Constitution of liquisol-quenched Al-W alloys

Formation of metastable phases by liquisol-quenching (also referred to as splat-cooling or rapid quenching from the melt) is well documented in the literature [1, 2]. These phases include supersaturated solid solutions, intermediate phases and, in some cases, amorphous alloys. By and large, X-ray diffraction procedures have been adopted to determine the crystal structures of the metastable phases, although electron diffraction has been resorted to in some cases [3]. Since it is difficult to obtain single crystals of alloys which display the metastable phases, a complete and accurate crystal structure determination often proves impossible. Further, reports are also available in the literature of different crystal structures for what is supposedly the same phase obtained by rapid solidification [4, 5].

An important characteristic of the metastable phases is that they disappear after a short anneal at a high enough temperature and give rise to the equilibrium phases. Hence, this can be utilized as a check for the metastability of these phases. For example, the formation of a new hcp phase during rapid solidification of Al was reported [6]; the phase was stable for 30 h at 600° C, and was later shown to be AlN [7]. Therefore, great care must be exercised in establishing the true metastability of the "new" phases. The present communication is an attempt to offer an alternative explanation for the metastable phases obtained in Al-rich Al-W alloys after rapid quenching from the melt [8].

It has been shown that supersaturated Al solid solutions can form up to a maximum of 6.3 wt % W, when the solidified foil is thinner than 10 μm. On the other hand, thicker foils were shown to contain the equilibrium ϵ (Al_4W) and metastable X and Y phases in addition to the supersaturated solid solution. Decomposition studies of the homogeneous solid solution revealed the existence of two more metastable intermediate phases, β' and β. The β' phase was found to be cubic with a = 6.92Å and β hexagonal with large unit cell dimensions of a = 7.87Å and c = 23.80Å. During continuous heating, the β' phase was stable up to 600° C, with simultaneous appearance of β, which continued even for 350 h at 650° C.

A critical comparison of the interplanar spacings reported by Tonejc [8] for the β' phase and those for the equilibrium $\gamma(Al_{12}W)$ phase reveals that the former can, in fact, be conveniently indexed on the basis of the latter. Table I brings out the satisfactory indexing of the d values on the basis of a bcc unit cell with a = 7.664Å (lattice parameter of the equilibrium γ phase = 7.580Å), which means that a slight expansion of the unit cell had taken place probably because of the higher W content present in the solid solution.

The appearance of γ during the decomposition of the metastable solid solution is not surprising since it is an equilibrium phase. As mentioned earlier, the rapidly-quenched alloy contained α-Al and $\epsilon(Al_4W)$ phases, indicating that the formation of the γ and $\delta(Al_5W)$ phases was prevented during the rapid solidification process. This can easily happen when alloys are quenched from about 900° C, at which temperature the equilibrium phases are liquid and ϵ. The liquid can solidify into α-Al with a composition characteristic of the high temperature and the ϵ phase continues to exist down to room temperature. Hence it appears that β' is not a new phase but is the equilibrium γ phase with a very slight change in the lattice parameter of the bcc unit cell.

Another new phase, designated as β by Tonejc [8], was assigned a hexagonal unit cell with a = 7.87Å, and c/a = 3.03. It is interesting to note that the equilibrium δ phase also has a hexagonal structure with a = 4.902Å, c = 8.857Å and c/a = 1.806. A comparison of the interplanar spacings of these two phases brings out the fact that about half of them are common to both the structures (Table II). The remaining

TABLE I Comparison of d_{hkl} values of the β' phase proposed by Tonejc and the equilibrium $\gamma(Al_{12}W)$ phase.

Line number	Proposed β' phase [8] (cubic, a = 6.92Å)		$\gamma(Al_{12}W)$ phase (bcc, a = 7.664Å)	
	hkl	d_{obs} (Å)	hkl	d_{calc} (Å)
1	—	—	110	5.368
2			200	3.832
3	012	3.13	211	3.128
4	112	2.82	220	2.684
5	—	—	310	2.423
6	013	2.18	222	2.212
7	—	—	321	2.047
8	023	1.92	400	1.916
9	—	—	330	1.789
10	—	—	420	1.714
11	033	1.63	332	1.634

TABLE II Alternative indexing of the β phase obtained by liquisol quenching Al-W alloys.

New tetragonal structure $a = 7.145$Å, $c = 7.874$Å, $c/a = 1.103$			Equilibrium hexagonal $\delta(Al_5W)$ phase $a = 4.902$Å, $c = 8.857$Å, $c/a = 1.806$	
hkl	d_{calc} (Å)	d_{obs} (Å)	*hkil*	d_{calc} (Å)
002	3.939	3.942	—	—
200	3.567	3.498	—	—
102	3.447			
112	3.103	3.134	—	—
211	2.958	2.976	—	—
301	2.277	2.271	—	—
311	2.169	2.175	—	—
222	2.124	2.128	$20\bar{2}0$	2.123
004	1.968	1.968	$10\bar{1}4$	1.963
321	1.919	1.919	$20\bar{2}2$	1.914
322	1.769	1.770	—	—
331	1.645	1.637	$10\bar{1}5$	1.634
402	1.625			
420	1.596	1.606	$21\bar{3}0$	1.604
314	1.484	1.486	0006	1.476
422	1.479			
333	1.416	1.413	$30\bar{3}0$	1.415
511	1.378	1.383	$10\bar{1}6$	1.393
423	1.363	1.355	$20\bar{2}5$	1.359
006	1.312	1.312	—	—
441	1.246	1.245	—	—
602	1.138	1.136	—	—
316	1.135			
533	1.109	1.107	0008	1.107
326	1.094	1.091	$31\bar{4}3$	1.093
444	1.062	1.059	$10\bar{1}8$	1.070
631	1.055			
416	1.046	1.045	—	—
604	1.018	1.017	$30\bar{3}6$	1.021
008	0.984	0.983	$20\bar{2}8$	0.982
642	0.960	0.959	—	—
228	0.917	0.917	—	—
644	0.884	0.885	—	—
626	0.856	0.858	—	—
822	0.895	0.844	—	—

extra reflections observed by Tonejc [8] cannot be explained on the basis of the equilibrium δ phase. Even though the annealing treatment necessary for the disappearance of this new phase looks a little unreasonable (one had to go into the liquid + γ region), its final disappearance suggests that it is probably a metastable phase.

Even assuming that β is a metastable phase, the hexagonal unit cell assigned to it appears to be too big. The unit cell contains ninety-six atoms on the basis of the assigned unit cell. However, the same interplanar spacings can be very satisfactorily indexed on the basis of a much smaller tetragonal unit cell with $a = 7.145$Å, $c = 7.874$Å and $c/a = 1.103$ (see columns 1 and 2 of Table II). These parameters are related to the unit cell dimension (a_α) of the primary α solid solution as

$$a_{tet} \simeq \sqrt{13}\, a_\alpha/2 \text{ and } c_{tet} \simeq 2a_\alpha\,.$$

This suggests that the unit cell contains twenty-six atoms and can as well be represented by the chemical composition $Al_{12}W$.

Regarding the stability of the β phase, it was reported to be stable above 600° C. At the present moment it may look too speculative, but it is likely that β is a stable (?) high-temperature phase with a possible chemical composition $Al_{12}W$. This might undergo a "polymorphic" transformation at low temperatures into the stable γ phase, thus explaining its appearance only at high temperature. A more precise determination of the Al-W equilibrium diagram may be able to shed more light on this aspect.

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