

## Multiphase reaction diffusion in transition metal-boron systems

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### Abstract

The formation of various diffusion layers in selected transition metal-boron systems was investigated by means of pack-boriding. Samples of commercially pure titanium, molybdenum and tantalum were packed in pre-calcined amorphous boron powder and annealed for 1–4 h at temperatures between 1200 and 1500°C. Experiments were carried out in a high-frequency furnace in inert gas atmosphere ( $\leq 500$  mbar Ar) or in rotary-pump vacuum ( $\leq 5 \times 10^{-2}$  mbar). Layered boride phases were observed metallographically and identified by XRD as a function of depth. In a series of experiments for the Ta-B system, small amounts of  $\text{KBF}_4$  (varied between 1 and 7.5 wt%) were added to the boron powder in order to activate a transport reaction supplying boron atoms to the sample surface via the gas phase. This was found to improve layer growth rates significantly. Also evidence was found that boron diffusivities in certain boride phases, like MoB or  $\text{TaB}_2$ , might be higher than in the corresponding less boron-rich phases ( $\text{Mo}_2\text{B}$ , TaB). © 1997 Elsevier Science S.A.

**Keywords:** Reaction diffusion; Layer growth; Transition metal borides; Pack-boriding

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### 1. Introduction

Boriding and boronizing are reliable and feasible techniques among a wide variety of thermochemical surface hardening processes known today [1,2]. It can be applied to ferrous and non-ferrous as well as cermet materials featuring surface layers that possess special advantages over conventional case-hardened layers, e.g. extremely high hardness values (up to 5000 HV) and improved resistance against mechanical and corrosive wear [3]. Superior material properties like that have long since attracted considerable interest for both technical applications (tools, high-performance gear parts [4]) and theoretical studies.

However, the huge majority of investigations in the field deals with boriding of steels and some of them with titanium alloy parts [2]. Only a very few studies are known concerning transition metals in general

[5,6]. Besides that, while most of the more important mechanical and chemical properties have been investigated for these boron compounds, the knowledge on multiphase layer formation and material transport properties, i.e. the diffusivities, are still lacking to a large extent [7]. Samsonov and Zhunkovskii [5] gave average diffusivities of boron in boride phases for one boride phase only for each of the transition metal-boron systems of group 4–6 investigated. Some metallographic investigations together with microhardness measurements were performed but the results are not in accordance with the recent versions of accepted phase diagrams [8].

In the present work initial investigations on the preparation of reaction diffusion couples within the systems Ti-B, Mo-B and Ta-B by pack-boriding in a high-frequency furnace are performed. These borides were chosen from the view of technical importance (Ti-B) and from a basic view of studying multiphase diffusion (Mo-B, Ta-B), because up to six intermediate phases occur in these systems.

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## 2. Experimental

The experiments were conducted in a Mo crucible inductively heated in a high-frequency furnace. Basic process parameters such as gas pressure and temperature (measured with two-colour IR pyrometry) were continuously monitored and recorded during annealing. Except where indicated separately, boronizing was carried out under high-purity inert gas atmosphere of typically 100–500 mbar Ar (> 99.999 vol% Ar).

Commercially pure sheets of titanium (> 99.6 wt% Ti), molybdenum (> 99.8 wt% Mo) and tantalum (> 99.8 wt% Ta) were used as starting materials. Plane-sheet (9 × 9 mm, thicknesses 0.5–3 mm) as well as small-angle wedge-type ( $\approx 20^\circ$ , length  $\leq 10$  mm) samples were cut from the sheets. Boriding agents applied were mixtures of powdered amorphous boron (> 99.7 wt% B purity, Fluka, Switzerland) and  $\text{KBF}_4$  (purum quality, Merck, Germany). Considerable amounts of oxygen ( $\sim 10\,000$  ppm, mostly as  $\text{B}_2\text{O}_3$ ) were contained in the boron powder. Therefore calcination was applied. This was done at about  $1500^\circ\text{C}$  in an Ar-backfilled rotary-pump vacuum (several  $10^{-2}$  mbar) for at least 2 h. Oxygen contents were reduced to values below the detection limit of vacuum hot-extraction ( $\sim 10$  ppm). The calcined boron had to be repowdered in an agate mortar and pestle where it was mixed with  $\text{KBF}_4$ .

Ground samples (4000 mesh SiC) were embedded in the boriding powder and put into the Mo crucible, which was then placed in the center of the HF inductor. After several cycles of evacuating and backfilling Ar gas the desired inert gas pressure was established and the HF power was turned on. Within typically 1–3 min equilibrium temperatures were reached and maintained constant (better than  $\pm 10^\circ\text{C}$ ). Samples were cooled down to below  $800^\circ\text{C}$  in less than a minute after turning off the HF power.

The borided samples were cut perpendicular to the surface, embedded in a cold-setting resin and ground with 75- $\mu\text{m}$  and 20- $\mu\text{m}$  diamond disks. Further polishing with 3- $\mu\text{m}$  diamond paste was applied for about 1–3 h after ultrasonic cleaning. An aqueous suspension of  $\text{SiO}_2$  was used for final polishing. Layer thicknesses and phase band sequences were examined by means of light-optical microscopy and XRD, respectively. Multiple-layered boride phases on plane-sheet samples were investigated by means of taking diffractograms as a function of depth after stepwise removal of material with an abrasive diamond disk. Boron concentration profiles were measured by electron-probe microanalysis [9,10].

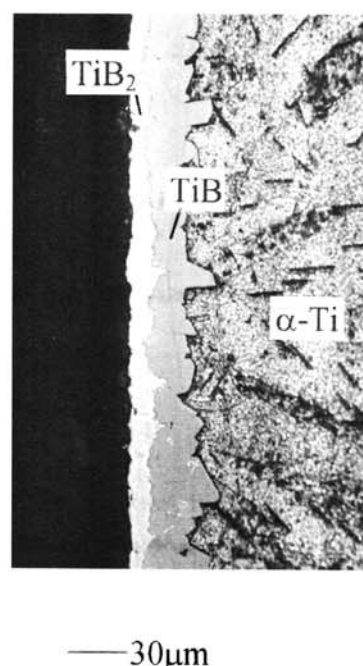


Fig. 1. Microstructure of a plane-sheet Ti-B diffusion couple annealed at  $1300^\circ\text{C}$  for 3 h (sample TiB02). Phase band sequence  $\text{TiB}_2$  ( $\sim 8\ \mu\text{m}$ ) —  $\text{TiB}$  ( $\sim 20\ \mu\text{m}$ ) —  $\alpha\text{-Ti}$ . Note the absence of the  $\text{Ti}_3\text{B}_4$  phase between  $\text{TiB}_2$  and  $\text{TiB}$ . The sample was etched with a mixture of hydrofluoric and hydrochloric acid (1:1).

## 3. Results and discussion

### 3.1. Ti-B

As titanium is known to have a high affinity with respect to oxygen, the use of virtually oxide-free boriding agents is inevitable. If uncalcined amorphous boron powder was used, mechanically completely unstable diffusion layers would be obtained that peeled off the sample. By using pre-calcined boron powder and annealing at  $1300^\circ\text{C}$  for 3 h, two boride layers (Fig. 1) were formed on the Ti substrate, identified by XRD as  $\text{TiB}_2$  (outermost layer,  $\sim 8\ \mu\text{m}$  thickness) and  $\text{TiB}$  ( $\sim 20\ \mu\text{m}$ ). For a series of XRD patterns obtained from this sample see Fig. 2. Interestingly, the  $\text{Ti}_3\text{B}_4$  phase, which should be present between  $\text{TiB}_2$  and  $\text{TiB}$ , was not observed in the diffusion couples. This is in accordance with the results obtained by Matsuda and Nakata [6].

### 3.2. Ta-B

Boriding experiments with Ta were performed with amorphous boron powder which was mixed with up to 7.5 wt%  $\text{KBF}_4$ . In addition, the gas pressure was varied systematically. Plane-sheet samples of 0.5-mm

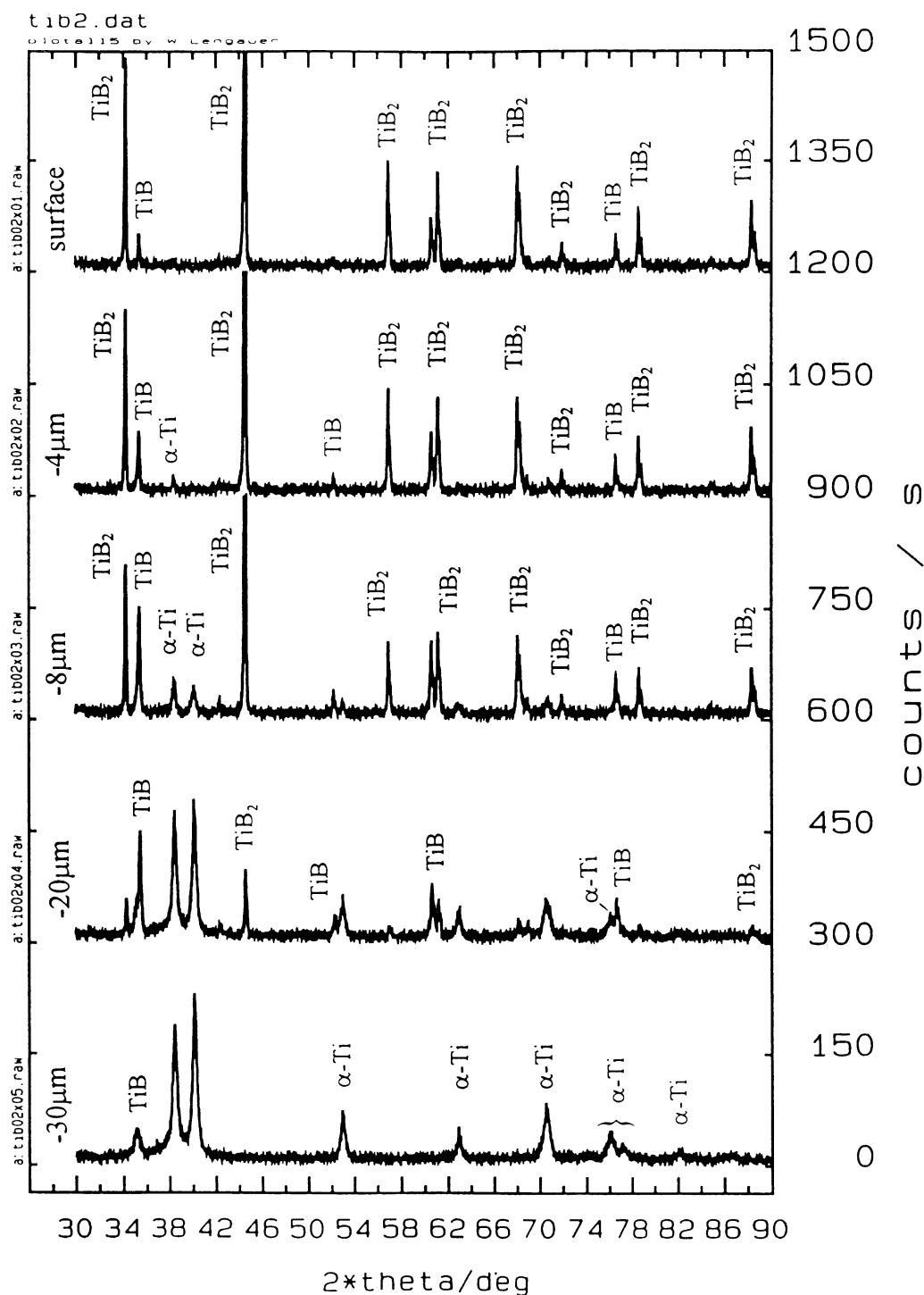


Fig. 2. XRD patterns of a Ti-B diffusion couple (TiB02) taken at the surface (top) and after removal of 4, 8, 20 and 30  $\mu\text{m}$  (bottom). Phase band sequence  $\text{TiB}_2$  —  $\text{TiB}$  —  $\alpha\text{-Ti}$  (see also Fig. 1).

thickness were annealed at 1400°C for 2 h. Experimental parameters and resulting layer thicknesses are listed in Table 1. Single-phase  $\text{TaB}_2$  layers were observed on all samples. The phases  $\text{Ta}_3\text{B}_4$ ,  $\text{TaB}$  and  $\text{Ta}_3\text{B}_2$  were not obtained, which is also in accordance with previous results [5,6]. As can be seen from the

data in Table 1, the total layer thickness can be increased by a factor of almost six when annealing under optimized conditions. An example of the observed microstructures of two samples annealed with and without  $\text{KBF}_4$  is shown in Fig. 3. One can further conclude that, given a constant amount of

Table 1  
Experimental parameters for Ta-B samples

Sample	Temperature (°C)	Time (h)	KBF <sub>4</sub> fraction (wt%)	Pressure (mbar)	Layer thickness (μm) <sup>a</sup>
TaB04	1400 ± 10	2	0	≤ 10 <sup>-2</sup>	29
TaB10	1400 ± 12	2	0	200	50
TaB07	1400 ± 7	2	5	≤ 10 <sup>-2</sup>	45
TaB12	1400 ± 8	2	5	500	~ 165
TaB08	1400 ± 10	2	5	200	~ 165
TaB09	1400 ± 10	2	5	100	~ 165
TaB11	1400 ± 13	2	7.5	100	~ 175
TaB13	1400 ± 7	2	1	200	~ 184

<sup>a</sup>Single-phase TaB<sub>2</sub> layers.

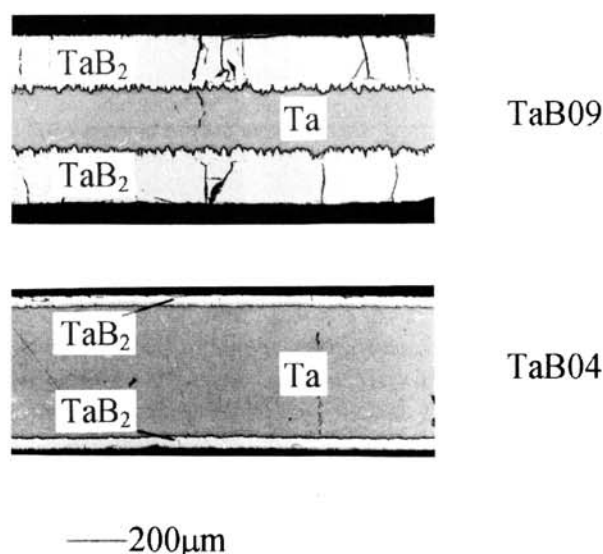


Fig. 3. Ta-B diffusion couples annealed with (top) and without (bottom) KBF<sub>4</sub> added (TaB09 and TaB04). For the corresponding experimental parameters see Table 1. Note the influence of KBF<sub>4</sub> on TaB<sub>2</sub> layer thickness (TaB09, 5 wt% KBF<sub>4</sub>, 165 μm; TaB04, without KBF<sub>4</sub>, 29 μm).

KBF<sub>4</sub> in the boriding agent, there is virtually no dependency of layer thicknesses on feeding gas pressure (samples 08, 09 and 10). Also the absolute amount of KBF<sub>4</sub> appears to be of minor importance (samples 11 and 13, Table 1), which is indicative of a cyclic transport reaction (loading/unloading of gaseous species with boron). It can be seen that the addition

of KBF<sub>4</sub> has no impact on enhancing layer growth rates if annealing is done in vacuum (samples 04 and 07).

On the basis of these results, it is clear that activating substances like KBF<sub>4</sub> enable the formation of volatile boron compounds, like BF<sub>3</sub>, which transport boron from the boriding powder to the sample surface via the gas phase and substantially increase the growth rate of at least one tantalum boride phase (TaB<sub>2</sub>). In the absence of an activator, the boron transport occurs through impurities and is much lower.

### 3.3. Mo-B

According to the ASM metals handbook [8] the following phases exist at 1450°C in the Mo-B system: Mo<sub>2</sub>B, MoB, Mo<sub>2</sub>B<sub>5</sub> and MoB<sub>4</sub>. Also a Mo<sub>3</sub>B<sub>2</sub> phase reported by [11] may exist as a thermodynamically stable binary compound, but probably at temperatures higher than 1450°C.

Annealing at 1450°C for 2.5 h (for experimental details see Table 2) yielded a 450-μm MoB layer on Mo metal (Fig. 4). The phase Mo<sub>2</sub>B, expected to occur between MoB and Mo, could not be observed. Also all other phases were not observable. In order to investigate whether this is due to the boron supply from the outside, this sample was re-annealed in vacuum. After this treatment the sample was covered with two boride layers (Fig. 5), MoB (thickness ca. 450 μm) and Mo<sub>2</sub>B (thickness ~ 19 μm). Fig. 6 shows the two EPMA scans across the annealed and the re-an-

Table 2  
Experimental parameters for Mo-B samples

Sample	Temperature (°C)	Time (h)	KBF <sub>4</sub> fraction (wt%)	Pressure (mbar)	Layer thickness (μm) <sup>a</sup>
MoB05	1400 ± 15	1	~ 15	500	315
MoB10	1400 ± 9	2.5	5	100	30–450 <sup>b</sup>
MoB11	1400 ± 7	2.5	5	100	450

<sup>a</sup>Total layer thickness for multiphase layers.

<sup>b</sup>See text.



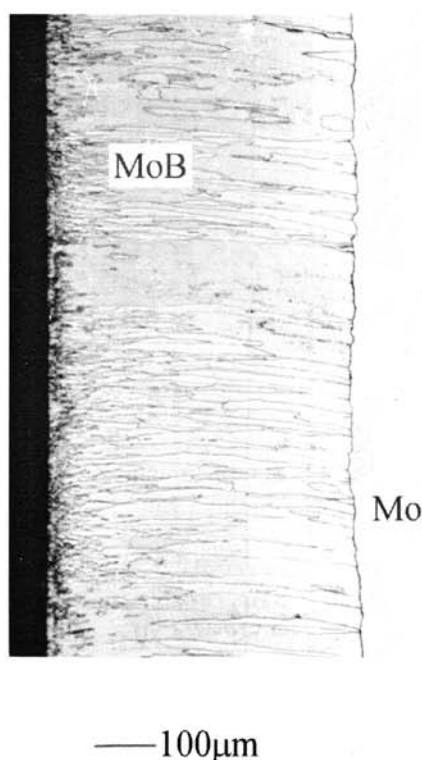


Fig. 4. Microstructure of a wedge-shaped Mo-B diffusion couple annealed at 1450°C for 2.5 h (sample MoB10, vapour-etched at 40°C with a mixture of 50% nitric and 50% hydrochloric acid). A single boride layer (MoB, 450  $\mu\text{m}$ ) was formed.

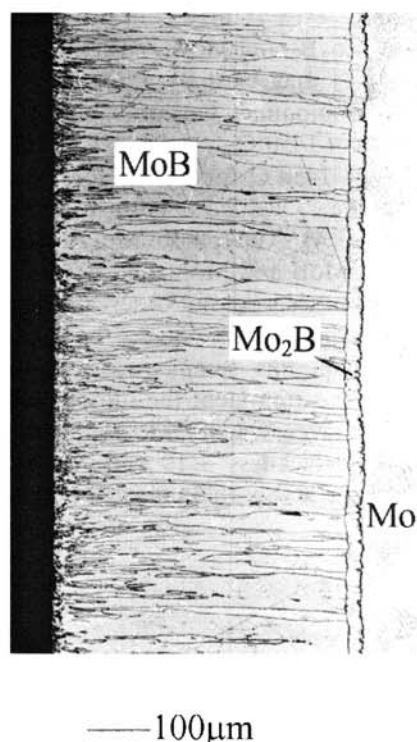


Fig. 5. Microstructure of the sample MoB10 (vapour-etched, see Fig. 4) after re-annealing at 1450°C for 2 h in vacuum. Phase band sequence MoB —  $\text{Mo}_2\text{B}$  — Mo.

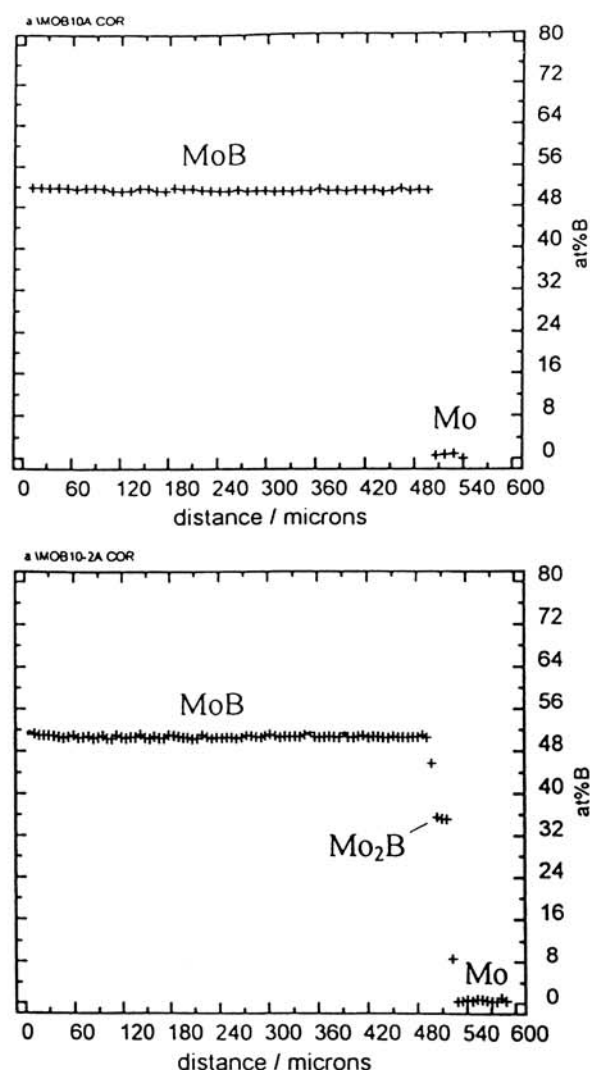


Fig. 6. Top: EPMA scan across the sample MoB10 shown in Fig. 4. The  $\text{Mo}_2\text{B}$  phase is absent. Bottom: after re-annealing, the  $\text{Mo}_2\text{B}$  phase can be identified (microstructure in Fig. 5).

nealed sample. The  $\text{Mo}_2\text{B}$  phase could be clearly identified also from the scan (bottom). Both, MoB and  $\text{Mo}_2\text{B}$  appear to be compounds with a very small homogeneity range (compare also Fig. 10).

Similar behaviour can also be observed in a sample that was annealed lying on top of a boron bed (Fig. 7). The side which was in contact with the boron bed showed a  $\sim 450\text{-}\mu\text{m}$  thick MoB layer. With increasing distance from the boron bed, the thickness of the MoB layer decreases and, interestingly, as the layer thickness of MoB becomes less than about 30  $\mu\text{m}$ , a second phase band ( $\text{Mo}_2\text{B}$ ,  $\sim 10\text{ }\mu\text{m}$ ) occurs.

From these two experiments it can be concluded, that  $\text{Mo}_2\text{B}$  only forms if there is a restricted supply of boron atoms to the sample surface. This is most probably due to the fact, that the diffusivities of boron atoms in the MoB phase are greater than that

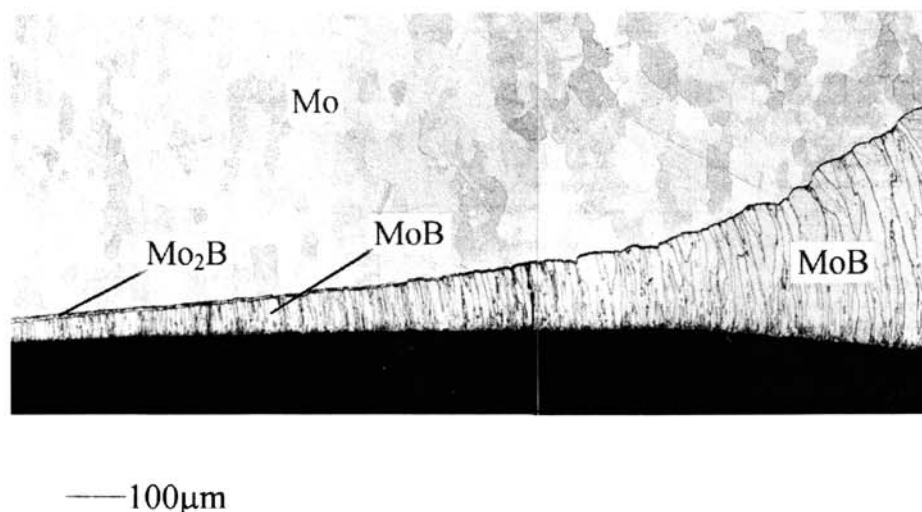


Fig. 7. Microstructure of a plane-sheet Mo-B diffusion couple annealed at 1450°C for 2.5 h (sample MoB11, vapour-etched, see Fig. 4). Note the appearance of the  $\text{Mo}_2\text{B}$  layer as the MoB phase band becomes thinner due to lacking boron supply (see text).

in the  $\text{Mo}_2\text{B}$  phase. In most other metal-metalloid systems the opposite is the case [12].

Fig. 8 shows the microstructure of a sample which was annealed at 1400°C for 1 h. A relatively high pressure of 500 mbar Ar and a very high fraction of  $\text{KBF}_4$  (~15 wt%) was applied. With these conditions the  $\text{Mo}_2\text{B}_5$  phase formed. This was the most B-rich phase we observed in our experiments, however, the  $\text{MoB}_4$  phase was still absent after this treatment as was also reported in [5,6]. Fig. 9 shows a diffractogram of  $\text{Mo}_2\text{B}_5$  taken from the surface of this sample. Obviously the most boron-rich phases only form if there is a high supply of boron atoms to the sample surface. A boron concentration profile measured by means of EPMA is presented in Fig. 10, where the phases can be clearly identified. The full composition range of MoB is accessible in this case. It was measured to be 51.0–52.3 at.% B.

#### 4. Conclusion

Upon boriding of Ti, Mo and Ta metal intermediate boride phases form, but — at least by inspection of standard XRD and light-optical microscopy — are lower in number than expected from the phase diagrams. In the Ti-B samples the  $\text{Ti}_3\text{B}_4$  phase was not observable, whereas in the Mo-B and Ta-B systems the phases  $\text{MoB}_4$  and TaB were absent. In the Mo-B system, a high supply of boron was necessary to observe the  $\text{Mo}_2\text{B}_5$  phase but this supply did not allow the  $\text{Mo}_2\text{B}$  phase to grow, the latter, however, grew upon restricted boron supply.

Further experiments with altering the experimental

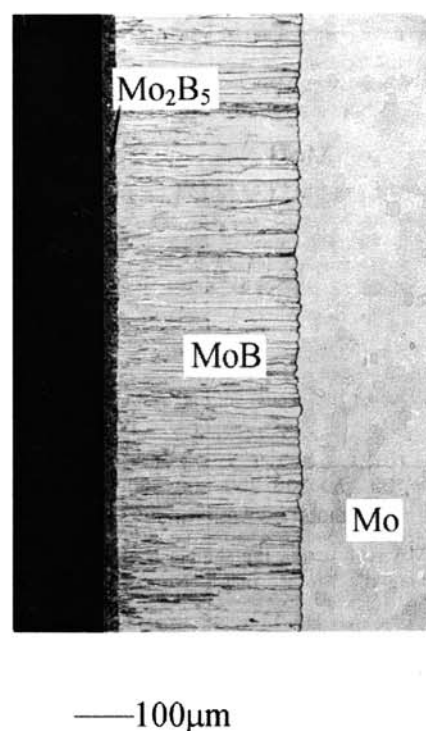


Fig. 8. Microstructure of a plane-sheet Mo-B diffusion couple annealed at 1400°C for 1 h (sample MoB05, vapour-etched). Phase band sequence  $\text{Mo}_2\text{B}_5$  — MoB — Mo.

conditions, the diffusion pairs, the sample geometry and the annealing time — as already performed in carbide and nitride systems [12] — will be conducted. However, a strong indication was obtained that the diffusion and layer growth behaviour in transition metal-boron systems is different from corresponding carbide and nitride systems.

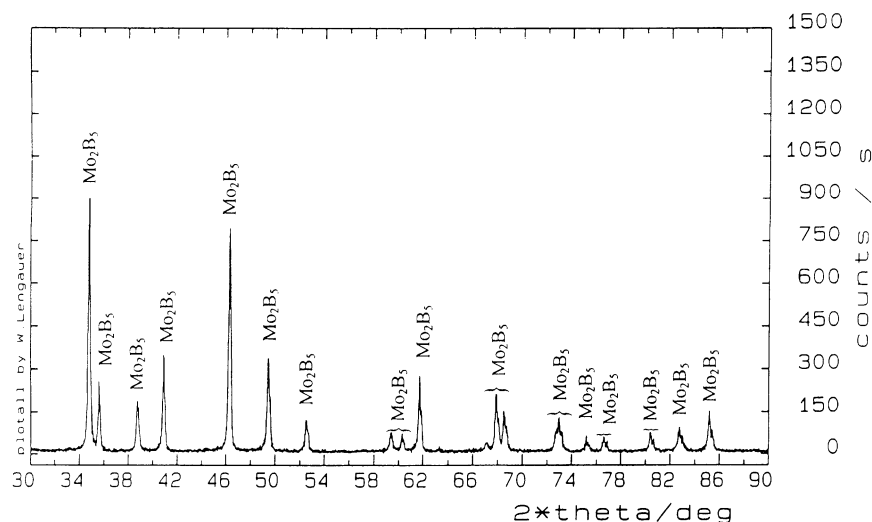


Fig. 9. XRD pattern taken from the surface of the MoB05 sample. For experimental parameters see Table 2. Identification of the  $\text{Mo}_2\text{B}_5$  layer.

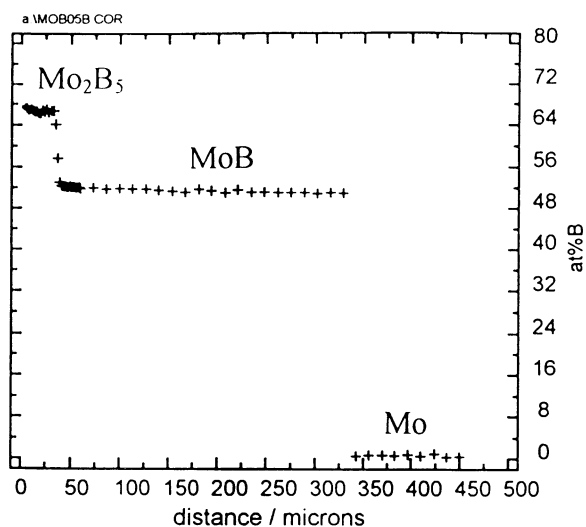


Fig. 10. EPMA scan across the sample MoB05 (microstructure in Fig. 8) showing the  $\text{Mo}_2\text{B}_5$  phase. Note the small homogeneity range of MoB.

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