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Calculations of Chemical Equilibria in the Mo–B–N System

Ewa Benko[a] & Andrzej Wyczesany[b]

[a] Institute of Metal Cutting, Ul. Wroclawska 37a, 30-011 Kraków, Poland
[b] University of Technology, Kraków, Poland

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Abstract

Calculations of chemical equilibria for the Mo–B–N system using the VCS algorithm were carried out for the 30–1727°C temperature range and the 1·3 × 10^{-3}–1 × 10^{7} Pa pressure range. Two BN:Mo molar ratios were selected: 1:1 and 2:1. It follows from these studies that Mo can react with BN in a very wide range of temperatures and pressures, giving new phases, namely Mo_2B, MoB, MoB_2, Mo_2B_5 and MoB_4. The formation of these phases is strongly influenced by pressure–temperature parameters. In order to verify theoretical calculations by experiment equimolar and 2:1 BN:Mo batches were prepared and heated at 1427°C in vacuum and in argon atmosphere. Phase identification carried out by X-ray diffraction fully corroborated the computational results.

Die chemischen Gleichgewichte des Mo–B–N-Systems wurden mit Hilfe des VCS-Algorithmuses im Temperatur- und Druckbereich von 30–1727°C bzw. 1·3 × 10^{-3}–1 × 10^{7} Pa berechnet. Es wurden zwei BN:Mo-Verhältnisse gewählt: 1:1 und 2:1. Aus den Berechnungen ergab sich, daß Mo in einem weiten Temperatur- und Druckbereich mit BN reagieren kann, und daß sich folgende neue Phasen bilden können: Mo_2B, MoB, MoB_2, Mo_2B_5 und MoB_4. Die Bildung dieser Phasen hängt stark von der Temperatur und vom Druck ab. Zur Bestätigung der theoretischen Ergebnisse wurden gleichmolare und 2:1 BN:Mo Proben hergestellt und im Vakuum bzw. in einer Argonatmosphäre auf 1427°C erwärmt. Die mittels Röntgenbeugung durchgeführte Phasenanalyse bestätigte die berechneten Ergebnisse.

On a calculé les caractéristiques de l'équilibre chimique du système Mo–B–N en utilisant l'algorithme VCS, ceci pour des températures comprises entre 30 et 1727°C, et des pressions de 1·3 × 10^{-3}–1 × 10^{7} Pa. Deux rapports molaires BN:Mo ont été sélectionnés: 1:1 et 2:1. Il ressort de cette étude que Mo et BN peuvent réagir dans un large domaine de température et de pression, donnant de nouvelles phases: Mo_2B, MoB, MoB_2, Mo_2B_5 et MoB_4. La formation de ces phases est fortement influencée par les paramètres de température et de pression. Afin de vérifier les prédictions théoriques de manière expérimentale, des lots équimolaires et 2:1 de BN et Mo ont été préparés, chauffés à 1427°C sous vide ou sous argon. L'identification des phases faite par diffraction X corrobore les résultats numériques.

1 Introduction

Polycrystalline materials produced from cubic boron nitride are widely used in machine building due to their unique properties, such as high resistance to oxidation, good thermal conductivity, and chemical inertness to iron and iron alloys. These materials are synthesized in special reactors by high-pressure and high-temperature treatment. The following two procedures are usually applied:

—direct transformation of the hexagonal modification to the cubic one,
—cubic boron nitride sintering with the activation of the sintering process.

The latter procedure is more frequently used. Metals of groups IV, V, VI periodic table and/or other metallic elements such as aluminium, cobalt and nickel are added to activate the sintering. Chemical reactions between the activators and boron nitride occur, resulting in the formation of some new phases. The prediction of the final products of the reactions taking place during the sintering as well as the elucidation of their mechanism is of crucial importance in the selection of the appropriate binding phase.

The reactions occurring in the system can, in principle, be predicted by thermodynamic calculations. Thus, the main goal of this paper is to

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elucidate the nature of the interactions between the metallic phase (in this case Mo) and boron nitride. In particular, the results of chemical equilibria calculations for the Mo–BN system are presented for a wide range of temperatures and pressures. Two BN : Mo molar rations are investigated: 1 : 1 and 2 : 1. Computational results are compared with X-ray diffraction phase identification.

2 Calculation of Phase Equilibria for the Mo–B–N System

Although a few papers devoted to the studies of interactions between boron nitride and molybdenum have been published[1–3] the discussed phenomena are still unclear. In particular, available literature data do not give clear classification of the phases created upon such interactions at various temperatures and pressures.

Molybdenum, a group VI element, exhibits significantly lower chemical affinity to BN than the metals from the IV and V periodic groups.[1] Mo can react with BN according to the following reaction schemes:[1–3]

$$2Mo + BN = Mo_2N + B \quad (1)$$

$$2Mo + BN = Mo_2B + \tfrac{1}{2}N_2 \quad (2)$$

$$4Mo + BN = Mo_2B + Mo_2N \quad (3)$$

$$Mo + BN = MoB + \tfrac{1}{2}N_2 \quad (4)$$

$$3Mo + BN = MoB + Mo_2N \quad (5)$$

$$\tfrac{1}{2}Mo + BN = \tfrac{1}{2}MoB_2 + \tfrac{1}{2}N_2 \quad (6)$$

$$\tfrac{5}{2}Mo + BN = \tfrac{1}{2}MoB_2 + Mo_2N \quad (7)$$

$$2Mo + 5BN = Mo_2B_5 + \tfrac{5}{2}N_2 \quad (8)$$

$$Mo + 4BN = MoB_4 + 2N_2 \quad (9)$$

The Gibbs energies calculated for these reactions are shown in Table 1; Gibbs energies of formation for the substrates and the products are taken from Refs 4–6. ΔG values of the reactions (1)–(9) between BN and Mo are positive at 25°C and 1×10^5 Pa. In a few papers the same interactions between Mo and BN have been published.[1–3] The formation of MoB at 1123°C within 1 h in vacuum 3×10^{-2} Pa was reported in Ref. 2, whereas according to Ref. 1, neither MoB nor Mo_2B were detected by XRD after synthesis at 1400°C in a vacuum of 3×10^{-2} Pa.

Thus the experimental data are scattered and incomplete. The authors have therefore undertaken a theoretical and experimental investigation for the Mo–B–N system. The calculations of chemical equilibria for the Mo–B–N system were carried out using the VCS algorithm,[7] i.e. an algorithm belonging to the so-called stoichiometric algorithms. In this procedure, the Gibbs energy of the whole reaction mixture is minimized subject to side conditions of elemental abundance and non-reactivity of the mole numbers. Reaction-extent variables derived from the transformation of the mass balance equations are the unknowns of the function being minimized. Thus, the problem can be reduced to the minimization of the unrestricted function and in each iteration the mass-balance equations are fulfilled. The details of the procedure can be found elsewhere.[7] In the calculation of chemical equilibria of the system investigated and related ones it is not known *a priori* which phases and components will appear in the equilibrium state (for given T, p and initial feed composition). The advantage of the VCS algorithm relies on the fact that only species which may, but do not need to, appear at equilibrium must be specified. Therefore, the program written on the basis of the VCS algorithm requires only the knowledge of the species which can occur at equilibrium together with their standard Gibbs energies of formation. In addition, the calculations require the knowledge of the exact number of moles of elements introduced to the system and the values of p and T as well as the initial estimate. It should be noted here that the user of the program does not need to specify the number and form of independent reactions possibly occurring in the system under consideration. The VCS algorithm is one of the most powerful tools for the calculation of chemical equilibria, especially for systems with a large number of condensed phases.

The calculations were performed for the temperature range of 27–1727°C and for the pressure range of 1×10^{-3}–1×10^7 Pa. Two BN : Mo molar

Table 1. Gibbs free energy values calculated for reactions (1)–(7)

Temperature (°C)	*ΔG (kJ/mol)*						
	Reaction						
	(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*
25	332·9	182·5	290·8	179	280·1	198·1	310·4

ratios were studied: 1:1 and 2:1. It was assumed that the following species can be present in the equilibrium state: B(g), B_2(g), N_2(g), BN(g), Mo(g), B(l), Mo(l), Mo(s), B(s), BN(s), MoB(s), Mo_2B(s), MoB_2(s), Mo_2B_5(s) and MoB_4(s) (g, l, and s denote gas, liquid and solid, respectively). Thermodynamic data necessary for calculations (Gibbs energies of formation of individual species) were taken from Refs 4–6.

The calculations were carried out in intervals of 100°C. Below 1427°C the equilibrium molar numbers of each phase change discretely, above this temperature the changes are more continuous. For these reasons for the data below 1427°C the pressure ranges are listed and above this temperature only representative pressures are given.

In Table 2 the calculated equilibrium compositions are listed for the mixture consisting of equimolar amounts of Mo and BN. At temperatures 27–427°C there is no reaction and the equi-

Table 2. Calculated equilibrium compositions for 1:1 molar BN : Mo mixture

Temperature (°C)	*Pressure (Pa)*	*N_2(g) (mol)*	*B(g) (mol)*	*BN(g) (mol)*	*Mo(g) (mol)*	*Mo(s) (mol)*	*BN(s) (mol)*	*MoB(s) (mol)*	*MoB_2(s) (mol)*	*Mo_2B_5(s) (mol)*	*Mo_2B(s) (mol)*
27–427	$1{\cdot}3 \times 10^{3}$–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
527	$1{\cdot}3 \times 10^{3}$	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
527	2×10^{3}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
627	$1{\cdot}3 \times 10^{3}$–8×10^{2}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
627	9×10^{2}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
727	$1{\cdot}3 \times 10$–$0{\cdot}2 \times 10$	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
727	$0{\cdot}3 \times 10$–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
827	$1{\cdot}3 \times 10^{3}$–2×10^{-2}	0·5000	—	—	—	—	—	1·0000	—	—	—
827	3×10^{2}–2×10	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
827	3×10–1×10^{7}	—	—	—	—	—	1·0000	1·0000	—	—	—
927	$1{\cdot}3 \times 10^{3}$–5×10^{1}	0·5000	—	—	—	—	—	1·0000	—	—	—
927	6×10^{1}–2×10^{2}	—	—	—	—	—	0·5000	—	—	—	0·5000
927	3×10^{2}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1027	$1{\cdot}3 \times 10^{3}$	0·5000	—	—	—	—	—	1·0000	—	—	—
1027	8×10–1×10^{3}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1027	2×10^{3}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1127	$1{\cdot}3 \times 10^{3}$–6×10	0·5000	—	—	—	—	—	1·0000	—	—	—
1127	7×10–7×10^{3}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1127	8×10^{3}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1227	$1{\cdot}3 \times 10^{3}$–3×10^{2}	0·5000	—	—	—	—	—	1·0000	—	—	—
1227	4×10^{2}–2×10^{4}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1227	3×10^{4}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1327	$1{\cdot}3 \times 10^{3}$–1×10^{3}	0·5000	—	—	—	—	—	1·0000	—	—	—
1327	2×10^{3}–9×10^{4}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1327	1×10^{5}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1427	$1{\cdot}3 \times 10^{3}$	0·5000	—	—	—	—	—	0·9999	—	—	—
1427	2×10^{3}–7×10^{3}	0·5000	—	—	—	—	—	1·0000	—	—	—
1427	8×10^{3}–2×10^{5}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1427	3×10^{5}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1527	$1{\cdot}3 \times 10^{3}$	0·5000	0·0004	—	0·0001	—	—	0·9994	—	—	0·0003
1527	5×10^{2}–2×10^{4}	0·5000	—	—	—	—	—	1·0000	—	—	—
1527	3×10^{4}–6×10^{5}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1527	7×10^{5}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1627	$1{\cdot}3 \times 10^{3}$	0·5000	0·0034	—	0·0008	—	—	0·9940	—	—	0·0026
1627	6×10^{2}	0·5000	0·0001	—	—	—	—	0·9999	—	—	0·0001
1627	8×10^{4}	0·5000	—	—	—	—	—	1·0000	—	—	—
1627	9×10^{4}–1×10^{6}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1627	2×10^{6}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—
1727	$1{\cdot}3 \times 10^{-3}$	0·5000	0·0265	—	0·0066	—	—	0·9537	—	—	0·0198
1727	1×10^{1}	0·5000	0·0003	—	0·0001	—	—	0·9994	—	—	0·0002
1727	2×10^{5}	0·5000	—	—	—	—	—	1·0000	—	—	—
1727	3×10^{5}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1727	2×10^{6}	0·2500	—	—	—	—	0·5000	—	—	—	0·5000
1727	3×10^{6}–1×10^{7}	—	—	—	—	1·0000	1·0000	—	—	—	—

Table 3. Calculated equilibrium compositions for 2:1 molar BN : Mo mixture

Temperature (°C)	*Pressure (Pa)*	*$N_2(g)$ (mol)*	*B(g) (mol)*	*BN(g) (mol)*	*Mo(g) (mol)*	*Mo(s) (mol)*	*BN(s) (mol)*	*MoB(s) (mol)*	*$MoB_2(s)$ (mol)*	*$Mo_2B_5(s)$ (mol)*	*$Mo_2B(s)$ (mol)*
27–427	$1{\cdot}3 \times 10^{-3}$–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
527	$1{\cdot}3 \times 10^{-3}$	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
527	2×10^{-3}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
627	$1{\cdot}3 \times 10^{-3}$–8×10^{-2}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
627	9×10^{-2}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
727	$1{\cdot}3 \times 10^{-3}$–$0{\cdot}2 \times 10$	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
727	$0{\cdot}3 \times 10$–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
827	$1{\cdot}3 \times 10^{-3}$–2×10^{2}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
827	3×10^{2}–2×10	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
827	3×10–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
927	$1{\cdot}3 \times 10^{-3}$–5×10^{-1}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
927	6×10^{1}–2×10^{2}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
927	3×10^{2}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1027	$1{\cdot}3 \times 10^{-3}$–$0{\cdot}7 \times 10$	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1027	8×10–1×10^{3}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1027	2×10^{3}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1127	$1{\cdot}3 \times 10^{-3}$–3×10^{-3}	1·0000	—	—	—	—	—	0·1342	—	0·8658	—
1127	4×10^{-3}–6×10	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1127	7×10–7×10^{3}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1127	8×10^{3}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1227	$1{\cdot}3 \times 10^{-3}$–2×10^{2}	1·0000	—	—	—	—	—	0·1342	—	0·8658	—
1227	3×10^{-2}–3×10^{2}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1227	4×10^{2}–2×10^{4}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1227	3×10^{4}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1327	$1{\cdot}3 \times 10^{3}$–2×10^{-1}	1·0000	—	—	—	—	—	0·1345	—	0·8658	—
1327	3×10^{-5}–1×10^{3}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1327	2×10^{3}–9×10^{4}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1327	1×10^{5}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1427	$1{\cdot}3 \times 10^{-3}$–$0{\cdot}1 \times 10$	1·0000	0·0048	—	—	—	—	0·1383	—	0·8617	—
1427	$0{\cdot}2 \times 10$–7×10^{3}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1427	8×10^{3}–2×10^{5}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1427	3×10^{5}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1527	$1{\cdot}3 \times 10^{-3}$	1·0000	0·0529	—	—	—	—	—	0·4142	0·5858	—
1527	$0{\cdot}2 \times 10^{3}$	1·0000	0·0338	—	—	—	—	—	0·3760	0·6240	—
1527	$0{\cdot}5 \times 10$	1·0000	—	—	—	—	—	—	0·3088	0·6912	—
1527	$0{\cdot}6 \times 10$–2×10^{4}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1527	3×10^{4}–6×10^{5}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1527	7×10^{5}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1627	$1{\cdot}3 \times 10^{-3}$	1·0000	0·5976	—	—	—	—	0·3837	0·6162	—	—
1627	2×10^{-3}	1·0000	0·3470	—	—	—	—	—	1·0000	—	—
1627	3×10^{-3}	1·0000	0·2483	—	—	—	—	—	0·8034	0·1966	—
1627	9×10^{-1}	1·0000	0·0007	—	—	—	—	—	0·3101	0·6899	—
1627	1×10	1·0000	0·0001	—	—	—	—	—	0·3089	0·6911	—
1627	2×10	0·8265	—	—	—	—	0·3470	—	1·0000	—	—
1627	3×10–8×10^{4}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1627	9×10^{4}–1×10^{6}	0·2500	—	—	—	—	1·5000	—	—	—	0·5000
1627	2×10^{6}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—
1727	$1{\cdot}3 \times 10^{-3}$	1·0000	1·0024	0·0001	0·0025	—	—	0·9975	—	—	—
1727	6×10^{3}	0·9999	0·9841	0·0001	0·0001	—	—	0·9765	0·0243	—	—
1727	1×10^{-2}	1·0000	0·4237	—	0·0001	—	—	0·1174	0·8825	—	—
1727	2×10^{-2}	1·0000	0·2787	—	0·0001	—	—	—	0·8641	0·1359	—
1727	4×10	1·0000	0·0001	—	—	—	—	—	0·3090	0·6910	—
1727	5×10	0·8265	0·0001	—	—	—	—	0·3469	—	1·0000	—
1727	2×10^{2}–2×10^{5}	0·5000	—	—	—	—	1·0000	1·0000	—	—	—
1727	3×10^{5}–2×10^{6}	0·2500	—	—	—	—	1·5000	0·5000	—	—	—
1727	3×10^{6}–1×10^{7}	—	—	—	—	1·0000	2·0000	—	—	—	—

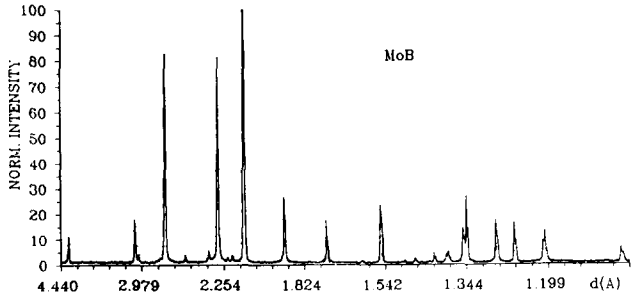

Fig. 1. X-Ray diffraction pattern of 1 : 1 molar BN : Mo mixture (T = 1427°C, p = 2 × 10^{-3} Pa).

librium state consists of BN and Mo phases. From 527°C molybdenum can react with boron nitride in very wide range of pressures and temperatures (p = 1·3 × 10^{-3}–2 × 10^6 Pa, T = 527–1727°C). Two new phases are formed, namely molybdenum borides (MoB, Mo_2B) whose amount is strictly dependent on the parameters of the process (T, p). Mo_2B is the only solid phase (0·5 mol) present in the temperature range 527–727°C and at low pressures. Beginning from 827°C MoB appears (1 mol) whose pressure range of existence widens as the temperature increases. In contrast, the range of coexistence of BN and MoB significantly narrows and shifts towards higher pressures.

In the 527–1727°C temperature range nitrogen gas appears in the system. Its content increases from 0·25 to 0·5 mol, depending on the values of the pressure and temperature. At high pressures molybdenum does not react with boron nitride in the whole temperature range investigated and the pressure range of BN and Mo coexistence diminishes as the temperature increases. Above 1527°C gaseous molybdenum and gaseous boron appear in the equllibrium state.

The results of calculations performed for BN:Mo 2 : 1 molar ratio mixture are listed in Table 3. Above 527°C the phase equilibrium composition depends on the pressure. Two equilibrium states can be distinguished (for low pressures). In the first one gaseous nitrogen (0·25 mol) appears, whereas in the second one two solid BN (1·5 mol)

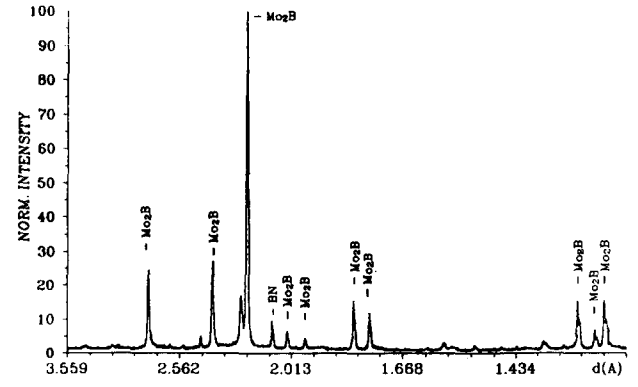

Fig. 2. X-Ray diffraction pattern of 1 : 1 molar BN : Mo mixture (T = 1427°C, p = 1 × 10^5 Pa).

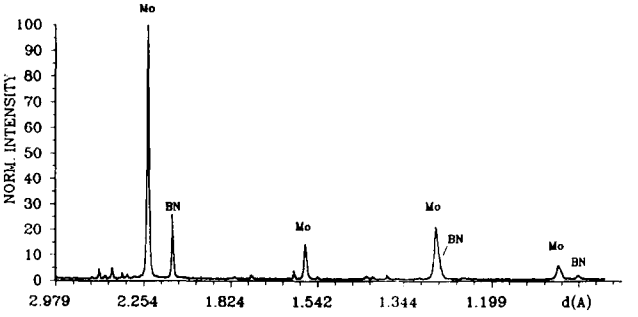

Fig. 3. X-Ray diffraction pattern of 1 : 1 molar BN : Mo mixture (T = 1427°C, p = 1 × 10^7 Pa).

and Mo_2B (0·5 mole) phases coexist. In the temperature range 527–1627°C, the pressure range in which the previously mentioned phases coexist varies. In the temperature range 827–1027°C (for low pressures) MoB (1 mol) and BN (1 mol) coexist at equilibrium. Between 1527 and 1727°C two equilibria can be distinguished: MoB coexisting with MoB_2 or MoB_2 coexisting with Mo_2B_5. Relative contents of these phases are strictly dependent on the parameters of the process (p, T). With increasing temperature the pressure range of coexistence of MoB_2 and Mo_2B_5 shifts towards higher pressures. Similarly, as in the case of the 1 : 1 BN : Mo system, Mo does not react with BN under high pressures. With increasing temperature the pressure under which BN and Mo do not react increases.

The ranges of gaseous nitrogen, molybdenum and boron existence are identical to those calculated for the 1 : 1 molar ratio.

3 Experimental

In order to verify the calculated equilibria with experiment BN:Mo mixtures of 1 : 1 and 2 : 1 molar ratios were prepared. Boron nitride (ABN-300, De Beers, 3–5 μm grain size) and molybdenum powder (HC Starck, 3–5 μm grain size) were mechanically mixed in ethyl alcohol medium and then pressed into pellets of 6 mm diameter using a pressure of 2 × 10^2 Pa. The pellets were then

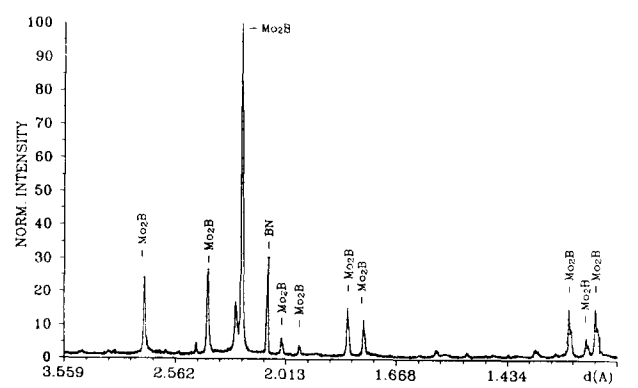

Fig. 4. X-Ray diffraction pattern of 2 : 1 molar BN : Mo mixture (T = 1427°C, p = 1 × 10^5 Pa).

Table 4. Comparison of calculated and experimentally determined equilibrium compositions for 1:1 and 2:1 molar BN:Mo mixture (T = 1427°C, $p = 2 \times 10^{-3}$ Pa, 1×10^5 Pa and 1×10^7)

Phases at equilibrium	*BN : Mo*							
	1 : 1 (mol) $p = 2 \times 10^{-3}$ Pa		*1 : 1 (mol) $p = 1 \times 10^5$ Pa*		*2 : 1 (mol) $p = 1 \times 10^5$ Pa*		*1 : 1 (mol) $p = 1 \times 10^7$ Pa*	
	Calculated	*Experimental*	*Calculated*	*Experimental*	*Calculated*	*Experimental*	*Calculated*	*Experimental*
N_2(g)	0·5000	—	0·2500	—	0·2500	—	—	—
B(g)	—	—	—	—	—	—	—	—
B_2(g)	—	—	—	—	—	—	—	—
BN(g)	—	—	—	—	—	—	—	—
Mo(g)	—	—	—	—	—	—	—	—
Mo_2N(s)	—	—	—	—	—	—	—	—
B(1)	—	—	—	—	—	—	—	—
Mo(1)	—	—	—	—	—	—	—	—
Mo(s)	—	—	—	—	—	—	1·0000	1·0000
BN(s)	—	—	0·5000	0·4700	1·5000	1·5000	1·0000	1·0000
B(s)	—	—	—	—	—	—	—	—
MoB(s)	1·0000	1·0000	—	—	—	—	—	—
Mo_2B(s)	—	—	0·5000	0·4900	0·5000	0·4900	—	—
MoB_2(s)	—	—	—	—	—	—	—	—
Mo_2B_5(s)	—	—	—	—	—	—	—	—
MoB_4(s)	—	—	—	—	—	—	—	—

heated at different temperatures around 1427°C and under various pressures for 1 h. Then they were immediately cooled to room temperature. The treated specimens were subjected to X-ray diffraction studies. Representative diffractograms are presented in Figs 1–4. Depending on the parameters of thermal treatment either single-phase MoB can be detected or a two-phase mixture of BN, Mo_2B and BN, Mo. Quantitative determination of the amount of each phase was performed by comparison of the relative intensities of the most intensive Bragg reflections.

The comparison of the calculated equilibrium compositions with the experimentally determined ones is presented in Table 4.

4 Conclusion

The results of X-ray diffraction studies unequivocally indicate good agreement of the experimental data with the calculated equilibrium compositions for both molar ratios studied, at least in the temperature and pressure ranges investigated experimentally. One (MoB) or two (BN, Mo_2B and BN, Mo) phases were detected, as predicted by the VCS algorithm. The calculated and experimentally determined contents of coexisting phases agree within the experimental error.

This agreement shows, in turn, that equilibrium conditions can reasonably easily be reached for the system investigated. Such calculations are extremely important from the technological point of view, since they facilitate the engineering of new materials with desired properties.

Acknowledgement

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