and 350 ℃ for 4 h, no new diffraction peaks appeared in alloy C except those of face center cubic α-Ag, which shows that the convex microstructure is still face center cubic solid solution α-Ag. However, diffraction peaks moves left. This shows that solubility of solute atoms Cu and Zn in solid solution α-Ag decreases during aging at the temperatures between 250 ℃ and 350 ℃, which makes lattice distortion decreasing.

After cold rolling, grains were obviously elongated in the rolling direction and lots of undulated slid slips appeared in four alloys, as shown in Fig.5. This shows that multisystem slip occurred in Ag925CuZn alloys during cold rolling[8]. When aged at the temperatures between 150 ℃ and 300 ℃, shapes of elongated grains of four alloys did not obviously change, at the same time, the convex microstructure also appeared along grain boundary of the matrix when aged at the temperatures between 200 ℃ and 300 ℃, as shown in Fig.6.

Table 2　EDS analysis on alloy C

The aged condition	Spots	Element content/wt%		
		Zn	Cu	Ag
200 ℃, 4 h, Fig.3b	1	2.59	3.48	93.93
	2	2.45	3.83	93.72
250 ℃, 4 h, Fig.3c	1	2.83	3.64	93.53
	2	2.68	3.49	93.84
350 ℃, 4 h, Fig.3d	1	2.63	3.71	93.66
	2	2.75	3.62	93.62

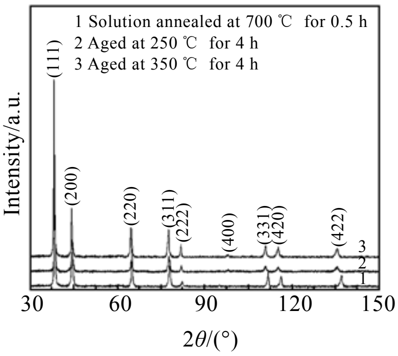

Fig.4　XRD spectra of alloys C in three heat treated states

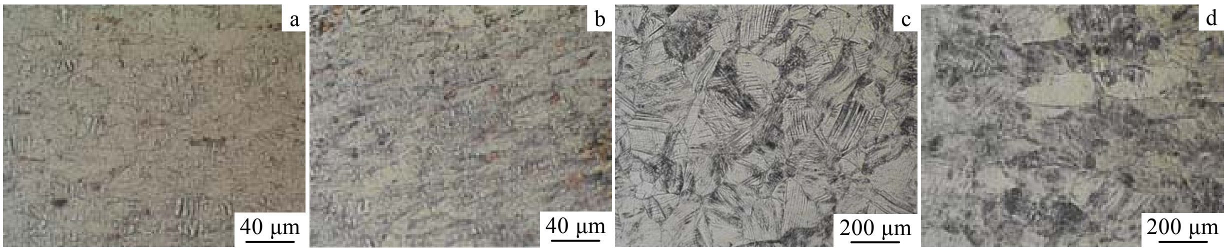

Fig.5　OM images of cold rolled alloys: (a) alloy A, cold rolled with 50% reduction in thickness; (b) alloy A, cold rolled with 70% reduction in thickness; (c) alloy C, cold rolled with 50% reduction in thickness; (d) alloy C, cold rolled with 70% reduction in thickness

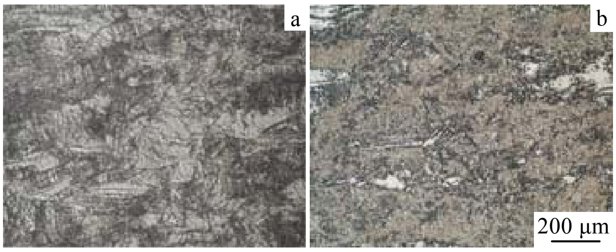

Fig.6　OM images of alloy C aged at 200 ℃: (a) 1 h; (b) 4 h (prior to cold rolling with 70% reduction in thickness)

2.2　Effect of Zn content on hardness

After solution-annealing at 700 ℃ for 0.5 h and water-quenching, in comparison with hardness HV0.2 621.3 MPa of alloy A, hardness of alloy B was HV0.2 53.9 MPa higher, and hardness of alloy D was HV0.2 57.8 MPa lower, as shown in table 3. Obviously, high Zn content decreased solution-annealed hardness of Ag925CuZn alloys. This is because the relative difference in atomic radius ($(R_{Ag}-R_{M})/R_{Ag}$) between Ag and Zn is 3.74% lower than that between Ag and Cu (atomic radius of Ag, Cu and Zn is 0.1444, 0.1278 and 0.1332 nm, respectively), and crystal lattice distortion caused by Zn is lower than that cause by Cu, therefore the solid-solution strength-thening effect of Zn on silver is weaker than that of Cu on silver.

When aged at the temperatures between 150 ℃ and 350 ℃ for various time from 1 h and 4 h, the changes of

Table 3　Hardness of four alloys solution-annealed at 700 ℃ for 0.5 h

Alloy	A	B	C	D
$HV_{0.2}$/MPa	621.3	675.2	625.2	563.5

hardness of four solution-annealed alloys with aging time are shown in Fig.7. For alloy A, when aged at the temperatures between 250 ℃ and 300 ℃, the hardening process was fairly fast and the hardness decreased slowly with the increase of aging time. For alloys B and C, when aged at the temperatures between 200 ℃ and 250 ℃, the hardening process was fairly fast and the hardness decreased slowly with the increase of aging time. After aging at 250 ℃ for 2 h, hardness of alloy B reached the peak 1350.4 MPa, which was 675.2 MPa higher than its solution annealed hardness and was also 120.5 MPa higher than the peak hardness $HV_{0.2}$ 1229.9 MPa of alloy A after aging at 250 ℃ for 2 h. After aging at 250 ℃ for 3 h, hardness of alloy C reached the peak hardness $HV_{0.2}$ 1230.9 MPa, which was 605.7 MPa higher than its solution-annealed hardness. However, in the same aged state, hardness of alloy D was lower than those of alloys B and C. It can be seen that the aged hardness of Ag925CuZn alloys with low Zn content is higher than those of Ag925CuZn alloys with high Zn content, and the former proper aging temperature are between 200 ℃ and 250 ℃.

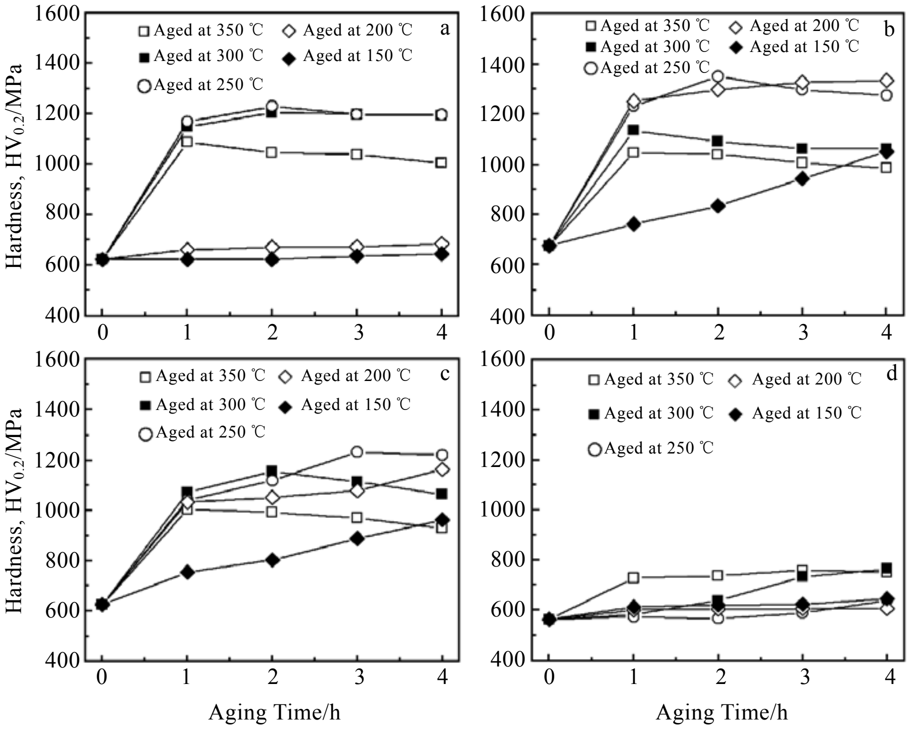

Fig.7　The changes in hardness of four solution-annealed alloys aged the temperatures between 150 ℃ and 350 ℃ as a function of aging time: (a) alloy A, (b) alloy B, (c) alloy C, and (d) alloy D

After cold rolling with 50% and 70% reduction in thickness, the hardness of four alloys is shown in table 4. It can be seen that the cold rolling greatly improves the hardness of Ag925CuZn alloys, and that high Zn content weakens the cold rolled hardness of Ag925CuZn alloys. When aged at the temperatures between 150 ℃ and 300 ℃ for various time from 1 h and 4 h, the changes in the hardness of four cold rolled alloys with aging time are shown in Fig.8. When aged at 150 ℃ for no more than 4 h, their hardness slightly increased, and when aged at 300 ℃ for more than 2 h, hardness obviously decreased, especially the hardness of alloys C and D. This shows that for cold rolled Ag925CuZn alloys, their proper aging temperatures are between 150 ℃ and 200 ℃.

Table 4　Hardness of four cold rolled alloys

Alloy	$HV_{0.2}$/MPa	
	50% reduction in thickness	70% reduction in thickness
A	1229.5	1457.3
B	1280.9	1427.9
C	1231.9	1370.0
D	1203.4	1396.5

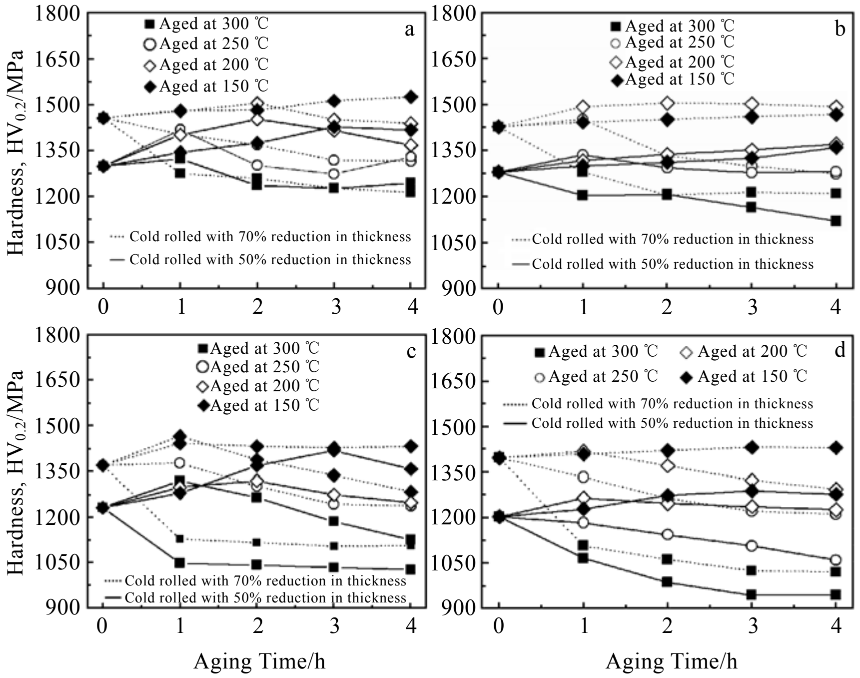

Fig.8 The changes in the hardness of four alloys aged the temperatures between 150 ℃ and 300 ℃ as a function of aging time: (a) alloy A, (b) alloy B, (c) alloy C, and (d) alloy D (prior to cold rolling)

3 Conclusions

1) For Ag925Cu alloys, alloying element Zn significantly reduces the porosity of as-cast microstructure, and induces grain coarsening during annealing-in-process. In addition, the composition and the crystal structure of convex microstructure which appears during aging are the same as those of the matrix *α*-Ag.

2) High Zn content will decrease the solution-annealed hardness and the aged hardness of Ag925CuZn alloys. For Ag925CuZn alloys with low Zn content, after solution-annealing, their proper aging temperatures are between 200 ℃ and 250 ℃, and after cold rolling, their proper aging temperatures are between 150 ℃ and 200 ℃.

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Zn含量对Ag925CuZn合金显微组织和硬度的影响

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摘　要：研究了 Zn 含量对 Ag925CuZn 合金显微组织和硬度的影响。结果表明：Zn 显著抑制 Ag925CuZn 合金铸态组织中孔洞的形成，且在中间退火过程中使其晶粒粗化，在时效过程中形成具有与基体 *α*-Ag 成分、结构相同的浮凸状组织。同时，高 Zn 含量降低 Ag925CuZn 合金的固溶态硬度和时效态硬度；对于低 Zn 含量 Ag925CuZn 合金，固溶退火后合理的时效温度为 200~250 ℃，冷变形后合理的时效温度为 150~200 ℃。

关键词：Ag925CuZn 合金；Zn 含量；显微组织；硬度

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