

# Phase transformations in Al-rich Al-W alloys rapidly quenched from the melt

A. TONEJC

*Institute of Physics of the University of Zagreb, 41000 Zagreb, POB 304, Yugoslavia*

Al-W alloys with a W content from 4.3 to 11.7 wt% were rapidly quenched, using the two-piston quenching method. X-ray examination showed that in as-quenched alloys two kinds of samples appeared; multiphase samples and single-phase samples. Multiphase samples contained supersaturated Al-W solid solutions ( $\alpha$ -Al),  $\text{Al}_4\text{W}$  and two unknown phases, all of which were metastable. In single-phase samples  $\alpha$ -Al was present as the only phase. In these samples  $\alpha$ -Al began to decompose at temperatures as low as  $100^\circ\text{C}$ . During the decomposition of these solid solutions two other new phases were observed, the unit cell constants of which were determined. Experiments with isochronal and isothermal annealing showed that the presence of metastable phases in as-quenched alloys highly increases the resistance to decomposition of Al-W solid solutions. The possible reason for this behaviour is discussed.

## 1. Introduction

The quenching of alloys from the liquid state has been given increasing attention by physicists since about ten years ago Duwez and Willens [1] developed new quenching techniques. The very high rate of cooling obtained by means of these techniques (from  $10^5$  to  $10^8^\circ\text{C sec}^{-1}$ ) has led to the formation of many metastable phases in many alloy systems. Much work has been done on Al-base alloys, the results being summarized by Furrer and Warlimont [2].

Several authors have dealt with rapidly quenched Al-rich Al-W alloys, but the results show certain disagreements. The Al-rich part of the Al-W phase diagram (after Clark [3] and Kubaschewski [4]) shows that the equilibrium solid solubility of W in Al is very small (0.15 wt% W at  $650^\circ\text{C}$  according to Elliot [5]), and that the intermediate phases  $\text{Al}_{12}\text{W}$  ( $\gamma$ ),  $\text{Al}_5\text{W}$  ( $\delta$ ) and  $\text{Al}_4\text{W}$  ( $\epsilon$ ) exist at approximately 35, 59 and 65 wt% W respectively (Fig. 1).  $\text{Al}_{12}\text{W}$  has the bcc structure with  $a = 7.580\text{\AA}$  [6],  $\text{Al}_5\text{W}$  is hexagonal with  $a = 4.902\text{\AA}$ ,  $c = 8.857\text{\AA}$  [7], and  $\text{Al}_4\text{W}$  is monoclinic with  $a = 5.272\text{\AA}$ ,  $b = 17.771\text{\AA}$ ,  $c = 5.218\text{\AA}$  and  $\beta = 100^\circ 12'$  [8].

Using lattice parameter measurements on Al-W alloys very rapidly quenched by the two-piston quenching method, Tonejc and Bonefačić

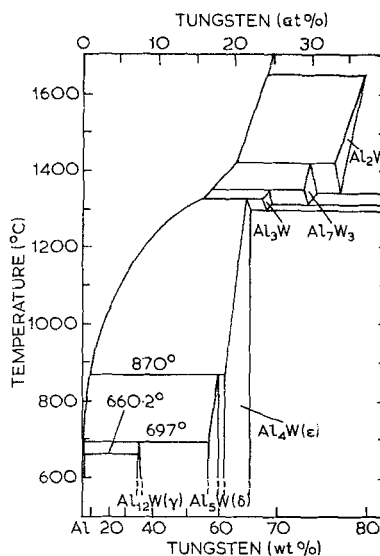


Figure 1 Aluminium-rich end of the Al-W equilibrium phase diagram [3, 4].

[9] found supersaturated Al-rich Al-W solid solutions of up to 6.3 wt% W. The slope of the line which gives the change of lattice parameter of the metastable  $\alpha$ -Al phase versus the concentration of W is in good agreement with the results of Varich *et al* [10], but differs considerably from

that obtained by Burov and Yakunin [11] (Fig. 2). Varich *et al* [10] also found that Al + 1 wt % W solid solution decomposes between 400 and 500°C, while Kolomoytseva *et al* [12] reported that Al-W solid solutions with a much higher W content (up to 6.4 wt % W) remain stable up to 600°C.

Because of these differences we decided to re-investigate the problem.

## 2. Experimental techniques

Seven Al-W alloys containing 4.3, 5.3, 6.3, 6.8, 6.9, 8.6 and 11.7 wt % W (in order to obtain at %, these values should be divided by a factor of approximately 6.5) were rapidly quenched using the two-piston quenching technique. The experimental details have been described earlier [9, 13].

Rapidly solidified samples of Al-W alloys ( $\approx 1.0$  to 50  $\mu\text{m}$  thick) were examined in a Siemens 114.6 mm diameter Debye-Scherrer camera with nickel-filtered  $\text{CuK}$  radiation, or by means of a Nonius Guinier-de Wolff quadruple focusing camera with crystal-monochromated  $\text{CuK}_\alpha$  radiation. The lattice spacings were computed taking  $\text{CuK}_{\alpha_1} = 1.54050 \text{ \AA}$  for resolved and  $\text{CuK}_\alpha = 1.54178 \text{ \AA}$  for unresolved doublets.

The isochronal and isothermal heat-treatments were carried out by placing the samples in a furnace with a nitrogen atmosphere. Annealing temperatures were controlled to within  $\pm 1^\circ\text{C}$ . Some samples were annealed *in vacuo* or in air. The results were always the same, regardless of the medium used for annealing. After each annealing the samples were air-quenched.

## 3. Experimental results

### 3.1. Results obtained from as-quenched samples

The effects of rapid quenching from the molten state on the structure and phase composition of Al-W alloys with a W content from 4.3 to 11.7 wt % were studied. The X-ray diffraction patterns obtained from these alloys exhibited the characteristic lines of  $\alpha$ -Al, monoclinic  $\epsilon$  and of two unknown phases. The distribution of phases in twenty-one samples is listed in Table I. The black dots before some sample numbers indicate those samples of which the  $\alpha$  lattice parameters are presented in Fig. 2.

$\alpha$ -Al phase with the composition of the original melt appeared only in samples thinner than 10  $\mu\text{m}$  (very high cooling rates) and with a

TABLE I Distribution of phases at room temperature in Al-W alloys rapidly quenched from the melt

Wt % W	Sample thickness		$\text{Al}_4\text{W}$	X	Y	
	No.	( $\mu\text{m}$ )				
4.3	●1	50	+	-	+	⊕
	●2	8	-	-	-	0
	3	5	-	-	-	0
5.3	●4	10	+	-	+	⊕
	●5	8	-	-	-	0
6.3	6	3	-	-	-	0
	●7	1	-	-	-	0
	8	5	+	+	-	⊕
6.8	9	15	+	+	-	⊕
	10	25	+	-	-	⊕
	●11	25	+	-	+	⊕
	●12	40	+	-	+	⊕
	●13	30	+	-	+	⊕
8.6	●14	15	+	-	+	⊕
	●15	40	+	-	+	⊕
	●16	50	+	-	+	⊕
11.7	17	5	+	+	+	⊕
	●18	20	+	+	+	⊕
	19	30	+	+	+	⊕
	●20	40	+	+	+	⊕
	21	45	+	+	+	⊕

+ Present.

- Absent.

0 Al-W solid solution with the composition of the original melt.

⊕ Al-W solid solution with a smaller W content than that contained in the original melt.

● Samples whose lattice parameters are presented in Fig. 2.

W content of up to 6.3 wt % (henceforth designated "A" alloys). In thicker samples or in alloys with a higher W content (more than 6.3 wt %) the  $\epsilon$  and the two unknown phases (we called them X and Y phases) could be detected (henceforth designated "B" alloys). The lattice parameters of  $\alpha$ -Al in these samples containing  $\epsilon$ , X and/or Y phases sharply increased relative to samples containing only  $\alpha$ -Al (Fig. 2).

$\epsilon$ , X and Y phases appeared together only in samples with 11.7 wt % W (Fig. 3a). For lower concentrations of W  $\epsilon$ -X and  $\epsilon$ -Y combinations appeared variously according to the sample (e.g. Fig. 3b).

### 3.2. Isochronal and isothermal annealing

The phase transformations and the decomposition of Al-W solid solutions were investigated using isochronal and isothermal annealing

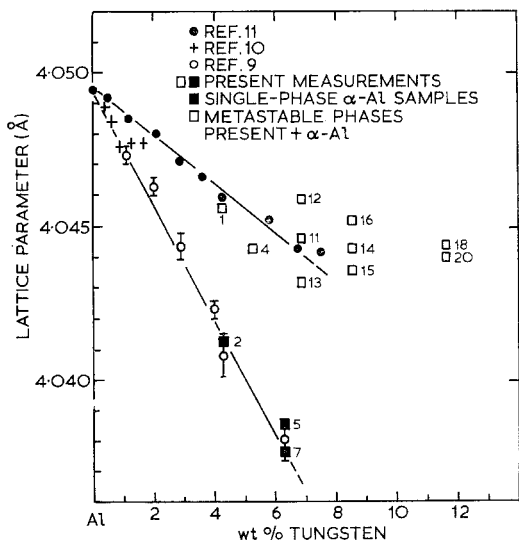


Figure 2 Lattice parameters of *fcc* solid solution in Al-rich Al-W alloys plotted against tungsten concentrations. Numbers indicate the samples listed in Table I.

experiments. The samples were first isochronally annealed for 30 min at temperatures from 50 to 650°C (with an interval of 50 or 100°C), when isothermal annealing began. The samples marked with black dots in Table I were used in the annealing experiments. The results obtained with four of them are presented in Fig. 4.

Fig. 4 records the variation in the lattice parameters of  $\alpha$ -Al in samples no. 2, 7, 15 and 16 as a function of the annealing temperature (up to 650°C) and as a function of the annealing time at 650°C. The dashed horizontal line in Fig. 4 represents the mean value of the lattice parameter of Al from five independent measurements obtained with the pure aluminium used in these experiments.

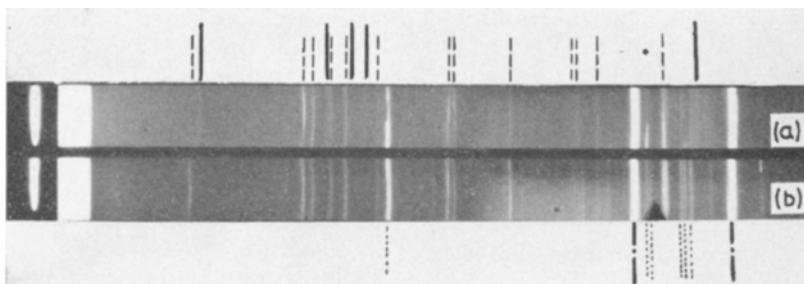


Figure 3 X-ray diffraction patterns of rapidly quenched: (a) Al + 11.7 wt % W alloy, immediately after quenching, showing reflections of  $\alpha$ -Al (---), of  $Al_4W$  (—), of X (····) and of Y phase (— · —); (b) Al + 6.8 wt % W alloy, immediately after quenching, showing reflections of  $\alpha$ -Al, of  $Al_4W$  and of X phase.

### 3.2.1. Multiphase "B" alloys

In the case of alloys no. 1, 4, 11, 12, 13, 14, 15, 16, 18 and 20 where metastable phases  $\epsilon$ , X and Y were present in as-quenched alloys, the lattice parameter of  $\alpha$ -Al remained unchanged up to 500°C (Fig. 4). At 600°C tungsten began coming out of the solution and the lattice parameters increased. At 650°C the lattice parameters showed a further increase, and with further annealing at 650°C the lattice parameters reached the value of pure aluminium, which indicates that the equilibrium solid solubility of W in Al is practically nil at 650°C.

In all these samples during the isochronal annealing procedure  $Al_4W$  ( $\gamma$ ) appeared at 400°C, i.e. before the  $\alpha$  began to disintegrate, while at the same time the quenched-in phases  $\epsilon$ , X and Y began to disappear. By further annealing, the entire matrix transformed to a mixture of  $Al_{12}W$  and Al, with the initial metastable phases tending to disappear. More precisely,  $\epsilon$  disappeared between 500 and 600°C, Y at 500°C, and X after 1.5 h at 650°C.

### 3.2.2. Single phase "A" alloys

In contrast to the multiphase samples (Section 3.2.1) where  $\alpha$ -Al was stable up to 500°C, in samples containing only the  $\alpha$ -Al phase (no. 2, 5 and 7) tungsten began to come out of the solution already at 100°C, and  $\alpha$  was decomposing throughout the whole temperature interval, with the highest increase in the lattice parameter between 50 and 200°C (Fig. 4).

In this decomposition process of  $\alpha$ , five lines of a phase (we called it  $\beta'$ ) could be detected on X-ray diffraction patterns at 200°C (Fig. 5b). At 300°C the lines of  $\gamma$  began to appear (Fig. 5c) to become increasingly intensive with annealing up to 500°C, while at the same time the lines of  $\beta'$

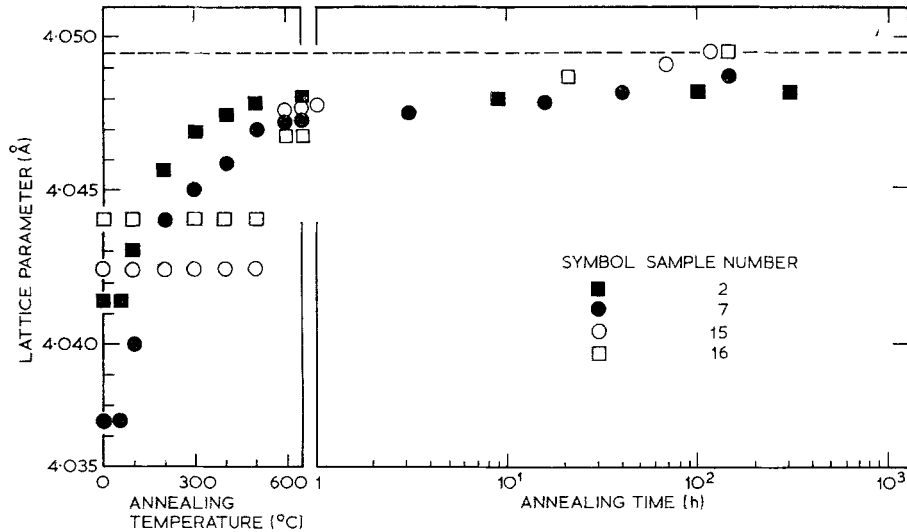


Figure 4 Change of the lattice parameters of Al-W solid solutions with annealing temperature after annealing for 30 min at several temperatures up to 650°C, and subsequently with annealing time at 650°C: ■ ● single-phase  $\alpha$ -Al samples; □ ○ multiphase samples.

were decreasing in intensity (Figs. 5d-e). At 600°C other lines of a phase (we called it  $\beta$ )\* appeared while at the same time the lines of  $\beta'$  disappeared (Fig. 5f). After annealing at 650°C the lines of  $\beta$  became more numerous and more intense. However, the lines of  $\gamma$  became less intense (Fig. 5g).

With further annealing at 650°C, the lines of  $\beta$  became more and more intense with the lines of  $\gamma$  tending to disappear. After 130 h  $\gamma$  completely disappeared and only the  $\beta$  lines remained (Fig. 5h). Further annealing for 350 h at 650°C appeared to have no effect on  $\beta$ .

After annealing for 1 h at 695°C (liquid +  $\gamma$  region according to Clark [3])  $\beta$  disappeared and  $\gamma$  reappeared (Fig. 5i). Repeated annealing at 650°C for 370 h did not lead to a reappearance of  $\beta$ .

#### 4. New phases and discussion

The results presented under Sections 3.1 and 3.2 enable us to draw a picture of the successive steps in the annealing processes for two kinds of alloys. These steps are shown schematically in Fig. 6.

Fig. 6 shows that the investigation of Al-W alloys, very rapidly quenched from the melt revealed seven phases:  $\alpha$ ,  $\epsilon$ , X and Y in as-

quenched alloys, and  $\beta'$ ,  $\beta$  and  $\gamma$  in annealed alloys. Structures are known only for  $\alpha$ ,  $\epsilon$  and  $\gamma$ .

As seen from the phase diagram in Fig. 1, the monoclinic  $\epsilon$  phase,  $\text{Al}_4\text{W}$ , does not exist at room temperature for W concentrations used in the present experiments. However, after rapidly quenching from the molten state  $\epsilon$  was formed at room temperature as a metastable phase for much lower concentrations of W in the as-quenched "B" alloys.

X and Y appeared as metastable phases in as-quenched "B" alloys. During the isochronal process Y disappeared between 500 and 600°C, but X behaved as a more stable phase and took 1.5 h at 650°C to disappear. X and Y phases could not be identified with any familiar intermediate phases in the Al-W system ( $\text{Al}_{12}\text{W}$ ,  $\text{Al}_5\text{W}$  or  $\text{Al}_4\text{W}$ ). However, there is some possibility that these phases are two of the high-temperature phases  $\text{Al}_3\text{W}$ ,  $\text{Al}_7\text{W}_3$  or  $\text{Al}_2\text{W}$  [4] which appeared as metastable phases in as-quenched samples, but this could not be checked because of the lack of structure data on these phases in existing literature, and because a synthesis of these phases was not possible at the present stage of experiments.

$\alpha$ -Al or Al-rich Al-W solid solution was present in the "A" and "B" alloys; in "A" as the

\*This phase we called  $\beta$  after Clark [3] who found an unidentified phase (he called it  $\beta$ ) in Al + 15 wt % W alloys as a result of reaction between  $\alpha$  and  $\gamma$ .

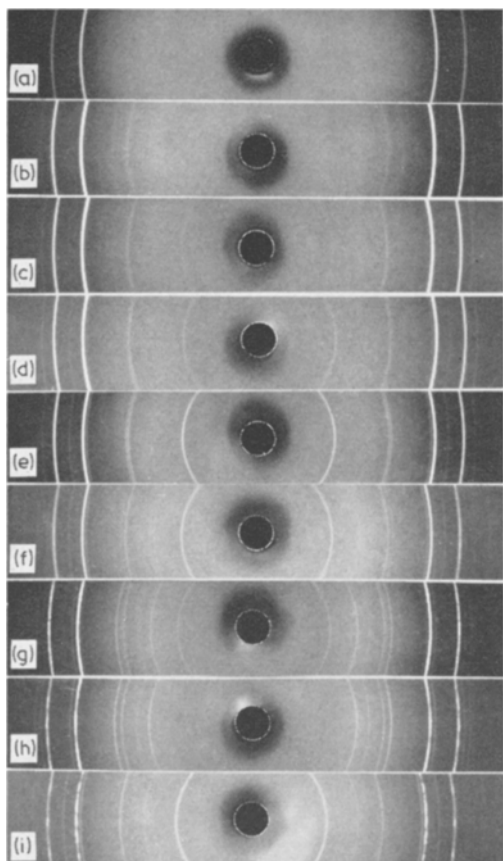


Figure 5  $\text{CuK}\alpha$  Debye-Scherrer patterns, showing: (a) the 111 and 200 reflections from Al + 6.3 wt% W solid solution; (b-i) phase transformations in this alloy after isochronal annealing for 30 min at temperatures of up to 650°C, and after isothermal annealing at 650 and 695°C: (a) room-temperature; (b) 200°C; (c) 300°C; (d) 400°C; (e) 500°C; (f) 600°C; (g) 650°C; (h) 130 h at 650°C; (i) 1 h at 695°C.

TABLE II Observed and calculated  $d_{hkl}$  values of the  $\beta'$  phase in Al-W alloys.

Structure: Cubic		
Lattice parameter: $a = 6.92 \pm 0.08 \text{ \AA}$		
$hkl$	$d_{\text{cal}}(\text{\AA})$	$d_{\text{obs}}(\text{\AA})$
012	3.10	3.13
112	2.83	2.82
013	2.19	2.18
023	1.92	1.92
033	1.63	1.63

only phase, with the same composition as that of the original melt; in "B" together with  $\epsilon$ , X and Y but with a lower W content than in the original melt. The maximum content of W in a

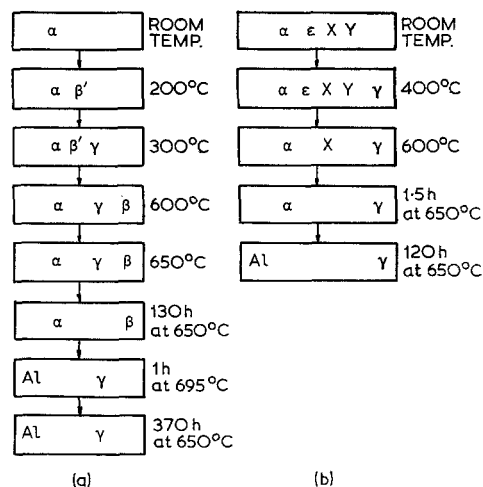


Figure 6 Transformation process in: (a) "A" alloys; (b) "B" alloys.

(in "A" alloys) represents the solubility limit of W in Al obtained by the two-piston quenching technique, already published by the same author [9].

During isochronal annealing,  $\alpha$  in "A" alloys began to decompose already at 100°C. The first phase to be detected was a new metastable phase  $\beta'$  which appeared at 200°C and which with further annealing at higher temperatures tended to disappear by transforming into  $\gamma$ . Five reflections from  $\beta'$  were detected and could be indexed with a cubic unit cell of  $a = 6.92 \pm 0.08 \text{ \AA}$ . The observed and calculated  $d_{hkl}$  values are given in Table II.

With further isochronal annealing,  $\gamma$ , together with remaining  $\alpha$ , transformed into  $\beta$  phase (Fig. 5h). Thirty reflections from the  $\beta$  phase could be detected and indexed with a hexagonal unit cell of  $a = 7.870 \pm 0.004 \text{ \AA}$  and  $c = 23.80 \pm 0.03 \text{ \AA}$ . The observed and calculated  $d_{hkl}$  values are listed in Table III.

Similar behaviour has been found by Clark [3] who reported that after annealing below 580°C,  $\gamma$  transformed into a new phase  $\beta$  by means of the provisionally written reaction  $\alpha + \gamma \rightarrow \beta$ . There were no other details in Clark's report, but we assume that his phase  $\beta$  is identical with that detected in "A" alloys during the annealing experiments.

During isochronal annealing,  $\alpha$  in "A" alloys began to decompose already at 100°C, while in "B" alloys it showed increased resistance to decomposition, and temperatures above 500°C were needed to ensure the disintegration of

TABLE III Observed and calculated  $d_{hkl}$  values of the  $\beta$  phase in Al-W alloys.

Structure: Hexagonal  
 Lattice parameters:  $a = 7.870 \pm 0.004 \text{ \AA}$   
 $c = 23.80 \pm 0.030 \text{ \AA}$   
 $c/a = 3.03$

$hkl$	$d_{\text{cal}}(\text{\AA})$	$d_{\text{obs}}(\text{\AA})$
110	3.938	3.942
113	3.527	3.498
023	3.133	3.134
008	2.980	2.976
024	2.959	
030	2.272	2.271
033	2.185	2.175
034	2.124	2.128
220	1.968	1.968
223	1.910	1.919
226	1.763	1.770
135	1.757	
044	1.638	1.637
045	1.605	1.606
140	1.487	1.486
145	1.420	1.413
146	1.393	1.383
052	1.354	1.355
330	1.312	1.312
335	1.246	1.245
244	1.243	
060	1.136	1.136
343	1.109	1.107
065	1.105	
250	1.091	1.091
251	1.090	
255	1.063	1.059
160	1.040	1.045
165	1.015	1.017
440	0.9838	0.9834
445	0.9635	0.9592
266	0.9195	0.9175
175	0.8870	0.8854
360	0.8587	0.8585
084	0.8434	0.8436

$\alpha$ . The precipitated phase first observed was  $\gamma$ , while  $\beta'$  and  $\beta$  were completely absent.

The increased resistance against decomposition of highly supersaturated  $\alpha$ -Al in the presence of a second component, was similar to the behaviour found by Vengrenovich and Psarev in Al-Cr [14, 15] and in Al-Mn [14] alloys. They showed that this increased resistance against decomposition of the  $\alpha$ -Al is due to a flow of Mn and Cr atoms towards the  $\alpha$ -Al, precipitated in the process of transformation of

the metastable phases  $\text{Al}_4\text{Mn}$  and  $\text{Al}_4\text{Cr}$  (or  $\text{Al}_{11}\text{Cr}_2$ ) into the equilibrium phases  $\text{Al}_6\text{Mn}$  and  $\text{Al}_7\text{Cr}$ .

When the transformation  $\epsilon + X + Y \rightarrow \gamma$  which was detected in "B" alloys at  $300^\circ\text{C}$  is accompanied by the precipitation of tungsten atoms, these atoms can partly combine with the aluminium atoms into  $\gamma$ , the rest of them being dissolved in the  $\alpha$ , preventing its disintegration. In order to give a full answer the crystal structures of X and Y, and even their composition formulae should be established. However, this was not possible in the present experiments.

In many rapidly quenched Al-phase alloys, during decomposition of supersaturated Al-base solid solutions, structural changes take place in one or more stages with the production of intermediate phases, until the equilibrium precipitates form [2]. So the fact that the first precipitate phase observed during annealing of  $\alpha$ -Al in "A" alloys is metastable  $\beta'$  rather than stable  $\text{Al}_{12}\text{W}$  is nothing unusual.

It was shown (Section 3.2.2) that  $\beta'$  reverts to  $\text{Al}_{12}\text{W}$  in "A" alloys. The absence of  $\beta'$  in "B" alloys is due to the high temperatures necessary for disintegration of  $\alpha$ . Since the precipitating phase can only be identified when precipitation is nearly complete, failure to observe  $\beta'$  in "B" alloys does not imply that it never forms. However, it remains unclear why  $\beta$  never appeared in "B" alloys.

The curve reported by Burov and Yakunin [11] (Fig. 2) was certainly obtained by means of samples with small contents of  $\text{Al}_4\text{W}$ , because the great resistance against decomposition of their  $\alpha$ -Al (up to  $600^\circ\text{C}$ ) was nearly the same as found in "B" alloys in the present experiments. It seems that the samples used by Burov and Yakunin were too thick\* (about  $50 \mu\text{m}$ ) to be quenched rapidly enough to produce single-phase  $\alpha$ -Al samples.

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\*Burov and Yakunin used the quenching method which was first developed by Duwez *et al* [16] in 1960. Samples which were cooled rapidly enough to allow effective quenching were always thinner than  $20 \mu\text{m}$  [17] or about  $10 \mu\text{m}$  [18].

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