Composition and morphology of diborides in Al-Ti-B alloys after annealing at 1873 K

Sestava in morfologija diboridov v zlitinah Al-Ti-B po žarjenju na 1873 K

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Received: January 13, 2008 **Accepted:** February 26, 2008

Abstract: In the investigation, Al-Ti-B alloys with different Ti/B ratios were annealed at 1873 K for 10 hours. Under this condition diboride particles were in contact with molten aluminium. During annealing considerable growth of remaining unmelted diboride particles took place. The composition of diboride particles shifted extremely close to the composition of pure TiB_2 regardless of the Ti/B ratios in the alloys, indicating that in equilibrium almost pure TiB_2 coexisted with a melt. Diboride particles were bound with well-defined crystal facets. Types and relative size of the facets depended on the Ti/B ratio. It is strongly indicated that an excess of Ti (B) in the melt over that needed to form TiB_2 stabilizes crystal planes having planar arrangement of Ti (B) atoms.

Izvleček: V tej raziskavi smo več zlitin Al-Ti-B, ki so imele različna razmerja Ti/B, žarili 10 ur pri 1873 K. V teh razmerah so bili delci diborida v kontaktu z aluminijevo talino. Med žarjenjem so diboridni delci močno zrasli. Njihova sestava se je v vseh raziskanih zlitinah močno približala sestavi čistega TiB_2, kar kaže, da je v termodinamskem ravnotežju s talino praktično čisti TiB_2. Diboridni delci so bili obdani s kristalnimi fasetami. Vrsta in relativna velikost faset je bila močno odvisna od razmerja Ti/B. Obstajajo trdni dokazi, da presežek Ti (B) nad vrednostjo, ki je potrebna za tvorbo TiB_2, stabilizira kristalne ravnine, ki imajo ravninsko razporeditev Ti (B) atomov.

Key words: Al-Ti-B alloys, diboride phase, high-temperature annealing, morphology, microstructure

Ključne besede: Al-Ti-B zlitine, diboridna faza, visokotemperaturno žarjenje, morfologija, mikrostruktura

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INTRODUCTION

It is believed that particles of the diboride phase (Al,Ti)B_2 present in Al-Ti-B alloys play the most important role in the grain-refining process in aluminium alloys[1,2]. Therefore, they were the subject of several investigations[1-5]. The results show that during manufacturing of Al-Ti-B alloys by an aluminothermic synthesis the diboride phase is formed with compositions ranging from that of the stoichiometric AlB_2 to that of the stoichiometric TiB_2[1-3]. All diborides, pure AlB_2 and TiB_2, as well as the mixed diboride $(Al_xTi_{1-x})B_2$ $(0 < x < 1)$ posses the same crystal structure (space group P6/mmm, Ref. 6) and very similar lattice parameters (see Figure 1). On this ground it was suggested that the mixed diboride phase $(Al_xTi_{1-x})B_2$ represents a thermodynamically stable phase in the aluminium-rich corner of the Al-Ti-B ternary system[7]. However, some experimental results do not support this assumption[2,8]. JOHNSSON and JANSSON[2] found out that the composition of the mixed diboride moved toward the compositions of pure TiB_2 and AlB_2 during holding in liquid aluminium. In addition, it was discovered that during synthesis of Al-Ti-B alloys by arc melting almost pure AlB_2 and TiB_2 formed. Furthermore, the formation of the mixed diboride $(Al_xTi_{1-x})B_2$ from pure diborides AlB_2 and TiB_2 did not take place even after exposure for 1000 h at 1073 K[8].

However, 1073 K is relatively low temperature since it amounts only 0.3 T_m of TiB_2, where T_m indicates melting temperature of pure TiB_2: 3498 K[9]. This could mean that even if the mixed boride would be a thermodynamically stable phase, the transfor-

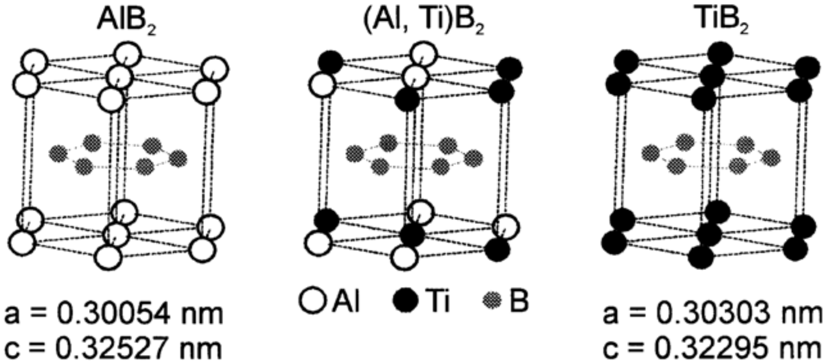


Figure 1. Crystal structures of diborides found in the ternary system Al-Ti-B. The diborides possess crystal structures belonging to the same space group P6/mmm. The lattice parameters are similar, mixed diboride having lattice parameters between those for AlB_2 and TiB_2. The crystal structure has layered form with alternate stack of planar hexagonal metal layers (m) and hexagonal boron layers (b).

Slika 1. Kristalne zgradbe diboridov v ternarnem sistemu Al-Ti-B. Kristalne zgradbe diboridov spadajo v isto prostorsko skupino P6/mmm. Mrežni parametri so podobni. Mrežni parametri zmesnega diborida so med parametri čistega AlB_2 in TiB_2. Zgradba diborida je plastna, sestavljena iz izmeničnih heksagonalnih kovinski plasti (m) in heksagonalnih borovih plasti (b).

mation of pure AlB_2 and TiB_2 to the mixed diboride $(Al_xTi_{1-x})B_2$ might be suppressed by kinetic reasons. Annealing of Al-Ti-B alloys containing both pure AlB_2 and TiB_2 is not possible at much higher temperatures that should allow completion of the transformation in shorter times, because AlB_2 would transform via a peritectic reaction to the liquid phase and α-AlB_{12} above 1253 K[10]. As a consequence, the diboride phase can be studied at higher temperatures only in equilibrium with other phases.

In this work some Al-Ti-B alloys with different Ti/B ratios were heated to 1873 K. This temperature exceeded 0.5 T_m of TiB_2, therefore in these conditions kinetic obstacles for achieving heterogeneous equilibrium between diboride phase and aluminium melt should be eliminated. The main purpose of the work was to determine the composition of the diboride phase coexisting with the liquid phase in order to contribute new information for the constitution of the ternary system Al-Ti-B. In addition, special attention was paid to the influence of Ti/B ratio on the morphology of diboride particles.

EXPERIMENTAL

Annealing of alloys

In this investigation samples of Al-Ti-B alloys were manufactured by an aluminothermic reduction of Ti and B from K_2TiF_6 and KBF_4 salts, respectively. The chemical compositions of the alloys are given in Table 1. Details of alloy preparation can be found elsewhere[12]. Before annealing at 1873 K the samples were put into small alumina crucibles situated inside a covered alumina vessel. The annealing took place in a high temperature furnace ASTRO in an argon atmosphere. Heating and cooling rates were 60 K/min, whereas the holding time at 1873 K was 10 hours.

Table 1. Composition of the investigated Al-Ti-B alloys prepared by an aluminothermic reduction of Ti from K_2TiF_6 and B from KBF_4
Tabela 1. Sestava preiskanih zlitin Al-Ti-B, ki so bile izdelane z aluminotermično redukcijo Ti iz K_2TiF_6 in B iz KBF_4

Alloy Zlitina	Ti / wt.% Ti / mas.%	B / wt.% B / mas. %	Ti/B weight ratio masno razmerje Ti/B	Ti + B / wt.% Ti + B / mas. %
A8	8.55	1.93	4.43	10.48
A6	7.34	2.86	2.56	10.2
A7-1	3.73	2.77	1.34	6.5
A7-2	3.14	2.85	1.1	5.99

Metallographic preparation

Samples for the light (LM) and scanning electron microscopy (SEM) were prepared using standard metallographic techniques[13]. The samples were polished directly before analyses with energy dispersive spectroscopy (EDS) to remove possible etching products and oxide layers on the investigated surface.

For investigation of the morphology of diboride particles deep etching was applied using two different etchants: (1) a solution consisting of 50 % HCl and water, and (2) a methanol-iodine solution (30 ml methanol, 3 g tartaric acid and 1 g iodine). Satisfying results were obtained after 10–15 min etching in the HCl solution and 1–2 hours etching in the methanol-iodine solution. It is important to stress that the morphology of diboride particles in each alloy was the same regardless of the applied etchant. This strongly indicates that both etchants dissolved only aluminium matrix and, what is of utmost importance, did not attack diboride particles.

Energy dispersive spectroscopy
EDS was performed in a scanning electron microscope SIRION 400 NC (FEI Company), equipped with an energy dispersive analyser INCA 350 (Oxford Analytical). Boron was mainly determined qualitatively, whereas titanium and aluminium were determined quantitatively in all observed phases. We used titanium and aluminium standard spectra obtained from pure titanium and aluminium, as well as from pure diborides AlB_2 (large AlB_2 particles in binary Al-B alloy) and TiB_2 (from pure arc-melted TiB_2).

X-ray diffraction
The phase composition of alloys was determined using an X-ray diffractometer Philipps PW 1710. The general diffraction curves were recorded at a scanning rate of 0.025 °/s (Bragg angle) scan range from 5° to 70° and the detailed diffraction curves with 0.025 °/10 s with a scan range between 33.5° and 35° (around the (100) diboride peak).

The results of X-ray diffraction were primarily used for the determination of the diboride lattice parameters. It was found out that lattice parameters *a* and *c* of the diboride phase can be calculated reliably if positions of at least five diffraction peaks can be determined. In some cases only (100) peak was well defined. In this case only the value of *a*-axis could be calculated.

The composition of the diboride phase – the atomic fraction of aluminium on the metallic sublattice of diboride phase C_{Al} – was estimated on the basis of two criteria:

- the deviation of the lattice parameter *a* from that of pure TiB_2[3]:

$$C_{Al} = \frac{a_{TiB_2} - a}{a_{TiB_2} - a_{AlB_2}} 100 \ \ \% \qquad (1)$$

- the deviation of the axis ratio *c*/*a* from that of pure TiB_2[4]:

$$C_{Al} = \frac{c/a - (c/a)_{TiB_2}}{(c/a)_{AlB_2} - (c/a)_{TiB_2}} 100 \ \ \% \qquad (2)$$

RESULTS AND DISCUSSION

The compositions of Al-Ti-B alloys were chosen so that the diboride phase should exists in the equilibrium with the liquid phase at the annealing temperature (1873 K). During heating of Al-Ti-B alloys all other phases present initially (e.g. Al_3Ti, α-AlB_{12}, AlB_2) were melted completely, only the titanium-rich diboride remained partly unmelted. To estimate the quantity of unmelted TiB_2 the solubility product proposed by SIGWORTH[14] was used:

$$\log\ (w_{Ti})(w_B)^2 = 8.526 - 16{,}043/T \qquad (3)$$

where T means temperature in K, and w_{Ti} and w_B contents of Ti and B (in wt.%) in the melt, respectively. Table 2 shows the results. It is obvious that 4–7.2 % TiB_2 remained unmelted. Since the solubility product defined by equation (3) may be too

Table 2. Concentration of titanium and boron in the liquid phase and the quantity of unmelted TiB_2 at 1873 K using equation (3)
Tabela 2. Koncentracija titana in bora v talini in količina nestaljenega TiB_2 pri 1873 K, izračunana z uporabo enačbe (3)

Alloy	Ti dissolved in the melt / wt.%	B dissolved in the melt / wt.%	estimated initial quantity of TiB_2 / wt.%	unmelted TiB_2 at 1873 K / wt.%
A8	5.22	0.42	6.2	4.8
A6	2.40	0.62	9.2	7.2
A7-1	0.53	1.32	5.4	4.7
A7-2	0.36	1.59	4.6	4

high, the amount of unmelted TiB_2 is to be slightly higher.

Morphology of diboride particles

The size of the diboride particles in the initial state (after aluminothermic reduction) rarely exceeded 1 μm (Figure 2). In alloys with hypostoichiometric and stoichiometric composition (Ti/B ≤ 2.21) agglomerates of diboride particles in Al-rich solid solution could be observed. In alloys with hiperstoichiometric composition, in addition to boride agglomerates also Al_3Ti particles were present.

However, during annealing at 1873 K very large hexagonal plates of the titanium-rich diboride formed. The height of the plates often exceeded 5 μm and their edge 10 μm (Figures 3 and 4).

All diboride particles were bound with very well defined crystal faces; however their morphology was not the same in all investigated alloys. In the alloy A7-1 having an excess of B over that needed for formation of TiB_2 (Ti/B) = 1.34, the basal {0001} facets dominate (Figure 4a). Note also traces of the prismatic $\{10\bar{1}0\}$ and pyramidal facets. It is not possible to determine the Miller-Bravais indices of these pyramidal planes by inspection of deep-etched specimens only. However, it seems possible that their indices could be $\{h\bar{k}01\}$, $h > l$, $h = -k$.

In the near-stoichiometric alloy A6 (Ti/B = 2.56) two additional types of facets were observed (Figure 4b): prismatic $\{11\bar{2}0\}$ and pyramidal $\{11\bar{2}1\}$ facets. In the alloy A8 having an excess of Ti over that to form TiB_2 (Ti/B = 4.43), the diboride particles were bound by basal {0001} and prismatic $\{10\bar{1}0\}$ facets (Figure 4c).

To explain the influence of Ti/B ratio on the observed morphology of the diboride particles we must take a closer look to the atomic arrangements in the following crystallographic planes: {0001}, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{11\bar{2}1\}$ and $\{2\bar{2}01\}$. In the {0001} planes, boron and titanium atoms form alternate planar layers (Figure 1). Thus, the outer layer in the contact with the liquid phase could be occupied only by boron or only by titanium atoms. In the family of $\{10\bar{1}0\}$ planes only titanium atoms can be arranged in a planar array, whereas the arrangement of boron atoms cannot be planar (Figure 5a). In both $\{11\bar{2}0\}$ and $\{11\bar{2}1\}$ families of planes it is not possible to get the planar outer layer occupied by only one kind of atoms, but in each case with both boron and titanium atoms (Figure 5a). On the other hand, boron atoms can be arranged in a planar manner, therefore the facets of this plane dominate in alloy A7-1.

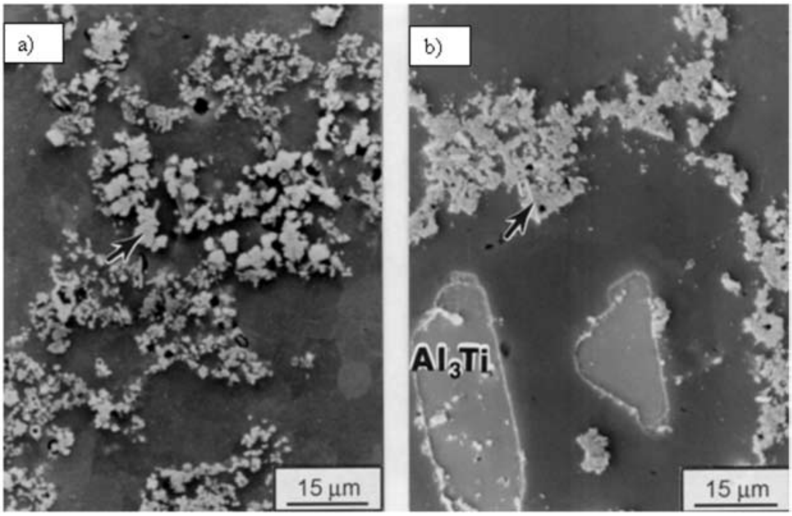


Figure 2. Secondary electron micrographs of a) alloy A7-1 and b) alloy A8. The arrows indicate diboride agglomerates.

Slika 2. Mikroposnetek z vrstičnim elektronskim mikroskopom (sekundarni elektroni) zlitin: a) A7-1 in b) A8. Puščici kažeta na diboridne agregate.

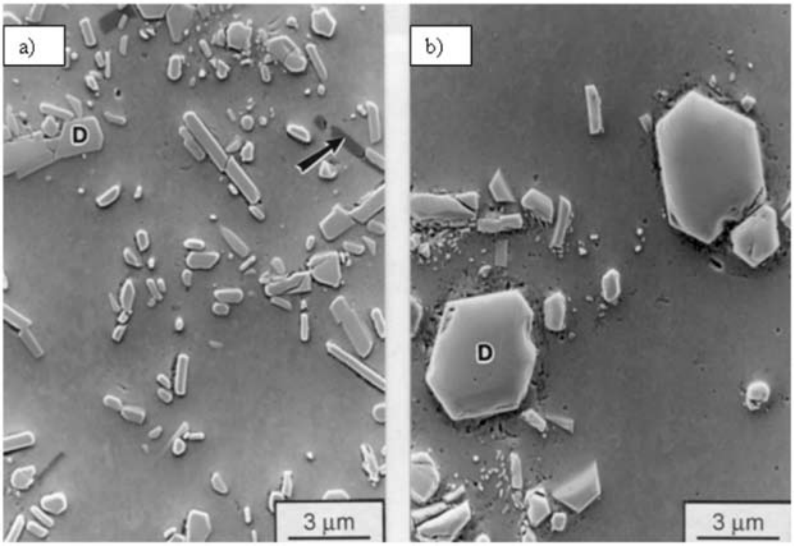


Figure 3. Secondary electron micrographs of a) alloy A7-1 and b) alloy A8. The arrow indicates AlB_2 particle. D indicates TiB_2.

Slika 3. Mikroposnetek z vrstičnim elektronskim mikroskopom (sekundarni elektroni) zlitin a) A7-1 in b) A8. Puščica kaže na delec AlB_2. D pomeni TiB_2.

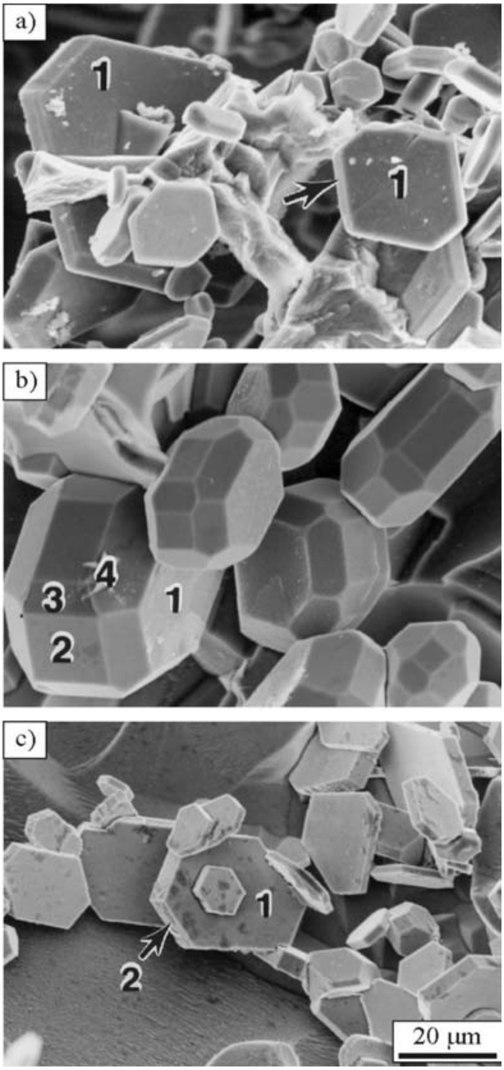


Figure 4. Secondary electron micrographs of diboride particles in the investigated alloys after deep-etching: a) Alloy A7-1, b) alloy A6 and c) alloy A8 after exposure for 10 hours and 1873 K (1: (0001), 2: $(10\bar{1}0)$, 3: $(11\bar{2}0)$, 4: $(11\bar{2}1)$, arrow in a: $(h\bar{k}01)$, $h > l$, $h = -k$)

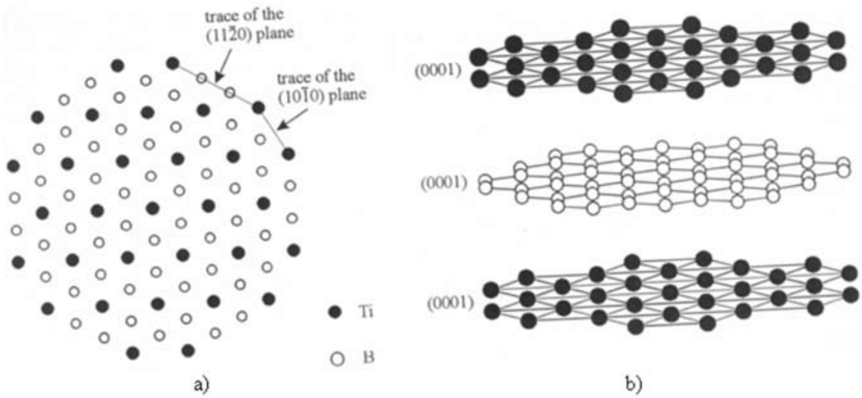
Slika 4. Mikroposnetek z vrstičnim elektronskim mikroskopom (sekundarni elektroni) zlitin diboridnih delcev v preiskovanih zlitinah po globokem jedkanju: a) Zlitina A7-1, b) zlitina A6 and c) zlitina A8 po desetih 10 urah pri 1873 K (1: (0001), 2: $(10\bar{1}0)$, 3: $(11\bar{2}0)$, 4: $(11\bar{2}1)$, puščica na sliki a: $(h\bar{k}01)$, $h > l$, $h = -k$)

According to this analysis it is very likely that diboride particles in the alloys with an excess of titanium are bound with {0001} and $\{10\bar{1}0\}$ planes, because in these planes titanium alloys are arranged in planar array. Similarly, in the alloys with an excess of boron {0001} planes dominate, since in these planes boron atoms form planar layers. On the other hand, $\{11\bar{2}0\}$ and $\{11\bar{2}1\}$ planes that contain both titanium and boron atoms are very important in the alloy A6 having near-stoichiometric composition. The above presented evidence indicates that an excess of Ti (B) tends to stabilize crystal planes with the planar arrangements of Ti (B) atoms.

Composition of the diboride phase

The results of EDS analyses showed that even after 1000 s live time aluminium peaks could not be resolved in EDS spectra of diboride particles present in the alloy A8. On the X-ray diffraction curve only two peaks arising from the diboride phase were identified thus it was not possible to reliably calculate its lattice parameters. Only the length of the *a*-axis from the position of (100) diboride phase was calculated. Using equation (1) we determined $C_{\mathrm{Al}} = 1.67$ at.% Al on the metallic sublattice. It is believed that in this case the results of EDS analysis were more reliable. Thus, apparently pure TiB_2 existed in the equilibrium with the liquid phase (Table 3).

EDS showed also that in the alloy A6 no aluminium peak could be resolved in spectra of diboride particles – similarly as in the alloy A8. On the other hand, several well-defined peaks arising from both Cu Kα_1 and Cu Kα_2 radiation could be easily resolved (Figure 6). The calculated lattice



a)

b)

Figure 5. Arrangement of atoms in some planes of TiB_2. In a) TiB_2 crystal is bound by traces of $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes (projection perpendicular to (0001) plane. In b) planar arrangement of titanium and boron atoms in (0001) plane is shown.

Slika 5. Razporeditev atomov v nekaterih ravninah TiB_2. Na sliki a) je TiB_2 kristal obdan z ravninama $\{10\bar{1}0\}$ in $\{11\bar{2}1\}$ (projekcija pravokotna na ravnino (0001). Na sliki b) je prikazana ravninska ureditev titanovih in borovih atomov v ravnini (0001).

parameters coincided completely with the lattice parameters of pure TiB_2. The aluminium content computed by equations (1) and (2) amounts 0 at.% Al. Therefore, the results of EDS analysis, as well as the results of XRD clearly indicate that in this alloy almost pure TiB_2 exists in the equilibrium with the melt (Table 3).

Both alloys A7-1 and A7-2 existed at 1873 K in the two-phase liquid + diboride region. On EDS spectra of some diboride particles very small aluminium peaks could be observed. The calculations gave us the result $C_{Al} \approx 0,3$ at.% Al. This is close to the detection limit of the EDS. On X-ray diffraction curves peaks arising from the diffraction of Cu Kα_1- and Cu Kα_2-radiation on the lattice planes of both AlB_2 and TiB_2 could be observed. Of course, AlB_2 was not present at 1873 K, but has crystallized from the melt during cooling below 1173 K. The lattice parameters of the titanium-rich and aluminium-rich diborides corresponded closely to the lattice parameters of pure TiB_2 and AlB_2. Also in these alloys the experimental results showed that almost pure TiB_2 existed in the equilibrium with the melt at 1873 K (Table 3).

During annealing at 1873 K the size of diboride particles increased considerably. In can be shown by a simple calculation that one such particle have formed from several thousands to several ten thousands of particles that were initially present in the microstructure. It is the most probable that diboride particles shown in Figures 3 and 4 had formed by a process similar to the Ostwald ripening; smaller particles have dissolved and the larger particles have grown. Therefore, for the attainment of the equilibrium composition of the diboride phase diffusivity inside particles is less important than the attachment/detachment kinetics during dissolution/growth of the diboride particles. Since under isothermal conditions diboride particles grow slowly, it is believed that he interface attachment/detachment kinetics should be fast enough to maintain the equilibrium composition of the diboride phase. On the basis of this discussion and the results of X-ray diffraction and EDS analyses we may conclude that at 1873 K apparently pure TiB_2 existed in the equilibrium with the liquid phase regardless of the Ti/B ratio.

CONCLUSIONS

During annealing at 1873 K considerable growth of unmelted diboride particles took place. They probably grew by a process similar to Ostwald ripening.

The composition of diborides was extremely close to the composition of pure

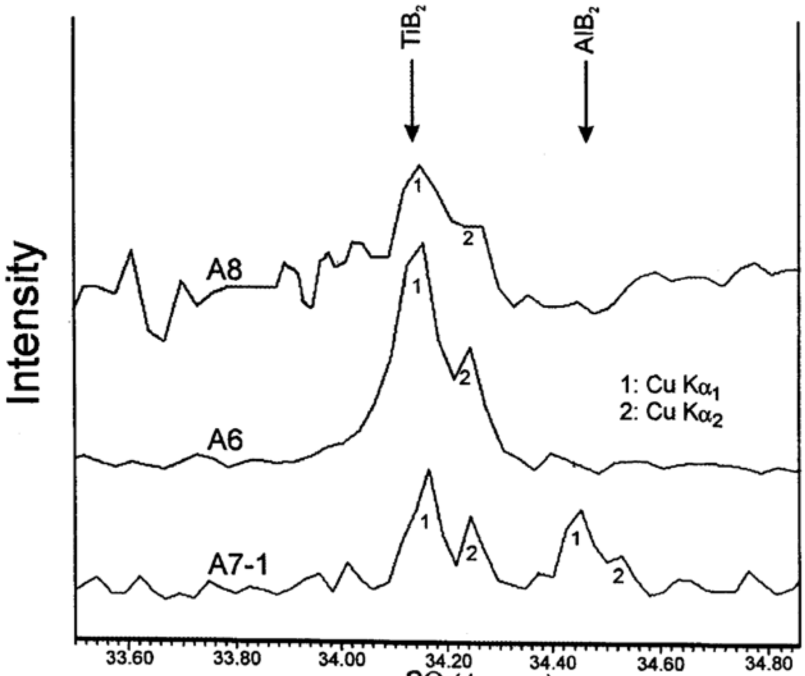


Figure 6. The results of X-ray diffraction. The shape and the position of the (100) diboride peak in different alloys after 10 hours exposure at 1873 K. In alloy A7-1 also peaks arising from AlB_2 that had formed during cooling could be seen. Arrows indicate the positions of (100) peaks of pure TiB_2 and pure AlB_2 by diffraction of Cu $K\alpha_1$ radiation.

Slika 6. Rezultati rentgenske difrakcije. Oblika in položaj vrhov (100) diborida v različnih zlitinah po 10 urah žarjenja pri 1873 K. V zlitini A7-1 se pojavi tudi vrh AlB_2, ker AlB_2 nastane pri ohlajanju. Puščici kažeta vrhova (100) čistega TiB_2 in čistega AlB_2 pri difrakciji Cu $K\alpha_1$.

Table 3. Aluminium content on the metallic sublattice of the diboride phase according to the results of XRD and EDS
Tabela 3. Vsebnost aluminija na kovinski podmreži diboridne faze skladno z rezultati XRD in EDS

alloy	C_{Al} / at.% Al (equation 1)	C_{Al} / at.% Al (equation 2)	C_{Al} / at.% Al (EDS)	remark pripomba
A8	1.5	-	0	TiB_2
A6	0	0	0	TiB_2
A7-1	0	0	0.3	TiB_2
A7-1	100	98.8	99.8	AlB_2

TiB_2 regardless of the Ti/B ratios in the investigated alloys. Therefore all evidence strongly suggests that at 1873 K almost pure TiB_2 existed in the equilibrium with the liquid phase in all investigated alloys.

Diboride particles were bound with well-defined crystal facets. Types and relative size of the facets were dependent on the Ti/B ratio. An excess of Ti (B) tended to stabilize crystal planes with the planar arrangement of Ti (B) atoms. In the alloy A8 with an excess Ti over that needed to form TiB_2 {0001} and {1010} planes dominated, whereas in alloy A7-1 and A7-2 having an excess of boron {0001} planes dominate, since in these planes boron atoms form planar layers. On the other hand, $\{11\bar{2}0\}$ and $\{11\bar{2}1\}$ planes that contain both titanium and boron atoms are very important in the alloy A6 having near-stoichiometric composition.

POVZETEK

Sestava in morfologija diboridov v zlitinah Al-Ti-B po žarjenju na 1873 K

Delci diboridne faze $(Al,Ti)B_2$ imajo pomembno vlogo pri udrobnitvi kristalnih zrn v aluminijevih zlitinah. Kadar zlitine Al-Ti-B izdelamo z aluminoternično sintezo imajo diboridi spekter sestav, ki se razteza od sestave čistega AlB_2 do sestave čistega TiB_2. V literaturi še vedno obstajajo razhajanja ali sta v sistemu Al-Ti-B termodinamsko stabilna čista diborida AlB_2 in TiB_2 ali pa zmesni diborid $(Al,Ti)B_2$.

V tej raziskavi smo raziskovali vzorce zlitine Al-Ti-B, ki smo jih izdelali z aluminotermično redukcijo Ti in B iz soli K_2TiF_6 in KBF_4. Zlitine Al-Ti-B so imele različno razmerje Ti/B. Zlitine smo nato žarili 10 ur pri 1873 K. Ta temperatura presega 0,5 T_t TiB_2 (T_t je temperatura tališča v kelvinih), zato so difuzijski procesi dovolj hitri, da se lahko vzpostavi ravnotežje v sorazmerno kratkem času.

Pri 1873 K so bili delci diborida v kontaktu z aluminijevo talino. Med žarjenjem so diboridni delci močno zrasli. Z analizo EDS in rentgensko difrakcijo (XRD) smo ugotovili, da se je njihova sestava v vseh raziskanih zlitinah močno približala sestavi čistega TiB_2. To kaže, da je v termodinamskem ravnotežju s talino praktično čisti TiB_2.

Ugotovili smo tudi, da so bili diboridni delci obdani s kristalnimi fasetami. Vrsta in relativna velikost faset je bila močno odvisna od razmerja Ti/B. V zlitini A8, v kateri je bil presežek titana glede na idealno stehiometrično razmerje (2,21:1) so bili diboridni delci obdani s fasetami osnovne ploskve $\{0001\}$ in prizmatičnimi ravninami $\{10\bar{1}0\}$. V zlitini s skoraj stehiometrično sestavo (Ti/B = 2,56) sta se pojavile še fasete dveh dodatnih ravnin: prizmatične $\{11\bar{2}0\}$ in piramidne $\{11\bar{2}1\}$. V zlitini A7-1, ki je imela presežek B (Ti/B = 1,34) je prevladovala faseta osnovne ravnine $\{0001\}$.

Z analizo rezultatov in primerjavo faset z razporeditvijo atomov v diboridu smo ugotovili, da presežek Ti nad vrednostjo, ki je potrebna za tvorbo TiB_2, stabilizira kristalne ravnine, ki imajo ravninsko razporeditev Ti atomov. Podoben učinek ima B, ki stabilizira ravnine, v katerih so atomi B razporejeni v ravnini.

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