

The Thermodynamic Properties Of Cu-O Solutions

Marian Kucharski

Retired professor of AGH University of Science and Technology,
Department of Metallurgy of Non-Ferrous Metals, 30 Mickiewicza Avenue, 30-019 Kraków, Poland
Corresponding author: Marian Kucharski

ABSTRACT: This study presents a novel method of thermodynamic properties description of liquid Cu-O solutions which is based on selection of infinite dilute solution as the reference state ($\gamma_{[O]} = 1$ for $x_{[O]} = 0$) for oxygen dissolved in copper. For this reference state the following relationships were established:

1. The equilibrium constant for the reaction of oxygen dissolution in liquid copper:

$$\ln K_{[O]} = \frac{9810}{T} - 5.085$$

2. The Gibbs energy of reaction of oxygen dissolution in liquid copper:

$$\Delta G_{[O]} = -81560 + 42.276 \cdot T \quad J \cdot (\text{mol } [O])^{-1}$$

3. The chemical potential of the oxygen in infinite dilute solution:

$$\mu_{[O]}^{\infty} = -60908 - 87.020 \cdot T \quad J \cdot (\text{mol } [O])^{-1}$$

4. The activity coefficient of the oxygen dissolved in liquid copper:

$$\ln \gamma_{[O]} = -7.204 \cdot x_{[O]}$$

KEYWORDS: copper; oxygen; thermodynamic description

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I. INTRODUCTION

In fire refining processes of copper, thermodynamic properties of the oxygen dissolved in copper are of considerable interest. These properties have been a subject of numerous investigations [1-35], however, reported results differ considerably. For example, values of the Gibbs energy for the process of oxygen dissolution in liquid copper show considerable disagreement which is illustrated in Fig. 1 [29]. The objective of this study was to reconcile this disagreement in Cu-O thermodynamic properties.

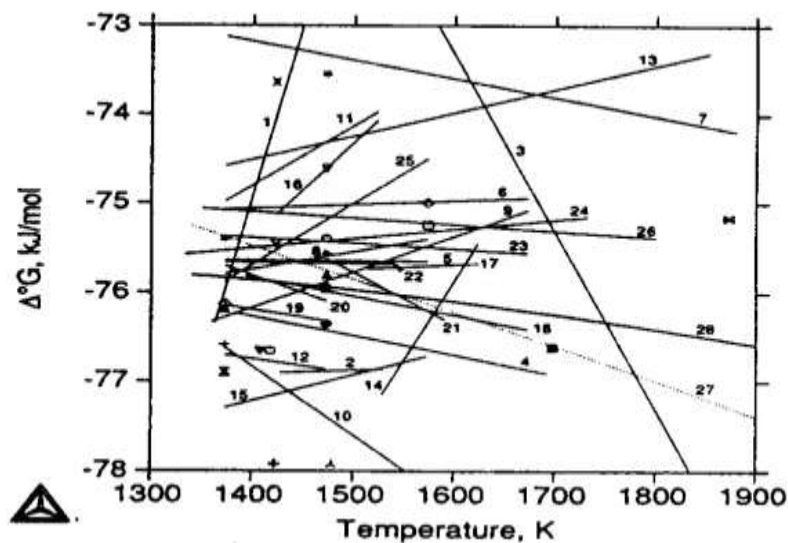


Fig. 1. The Gibbs energy of dissolution of oxygen in liquid copper as a function of temperature reported by different authors (Fig. 1 is taken from [29]).

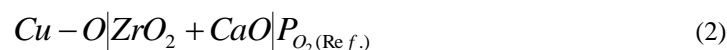
The process of oxygen dissolution in liquid copper can be written in form of the reaction:



Thermodynamic properties of the dissolved oxygen in liquid copper have been investigated with two distinct methods.

The first method is based on equilibration of liquid copper with a gas atmosphere with strictly defined oxygen pressure. In order to obtain a desired oxygen pressure the following gas mixtures were used: $H_2O_{(g)}/H_2$ – [2, 15], CO_2/CO – [1], Ar/O_2 – [21], or pure oxygen under low pressure – [30]. Results of this kind of experiments are the oxygen dissolved in liquid copper, and its concentration depends on oxygen pressure and temperature.

The second method employed electromotive force (emf) measurements of galvanic cell with solid electrolyte conducting oxygen ions (O^{2-}). One electrode consists of liquid copper with dissolved oxygen which is in equilibrium with oxygen in the gas phase with the partial pressure P_{O_2} . The second electrode is the reference electrode with oxygen partial pressure $P_{O_2(Ref.)}$. Schematically, such galvanic cell, for example can be written by:



The electrolyte is zirconia stabilized by addition of calcium oxide (or others oxides MgO , Y_2O_3), which makes electrolyte resistant to thermal shock. The emf of a galvanic cell is described by the relation:

$$-4FE = RT \ln \frac{P_{O_2}}{P_{O_2(Ref.)}} \quad (3)$$

where: F – the Faraday constant ($96487 J \cdot V^{-1}$), E – the electromotive force of the cell (V), R – the universal gas constant ($8.3143 J \cdot K^{-1}$), T – the absolute temperature, P_{O_2} – oxygen partial pressure above liquid copper (bar), $P_{O_2(Ref.)}$ – oxygen partial pressure in reference electrode (bar).

Oxygen partial pressure in the reference electrode can be fixed by:

1. Using air ($P_{O_2(\text{Ref.})} \approx 0.21 \text{ bar}$) - [3, 6, 7, 10, 11, 16, 17, 18].
2. Employing pure oxygen ($P_{O_2(\text{Ref.})} = 1 \text{ bar}$) - [26, 23].
3. Using a mixture of Ni and NiO ($P_{O_2(\text{Ref.})} = \exp(-2 \cdot \Delta G_{NiO}^0 / (R \cdot T))$) - [5, 8, 12, 14, 20, 22, 24, 32].

Using experimental data, the equilibrium constant for the reaction (1) can be determined under condition that the standard state ($a_{[O]} = 1$) or the reference state ($\gamma_{[O]} = 1$) is defined:

$$K_{[O]} = \frac{a_{[O]}}{P_{O_2}^{1/2}} = \frac{x_{[O]} \cdot \gamma_{[O]}}{P_{O_2}^{1/2}} \quad (4)$$

Where: $a_{[O]}$ – the activity of oxygen dissolved in liquid copper, P_{O_2} – oxygen partial pressure above liquid copper, $x_{[O]}$ – oxygen mole fraction in liquid copper, $\gamma_{[O]}$ – the activity coefficient of oxygen dissolved in liquid copper.

Utilizing equations (3) and (4) the following relation is obtained:

$$-2FE = RT \ln a_{[O]} + \Delta G_{[O]} - \frac{1}{2} RT \ln P_{O_2(\text{Ref.})} \quad (5)$$

where: $\Delta G_{[O]}$ – the Gibbs free energy of the reaction (1).

The equation (5) has two unknown quantities ($a_{[O]}$, $\Delta G_{[O]}$), and therefore without additional assumption, that for a certain composition $a_{[O]} = 1$ or $\gamma_{[O]} = 1$, equation (5) is unsolvable.

Some authors e.g. [7, 23] tried to find another solution to this problem. They assumed that the chemical potential of oxygen in liquid copper is equal to half the standard chemical potential of oxygen in gaseous state ($\mu_{[O]} = 0.5\mu_{O_2}^0$). However under such an assumption, the Gibbs energy for reaction (1) is equal zero.

$$\Delta G_{[O]} = \mu_{[O]} - 0.5\mu_{O_2}^0 = 0 \quad (6)$$

II. THE CU-O MIXTURE AT INFINITE DILUTION AS A REFERENCE STATE FOR OXYGEN

In the case of infinite diluted Cu-O solution, equation (4) can be expressed as the following relation:

$$K_{[O]} = \frac{x_{[O]} \cdot \gamma_{[O]}}{P_{O_2}^{0.5}} \rightarrow \frac{x_{[O]}}{P_{O_2}^{0.5}} \text{ for } x_{[O]} \rightarrow 0 \quad (7)$$

In other words we assume that the activity coefficient of dissolved oxygen in liquid copper at infinite dilution is equal to 1. For such defined reference state, the equilibrium constant for reaction (1) is equal to limiting value of the ratio $x_{[O]}/P_{O_2}^{0.5}$ for $x_{[O]} \rightarrow 0$.

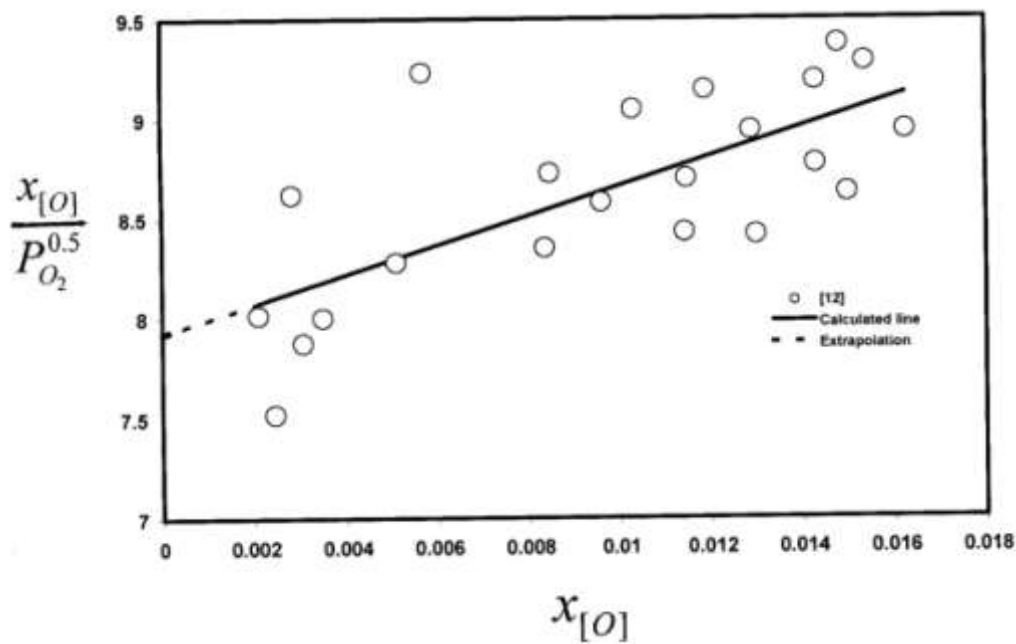


Fig.2. Variation of $x_{[O]}/P_{O_2}^{0.5}$ with mole fraction of oxygen dissolved in liquid copper. Points were estimated from data given in paper [12], and obtained at 1373 K. Solid line was calculated with the list square method and dashed line is extrapolation of $x_{[O]}/P_{O_2}^{0.5}$ ratio to $x_{[O]} = 0$.

Utilizing experimental data from several sources [1, 3, 5-12, 14-16, 18, 20-24], the equilibrium constants ($K_{[O]}$) for reaction (1) were estimated by extrapolation of a function $x_{[O]}/P_{O_2}^{0.5} = f(x_{[O]})$ to $x_{[O]} = 0$. Fig. 2 demonstrates an example of $K_{[O]}$ estimation. Obtained results are demonstrated in Fig 3. These results were used for calculation of the equilibrium constant as a function of temperature:

$$\ln K_{[O]} = \frac{9810}{T} - 5.085 \quad (8)$$

In these computations, experimental data from Ref. [1] were omitted. It was because these data have been produced by equilibrating liquid copper with $CO - CO_2$ mixtures with a low CO partial pressure. In such a situation it is very difficult to maintain constant ratio of P_{CO_2}/P_{CO} during experimental course. And relatively a small error in determination of CO pressure ($\Delta(P_{CO})$), can produce quite large error in generated oxygen pressure ($\Delta(P_{O_2}^{0.5})$):

$$\Delta(P_{O_2}^{0.5}) \approx K \frac{-\Delta(P_{CO})}{P_{CO}^2} \quad (9)$$

where: K is equilibrium constant for the reaction (10).



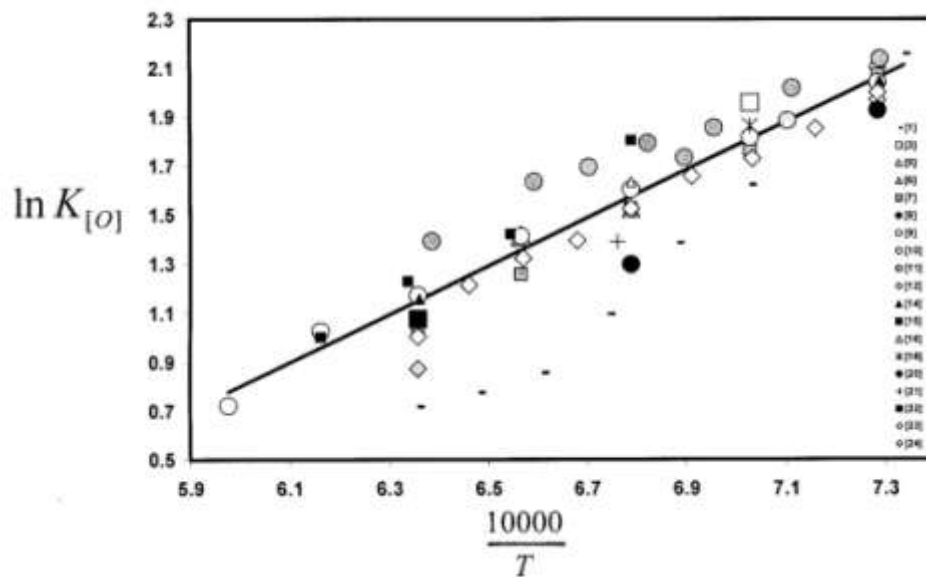


Fig. 3. Dependence of the equilibrium constant of reaction (1) versus temperature. The points were calculated with experimental data reported in papers [1, 3, 5-12, 14-16, 18, 20-24]. The solid line represents Eq. 8.

The equilibrium constant $K_{[O]}$ enables us to determine the Gibbs energy for the reaction (1):

$$\Delta G_{[O]}(J \cdot mol^{-1}) = -RT \ln K_{[O]} = -81560 + 42.276 \cdot T \tag{11}$$

The calculated values of $\Delta G_{[O]}$ enable to estimate the chemical potential of oxygen dissolved in liquid copper:

$$\mu_{[O]}^\infty = \Delta G_{[O]} + 0.5\mu_{O_2}^0 \tag{12}$$

Making use of $\mu_{O_2}^0$ given in data base of the HSC Chemistry 7 software and Eq. (11), we can determine a function describing $\mu_{[O]}^\infty$:

$$\mu_{[O]}^\infty(J \cdot mol^{-1}) = -60908 - 87.020 \cdot T \tag{13}$$

This function is very impotent in thermodynamic analyzes of copper refining processes. In consequence the chemical potential of oxygen in liquid copper can be expressed by the relation:

$$\mu_{[O]} = \mu_{[O]}^\infty + RT \ln a_{[O]} \tag{14}$$

Coupling Eq. (4) and Eq. (8) the following relation can be obtained:

$$\frac{9810}{T} - 5.085 = \ln \left(\frac{x_{[O]} \cdot \gamma_{[O]}}{P_{O_2}^{0.5}} \right) \tag{15}$$

Rearranging Eq. (15) and utilizing experimental data given in [23], the activity coefficient of oxygen dissolved in liquid copper can be determined:

$$\ln \gamma_{[O]} = \frac{9810}{T} - 5.085 - \ln \left(\frac{x_{[O]}}{P_{O_2}^{0.5}} \right) \quad (16)$$

For these computations experimental data given by Taskinen [23] were selected because:

1. Data are given as they were acquired from experiments.
2. This study was carried out for considerable concentration range of the oxygen dissolved in liquid copper and comprises homogeneous liquid as well as two phase area.
3. Experiments were conducted in the large temperature range (1375-1548 K).
4. Obtained results are internally consistent and show good reproducibility.

Computation results came as a surprise, because activity coefficient of oxygen does not show temperature dependence, which is demonstrated in Fig.4. Making use of the least square method and values computed with equation (16), the activity coefficient of oxygen was described by the relation:

$$\ln \gamma_{[O]} = -7.204 \cdot x_{[O]} \quad (17)$$

Utilizing the Gibbs-Duhem equation and relation (17), the activity coefficient of copper can be derived:

$$\ln \gamma_{Cu} = 7.204 \cdot (-x_{[O]} - \ln(1 - x_{[O]})) \quad (18)$$

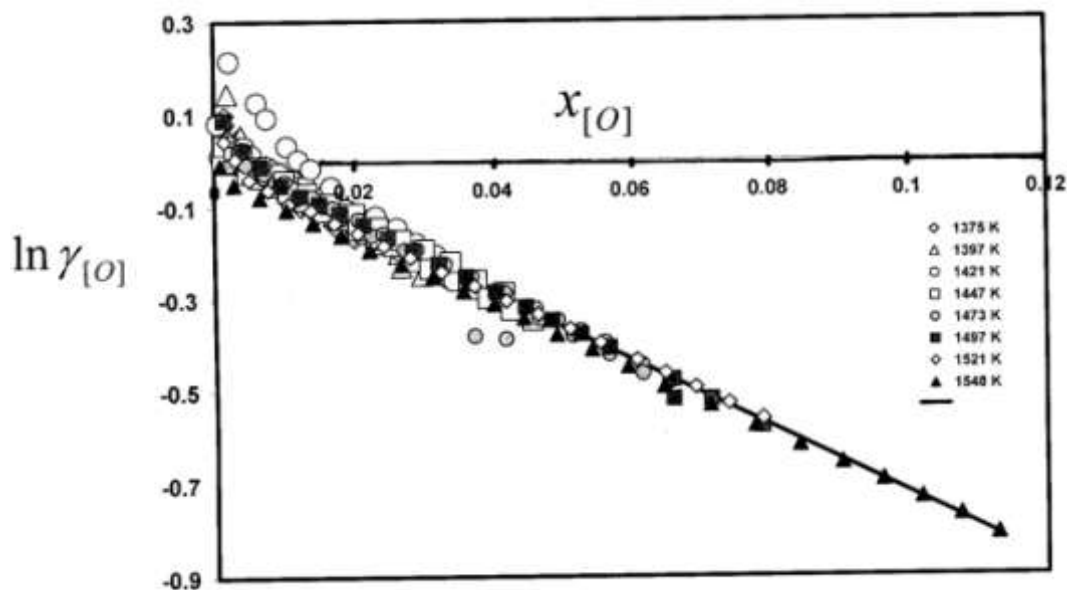


Fig. 4. The relation between activity coefficient of oxygen and its concentration in Cu-O solution. Points were calculated with experimental data given in paper [23]. Solid line represents equation (17).

Expanding $\ln(1 - x_{[O]})$ in series, and taking into account two first terms one can obtain:

$$\ln \gamma_{Cu} = 3.602 \cdot x_{[O]}^2 \quad (19)$$

Equation (19) is very good approximation of the relation (18) for small values of $x_{[O]}$, which is the case for homogenous Cu-O solution (see Fig. 4). For the same reason, the activity coefficient of copper is close to unity.

III. CONCLUSION

1. For thermodynamic description of liquid mixtures Cu-O, an infinite diluted solution was taken as the reference state for oxygen ($\gamma_{[O]} = 1$). As for copper the reference state as well as the standard state ($\gamma_{Cu} = 1, a_{[Cu]} = 1$) is pure liquid copper.
2. For such chosen the reference state for oxygen in liquid copper, its activity coefficient does not show temperature dependence (Fig. 4), which came as a surprise. One can argue for example that such behavior is because the equilibrium constant was determined with various author experimental data. And at the same time, the activity coefficients of the oxygen were computed with experimental data given by Taskinen [23]. It was found that the use of Taskinen data [23] for determination of the equilibrium constant as well as the activity coefficient of oxygen does not alter this picture.
3. However, the activity coefficient of oxygen depends on temperature in a hidden manner, because oxygen concentration in copper ($x_{[O]}$) is a function of temperature for fixed oxygen pressure above the melt Cu-O as can be seen in Fig. 5.

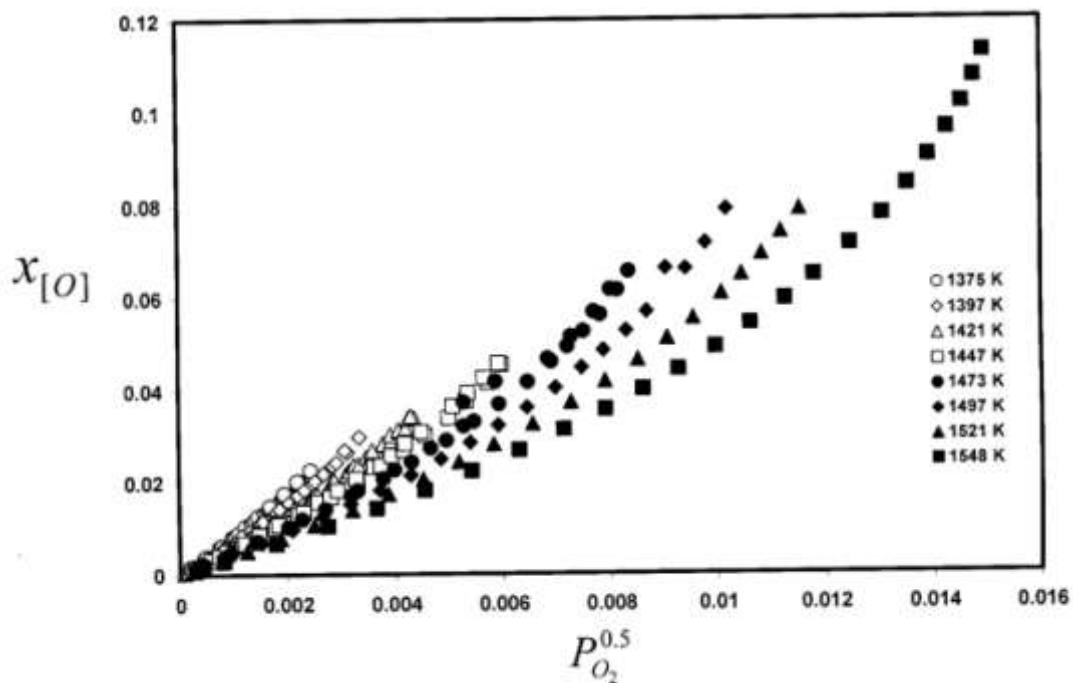


Fig. 5. Dependence of oxygen concentration in liquid copper on oxygen pressure above liquid Cu-O solution and temperature. Experimental points were taken from paper [23].

4. Values of the Gibbs energy of oxygen dissolution in liquid copper calculated with Eq. (11) are about 3 times smaller than those presented in Fig. 1 in the absolute numbers.

REFERENCES

- [1]. D.J. Girardi, C.A. Siebert, Trans. AIME 188 (1950) 1168-1170.
- [2]. E.S.Tankins, J.F.Erthal, M.K.Thomas, J.Electrochemical Soc. 112 (1965) 446-450.
- [3]. W. Pluschkell, H.-J. Engel, Z. Metallk. 56 (1965) 450-452.
- [4]. G.R. Belton, E.S. Tankins, Trans. AIME 233(1965) 1892-1898.
- [5]. T.C. Wilder, Trans. AIME 236 (1966) 1035-1040.
- [6]. W.A. Fischer, W. Ackermann, Arch. Eisenhüttenwes. 37 (1) (1966) 43-47.
- [7]. W. Stichel: Doctor-Ingenieur Dissertation, Elektrochemische Gleichgewichtsmessungen im System Kupfer-Silber-Sauerstoff, Technischen Universität Berlin, Berlin (1967).
- [8]. R.J. Freuhan, F.D. Richardson, Trans. TMS-AIME 5 (1969)1721-1726.
- [9]. . Osterwald, G. Reimann, W. Stichel, Z. physic. Chem. Neue Folge, 66 (1969)1-7.
- [10]. C.R. Nanda, G.H. Geiger, Metall. Trans., 1(1970)1235-1243.
- [11]. M.M.A. El-Naggar, N.A.D. Parlee, Metall. Trans., 1(1970) 2975-2977.
- [12]. K.T. Jacob, J.H.E. Jeffes, Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.), 80(1971)C32-C41.

- [13]. W.T. Thompson, P. Tarassoff, *Can. Metall. Q.*, 10(1971)315-321.
- [14]. A.D. Kulkarni, *Metall. Trans.*, 4(1973)1713-1721.
- [15]. H.P. Seow, A.K. Biswas, *Proc. Australas. Inst. Min. Metall.*, 245(1973)39-45.
- [16]. L.-I. Staffansson, L. Bentell, I. Svensson, *Scand. J. Metallurgy*, 3(1974)153-157.
- [17]. Z. Moser, K. Fitzner, *Rudy Metale*, 20(1975)510-513.
- [18]. Z. Moser, K. Fitzner, *Bull. Acad. Pol. des Sci., Ser. Sci. Techn.*, 24(1976)215-220.
- [19]. D. Janke, *Z. Metallkde.*, 69(1978)302-307.
- [20]. K. Fitzner, Z. Moser, *Metals Tech.*, 6(1979)273-275.
- [21]. M.G. Frohberg, F. Puchi, *Erzmetall*, 33(1980)264-270.
- [22]. N. Kemori, I. Katayama, Z. Kozuka, *Trans. JIM*, 21(1980)276-284.
- [23]. P. Taskinen, *Acta Polytech. Scand. Chem. Metall. Ser.*, 145(1981)1-45.
- [24]. Y. Kayahara, K. Ono, T. Oishi, J. Moriyama, *Trans. JIM*, 22(1981)493-500.
- [25]. R. Schmid, *Metall. Trans. B*, 14B(1983)473-481.
- [26]. P. Taskinen, *Scand. J. Metall.*, 13(1984)75-82.
- [27]. J.P. Neumann, T. Zhong, Y.A. Chang, *Bulletin of Alloy Phase Diagrams*, 5(1984)136-140.
- [28]. Y.A. Chang, K. Fitzner, Zhang Min-Xian, *Prog. Mater. Sci.*, 32(1988)97-259.
- [29]. B. Hallstedt, D. Risold, L.J. Gauckler, *J. Phase Equilib.*, 15(1994)483-499.
- [30]. A.V. Kosenko, G.A. Emel'chenko, *J. Phase Equilib.*, 22(2001)12-19.
- [31]. B. Hallstedt, L.J. Gauckler, *CALPHAD*, 27(2003)177-191.
- [32]. A. Vázquez, A. Romero, M.A. Garcia, S. González, J. Araujo, *Yazawa International Symposium, Metallurgical and Materials Processing, Principles and Technologies, Volume I: Materials Processing Fundamentals and New Technologies*, Edited By F. Kongoli, K.Itagaki, C. Yamauchi, H.Y Sohn, TMS (2003)187-196.
- [33]. R. Aune, P. Fredriksson, S. Seetharaman, *Yazawa International Symposium, Metallurgical and Materials Processing, Principles and Technologies, Volume I: Materials Processing Fundamentals and New Technologies*, Edited By F. Kongoli, K.Itagaki, C. Yamauchi, H.Y Sohn, TMS, (2003)119-130.
- [34]. L. Schramm, G. Behr, W. Löser, K. Wetzig, *J. Phase Equilib. Diffus.*, 26(2005)605-612.
- [35]. D. Shishin, S.A. Decterov, *CALPHAD*, 38(2012)59-70.

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