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Nonstoichiometry of Al-Zr Intermetallic Alloys

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NONSTOICHIOMETRY OF Al-Zr INTERMETALLIC PHASES

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Abstract

Nonstoichiometry of metastable cubic β' and equilibrium tetragonal β Al-Zr intermetallic phases of the nominal composition Al_3Zr in Al-rich alloys has been extensively studied. It is proposed that the "dark contrast" of β' core in β'/δ' complex precipitates, in Al-Li-Zr based alloys, is caused by incorporation of Al and Li atoms into the β' phase on Zr sublattice sites, forming nonstoichiometric Al-Zr intermetallic phases, rather than by Li partitioning only. β' particles contain very small amounts of Zr, approximately 5 at.%, much less than the stoichiometric 25 at.% in the Al_3Zr metastable phase. These particles are, according to simulation of high resolution images, of the $\text{Al}_3(\text{Al}_{0.4}\text{Li}_{0.4}\text{Zr}_{0.2})$ type. Nonstoichiometric particles of average composition Al_4Zr and Al_6Zr are observed also in the binary Al-Zr alloy, even after annealing for several hours at 600°C.

Introduction

The Al-Zr system is of scientific as well as technological interest, mainly because of the beneficial effect of Zr on the properties of Al rich alloys. The improved properties are due to the formation of metastable cubic β' (Al_3Zr) precipitates [1-7], nonhomogeneously distributed in the Al-matrix, causing less pronounced subgrain and grain growth, especially in the regions with a higher particle density. The beneficial effect of Zr additions to ingot processed (0.1 -0.15%Zr) or powder processed (~0.5%Zr) Al-rich alloys could be summarized as: 1. inhibiting recrystallization and control grain size [1, 3, 4, 8-11] by the presence of the coherent cubic β' (Al_3Zr) particles, 2. improve toughness and stress corrosion cracking resistance [3, 5]. 3. control quench rate sensitivity [5, 6, 9], and 4. β' serve as preferential nucleation sites for δ' and other strengthening precipitates in Al-Li based alloys [3, 12, 13].

Special attention to the role of Zr in Al-Li base alloys has been given because δ' (Al_3Li) precipitates heterogeneously around the coherent cubic β' (Al_3Zr) phase due to reduction in strain and surface energy, forming the so-called composite β'/δ' precipitates [1-3, 7, 10, 13-16]. It has been assumed [4, 5, 16, 17] that β' particles are stoichiometric Al_3Zr phase, regardless if β' is coherent (typical for annealing below 500°C) or incoherent (typical for annealing above 500°C). In previous studies the presence of the nonstoichiometric β' (Al-Zr based particles) was reported by Vecchio and Williams [18] on ingot processed binary Al-Zr alloy, Gayle and Vander Sande [13, 19, 20] and Vecchio and Williams [18] on ternary Al-Li-Zr alloys. However, the origin of the nonstoichiometric ratio between Al and Zr is not yet clarified. Gayle and Vander Sande [13] assumed, based on the work of other authors [4, 5, 21, 22] that β' is the metastable L_{12} ordered cubic phase or the equilibrium

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tetragonal β DO_{23} phase (first described by Brauer [23]; $a = 4.005 \text{ \AA}$ and $c = 17.285 \text{ \AA}$), having identical first nearest neighbor configuration. β' L_{12} cubic particles exhibit high stability because of the small misfit with the matrix, low Zr diffusivity and low solubility in aluminum [1, 4, 5, 10, 24]. Recently, quantum mechanical calculations [25] show that cubic β' under constraint could be even more stable than tetragonal β equilibrium phase, in a certain temperature range. Any discrepancy between the Zr content and the amount of Al-Zr based particles in the Al alloys has not received too much attention.

Radmilovic et al. [26] already reported that the volume fraction of β' particles in powder processed Al-Li-Zr based alloys is larger than is to be expected according to the Zr content in Al rich alloys. This suggests that the Al:Zr ratio is probably not stoichiometric, and might be caused by the partitioning of other elements on the Zr sublattice sites. Gayle and Vander Sande [13, 19, 20] suggested that the dark contrast, in the dark field transmission electron imaging using L_{12} superlattice reflections, of β' core in complex β'/δ' precipitate is due to incorporation of Li into the β' superlattice. They proposed that the composition of β' is very close to $\text{Al}_3(\text{Zr},\text{Li})$ with Li:Zr ratio between 2:1 and 1:4. It has been confirmed [26], based on high resolution electron microscopy and image simulation that, if there is partitioning of Li in β' , then the composition of these particles is close to the $\text{Al}_3(\text{Zr}_{0.4}\text{Li}_{0.6})$. However, preliminary investigation of the binary Al-Zr alloy also revealed the existence of non-stoichiometric cubic Al-Zr based particles. The aim of this paper is to clarify these issues for particles in powder and ingot processed Al-Zr and Al-Li-Zr based alloys, utilizing electron microscopy and different spectroscopy and diffraction techniques.

Experimental procedure

The AlLiCuMgZr and AlZr powder processed alloys produced by Allied-Signal Inc. were provided in extruded strips and ribbons with chemical compositions listed in Table I, and treated as follows: solution treatment 2h at 470, 540 and 580°C, ice brine quenched, followed by aging a) 16h at 135°C (underaged condition) and b) 100h at 150°C (peak aged condition).

Table I - Chemical composition of Al-Zr and Al-Li-Zr alloys [in wt.%].

Alloy	Zr	Li	Cu	Mg	Al
		<u>AlLiCuMgZr-powder processed</u>			
C762	0.6	2.6	1.0	0.5	95.3
		<u>AlZr-powder processed</u>			
6971	0.92	-	-	-	99.08
		<u>AlZr-ingot processed</u>			
AZ-1	3.00	-	-	-	97.0

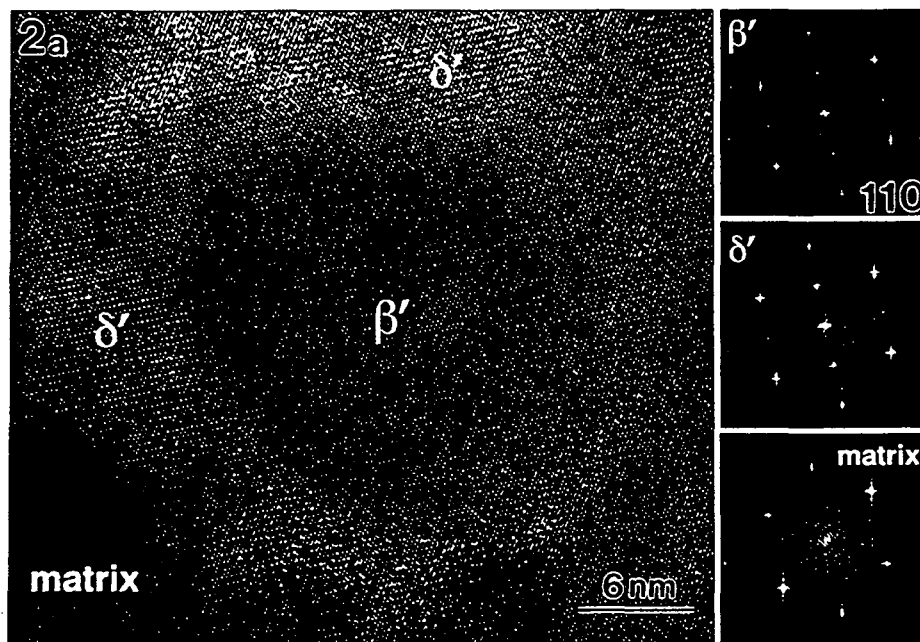
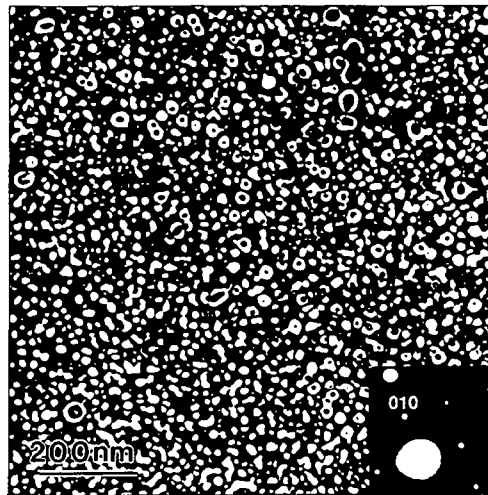
The AlZr ingot processed alloy was produced in an electric arc furnace in Ar atmosphere at -15 mmHg, following by fast cooling in Cu water cooled mold. The AlZr cast rods were remelted 3 times to ensure homogeneous distribution of Zr. The as-cast rods were annealed in a quartz tube in Ar atmosphere for 24 hrs at 600°C to obtain equilibrium Al_3Zr phase, and then air cooled. Al-Li-Zr based alloys with different Zr contents have been also investigated in the overaged condition (700h at 150°C). For transmission electron microscopy (TEM) 3 mm discs were punched from the slices, cut by a slow-speed diamond saw, and jet electropolished with a 1/3 nitric acid 2/3 methanol solution at -25°C in the range between 12 and 14 V. The TEM specimens were examined in the Philips 400 EM, Jeol 200CX analytical electron microscopes at -160°C, and in the high resolution transmission electron microscopes (ARM and Jeol 200CX). Symmetry in convergent beam electron diffraction patterns is defined according to Vecchio and Williams [18]. For high resolution electron microscopy, through focus series of images were taken in 12 nm increments, starting at the minimum contrast condition. With respect to the Gaussian image plane the Scherzer defocus value is around -55 nm. The ARM microscope parameters are: defocus step, $D_f=12 \text{ nm}$, half convergence angle value, $\alpha=0.6 \text{ mrad}$ and spread of focus $D=10 \text{ nm}$. Simulated high resolution TEM images of the structure of interest were calculated using the NCEMSS multislice program [27]. The

calculations were performed for foil thicknesses ranging from 2 to 10 nm, and for defocus range between -36 and 108 nm with respect to the Gaussian image plane. The volume fraction of phases were analyzed using the commercially available "Prism" image analysis system.

Results

Fig. 1 shows the typical distribution of δ' and β'/δ' precipitate in the C762 peak-aged alloy developed after 94h at 148°C. A large number of coherent β' particles are encapsulated by δ' Al_3Li L_{12} phase. The estimated volume fraction of cubic β' and (dark regions inside δ' shell in the dark field electron micrograph in Fig. 1) and tetragonal β in the C762 alloy containing 0.6 wt.% Zr is larger than is expected according to the Zr amount in this alloy, e.g. ~7 vol.%. The volume fraction of δ' Al_3Li phase is for all measurements above 45%, is also larger than is expected for 2.6 wt.% Li. This fraction should be less than ~40% if all the Li comes out as the metastable cubic Al_3Li stoichiometric phase. High resolution electron microscopy (HREM), Fig. 2a, shows dark regions in the β'/δ' core, that are in fact a disordered structure, having a contrast very much like that of the matrix. Calculations of high resolution images for different composition are shown in Figs. 2b. β' particle of the composition $\text{Al}_3(\text{Li}_{0.6}\text{Zr}_{0.4})$ or (and) $\text{Al}_3(\text{Al}_{0.4}\text{Li}_{0.4}\text{Zr}_{0.2})$ will produce very similar structural images as the Al matrix.

Fig. 1- Dark field image of Al-Li-Zr based alloy aged 100 h at 150°C, using 001 superlattice reflection. Metastable cubic β' (Al_3Zr) precipitates are encapsulated in metastable cubic δ' (Al_3Li) phase.



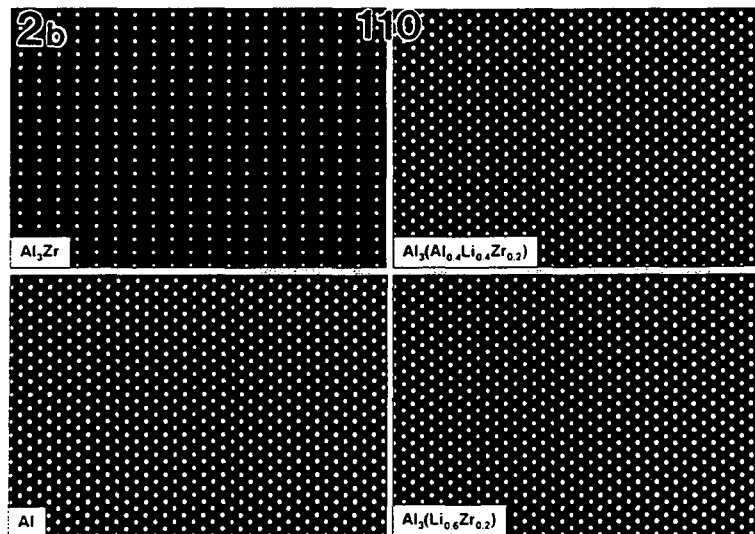
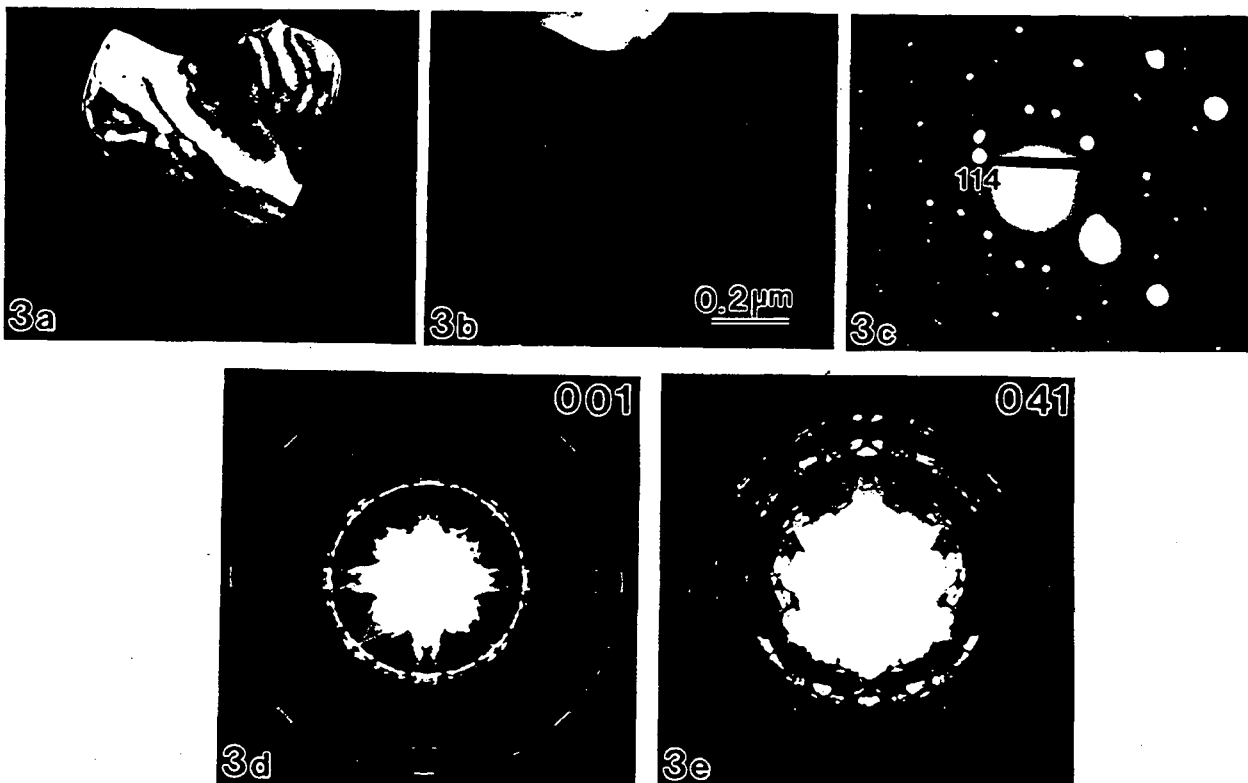


Fig. 2- a) High resolution electron micrograph of complex cubic β'/δ' . Note similarity between contrast of β' core and Al matrix. Optical diffractograms are taken from appropriate regions in the high resolution image, b) calculated structural images for thickness 10 nm, and defocus setting -55 nm (Scherzer defocus value).

In the Al-0.92 wt.% Zr alloy, Al-Zr tetragonal particles are present mostly at the grain boundaries. A typical morphology is shown in Fig. 3. Convergent beam electron diffraction (CBED) patterns (Fig. 3d and e) and microdiffractions (f and g) confirm that it is equilibrium tetragonal phase.



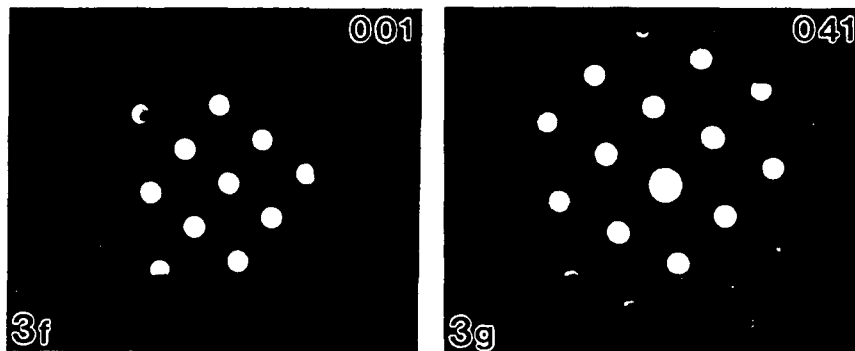


Fig. 3- a) Dark and b) bright field images of β phase, c) 114 reflection used for dark field imaging; CBED patterns (d and e) and microdiffraction patterns (f and g) in 001 and 041 zone axis from the same particle.

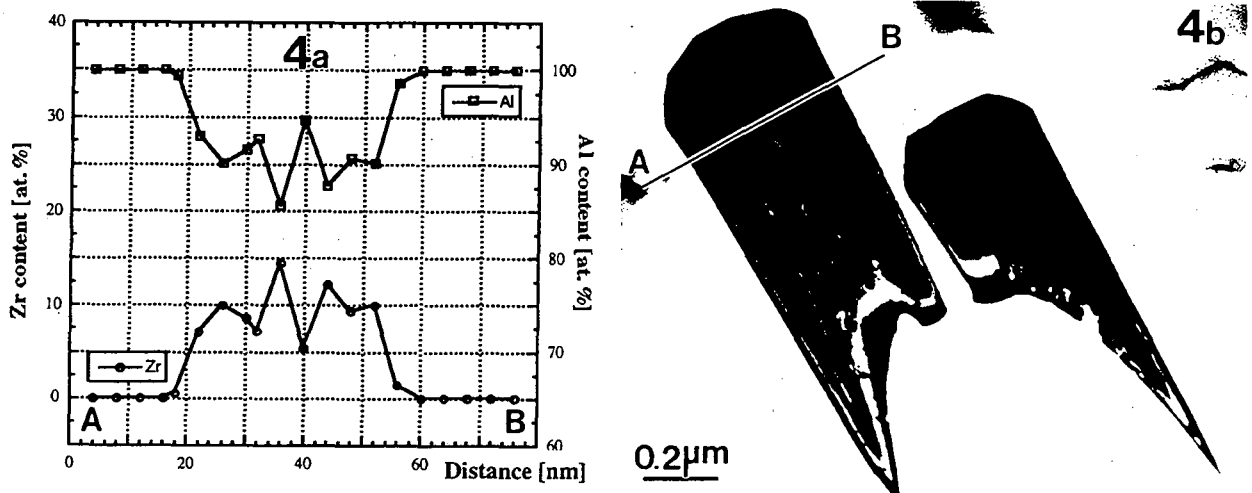


Fig. 4- Composition profile (a) measured across β particle (b) located at the grain boundary. Note significant variation in Zr content across the particle.

001 and 041 CBED patterns have 4mm and 2mm symmetries, respectively. The composition of these particles is close to Al_4Zr . Line profile microchemical analysis (Fig. 4a) taken from the particle in Fig. 4b shows significant variation of the composition within the phase. The metastable cubic β' phase with composition close to Al_6Zr is also found in Al-Zr binary alloy, annealed 2 hrs at 540°C . The cubic metastable β' phase is predominantly of the ordered L_{12} type structure. However, occasionally the disordered cubic structure has been also observed. The latter occurs in spherical and polygonal shape, and tetragonal only in plate and rod like faceted shapes. Possible models of stable and metastable nonstoichiometric equilibrium tetragonal β phase of the composition Al_4Zr are shown in Fig. 5.

X-ray microanalysis (EDX) revealed that investigated cubic β' and tetragonal β particles are of the Al-Zr type with Al:Zr ratio higher than 3, e.g. with Zr content less than 25 at.%. The results of microchemical analysis are shown in Table II. The Al/Zr atomic ratio in powder processed Al-0.92wt.% Zr, annealed 2 hrs at 540°C , was found to be in the range from 4.3 to 6.4. In ingot processed Al-3wt.% Zr alloys annealed 24 hrs at 600°C , the average value of Al/Zr ratio is found to be 4. In powder processed Al-0.6 Zr-2.6 Li-1.0 Cu-0.5 Mg (wt.%), and heat treated $540^\circ\text{C}/2\text{hrs}/135^\circ\text{C}/16\text{hrs}$, β' particles were found to have Al/Zr ratio in the range from 8.8 to 20.1. Even if all analyzed particles were on the edge of the foil, and probe size were kept below 2.5 times

less than particle size, possible matrix contribution can not be excluded. Microchemical analysis based on extraction replicas were also performed, but with very limited success. However, several analyzed Al-Zr particles in extraction replicas contained much less than 25 at.% of Zr.

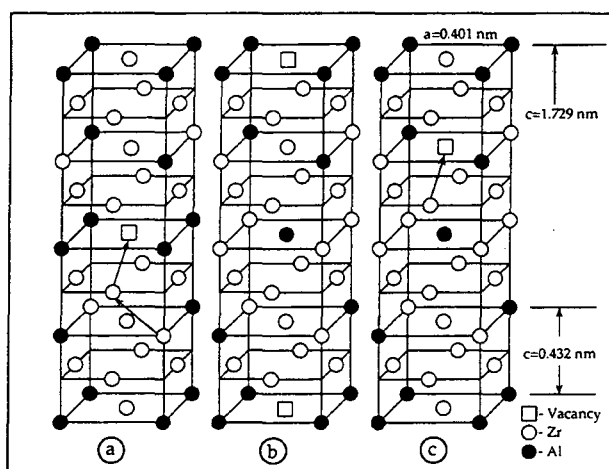


Fig. 5- Models of stable (a and b) and metastable (c) configuration for nonstoichiometric equilibrium tetragonal β phase of the composition Al_4Zr .

Table II. Chemical composition of Al-Zr particles [%]

Particle	Al		Zr		Al/Zr at.
	wt.	at.	wt.	at.	
<u>Al-0.92 wt.%Zr- annealed 2hrs at 540°C</u>					
1.	65.47	86.50	34.53	13.50	6.4
2.	57.37	81.98	42.63	18.02	4.5
3.	65.52	86.53	34.48	13.47	6.4
4.	55.91	81.09	44.09	18.91	4.3
<u>Al-0.6wt.%Zr-2.6 wt.%Li-1wt.%Cu-0.5wt.%Mg-underaged</u>					
5.	85.20	95.11	14.80	4.89	19.4
6.	85.62	95.27	14.38	4.73	20.1
7.	78.88	92.66	21.12	7.34	12.6
8.	72.20	89.77	27.80	10.23	8.8
9.*1	77.02	91.89	22.98	8.11	11.3
9.*2	75.61	91.29	24.39	8.71	10.5
10.*3	81.63	93.76	18.37	6.24	15
10.*4	79.69	92.99	20.31	7.01	13.3
<u>Al-3wt.%Zr alloy-annealed 24 hrs at 600°C</u>					
11.	55.05	80.55	44.95	19.45	4.14
12.	54.10	79.94	45.90	20.06	3.98
13.	54.50	80.20	45.50	19.80	4.05
14.	53.75	79.71	46.25	20.29	3.93
15.	53.67	79.66	46.33	20.34	3.92
16.	54.56	80.24	45.44	19.76	4.06
17.	54.92	80.47	45.08	19.53	4.12
18.	54.70	80.33	45.30	19.67	4.08
19.	54.04	79.90	45.96	20.10	3.98
20.	55.02	80.53	44.98	19.47	4.14
21.	55.20	80.64	44.80	19.36	4.17

*Probe size: 1- 20 nm, 2- 30 nm, 3- 40 nm, and 4- 30 nm.

Discussion

According to Ryum [4], the precipitation sequence of Al-Zr based particles in Al-alloys is: Saturated solid solution \rightarrow cubic β' \rightarrow tetragonal β . However, the coexistence of agglomerates of cubic β' and tetragonal β , of approximately the same size, suggests that under certain conditions both phases could precipitate simultaneously. It could happen if the stress developed around β' cubic phase is large enough to cause its stability. The observed tetragonal (called equilibrium) β phase of composition close to Al_4Zr , does not really mean it is an equilibrium phase. It has been found by several authors [4, 28], that β can reach equilibrium only after annealing for several hours at 640°C . However, the fact that many tetragonal β particles after such annealing have compositions approximately Al_4Zr indicates the stability of this configuration, schematically shown in Fig. 5. In this case it is possible to expect some kind of long range vacancy ordering in the equilibrium β phase. An orthorhombic phase of the same composition, Al_6Zr , has been observed in Cu-Ti thin films [29]. A limited number of analyzed Al-Zr particles suggests that the amount of Zr in β decreases with decreasing annealing temperature. However, this has to be studied in more details.

The identification of Al-Zr based particles in the 8090 Al-Li alloy as Al_3Zr [8] seems to be based on an assumption that every cubic Zr containing particle has to be of the L_{12} Al_3Zr type. Similar to Gayle and Vander Sande's results [20] we found no superlattice reflections in some Al-Zr cubic particles. However, in most of the investigated particles, superlattice reflections have been confirmed, which is consistent with the results of Tosten et al. [2]. It is quite possible that the presence of superlattice spots in patterns taken by Tosten et al. [2] is a consequence of averaging from the particles with and without the L_{12} superstructure. Which particle will have the L_{12} structure depends on their chemical composition.

It is very interesting that the amount of β' particles in Al-Li-Zr alloys is higher than the amount of manganese dispersoids in Al-Li-Mn alloy having comparable Mn and Zr contents [3]. This could be explained by the nonstoichiometric nature of the β' phase as is shown in Table II.

The possible disordering of β' phase has been anticipated by Gayle and Vander Sande [20], emphasized that it is thermodynamically unfavorable. Our results in Table II show that the Al:Zr ratio is always higher than 3:1, regardless of the heat treatment and bulk Zr content. Although it has been claimed that Al-Zr particles, which are the product of a discontinuous reaction, are of the metastable cubic Al_3Zr type [4, 5, 30], the presence of superlattice spots in diffraction patterns is not sufficient evidence to conclude that the Al:Zr ratio is 3:1, e.g. is stoichiometric.

β' cubic coherent precipitates are very often slightly misoriented with respect to the surrounded δ' shell, e.g. $\sim 1^\circ$, which is in agreement with Stimson et al. [16]. However, very low Zr content in some β' particle (see Table II) that is far from stoichiometric 25 at.%, suggests that "dark imaging" of the β'/δ' core is not related to this misorientation. Also, since the amount of δ' phase is larger than is expected according to the amount of Li in the system, the dark contrast is not only related to Li diffusion into the β' . If there is Li diffusion into β' , Li can certainly reduce the structure factor value to zero for the possible composition $\text{Al}_3(\text{Li}_{0.6}\text{Zr}_{0.4})$, as has been proposed by Gayle and Vander Sande [13, 20], and later confirmed by computer simulation of HREM images [26]. Based on experimental observations and appropriate calculations, there is reason to believe that the "dark imaging" of the β'/δ' core is predominantly caused by replacing Zr atoms on the Zr sublattice sites by Al and Li atoms. β' particles in fact contain very small amounts of Zr, and they can be, according to simulation of high resolution images, of the $\text{Al}_3(\text{Al}_{0.4}\text{Li}_{0.4}\text{Zr}_{0.2})$ type. However, it is important to emphasize that incorporation of Li into β' has not been established yet [18]. The ratio between Al, Li, and Zr atoms present on Zr sublattice sites can vary. Thus, the amount of Zr in these particles is significantly smaller than 25 at.%, but still well above the values typical for solid solution of Zr in Al. It is concluded that the main reasons for the nonstoichiometric nature of the Al-Zr particles in Al-rich alloys are very slow diffusion rate of Zr in Al, at the temperatures typical for their heat

treatment, and the very high binding energy of Zr atom and vacancy, which is in the order of 0.24 ± 0.02 eV [9].

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