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Thermodynamic re-assessment of binary Cr-Nb system down to 0 K

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ABSTRACT

Based on the recently proposed physically-based segmented model, the descriptions for Gibbs energy of pure Cr and Nb down to 0 K were first established. After that, a thermodynamic re-assessment of binary Cr-Nb system down to 0 K was then performed by taking into account all the experimental phase equilibria and thermodynamic properties. Especially, the experimental heat capacities of Cr_2Nb at low temperatures ignored in previous assessments were utilized in the present assessment. The calculated phase equilibria and thermodynamic properties according to the presently obtained thermodynamic descriptions of binary Cr-Nb system agree well with most of the experimental data, and show better agreement than the previous assessments.

1. Introduction

Cr and Nb are two important additional elements in different technical alloys [1]. Moreover, the Laves Cr_2Nb alloy, which owns high melting points, high strength and superior oxidation resistance [2–8], has also shown its potential in development of new high-temperature structural materials. Nowadays, computational thermodynamics in the framework of CALculation of PHAse Diagram (CALPHAD) approach, which heavily depends on the quality of the thermodynamic descriptions for the target system, has been proved to be a promising approach for speeding up the process of novel alloy design [9]. Thus, in order to perform a computational thermodynamics-aided design of novel alloys with Cr and Nb, an accurate CALPHAD thermodynamic description of the binary Cr-Nb system is the prerequisite.

In fact, there are already several sets of thermodynamic descriptions for the binary Cr-Nb system in the literature [10–13]. Neto et al. [10] first optimized the binary system using the CALPHAD approach in 1993. Around 16 years later, Pavlů et al. [11] performed a re-modeling of the Laves phase by applying their own first-principle results. However, Laves_C14 phase was treated as one thermodynamically stable phase in both reports [10,11]. Then in year 2014, Schmetterer et al. [12] analyzed the existence of Laves_C14 phase in detail based on the available experimental [14] and theoretical reports and concluded that the Laves_C14 phase is metastable. Furthermore, the authors [12] also performed a thermodynamic assessment of the Cr-Nb system by excluding Laves_C14 phase and employing *ab initio* calculations to fix the enthalpies of formation for the end members of the Laves_C15 phase. Very recently, Lu et al. [13] confirmed the absence of Laves_C14 phase in the Cr-Nb phase equilibria by using *ab initio* calculations, which indicate that the Gibbs energy difference between Laves_C14 and Laves_C15 (i.e., $\Delta G^{\text{Laves\_C15}-\text{Laves\_C14}}$) is always negative over the wide temperature range of 0~3000 K. After that, Lu et al. [13] further conducted a new thermodynamic assessment of the binary Cr-Nb system.

Despite that great efforts in ascertaining the stability of controversial Laves_C14 phase as well as refining the Cr-Nb phase diagram have been made in the literature, there still exist two drawbacks in the previous thermodynamic assessments. The first one lies in that most of the thermodynamic assessments employed their own first-principles computed enthalpies of formation of Laves_C15 phase at 0 K to optimize the thermodynamic parameters of Laves_C15 phase above room temperature, but the values for enthalpies of formation of Laves_C15 phase at 0 K from different authors show large differences (i.e., ranging from the −1.83 to −4.16 kJ/mole-atom). Such large differences leave a matter for consideration on the reliability of the obtained Gibbs energy for Laves_C15 phase. Fortunately, Syutkin et al. [8] measured the standard enthalpy of formation for Laves_C15 phase by means of drop solution calorimetry technique in 2016. This piece of information is very important to verify the reliability of the theoretically-predicted enthalpies of formation. The other drawback lies in that the heat capacites of Laves Cr_2Nb phase between 10 and 350 K measured by Martin et al. [15] using an adiabatic calorimeter have not been included in all the previous thermodynamic modeling. Moreover, their measured heat capacities of Laves Cr_2Nb phase are consistent with the very recent standard enthalpy of formation by [8]. The reason lies in that most of the experimental data from [15] are below the room temperature, and thus cannot be included in the 2nd generation CALPHAD thermodynamic modeling. Thus, in order to take those heat

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capacities into account, a modeling strategy in the framework of the 3rd generation CALPHAD databases down to 0 K should be applied.

One core research task towards the 3rd generation thermodynamic database is to establish the reliable and robust physically-based thermodynamic description from 0 K up to the melting point and far above it. Currently, several alternative physics-based models [16–18] have been proposed to replace the standard SGTE polynomial description [19]. Many authors contributed to this direction since 1995 to develop the 3rd generation CALPHAD-type thermodynamic descriptions for some pure elements [16–18,20–25], several compounds [16,26], limited binary [27–29] and ternary systems [30,31]. The main two requirements to modeling functions for the 3rd generation of CALPHAD databases can be summarized as follows: (1) the modeling function should be a physically-based formulation, which is valid from 0 K; (2) some of fitting parameters should be associated with physical meaning such that their estimated values can be validated with available experiments and DFT calculations. One of the successful attempts in this direction, which fulfilled the modeling requirements listed above, is the segmented regression (SR) model [18] for the description of the thermodynamic properties of pure elements and stoichiometric compounds from 0 K. The SR modeling approach is based on a combination of a statistical fit of the heat capacity data with several physically-based models, for example, the Debye model. Therefore, several SR modeling parameters are associated with physical constants and their estimated values can be verified versus the available experimental and DFT data. Very recently, in order to integrate the Debye model into the existing thermodynamic databases, Roslyakova et al. [32] proposed an efficient and accurate method by approximating the Debye model for the heat capacity through the weighted linear combination of the Einstein functions. The segmented modeling approach has been successfully applied for the modeling of thermodynamical properties of pure Al, Cr and Fe [18] and currently its application has been extended to other 11 pure elements [24]. Combining the segmented regression model and the newly proposed approximation method of the Debye model, a robust and accurate description of key thermodynamic properties of pure elements and some stoichiometric compounds over the wide temperature range (i.e., 0 ~ 6000 K) can be obtained.

Consequently, a re-assessment of binary Cr-Nb system down to 0 K is to be conducted in this paper. The low-temperature heat capacities [15] missing in all the previous thermodynamic modelings and the newly reported standard enthalpy of formation [8] for Laves_C15 phase will be taken into account. Moreover, the extended segmented model developed by Roslyakova et al. [32] will be applied to model the Gibbs energy of pure elements and stoichiometric Cr_2Nb phase down to 0 K.

2. Literature review

All the experimental phase equilibria and thermodynamic properties of the binary Cr-Nb system available in literature are summarized in Table 1 and concisely categorized in the following.

2.1. Phase equilibria information

The liquidus in the Cr-Nb system were investigated by several groups of authors around 1960s [34,35,2,36,33] using thermal analysis (TA) technique, but the experimental data from different sources are scattering. Elyutin and Funke [34] determined liquidus data from 0 to 100 at.% Nb using TA technique. However, the results in the Nb-rich part are questioned obviously, since the alloys reacted with the ZrO_2 crucible they applied during experiment, resulting in significant reduction of measured liquidus temperature in Nb-rich part. Another set of liquidus data over the entire composition range measured by Goldschmidt and Brand [2] are regarded to be inaccurate, because the melting points were recorded by [2] at the time when the samples "collapsed", and thus the recorded values should be lower than the true liquidus temperatures where the solid phase transforms into liquid phase completely. Futhermore, the liquidus temperatures given by Goldschmidt and Brand [2] perfectly fit the solidus line and the questioned liquidus line from Elytin and Funke [34] in the Cr-rich part and Nb-rich part, respectively. In fact, their melting points of pure elements Cr and Nb are relatively lower than that of SGTE data [19] by several tens of Kelvin. Rudy [33] also investigated the system using a crucible free thermal analysis technique on heating. However, those data are also recorded when samples "collapsed", thus they can only represent temperatures below liquidus in an analogous manner compared with the work by Goldschmidt and Brand [2]. Eremenko et al. [35] measured the liquidus temperatures from 0 to 66 at.% Nb by means of a pyrometer in an induction furnace using a BeO crucible, but their samples contained considerable amounts of impurities as illustrated by Schmetterer et al. [12]. Pan [36] determined the liquidus temperatures over the composition range between 0 and 55 at.% Nb by using the differential thermal analysis (DTA) technique. Their results are in general agreement with the Cr-rich data by Elyutin et al. [34]. All the liquidus data mentioned above will not be considered during thermodynamic assessment, but just for comparison.

The solidus line in the Cr-rich part was studied by Elyutin and Funke [34] and Eremenko et al. [35], but the results reported by the later authors exhibit apparent problems due to contamination. Elyutin and Funke [34] and Rudy [33] determined the Nb-rich solidus. But the temperatures reported by the preceding authors [34] are too low. While for the data in Ref. [33], the accuracy is also questioned as discussed above. Thus the solidus data from Elyutin and Funke [34], Eremenko et al. [35] and those from Rudy [33] are also used for comparison, but no data are involved in the present optimization.

The Cr-rich solvus, Nb-rich solvus and Cr_2Nb homogeneity range were measured by Thoma and Perepezko [4] through energy dispersive

Table 1
Summary of the phase diagram and thermodynamic data in the Cr-Nb system available in the literature.

Type of data	Reference	Experimental method	Quoted mode[a]
Liquidus			
0–100 at% Nb	[2]	TA	–
0–100 at% Nb	[33]	TA	–
0–100 at% Nb	[34]	TA	–
0–66 at% Nb	[35]	TA	–
0–55 at% Nb	[36]	DTA	–
Solidus in Cr-rich part	[34]	TA	–
	[35]	TA	–
Solidus in Nb-rich part	[34]	TA	–
	[33]	TA	–
Cr-solvus,Nb-solvus &	[4]	EDS	+
homogeneity range	[34]	Microhardness	+
of Cr_2Nb	[37]	XRD	+
Congruent melting point	[38]	DTA	+
	[2]	TA	–
	[36]	DTA	–
	[34]	TA	–
Eutectic temperatures	[39]	TA	–
	[2]	TA	–
	[36]	DTA	–
	[35]	TA	–
	[34]	TA	–
	[38]	DTA	+
Enthalpy of formation	[8]	Tian-Calvet calorimetry	+
Heat capacities of Cr_2Nb	[15]	Adiabatic calorimetry	+
Chemical potential of Cr in (Nb) + Cr_2Nb region at 1472 K	[15]	Knudsen cell effusion	+

TA = Thermal analysis.
DTA = Differential thermal analysis.
EDS = Energy dispersive spectroscopy.
XRD = X-Ray Diffraction.
[a] indicates whether the data are used or not used in the parameter optimization: +, used; -, not used but employed for comparison.