Vol. 14 № 2 Trans. Nonferrous Met. Soc. China Apr. 2004
Article ID: 1003 - 6326(2004)02 - 0356 - 06

Evolution of undissolved phases in high-zinc content super-high strength aluminum alloy during ageing①

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Abstract: The evolution of undissolved phases in the high-zinc content super-high strength aluminum alloy during ageing was investigated by means of SEM and EDS. The results show that undissolved phases of Cu-rich *M*(AlZnMgCu) exist in the silver-free alloy at solid-solution state. With increasing the ageing time, the precipitation of age-hardening precipitates $MgZn_2$ stimulates Zn atoms within the undissolved phases to diffuse into the matrix, and thus the Cu content in the *M*(AlZnMgCu) phase increases relatively. For the silver-bearing alloy, small addition of Ag promotes the formation of Ag-rich *M*(AlZnMgCuAg) undissolved phases and deteriorates mechanical properties of the alloy. At the early stage of ageing, Ag content within the *M*(AlZnMgCuAg) phases greatly decreases due to rapid diffusing of Ag atoms into the matrix and the co-clustering of Ag and Mg atoms. As the ageing time prolonging, the precipitation of $MgZn_2$ results in the decrease of Zn content in the undissolved phases, and the relative increase of Ag and Mg contents.

Key words: Al-Zn-Mg-Cu; undissolved particles; ageing; SEM; EDS
CLC number: TG 146.2 **Document code:** A

1 INTRODUCTION

There are generally three types of the second phase particles in commercial 7XXX series aluminum alloys which are dispersoids, fine age-hardening precipitates and coarser constituent phases[1]. Dispersoids are insoluble intermetallic compounds of Cr or Zr, intentionally added to retard recrystallization and to control grain size. Precipitates are extremely fine and homogeneously distributed. They form during ageing and are responsible for the high strength. Coarser particles are inherited from the original cast ingot, consisting of insoluble or partially soluble intermetallic compounds and eutectic phases. The former compounds form primarily because of the interaction of the alloying elements with impurities such as Fe and Si, and the latter attributed to the non-equilibrium phase transformation during casting. These coarser particles are sites of stress concentration and micro-crack initiation, which may do harm to the fracture toughness, fatigue-resistance and resistance of stress corrosion cracking[2, 3]. CHEN[4] studied the promotive-homoginization process of LC4. It was found that multiple eutectic phases may dissolve at different temperatures. CHEN[5-7] studied the effect of promotive-solution heat treatment on the microstructure and mechanical properties of 7075 and 7055 aluminum alloys. It was pointed out that the temperature-incremental solutionizing heat treatment made the solutionizing temperature limit higher than the multi-phase eutectic temperature without the formation of over-heated structure and effectively promoted solutionizing and improved the mechanical properties of 7XXX series aluminum alloys. Employed alloy in present study was promotive-homoginized, promotive-solutionized and then aged for various periods of time. The purpose is to investigate the influence of element composition changes of undissolved phases on mechanical properties of the studied alloy, accommodating a basis to the alloy composition design and optimization of heat treatment process.

2 EXPERIMENTAL

The cast ingots of two employed alloys in present study were made by low frequency electromagnetic casting and their chemical compositions are listed in Table 1. Alloy 2 is 0.2% (mass fraction) silver-bearing and 0.01% (mass fraction) beryllium-bearing. The ingots were homogenized at 400 ℃ for 12 h, 460 ℃ for 32 h and then hot squeezed into cylindrical rod of 11mm in diameter. Different promotive-solution treatments were applied to the two alloys as 450 ℃, 2 h+ 460 ℃, 1 h for alloy 1 and 450 ℃, 2 h+ 470 ℃, 1 h for alloy 2, respectively. Subsequently the two alloys were quenched in cold water and aged at 120 ℃ for various lengths of time. Mechanical prop-

① **Foundation item:** Project(2001AA332030) supported by the National Advanced Materials Committee of China
Received date: 2003 - 06 - 05; **Accepted date:** 2003 - 11 - 24
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erties test was performed on an universal tensile testing machine of CSS-44100 type. A JSE-5600LV scanning electron microscope and its energy dispersive analyzer were used for the microstructure inspection and the determination of the constituent elements in undissolved phases.

Table 1 Chemical compositions of studied alloy

Alloy No.	Composition (mass fraction) / %						
	Zn	Mg	Cu	Ag	Be	Zr	Al
1	12.2	2.00	2.48	0	0	0.15	Bal.
2	12.1	2.27	2.40	0.2	0.01	0.15	Bal.

3 RESULTS

The distribution and morphology of the undissolved phases of both alloys are shown in Fig. 1. By comparing Fig. 1(a) with Fig. 1(b), the silver-bearing alloy has a larger number of constituent particles than the silver-free one does. According to the EDS analysis results (Table 2), undissolved particles found in the silver-bearing alloy contain Zn, Mg and especially much high contents of Ag and Cu. The kind of compound found in the silver-free alloy is indentified as Cu-rich *M* (AlZnMgCu) phase.

The curves in Fig. 2 show the changes of mechanical properties of the two alloys aged for various lengths of time at 120 ℃. The ultimate tensile strength of the two as-quenched alloys is at the same level of about 530 − 550 MPa. At the initial stage of ageing (1 h), the tensile strength of alloy 2 is up to 700 MPa rapidly, which shows that the alloy has strong age-hardening ability, while that of alloy 1 is only about 630 MPa. Both alloys obtain the maximum strength of 770 MPa at the peak-age hardening stage, but the elongation of alloy 1 is higher than that of alloy 2.

The SEM images in Fig. 3 reveal the fractographs of samples at peak-age hardening stage, which demonstrates that the fractures of the two alloys are all in transgranular/intergranular combined mode. Quite a number of transgranular dimples and intergranular cracks exist in the fracture surface, and the second phases within the dimples have the same size level as the undissolved coarser phase in Fig. 2. From Fig. 3, it can also be found that the amount of dimples in alloy 2 is larger than that of alloy 1.

The microstructures of the two alloys after ageing for 1 h, 16 h, 36 h at 120 ℃ are shown in Fig. 4 (a), (b), (c), (d), (e) and (f), respectively. Corresponding to the EDS analysis of the undissolved phases (Table 3), it is found that the undissolved phases within alloy 1 are Cu-rich *M* (AlZnMgCu) compounds. In contrast to those contained in the solid-solution structure, zinc content decreases in *M* (AlZnMgCu), while increases in the matrix. With the ageing time extending, Cu content in the *M* (AlZnMgCu) compounds gradually increases. EDS results (Table 4) show that un-

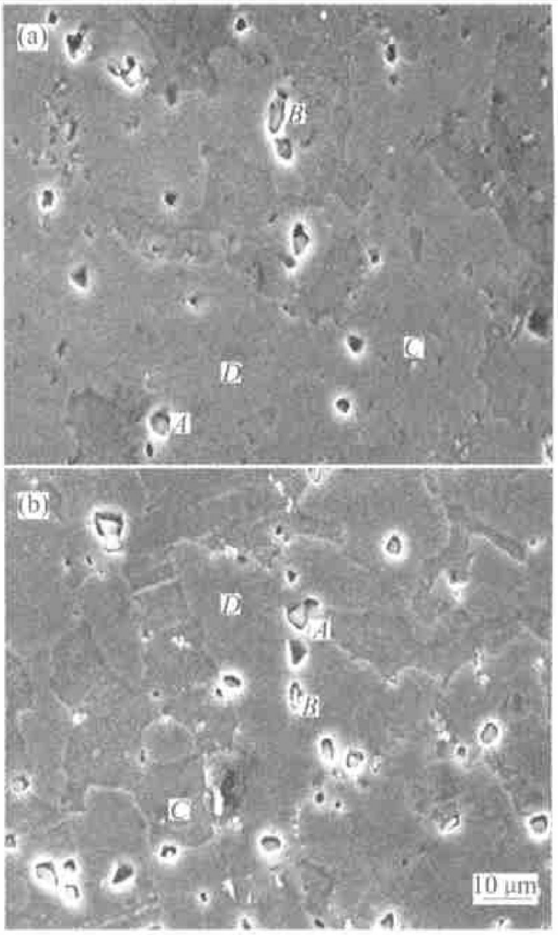

Fig. 1 SEM images of two alloys after solution treatment
(a) —Alloy 1 (450 ℃, 2 h + 460 ℃, 1 h);
(b) —Alloy 2 (450 ℃, 2 h + 470 ℃, 1 h)

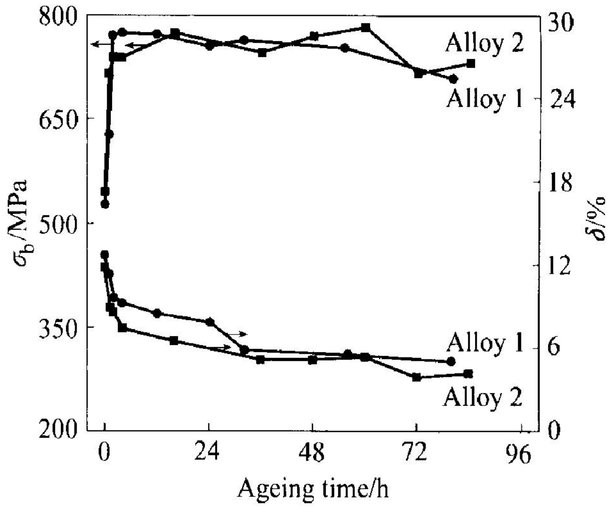

Fig. 2 Change of mechanical properties of two alloys with ageing time

Table 2 EDS analysis results of undissolved particles within as-quenched alloys

Alloy No.	Location	Element content (mass fraction) / %					
		Zn	Cu	Mg	Ag	Fe	Al
1	*A* in Fig. 1(a)	15.66	44.21	1.18	–	–	38.94
	Matrix	16.40	1.91	1.27	–	–	80.42
2	*A* in Fig. 1(b)	4.24	27.98	2.43	32.44	–	32.90
	B in FIg. 1(b)	6.49	35.81	2.28	17.75	–	37.67
	Matrix	13.27	2.02	0.78	–	–	83.93

Table 3 EDS analysis results of undissovled phases within alloy 1

Type of particles	Ageing time/ h	Composition (mass fraction) / %				
		Zn	Cu	Mg	Fe	Al
Cu-rich particles	1	12.79	43.69	1.36	0.20	39.96
	16	4.60	63.19	2.76	0.10	29.35
	36	3.50	72.06	1.35	0.20	22.88
Particles in matrix	As-quenched	16.40	1.91	1.27	0	80.42
	1	20.93	2.63	1.21	0.17	75.06
	16	17.38	2.99	1.58	0.00	78.05
	36	18.55	3.21	1.15	0.21	76.89

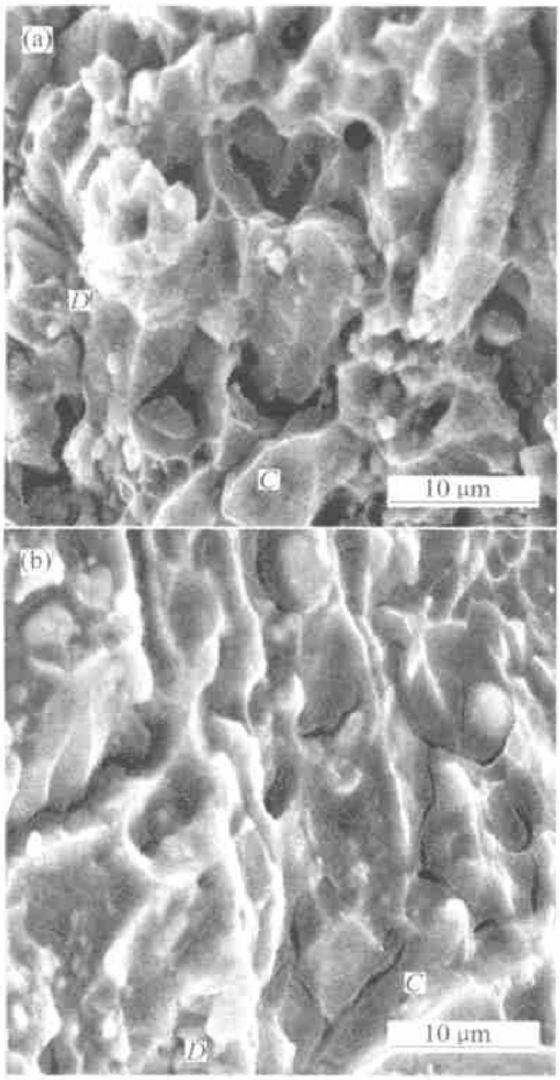

Fig. 3 SEM fractographs of samples at peak-age hardening stage
(a) —Alloy 1; (b) —Alloy 2

dissolved particles existing in alloy 2 are *M* (AlZnMgCuAg) compounds. According to the Ag content, the *M* (AlZnMgCuAg) compounds of each sample undergoing different ageing time are divided into two patterns: one with higher Ag content and the other with lower Ag content. Compared with the undissolved particles within the solid-solution microstructure, Ag content in the undissolved *M* (AlZnMgCuAg) phases greatly decreases at the early stage of ageing. As ageing time is prolonged, Zn content decreases gradually in undissolved particles and Ag, Mg contents increase again. Correspondingly, Ag content in the matrix increases.

4 DISCUSSION

The EDS results of both alloys in Table 2 show that the undissolved phases at the solid-solution state are mostly Cu-rich or Cu/Ag-rich phases. It is attributed to the different solid-solution velocities of the remaining eutectic phases. For high alloying 7XXX series aluminum alloy, coarse non-equilibrium eutectic phases inherited from the cast ingot is generally composed of $\alpha(Al) + T$, $\alpha(Al) + T + S$, $\alpha(Al) + MgZn_2 + t$ or $\alpha(Al) + MgZn_2 + T + S$[4]. Generally, Mg/Zn-rich coarse non-equilibrium eutectic phases can dissolve into the matrix more easier than the Cu-rich phases during the process of solid-solution treatment[8]. So the remaining undissolved phases in the solid-solution structure contain high Cu content. For alloy 2, in addition to the high Cu content, Ag element also slightly dissolves in the matrix and aggregates within the undissolved phases mostly. The effect may become significant because of the small con-

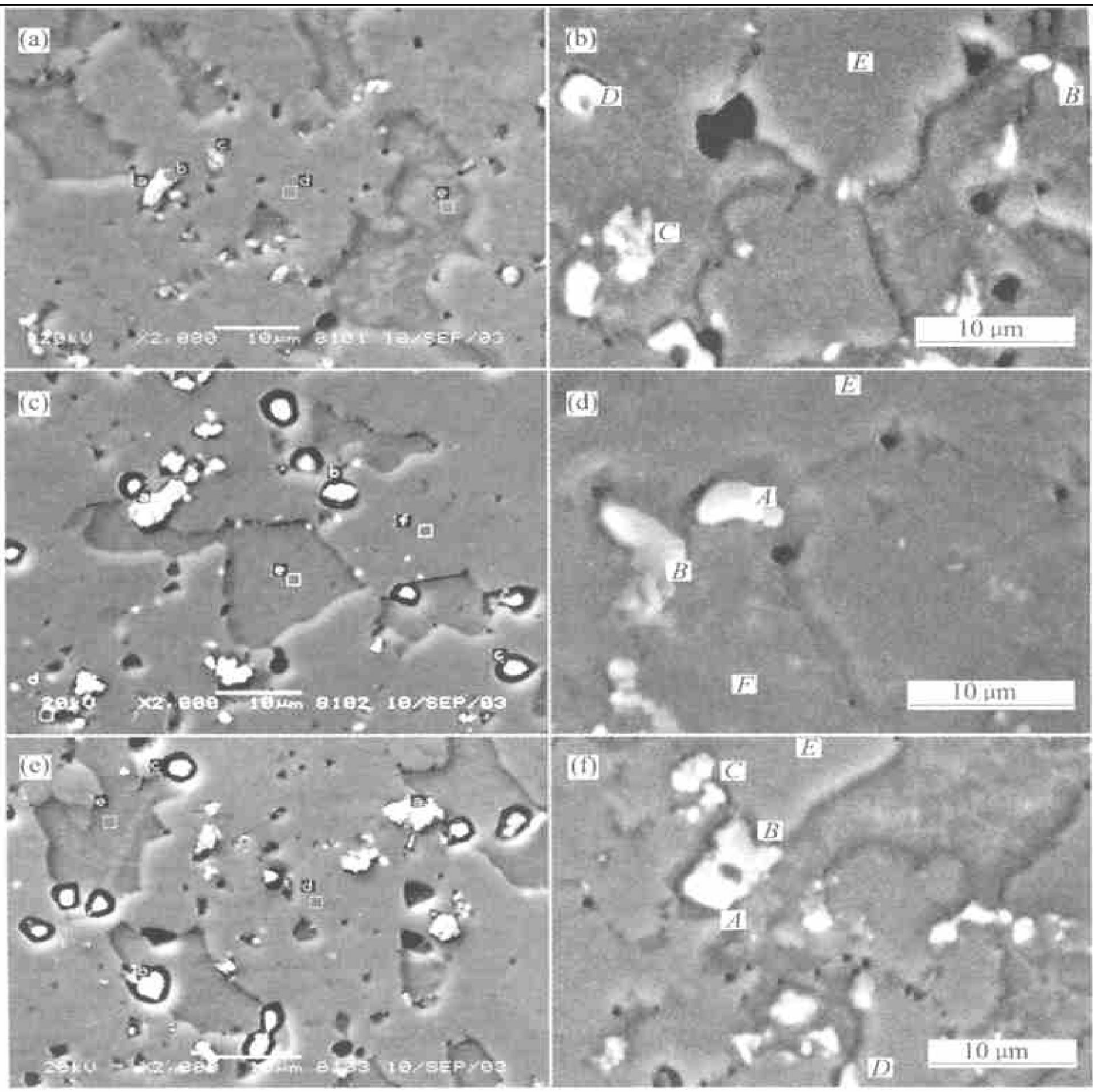

Fig. 4 SEM images of two alloys aged at 120 ℃ for different durations
(a) —1 h(alloy 1); (b) —1 h(alloy 2); (c) —16 h(alloy 1); (d) —16 h(alloy 2); (e) —36 h(alloy 1); (f) —36 h(alloy 2)

Table 4 EDS analysis results of undissovled phases within alloy 2

Type of particles	Ageing time/h	Composition(in mass fraction)/%				
		Zn	Cu	Mg	Ag	Al
High Ag content	1	53.96	15.28	0.46	2.98	27.33
	16	43.55	16.09	9.37	6.09	24.90
	36	37.50	13.33	10.47	8.23	30.75
Low Ag content	1	67.48	24.49	0.81	0.04	7.17
	16	59.76	21.02	1.11	1.33	16.78
	36	50.20	13.43	3.33	2.26	30.78
Particles in matrix	As-quenched	13.27	2.02	0.78	0	83.93
	1	12.70	2.10	0.07	1.47	83.66
	16	16.94	2.99	1.14	1.50	77.43
	36	13.47	1.44	0.43	0.96	83.70

junction energy of 0.1 eV among Ag atoms. Even at high temperature Ag atoms existing in the solid solution have an aggregation tendency. In addition, the Mg and Zn alloying elements can greatly reduce the Ag solubility in Al matrix. The aluminum alloy contained 8% Zn and 1% Mg can only dissolve 0.1% Ag (mass fraction)[9]. For alloy 2, it is subject to the Ag segregation within the undissolved phases due to its high zinc content and alloying of magnesium. By comparing the Mg and Zn contents of the two as-quenched alloys, it is found that small addition of silver also reduces the Zn, Mg solubility and promotes the formation of undissolved phase *M* (AlZnMgCuAg). Lee et al[10] studied 7055 aluminum alloy with 0.37% (mass fraction) silver addition. It is indicated that small particles are imbedded in a large Al-Zn-Mg-Cu-Ag constituent particles and these small particles are connected with silver segregation in the as-quenched alloy and act as a seed to promote the formation of constituent particles. From the age-hardening curves in Fig. 2, it is investigated that alloy 1 obtains a higher elongation at the initial stage of ageing because of its smaller amount of undissolved phases in its microstructure, although the ultimate tensile strength of the two alloys is at a same level.

From Table 2 and Table 3, it is revealed that Zn content within the Cu-rich *M*(AlZnMgCu) compounds of the silver-free alloy decreases during ageing, while the Cu content increases relatively. In contrast, Zn content in the matrix increases, and Cu content changes a little. The phenomenon can be explained with the kinetic equilibrium system of element compositions between the matrix and the undissolved phases. For Al-Zn-Mg-Cu alloy with relatively high mass ratio of Zn to Mg, the pattern of precipitation sequence is SSS> GP zone> η' (metastable phase) > η($MgZn_2$) during artificial ageing[11]. Therefore the main age-hardening precipitates in both studied alloys are $MgZn_2$. The continuous precipitation of $MgZn_2$ during ageing consumes Zn elements in the matrix and breaks the kinetic equilibrium of Zn content between the matrix and the undissolved phases. So the Zn atoms spontaneously diffuse from the undissolved phases to the matrix to set up a new balance of Zn content between them, which results in the decrease of Zn content in the undissolved phases and relatively higher Cu content.

EDS results of silver-bearing alloy 2 (Table 4) show that Ag content in the undissolved particles greatly decreases at the early ageing stage (1 h); while the Zn content has a marked increase. With the aging time prolonging, Ag and Mg contents increase again in contrast to the Zn content. This can be explained with the vacancy diffusion mechanism[12, 13]. At the initial stage of ageing, there is a large amount of over-saturated vacancy in the as-quenched alloy. Ag atoms that aggregate to the undissolved particles at the solid-solution state rapidly diffuse into the matrix because of its low conjunction energy with vacancy, and thus Ag content decreases accompanying with the great increase of the Zn content within the undissolved phases. Correspondingly, Ag content in the Al matrix increases significantly. At the same time, due to the strong interaction between Mg and Ag atoms, they combine with vacancies to form co-clusters rapidly according to the mass ratio of Mg to Ag closing to 1∶1[14]. Therefore the diffusion of Ag atoms from the undissolved phases to the matrix results in the migration of Mg atoms at the same direction, which causes Mg content within the undissolved phases to decrease. With the ageing process going on, Mg element in the silver-bearing alloy is divided into two parts as follows: one part dissolves into Al matrix and precipitates according to the precipitate sequence as SSS> GP> η' > η during the ageing process; the other incorporates with vacancies to form Mg-Ag co-clusters. The diffusion of Ag and Mg atoms reduces the amount of the over-saturated vacancies in the Al matrix and thus weakens the concentration of mobile Zn-vacancy or Mg-vacancy, causing aggregation of Zn, Mg atoms rapidly to form GP zones. In addition, the misfit strain energy accommodated by Mg and Ag segregation to undissolved-particle/ α interface stimulates the formation of precipitates in the early stage of decomposition and provides nucleation sites for the age-hardening precipitates[10, 15]. Accordingly, the formation of GP zones consumes Zn element in the Al matrix and enhances diffusion of Zn atoms from the undissolved phases to the matrix, which causes the reduction of Zn content in the *M* (AlZnMgCuAg) compounds and the increase of Ag, Mg content gradually. Due to the effect of silver additions, alloy 2 has stronger age-hardening ability than alloy 1 does at the initial stage of ageing as shown in Fig. 2, in which the tensile strength of alloy 2 after ageing for 1 h is up to 700 MPa rapidly, while that of alloy 1 is only about 630 MPa.

5 CONCLUSIONS

1) For silver-free high-Zn content super-high strength aluminum alloy, undissolved Cu-riched phase *M* (AlZnMgCu) exists in its solid-solution microstructure. Zn content in *M* (AlZnMgCu) compounds gradually decreases during ageing, and Cu content becomes higher.

2) For silver-bearing high-Zn content super-high strength aluminum alloy, undissolved Cu or Ag riched phase *M* (AlZnMgCuAg) exists in its solid-solution microstructure. At the early stage of ageing, the amount of Ag contained in the *M* (AlZnMgCuAg) compounds greatly decreases and Zn content increases largely. With the ageing time prolonging, Zn content

in the undissolved phases gradually decreases, while Mg and Ag contents increase.

3) Small addition of Ag promotes a larger amount of undissolved phases within the microstructure of the as-quenched high-Zn content super-high strength aluminum alloy. These undissolved phases change a little in their size and amount during ageing and become sites of stress concentration and micro-crack initiation, which reduces the elongation of alloy at early stage of ageing.

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(Edited by YANG Bing)