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Thermodynamic assessment of Ni-Ta-C ternary system①

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Abstract: By means of the CALPHAD technique, an ideal calculation, i.e. without ternary interaction parameter, was applied to assess the Ni-Ta-C ternary system. The calculated and experimental data were in reasonable agreements. It proved the CALPHAD technique of a powerful approach of the extrapolation, as well as the good feasibility of the thermodynamic descriptions of three binary systems, Ni-C, Ni-Ta and Ta-C.

Key words: nickel-tantalum-carbon systems; phase diagrams; thermody namics **Document code**: A

1 INTRODUCTION

The introduction of tantalum in Ni-base superalloys can improve their high temperature strength and hot corrosion resistance. The presence of the TaC in Ni-base superalloys positively contributes to their strength, especially in directionally solidified eutectic alloys reinforced by the carbides aligned lamellae. The Ni-Ta-C ternary system is therefore of importance to make alloy modifications and optimize the process schedule.

Over the years, the Ni-Ta-C system has been investigated to a limited extent. By means of composition analysis and thermal arrest, Lemkey and Thompson[1] observed a pseudobinary eutectic between Ni and TaC, and sequently established its composition and formation temperature. Later, Frey and Holleck[2] also reported a schematic Ni-TaC pseudobinary section. Examining the directionally solidified Ni-TaC alloys by chemical analysis, X-ray lattice parameter measurement, electron probe microanalysis and metallography, Jackson[3] constructed a tentative Ni-rich isothermal section of the Ni-Ta-C system at 1 473 K. Holleck[4] published another isothermal section at 1 373 K where a ternary carbide Ni_2Ta_4C was found. This ternary carbide was further confirmed by his another work[5]. Recently, Wang *et al*[6] studied the diffusion paths in the Ni-Ta-C system at 1 373 K and 1 473 K by means of diffusion couple and EPMA analysis. However, they reported several probable diffusion paths rather than phase equilibrium data. The modern CALPHAD technique, as a pwerful approach to thermodynamics and phase diagrams calculation, enables us to apply various experimental quantities simultaneously to obtain consistent thermodynamic description of a system. Accordingly, it is the aims of this paper to assess the Ni-Ta-C ternary using the CALPHAD technique.

2 EVALUATION OF LITERATURE DATA

2.1 Binary systems

2.1.1 Ni-C system

The Ni-C binary system was thoroughly assessed by Gabriel *et al*[7]. Recently, considering more experimental data on the carbon solubility in the fcc-(Ni) phase[8], Lee[9] modified the thermodynamic description of the Ni-C system. The version of Lee[9] was accepted in present assessment. In addition, similar to the treatment of Du[10], the regular interaction parameter ${}^{0}L^{bcc}_{Ni,C}$ of the metastable bcc phase was fixed to

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be a positive value, 300 kJ, to prevent it from being stable at high temperature.

2.1.2 Ta-C system

By applying the mathematical model and a computer optimization procedure, Frisk *et al*[11] critically assessed the Ta-C binary system. However, due to the lack of available information, the ξ-Ta_4C_{3-x} phase was excluded in their assessment. Before long, mainly concentrating on binary carbides, Lengarure[12] and Wiesenberger *et al*[13] carried out the systematic investigations of the Ta-C binary system by applying an advanced wedge-type diffusion couple method. The late paper[13] showed the homogeneity range of ξ-Ta_4C_{3-x} was 38.2% ~ 39% (mole fraction, %)C, and the measured phase boundaries of the Ta_2C phase were somewhat richer carbons than the calculated ones[11]. Also, they located the decomposition temperature of the ξ-Ta_4C_{3-x} phase in the range of 2150~2175 ℃. As a consequence, it still requires to modify the thermodynamic description due to Frisk *et al*[11]. However, since the presence of this carbide has a small effect on overall phase relation of the Ta-C system, no modification was performed in this work.

2.1.3 Ni-Ta system

The Ni-Ta system was assessed by Kaufman[14], and Ansare and Selleby[15]. Recently, Cui and Jin[16] reassessed this system based upon the new experimental data and internationally accepted modeling of the NiTa phase. The thermodynamic assessment of Cui and Jin[16] was adopted in present work.

2.2 Ternary system

Lemkey and Thompson[1] reported the Ni-TaC pseudobinary eutectic temperature was 1623 K, and the eutectic composition was 16% TaC. Frey and Holleck[2] located this eutectic reaction at 1643 K. These two sets of data were preferred to assess the vertical section from Ni to TaC.

Jackson[3] determined the fcc-(Ni) solvus at 1 473 K, as well as the tentative three-phase boundaries of fcc-(Ni) + TaC + graphite and fcc-(Ni) + TaC + Ni_3Ta. As stated by the author, however, the phase relations developed were for as-directionally solidified composites and did not represent a particular equilibrium isotherm. Furthermore, it was discovered that the fcc-(Ni) solvus determined was mainly approximated from the volume fraction data of the TaC phase in the directionally solidified fcc-(Ni) + TaC composites. The experimental data from Jackson[3] were therefore considered not reliable enough. Accordingly, their data were used in the present work, but were given a low weight. The denotation of weight will be discussed in Section 4. The isothermal section constructed at 1373 K by Holleck[4] shows a little discrepancy with the section from Jackson[3] except for the formation of the ternary carbide Ni_2Ta_4C. Since such a compound was not confirmed by other research groups and its nature was also isolated, it was thus excluded in the present work.

Since no equilibrium data were reported by Wang *et al*[6], their data can not be utilized in the assessment. But the diffusion paths according to Wang *et al* were served to compare with the calculated results.

3 THERMODYNAMIC MODELS

3.1 Liquid phase

The liquid phase was described by the substitutional solution model. Its Gibbs energy can be expressed by Redlich-Kister polynomial[17]:

$$\begin{aligned} G_m = {} & x_{Ni}{}^0G^h_{Ni} + x_C{}^0G^h_C + x_{Ta}{}^0G^h_C + RT \cdot \\ & (x_{Ni}\ln x_{Ni} + x_C\ln x_C + x_{Ta}\ln x_{Ta}) + \\ & x_{Ni}x_C L_{Ni,C} + x_{Ni}x_{Ta}L_{Ni,Ta} + \\ & x_C x_{Ta} L_{C,Ti} + x_{Ni}x_C x_{Ta} L_{Ni,C,Ta} \end{aligned} \tag{1}$$

where the parameter ${}^0G^h_{Ni}$ is the Gibes energy of pure component i in a hypothetical non-magnetic state, and is taken from the SGTE database[18]. $L_{i,j}$ is the binary interaction parameter from the corresponding binary system. The ternary interaction parameter $L_{Ni,C,Ta}$ can be expressed by the following equation:

$$L_{Ni,C,Ta} = x_{Ni}L_{Ni} + x_C L_C + x_{Ta}L_{Ta} \tag{2}$$

L_i is composition independent. Owing to the lack of the experimental data associated with the ternary liquid phase, the term $L_{\mathrm{Ni,C,Ta}}$ was fixed to be zero.

3.2 Solid solution phases

The Gibbs energies of the solid solution phases, i.e. fcc phase (fcc-Ni and TaC_x), bcc-Ta and hcp ($\mathrm{ta_2C}_x$), were modeled using the two-sublattice model[19] $(\mathrm{Ni, Ta})_a(\mathrm{C, Va})_b$. For fcc-Ni and TaC_x, $a = b = 1$; for bcc-Ta and hcp, $a = 1$ and $b = 3$. Their Gibbs energies can be expressed as

$$\begin{aligned} G_{\mathrm{m}} = {} & y^1_{\mathrm{Ni}} y^2_{\mathrm{C}} \cdot {}^0G^{\varphi}_{\mathrm{Ni:C}} + y^1_{\mathrm{Ni}} y^2_{\mathrm{Va}} \cdot {}^0G^{\varphi}_{\mathrm{Ni:Va}} + \\ & y^1_{\mathrm{Ta}} y^2_{\mathrm{C}} \cdot {}^0G^{\varphi}_{\mathrm{Ta:C}} + y^1_{\mathrm{Ta}} y^2_{\mathrm{Va}} \cdot {}^0G^{\varphi}_{\mathrm{Ta:Va}} + \\ & aRT(y^1_{\mathrm{Ni}} \ln y^1_{\mathrm{Ni}} + y^1_{\mathrm{Ta}} \ln y^1_{\mathrm{Ta}}) + \\ & bRT(y^2_{\mathrm{C}} \ln y^2_{\mathrm{C}} + y^2_{\mathrm{Va}} \ln y^2_{\mathrm{Va}}) + \\ & y^1_{\mathrm{Ni}} y^1_{\mathrm{Ta}} y^2_{\mathrm{C}} \cdot L^{\varphi}_{\mathrm{Ni,Ta:C}} + y^1_{\mathrm{Ni}} y^1_{\mathrm{Ta}} y^2_{\mathrm{Va}} \cdot \\ & L^{\varphi}_{\mathrm{Ni,Ta:Va}} + y^1_{\mathrm{Ni}} y^2_{\mathrm{C}} y^2_{\mathrm{Va}} \cdot L^{\varphi}_{\mathrm{Ni:C,Va}} + \\ & y^1_{\mathrm{Ta}} y^2_{\mathrm{C}} y^2_{\mathrm{Va}} \cdot L^{\varphi}_{\mathrm{Ta:C,Va}} + G^{mg}_{\mathrm{m}} \end{aligned} \tag{3}$$

in which, y^i_j is the site fraction of species j sublattice i, the parameters ${}^0G^{\varphi}_{\mathrm{Ni:C}}$ and ${}^0G^{\varphi}_{\mathrm{Ta:C}}$ are the Gibbs energies of the compounds $\mathrm{Ni}_a\mathrm{C}_b$ and $\mathrm{Ta}_a\mathrm{C}_b$, respectively. The parameters ${}^0G^{\varphi}_{\mathrm{Ni:Va}}$ and ${}^0G^{\varphi}_{\mathrm{Ta:Va}}$ are the Gibbs energies of pure nickel and tanktalum with the structure of the φ phase. The G^{mg}_{m} term denotes the magnetic contribution to the Gibbs energy which can be described by Hiller and Jarl model[20]. In Eqn. 3, $L^{\varphi}_{\mathrm{Ni,Ta:C}}$ is the unique ternary interaction parameter which can be expressed as

$$\begin{aligned} L^{\varphi}_{\mathrm{Ni,Ta:C}} = {} & {}^0L^{\varphi}_{\mathrm{Ni,Ta:C}} + (y^1_{\mathrm{Ni}} - y^1_{\mathrm{Ta}})^1 \cdot \\ & L^{\varphi}_{\mathrm{Ni,Ta:C}} \end{aligned} \tag{4}$$

This value for the bcc phase was neglected with regards to the lack of the experimental data, for hcp ($\mathrm{Ta_2C}_x$) was also fixed to be zero since only negligible solubility for Ni was proved by Holleck[4].

As demonstrated by the existing literature data, none of five intermediate phases in the Ni-Ta system shows noticeable solubility for carbon, and thus no additional treatment was taken into account in the ternary system.

4 RESULTS AND DISCUSSION

The optimization was carried out in Parrot module of Thermo-Calc program[21], which was made by minimizing the square sum of the differences between experimental and computed values. In the assessment procedure, each experimental value is given a certain weight. The weights were changed systematically during the assessment until most of the experimental data were accounted for within the claimed uncertainty limits.

At first, an ideal calculation, i.e. no ternary interaction parameters were employed, was performed. The agreement between the calculated and experimental data, even in this case, was satisfactory. Then, a ternary interaction parameter of the fcc-(Ni) phase was introduced to give a better reproduction of the overall phase relation determined experimentally, especially for the fcc-(Ni) solvus from Jackson[3]. However, such an attempt only offers a limited improvement unless some unrealistic parameters were introduced, and thus was considered to be unnecessary and improbable[22]. As a result, only an ideal calculation was discussed in present work.

Fig. 1 presents the calculated isothermal section of the Ni-Ta-C system at 1 473 K. The calculated and the experimental values are in reasonable agreement, as shown in Fig. 2. The calculated three-phase boundaries of fcc-(Ni) + TaC + graphite and fcc-(Ni) + TaC + $\mathrm{Ni_3Ta}$ fit the estimated ones by Jacson very well, but the calculated fcc-(Ni) solvus presents in excess of the Ni content. As already mentioned and the evaluation in section 2.3, a better fitness to the data from Jackson[3] was not made. Since the $\mathrm{Ni_8Ta}$ phase and not observed in the Ni-Ta-C ternary system according to Jacson[3] and Holleck[4], the $\mathrm{Ni_8Ta}$ phase was suspended in these tow figures, as well as in Fig. 3 and 4, in order to facilitate the comparing between the calculation and the experimental data.

The calculated isothermal section at 1 373 K is presented in Fig. 3. It can be claimed that,

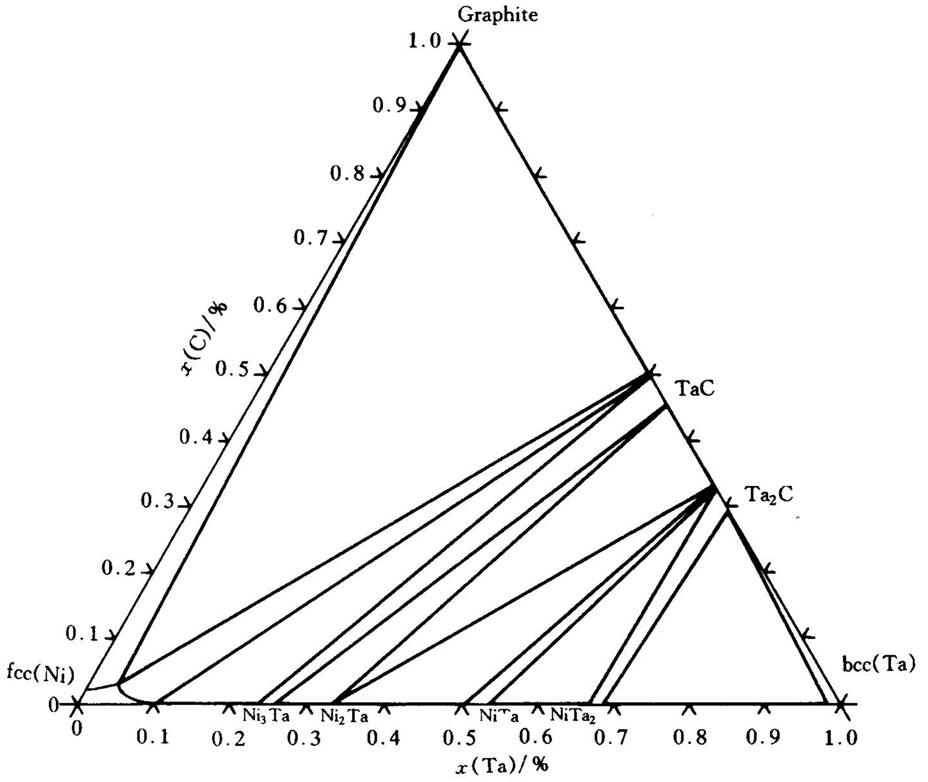

Fig.1 Calculated isothermal section of the Ni-T-C termary system at 1 473 K, in which Ni_8Ta phase was suspended

the calculated phase relation were in accord with the observation of Hollect[4] apart from the absence of the ternary carbide. In view of the study of Wang *et al*[6], the second group couples used to establish the diffusion paths at 1 373 K or 1 473 K were first annealed at 1 473 K for 5 d and then at 1 373 K for just one day, this treatment schedule was certainly dubious. Moreover, one couple of their first samples group contained one end member with non-homogenous binary structure, $Ni_2Ta + Ni_3Ta + NiTa_2$, and thus was believed to be doubtful. Thereby, only two diffusion paths determined by Wang *et al*[6] were selected and marked in Fig.3. As indicated, the calculation describe the selected paths[6] successfully.

The calculated Ni-TaC vertical section shows that, in Fig.4, the experimental points[1] together with the eutectic temperature from Frey *et al*[2] were represented by present modeling satisfactorily.

Fig.5(a) depicts the calculated liquid projection of Ni-Ta-C system in comparison with the experimental data. As shown in it, the melting points of the ternary alloys measured in Jackson[3] thermal arrest analysis were reproduced in present work. Fig.5(b) gives the enlarged projection in the vicinity of the Ni-Ta binary system. The ternary reaction temperatures are also marked in these two figures. The calculations show the Ni-Ta-C system possesses a very wide primary field of TaC_x, it almost reaches the vicinity of the Ni-Ta binary system. Obviously, it demonstrates that the composites of fcc-(Ni) + TaC in the Ni-Ta-C ternary system can be prepared over a wide range of composi-

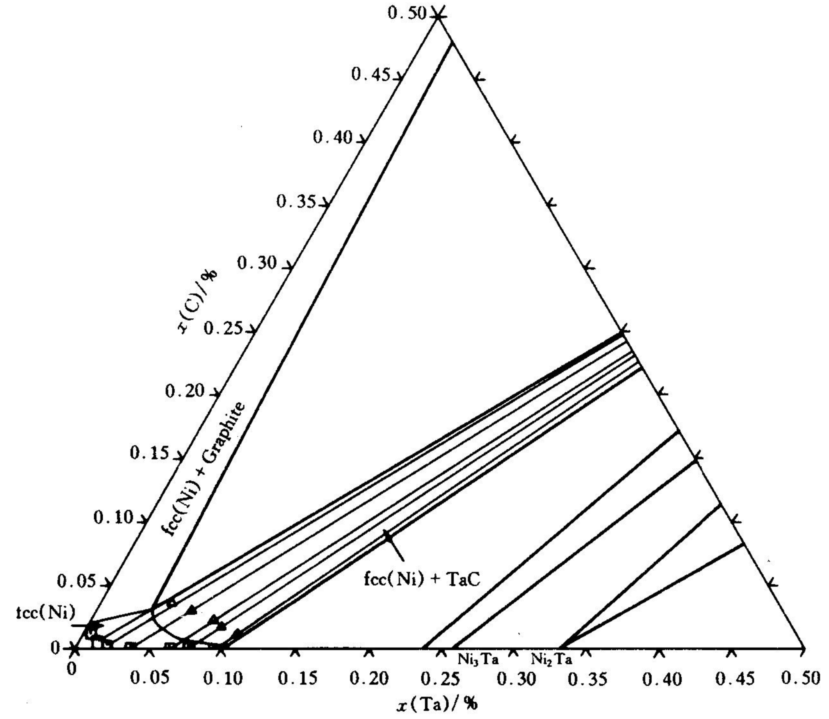

Fig.2 Calculated Ni-rich isothermal section of the Ni-T-C termary system at 1473 K, together with experimental data[3]

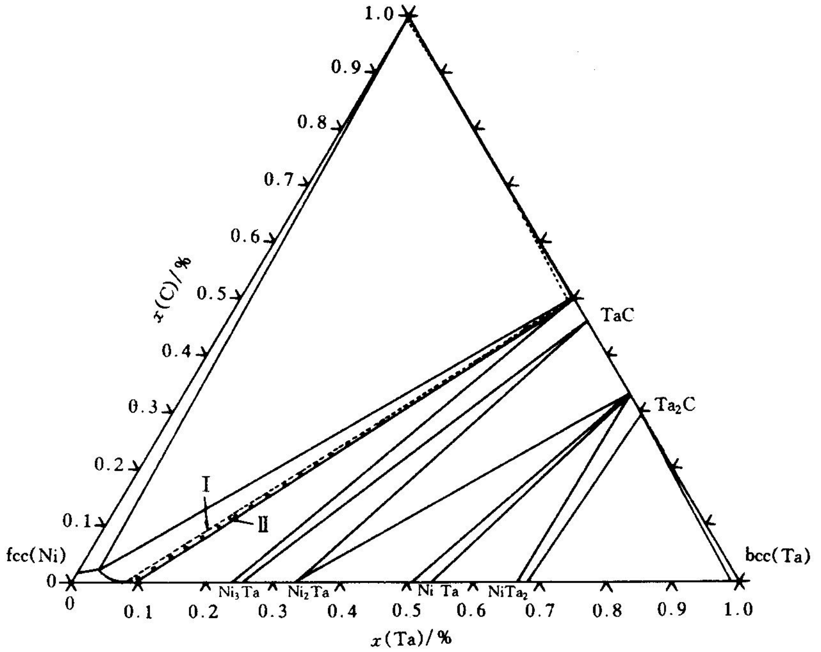

Fig.3 Calculated isothermal section of the Ni-T-C ternary system at 1373 K
I —fcc-TaC-graphite; II —Ni_3Ta-fcc-graphite[6]

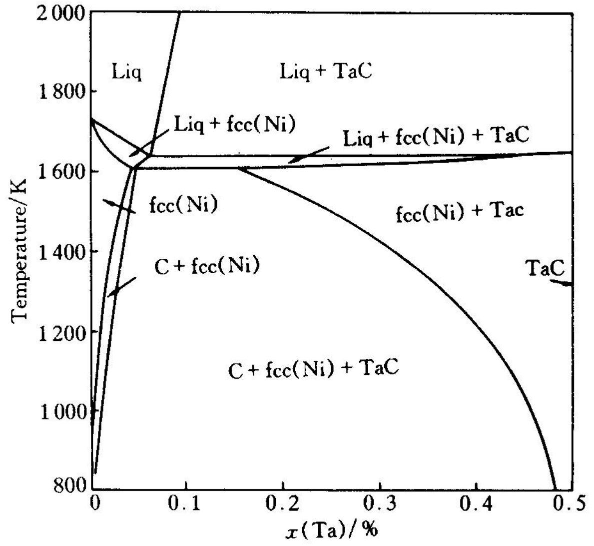

Fig. 4 Calculated vertical section from Ni to TaC, as well as experimental data[1]

tions, as proposed by Jacson[3].

5 CONCLUSIONS

By means of CALPHAD technique, an ideal calculation was used to assess the Ni-Ta-C ternary system. The comparison between the calculated and experimental data was made, and the agreement was reasonable. It proves the CALPHAD technique of a powerful approach of the extrapolation, as well as the feasibility of the thermodynamic descriptions of Ni-C, Ni-Ta and Ta-C systems.

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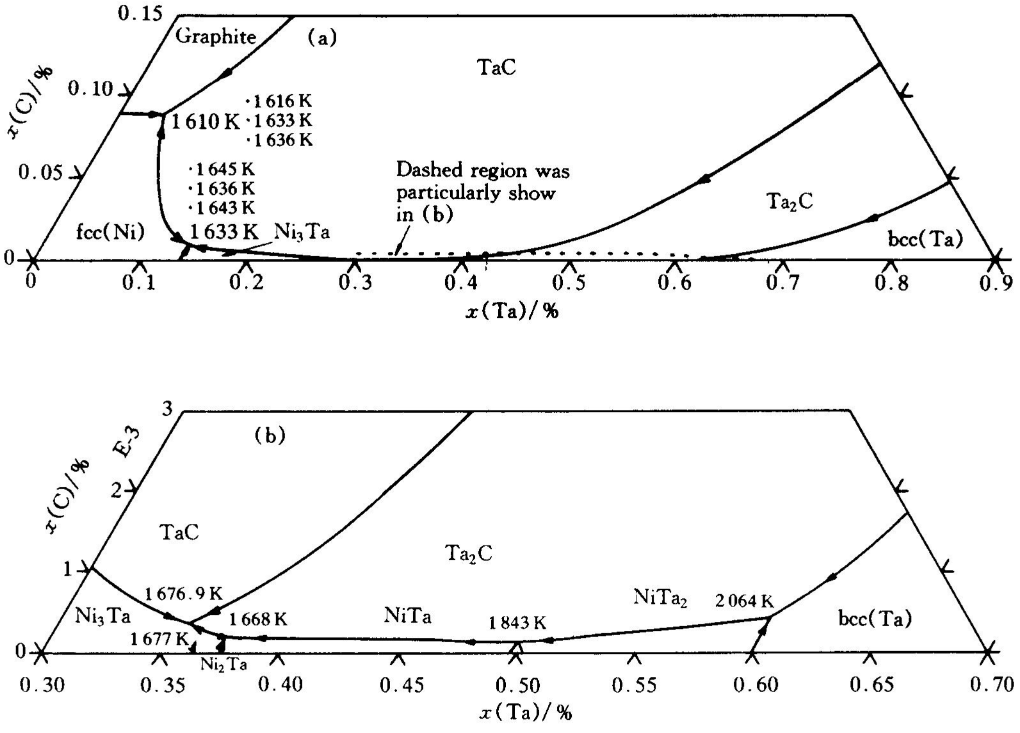

Fig. 5 Calculated liquidus projection of Ni-Ta-C ternary system (a) and enlarged portion of dashed region in the top figure (b)

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