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Thermodynamic modelling of the ternary B–Mo–Ti system with refined B–Mo description

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ABSTRACT

In the present paper, the constituent binary B–Mo system is re-modelled in order to reproduce genuine homogeneity ranges of the molybdenum borides. Based on this, available descriptions of the constituent B–Ti and Mo–Ti systems as well as new experimental data reported in the literature for the ternary B–Mo–Ti system are used to model the B–Mo–Ti system in the entire composition and temperature ranges. The elaborated thermodynamic description is further applied to calculate selected phase equilibria as to provide a comparison between calculated and experimental results. The calculations are shown to reproduce the experimental data reasonably well, however for few alloys belonging to the domain of primary $(Ti,Mo)B_2$ crystallization the computed solidus temperatures are about 200 K higher than incipient melting temperatures measured by pyrometry.

1. Introduction

The B–Mo–Ti system is of interest for alloy design and processing of new materials for high-temperature applications. Particularly, molybdenum is an alloying element for the Ti- and TiAl-based materials serving as a solid solution hardener and stabilizing the A2 (β) and B2 (β_o) phases, respectively [1–5]. Furthermore, boron is an effective grain refiner for TiAl-based alloys [6–8], but may also be added in higher amounts as to form boride reinforcement particles in composite materials design strategies. Ravi Chandran et al. [9] reported that the tensile strength and elongation of powder metallurgical composites with β metallic matrix 75.7Ti–24.3Mo (wt.%) reinforced by 34 vol.% TiB were 1105 MPa and 0.85% respectively at good stiffness (elasticity modulus of 171 GPa).

More generally, mechanical properties of Ti- and TiAl-based alloys are sensitive to their microstructure and phase constituents, which are strongly dependent on composition. That is why a consistent thermodynamic description of the B–Mo–Ti ternary system is important also from the perspective of its integration into multicomponent databases for Ti-, TiAl-based and other alloys [10–16].

Critical assessments of literature data for the constituent binary B–Mo system were performed in numerous works [17–24]. In few of them and some others, the phase equilibria and thermodynamic properties were equally modelled by the CALPHAD approach (Computer Coupling of Phase Diagrams and Thermochemistry) [18,19,24,25]. Unfortunately, all the thermodynamic descriptions including the latest one [24] are not reliable since they describe boride phases as stoichiometric compounds, whereas available experimental data show that they display rather broad (from ~2 to ~5 at% B) homogeneity ranges.

Literature data on the B–Mo–Ti system were critically assessed by Velikanova and Turchanin [26], who provided a comprehensive description of all experimental data on phase equilibria and thermodynamic properties of the system up to the year 2008. Table 1 summarizes the crystallographic data for all known phases of the system, taken from this work. After this review further experimental results were published by Potazhevska et al. [27], focussing on the analysis of phase equilibria in the range of melting/solidification by means of SEM/EPMA, XRD, DTA and Pyrani-Alterthum techniques. They investigated 22 samples and presented tentative liquidus and solidus surface projections.

The work reported here aimed to provide an improved thermodynamic description of the entire B–Mo–Ti system including a

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Table 1
Crystal structure data for B–Mo–Ti phases [10,19,26,85] and their modelling.

Phase	Pearson symbol	Space group	Prototype	Structurbericht designation	Model applied
Liquid[a]					$(B,Mo,Ti)_1$
α, αTi, hcp-Ti	*hP2*	$P6_3/mmc$	Mg	A3	$(Mo,Ti\%)_{1.0}$: $(B\%,Va)_{0.5}$
β, **A2**, Mo, βTi, $A2_{Mo}$, $A2_{Ti}$, bcc-Ti, bcc-Mo, (βTi,Mo)	*cI2*	$Im\bar{3}\,m$	W	A2	$(Mo,Ti)_1$: $(B,Va)_3$
βB	*hR*105(*hR*111)	$R\bar{3}\,m$	βB	–	$(B\%,Mo,Ti)_1$
TiB	*oP8*	*Pnma*	FeB	B27	$(Mo,Ti)_1$: $(B\%,Mo,Ti)_1$
Ti_3B_4	*oI14*	*Immm*	Ta_3B_4	$D7_b$	$(Mo,Ti)_3$: $(B)_4$
MoB_{2-x}, TiB_2 **MB_2**, $(Ti,Mo)B_2$	*hP3*	*P6/mmm*	AlB_2	C32	$(B,Mo\%,Ti)_1$:$(B\%,Mo,Ti)_2$
Mo_2B	*tI12*	I4/mcm	Al_2Cu	C16	$(Mo,Ti,Va)_{0.667}$: $(B,Va)_{0.333}$
Mo_3B_2[b]	*tP10*	*P4/mbm*	U_3Si_2	–	Not considered
αMoB	*tI16*	$I4_1/amd$	αMoB	B_g	$(Mo,Ti,Va)_{0.5}$: $(B,Va)_{0.5}$
βMoB	*oC8*	*Cmcm*	CrB	B33	$(Mo,Ti,Va)_{0.5}$: $(B,Ti,Va)_{0.5}$
Mo_2B_5, Mo_2B_{5-x}	*hR7*	$R\bar{3}\,m$	Mo_2B_5	$D8_i$	$(Mo,Ti,Va)_{0.32}$:$(B,Va)_{0.68}$
$Mo_{1-x}B_3$, MoB_4	*hP20*	$P6_3/mmc$	$W_{1-x}B_3$	–	$(Mo,Ti,Va)_{0.2}$:$(B,Va)_{0.8}$
$MoTi_2B_4$[b]	–	–	–	–	Not considered
Mo_2TiB_2[b]	–	–	–	–	Not considered

[a] Designations given in bold letters are used throughout the present work.
[b] The phase is rejected as stabilized by contaminants.

refinement of the constituent binary B–Mo system. Published data about phase equilibria in these systems, as well as thermodynamic properties of molybdenum borides were critically analysed. The available experimental data and the most reliable descriptions of the constituent binary systems B–Ti [10] and Mo–Ti [28] were used for CALPHAD modelling and optimization.

The paper is structured as follows: Section 2 contains a brief description of the thermodynamic models used for expressing the Gibbs free energy of the individual phases and a description of the optimization procedure. The resulting thermodynamic database is given in Appendix A as supplementary material. Section 3 contains a large number of calculations performed with the elaborated thermodynamic description, including the complete Scheil's reaction scheme, liquidus and solidus surface projections, isothermal

Table 2
Summary of the thermodynamic parameters for the phases in the ternary B–Mo–Ti system.

Phase	Model/Sites/Constituents	Parameters (in SI units)	Ref.
BCC_A2	2 SUBLATTICES /1: 3 /MO,TI: B,VA	L(BCC_A2,MO,TI:VA; 0) = 20249−13.474T; L(BCC_A2,MO,TI:VA; 1) = −22963 + 8.598T; L(BCC_A2,MO,TI:VA; 2) = −8171	[28]
		G(BCC_A2,MO:VA; 0)-H298(BCC_A2,MO; 0) = GHSERMO; G(BCC_A2,TI:VA; 0)-H298(HCP_A3,TI; 0) = GBCCTI	[30]
		G(BCC_A2,TI:B; 0)-3 H298(BETA_RHO_B,B; 0)-H298(HCP_A3,TI; 0) = GBCCTI+3 GBBCC-207312; L(BCC_A2,MO,TI:B; 0) = −105000	PW[a]
		G(BCC_A2,MO:B; 0)-3 H298(BETA_RHO_B,B; 0)-H298(BCC_A2,MO; 0) = GHSERMO+3 GBBCC-240000 + 100T	PW
		L(BCC_A2,MO:B,VA; 0) = −150000 + 75T; L(BCC_A2,TI:B,VA; 0) = −14722.577	PW
BETA_RHO_B	1 SUBLATTICE /1 /B,MO,TI	G(BETA_RHO_B,B; 0)-H298(BETA_RHO_B,B; 0) = GHSERBB	[30]
		G(BETA_RHO_B,TI; 0)-H298(HCP_A3,TI; 0) = GHSERTI+10000	[10]
		G(BETA_RHO_B,MO; 0)-H298(BCC_A2,MO; 0) = GHSERMO+5000; L(BETA_RHO_B,B,MO; 0) = −27457	PW
HCP_A3	2 SUBLATTICES /1: 0.5 /MO,TI: B,VA	G(HCP_A3,TI:B; 0)-0.5H298(BETA_RHO_B,B; 0)-H298(HCP_A3,TI; 0) = GHSERTI+0.5 GHSERBB-53603; L(HCP_A3,TI:B,VA; 0) = 9115.367	[10]
		G(HCP_A3,MO:VA; 0)-H298(BCC_A2,MO; 0) = GHCPMO; G(HCP_A3,TI:VA; 0)-H298(HCP_A3,TI; 0) = GHSERTI	[30]
		L(HCP_A3,MO,TI:VA; 0) = 27144	[28]
		G(HCP_A3,MO:B; 0)-0.5H298(BETA_RHO_B,B; 0)-H298(BCC_A2,MO; 0) = GHSERMO+0.5 GHSERBB; L(HCP_A3,MO,TI:B; 0) = 25000;	PW
LIQUID	1 SUBLATTICE /1 /B,MO,TI	G(LIQUID,B; 0)-H298(BETA_RHO_B,B; 0) = GLIQB; G(LIQUID,MO; 0)-H298(BCC_A2,MO; 0) = GLIQMO; G(LIQUID,TI; 0)-H298(HCP_A3,TI; 0) = GLIQTI	[30]
		L(LIQUID,MO,TI; 0) = 5487−9.727T	[28]
		L(LIQUID,B,MO; 0) = −181658 + 24.187T; L(LIQUID,B,MO; 1) = 22000−16.103T; L(LIQUID,B,MO; 2) = 29223; L(LIQUID,B,MO,TI; 1) = −41953	PW
		L(LIQUID,B,MO,TI; 2) = 39339 + 31.11T; L(LIQUID,B,TI; 0) = −244933 + 22.054T; L(LIQUID,B,TI; 1) = −82544 + 3.016T	PW
		L(LIQUID,B,TI; 2) = 28288 + 7.734T; L(LIQUID,B,TI; 3) = 39360;	PW
MB2	2 SUBLATTICES /1: 2 /B,MO,TI: B,MO,TI	G(MB2,B:B; 0)- 3H298(BETA_RHO_B,B; 0) = 3 GHSERBB+89628; L(MB2,B:B,TI; 0) = 98091; L(MB2,TI:B,TI; 0) = 98091	[10]
		G(MB2,B:TI; 0)-H298(BETA_RHO_B,B; 0)- 2H298(HCP_A3,TI; 0) = 2 GHSERTI + GHSERBB; G(MB2,TI:TI; 0)-3 H298(HCP_A3,TI; 0) = 3 GHSERTI+18000	[10]
		G(MB2,MO:B; 0)- 2H298(BETA_RHO_B,B; 0)-H298(BCC_A2,MO; 0) = +GHSERMO+2 GHSERBB-110325-7.281T	PW
		G(MB2,TI:B; 0)- 2H298(BETA_RHO_B,B; 0)-H298(HCP_A3,TI; 0) = −36600 + 0.14T LN(T)-3.7E-4 T^2+**GTIB2**	PW
		G(MB2,B:MO; 0)-H298(BETA_RHO_B,B; 0)- 2H298(BCC_A2,MO; 0) = 2 GHSERMO + GHSERBB-29580	PW
		G(MB2,MO:MO; 0)- 3H298(BCC_A2,MO; 0) = 3 GHSERMO+165000	PW
		G(MB2,TI:MO; 0)-2 H298(BCC_A2,MO; 0)-H298(HCP_A3,TI; 0) = 2 GHSERMO + GHSERTI+65000	PW
		G(MB2,MO:TI; 0)-H298(BCC_A2,MO; 0)-2 H298(HCP_A3,TI; 0) = GHSERMO+2 GHSERTI+65000; L(MB2,B,MO:B; 0) = 1848975	PW
		L(MB2,MO,TI:B; 0) = 246400-236T + 0.0538 T^2; L(MB2,MO,TI:B; 1) = −81315 + 34.26T; L(MB2,MO:B,MO; 0) = −588240 + 118.881T	PW

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