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The Ta-B system: Key experiments and thermodynamic modeling

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ABSTRACT

In the present work, the Ta-B system was thermodynamically optimized based on the CALPHAD method using data of *liquidus* temperatures, invariant transformations and enthalpy of formation from the literature as well as new experiments performed in our group. The phases Ta_3B_2, TaB(rt), Ta_5B_6, Ta_3B_4 were modeled as stoichiometric compounds. On the other hand, L (liquid), BCC, Ta_2B, TaB(ht) and TaB_2 were modeled as solution phases using the Compound Energy Formalism (CEF), with excess terms described by the Redlich-Kister polynomials. (βB) was treated as a pure element without any Ta solubility. The present thermodynamic modeling is in good agreement with the experimental data.

1. Introduction

The development of new high-temperature structural materials is essential for future generations of aircraft engines and land-based gas turbines. RM-boron-silicide-based alloys (RM: refractory metal) represent good candidates for high-temperature applications due to a suitable balance of properties required in these severe conditions [1,2].

The currently accepted Ta-B phase diagram [3], shown in Fig. 1, is mainly based on the proposals of Rudy [4] and Portnoi et al. [5]. However, more recent data from Chad et al. [6,7] have shown that: (i) the liquid composition in the Ta-rich eutectic reaction ($L \leftrightarrow Ta_{ss} + Ta_2B$) is placed at 18 at% B instead of 23 at% B; (ii) the liquid composition in the Ta-rich peritectic reaction ($L + TaB \leftrightarrow Ta_2B$) is placed at 22.5 at% B instead of 27 at% B; (iii) the eutectoid decomposition of Ta_2B occurs at 1925 ± 25 °C instead of 2040 °C; (iv) unknown peaks appears on diffractograms of as-cast Ta-B alloys with composition in the 33–45 at% B range but not in samples with B contents higher than 50 at% B. Furthermore, Okada et al. [8,9] proposed the stability of Ta_5B_6 in the Ta-B system and discrepancies exist about the homogeneity range of TaB_2 [4,8]. In the present work, experiments were designed to investigate these aspects.

The thermodynamic data available for this system concern the experimental determination of TaB_2 enthalpy of formation [10–13] and its dependence on temperature [14]. In addition, there are data on the enthalpies of formation of the intermetallic compounds from ab-initio calculations [15–19].

The first optimization of the Ta-B system available in the literature is due to Kaufman [20]. In his work: (i) all solid phases were modeled as stoichiometric compounds; (ii) the composition of Ta_2B was considered to be at 33.3 at% B and not between 29 at% B and 31 at% B, as suggested by Rudy [4] and Portnoi et al. [5]. Furthermore, most of the modern thermodynamic databases use the Stable Element Reference (SER), adopted by SGTE (Scientific Group Thermodata Europe), which is not compatible with the reference state adopted by Kaufman [20]. In a recent work, Yang et al. [19] (Fig. 2) re-optimized the Ta-B system considering the data of Chad et al. [6] except for the non-stoichiometric composition of Ta_2B. Thus, based on the previous information and the experimental data from the present work, a new thermodynamic modeling for the Ta-B system has been carried out.

2. Experimental procedure

In this work, key experiments were carried out in order to: (i) determine the homogeneity range of TaB_2 phase at 1500 °C; (ii)

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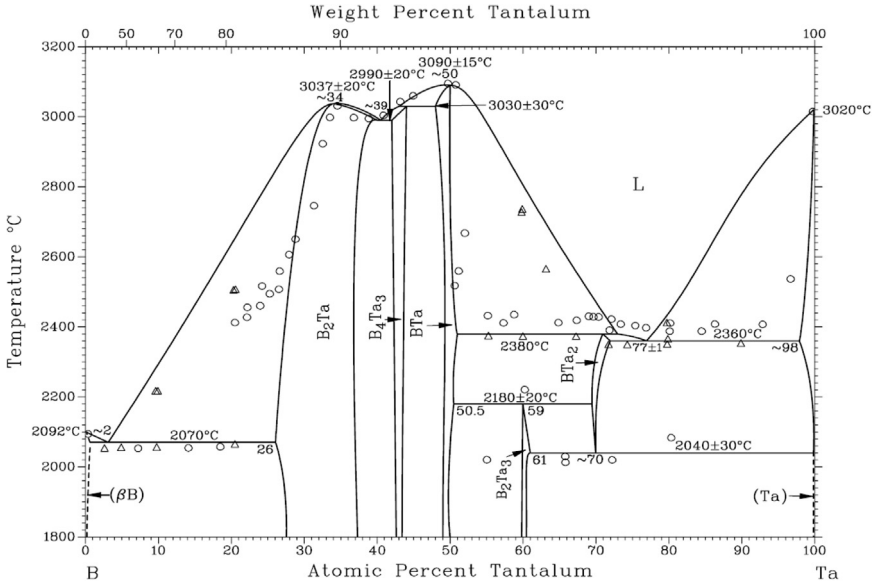

Fig. 1. Currently accepted phase diagram of the Ta-B system [3] along with experimental data from: ○ Rudy [4] and Δ Portnoi et al. [5].

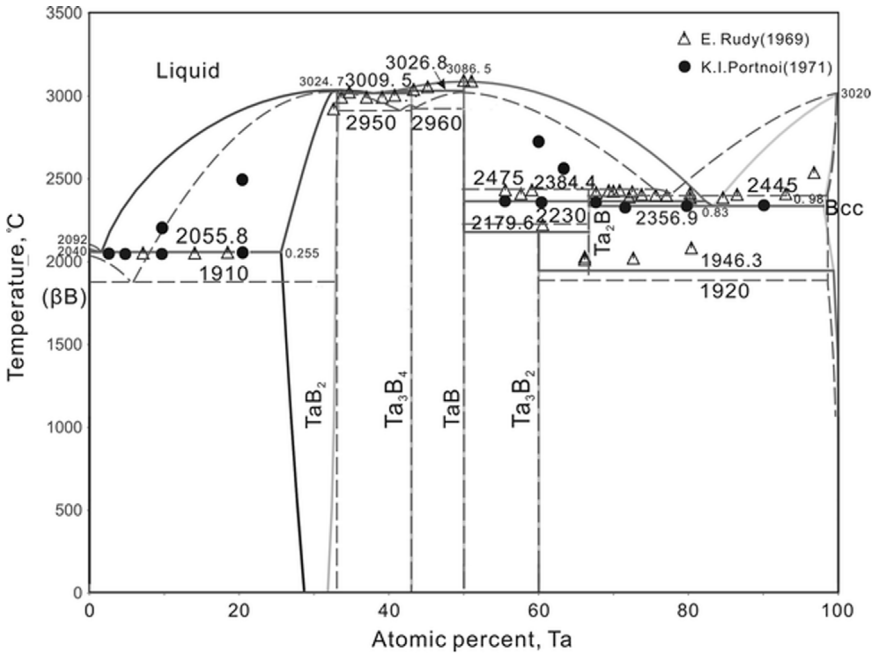

Fig. 2. Ta-B phase diagram published by Yang et al. [19] calculated with their parameters (solid lines) and Kaufman's [20] (dotted lines) along with selected experimental data from Rudy [4] and Portnoi et al. [5].

investigate the possible existence of a high-temperature polymorph TaB-phase; (iii) evaluate the possible stability of Ta_5B_6. Arc-melted samples were used for (i) and (ii) investigations and powder sintered samples for (iii), as detailed below.

Arc-melted samples were prepared from high-purity Ta (min. 99.95 wt%) and B (min. 99.5 wt%) in powder form. The powders were intimately mixed and cold pressed in the form of pellets (~ 3 g) and then arc-melted under titanium-gettered argon (min 99.995 wt%) on a water-cooled copper hearth using a non-consumable tungsten electrode. At least three melting steps were carried out for better chemical homogeneity of the samples.

For the determination of the homogeneity range of TaB_2, arc-melted alloys with compositions varying from 64 to 78 at% B were heat treated under high-purity, niobium-gettered argon, at 1500 °C for 6 h. The solubility limits of TaB_2 were evaluated through the determination of lattice parameters of this phase from the different samples. Within the single-phase region, the lattice parameters of a non-stoichiometric phase varies with composition and depends on the defect structure of the particular phase (substitutional atoms; interstitial atoms; vacancies). When the solubility limit is reached, new phases precipitate (Ta_3B_4 or (βB) in this case) and the lattice parameters of the considered phase (TaB_2) is kept constant in each of the neighbor two-phase fields (Ta_3B_4 + TaB_2; TaB_2 + (βB)).

The investigation of the existence of a high temperature TaB-phase was based on an arc-melted alloy with composition 45 at% B (referred as Ta-45at%B) analyzed in the as-cast state.

For the Ta_5B_6 stability study, two alloys with compositions 54.54 and 60 at% B (referred as Ta-54.54at%B and Ta-60at%B, respectively) were prepared from pure B (min. 99.5 wt%) and TaB powders. The TaB powder was prepared by arc-melting pure Ta and B, following the same