Journal of University of Science and Technology Beijing
Vol.7(2000), No.4, p.246

Metallurgy

Calculating Models of Mass Action Concentrations for Ni-Mn and Co-Mn Melts and Optimization of Their Thermodynamic Parameters

Jian Zhang

Metallurgy School, University of Science and Technology Beijing, Beijing 100083, China
(Received 2000-02-22)

Abstract: According to phase diagrams, measured activities as well as the coexistence theory of metallic melts structure involving compound formation, the calculating models of mass action concentrations for Ni-Mn and Co-Mn melts are formulated and their thermodynamic parameters are optimized. As a result, the calculated mass action concentrations agree well with the corresponding measured activities, showing that these models can reflect the structural characteristics of both Ni-Mn and Co-Mn melts.

Key words: activity; metallic melts; coexistence theory; mass action concentration

Ni, Mn and Co are important alloy elements in metallurgy. Mn is also a commonly used reducing agent of steelmaking. These three elements exist in great amount in the seabed mineral intergrowth of manganese concretion. Hence investigations on the thermodynamic properties of Ni-Mn and Co-Mn melts is not only useful for the improvement of alloying and deoxidizing technologies of the metals, but also is meaningful for the exploitation of seabed manganese resources. There are some works about the phase diagrams of Ni-Mn and Co-Mn systems [1–4]. Though their conclusions are not yet consistent, but they are reliable enough to serve as the clue for choosing the structural units of both Ni-Mn and Co-Mn melts. In the meantime, some results about thermodynamic properties of both Ni-Mn and Co-Mn melts are attained [5–7]. However, there aren't any models for calculating the activities of both Ni-Mn and Co-Mn melts yet, the calculated results of which not only agree with practice, but also are consistent with the law of mass action. This paper aims at formulating the calculating models of mass action concentrations for Ni-Mn and Co-Mn melts on the basis of reference data as well as the coexistence theory of metallic melts structure involving compound formation [8], so as to serve as the theoretical basis for further study.

1 Calculating Models

1.1 Ni-Mn melts

According to the phase diagram [1–4], there are several compounds Ni_3Mn, Ni_2Mn, NiMn, $NiMn_2$ and $NiMn_3$ formed in the solid state in this system. Comparison by different calculating models shows that at 1799.45–1 893 K there are Ni_3Mn, NiMn and $NiMn_3$ formed, while at 1 743–1 799.45 K the compounds formed are Ni_3Mn and NiMn. In this case the calculated results agree best with practice, and the calculation has the highest accuracy. From this, the structural units of these melts can be determined at $T>1\,799.45$ K as Ni, Mn as well as Ni_3Mn, NiMn and $NiMn_3$ compounds, while at $T<1\,799.45$ K as Ni, Mn atoms as well as Ni_3Mn and NiMn compounds.

Thus, assume (1) the composition of the melts as $b=\Sigma x_{Ni}$, $a=\Sigma x_{Mn}$, (2) the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Ni}$, $y=x_{Mn}$, $z_1=x_{Ni_3Mn}$, $z_2=x_{NiMn}$, $z_3=x_{NiMn_3}$, (3) the mass action concentration of every structural unit after normalization as $N_1=N_{Ni}$, $N_2=N_{Mn}$, $N_3=N_{Ni_3Mn}$, $N_4=N_{NiMn}$, $N_5=N_{NiMn_3}$, and (4) Σx is the sum of all equilibrium mole fractions. Then the following equations are given:

(1) Chemical equilibria

$3Ni_{(l)}+Mn_{(l)}=Ni_3Mn_{(l)}$,

$$K_1=\frac{N_3}{N_1^3N_2},\ N_3=K_1N_1^3N_2,\ z_1=K_1\frac{x^3y}{(\Sigma x)^3} \tag{1}$$

$Ni_{(l)}+Mn_{(l)}=NiMn_{(l)}$,

$$K_2=\frac{N_4}{N_1N_2},\ N_4=K_2N_1N_2,\ z_2=K_2\frac{xy}{\Sigma x} \tag{2}$$

$Ni_{(l)}+3Mn_{(l)}=NiMn_{3(l)}$,

$$K_3=\frac{N_5}{N_1N_2^3},\ N_5=K_3N_1N_2^3,\ z_3=K_3\frac{xy^3}{(\Sigma x)^3} \tag{3}$$

(2) Mass balance

$$N_1+N_2+N_3+N_4+N_5-1=0 \tag{4}$$

$$b=\Sigma x\,(N_1+3N_3+N_4+N_5)=x+3z_1+z_2+z_3 \tag{5}$$

$$a=\Sigma x\,(N_2+N_3+N_4+3N_5)=y+z_1+z_2+3z_3 \tag{6}$$

From equations (5) and (6),

$$aN_1-bN_2+(3a-b)N_3+(a-b)N_4+(a-3b)N_5=0 \quad (7)$$

Combining equation (4) with (7),

$$1-(a+1)N_1-(1-b)N_2=K_1(3a-b+1)N_1^3N_2+$$
$$K_2(a-b+1)N_1N_2+K_3(a-3b+1)N_1N_2^3 \quad (8)$$

Canceling of the terms K_3, N_5 and z_3 from the abovementioned equations at $T<1\,799.45$ K will give the calculating model of mass action concentrations for Ni-Mn melts without $NiMn_3$, hence further deduction is not needed.

The foregoing equations (1)–(8) are the calculating model of mass action concentrations for Ni-Mn melts, in which equations (1)–(3) and (4)–(7) are used for calculating the mass action concentrations, while equations (4) and (8) are applied for determining equilibrium constants by regression. As there aren't any suitable thermodynamic parameters for these melts yet, before using the model for calculation, these parameters should be determined firstly. For this reason, the following empirical equations from reference [5] for computing γ_{Ni} and γ_{Mn} at different temperatures are used:

T=1 743 K,

$$\lg\gamma_{Ni}=-1.751\,6a^2-0.375\,4a^3+1.294\,4a^4,$$
$$\lg\gamma_{Mn}=0.274\,2b^2-3.076\,4b^3+1.294\,4b^4 \quad (9)$$

T=1 793 K,

$$\lg\gamma_{Ni}=-1.665\,8a^2-0.156\,7a^3+0.929\,4a^4,$$
$$\lg\gamma_{Mn}=-0.042\,0b^2-2.321\,8b^3+0.929\,4b^4 \quad (10)$$

T=1 843 K,

$$\lg\gamma_{Ni}=-2.341\,9a^2+2.377\,0a^3-1.012\,7a^4,$$
$$\lg\gamma_{Mn}=-0.801\,8b^2+0.323\,5b^3-1.012\,7b^4 \quad (11)$$

T=1 893 K,

$$\lg\gamma_{Ni}=-1.750\,4a^2+1.239\,3a^3-0.467\,0a^4,$$
$$\lg\gamma_{Mn}=-0.825\,4b^2+0.006\,1b^3-0.467\,0b^4 \quad (12)$$

Regression by inserting $N_1=\gamma_{Ni}b$ and $N_2=\gamma_{Mn}a$ into equation (8) gives

T=1 893 K,

K_1=8.394 793, K_2=5.837 843, K_3=1.983 433,

(F=17 085.2, R=0.999 842 060);

T=1 843 K,

K_1=13.901 47, K_2=6.314 903, K_3=1.387 639,

(F=8 147.172, F=0.999 652 412);

T=1 793 K,

K_1=13.628 93, K_2=7.779 898,

(F=31 057.97, R=0.999 851 978);

T=1 743 K,

K_1=17.880 64, K_2=8.103 704,

(F=5 596.542, R=0.999 196 901).

From these the following equations can be given:

$$\lg K_1=\frac{6\,405.485}{T}-2.413\,2 \quad (r=0.913\,21),$$
$$\Delta G^{\ominus}=-122\,694.57+46.224T \text{ (J/mol)} \quad (1\,743\text{–}1\,893 \text{ K}) \quad (1a)$$

$$\lg K_2=\frac{3\,409.732}{T}-1.0357 \quad (r=0.965\,81),$$
$$\Delta G^{\ominus}=-65\,312.09+19.84T \text{ (J/mol)} \quad (1\,743\text{–}1\,893 \text{ K}) \quad (2a)$$

$$\lg K_3=\frac{-10\,825.117}{T}+6.015\,9 \quad (r=1),$$
$$\Delta G^{\ominus}=207\,351-115.23T \text{ (J/mol)} \quad (1\,799.45\text{–}1\,893 \text{ K}) \quad (3a)$$

Having both the calculating model and the thermodynamic parameters, the calculation of mass action concentrations for these melts can be easily performed.

1.2 Co-Mn melts

According to reference [4], at temperatures lower than 545℃, σ phase (the CoMn compound) forms in the Co-Mn system. In light of the opinion of Y. S. Kulikov: "If a cluster or covalent compound is stable in solid state, then its stability should strengthen during melting" [9]. CoMn formed in the solid state is capable to be retained in liquid state after melting. In view of the above, during the following data from reference [6]

T=1 743 K,

$$\lg\gamma_{Co}=-0.179\,0a^2-0.610\,6a^3+0.492\,4a^4,$$
$$\lg\gamma_{Mn}=-0.110\,1b^2-0.702\,4b^3+0.492\,4b^4 \quad (13)$$

T=1 793 K,

$$\lg\gamma_{Co}=-0.231\,6a^2-0.168\,9a^3-0.012\,2a^4,$$
$$\lg\gamma_{Mn}=-0.509\,3b^2+0.201\,4b^3-0.012\,2b^4 \quad (14)$$

T=1 843 K,

$$\lg\gamma_{Co}=-0.412\,4a^2+0.518\,4a^3-0.506\,6a^4,$$
$$\lg\gamma_{Mn}=-0.647\,9b^2+0.832\,5b^3-0.506\,6b^4 \quad (15)$$

T=1 893 K,

$$\lg\gamma_{Co}=-0.261\,6a^2-0.232\,3a^3+0.183\,3a^4,$$
$$\lg\gamma_{Mn}=-0.243\,4b^2-0.256\,6b^3+0.183\,3b^4 \quad (16)$$

being treated, it was found that at about 0.25 mole fraction of Co, there had been great errors in the calculated mass action concentrations relative to the measured activities. Further, according to the information of reference [1] about the possibility of formation of $CoMn_3$ and Co_2Mn in the Co-Mn alloy, comparison by calculating with different models showed that the model including Co, Mn atoms as well as CoMn and $CoMn_3$ metastable compounds gives the best agreement between the calculated and practical values. Thus the structural units of Co-Mn melts can be determined as Co, Mn atoms as well as CoMn and $CoMn_3$ metastable compounds.

From this, assume (1) the composition of the melts as $b=\Sigma x_{Co}$, $a=\Sigma x_{Mn}$, (2) the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Co}$, $y=x_{Mn}$, $z_1=x_{CoMn}$, $z_2=x_{CoMn_3}$, (3) the mass action concentration of every structural unit after normalization as $N_1=N_{Co}$, $N_2=N_{Mn}$, $N_3=N_{CoMn}$, $N_4=N_{CoMn_3}$, and (4)Σx is the sum of all equilibrium mole fractions. Then the following are given:

(1) Chemical equilibria

$Co_{(l)}+Mn_{(l)}=CoMn_{(l)}$,

$$K_1=\frac{N_4}{N_1N_2},\ N_3=K_1N_1N_2,\ z_1=K_1\frac{xy}{\Sigma x} \tag{17}$$

$Co_{(l)}+3Mn_{(l)}=CoMn_{3(l)}$,

$$K_2=\frac{N_5}{N_1N_2^3},\ N_4=K_2N_1N_2^3,\ z_2=K_2\frac{xy^3}{(\Sigma x)^3} \tag{18}$$

(2) Mass balance

$$N_1+N_2+N_3+N_4-1=0 \tag{19}$$

$$b=\Sigma x(N_1+N_3+N_4)=x+z_1+z_2 \tag{20}$$

$$a=\Sigma x(N_2+N_3+3N_4)=y+z_1+3z_2 \tag{21}$$

From equations (20) and (21),

$$aN_1-bN_2+(a-b)N_3+(a-3b)N_4=0 \tag{22}$$

Combining equation (19) with (22),

$$1-(a+1)N_1-(1-b)N_2=$$

$$K_1(a-b+1)N_1N_2+K_2(a-3b+1)N_1N_2^3 \tag{23}$$

Equations (17)–(23) are the calculating model of mass action concentrations for these melts. Similarly, there aren't any suitable thermodynamic parameters for these melts, hence, these parameters should be determined by optimization according to the equations for computing γ_{Co} and γ_{Mn} from reference [6], the measured activities from reference [7] as well as equation (23). The results are as follows:

T=1 843 K,

K_1=0.879 226 6, K_2=0.361 267 4,

(F=3 844.163, R=0.998 896 258);

T=1 793 K,

K_1=1.084 112, K_2=0.432 938 1,

(F=314 147.8, R=0.999 986 472);

T=1 050 K,

K_1=5.868 919, K_2=4.759 081,

(F=104.293 1, R=0.961 582 446 1).

Thus,

$$\lg K_1=\frac{1\,940.99}{T}-1.078\,85\ (r=0.997\,673\,2),$$

$$\Delta G^{\ominus}=-37\,178.907+20.665T\ \text{(J/mol)}\ (1\,050\text{–}1\,893\ \text{K}) \tag{17a}$$

$$\lg K_1=\frac{2\,688.728}{T}-1.8825\ (r=0.999\,539\,4),$$

$$\Delta G^{\ominus}=-51\,501.545+36.06T\ \text{(J/mol)}\ (1\,050\text{–}1\,893\ \text{K}) \tag{18a}$$

Having these thermodynamic parameters, calculation of the mass action concentrations for Co-Mn melts can accordingly be carried out.

2 Calculated Results and Discussion

2.1 Ni-Mn melts

By the use of equations (1)–(3), (5) and (6), the calculated N_{Ni} and N_{Mn} at different temperatures are compared respectively with the measured a_{Ni} and a_{Mn} from reference [5] as shown in **figure 1**. It is seen that irrespective of the variations of composition and temperature, the calculated and measured values agree excellently, showing that the calculating model can reflect the structural characteristics of these melts.

In order to have a full view of the variation of the structural units with composition for the melts, the calculated results of mass action concentrations for the melts at 1 743 and 1 893 K are respectively given in **figure 2**. From this figure it can be seen that at higher temperatures $NiMn_3$ exists in the melts, while at 1 743 K there isn't that metastable compound.

It is necessary to point out that the models including respectively (1) Ni, Mn, Ni_2Mn, NiMn and $NiMn_2$, (2) Ni, Mn, Ni_3Mn and NiMn, and (3) Ni, Mn, Ni_2Mn, NiMn and $NiMn_3$ *etc.*, have also been tested, and that considerably good agreement between the calculated and measured values have been obtained. However, their accuracy is a little worse than the preceding model, hence they are not selected in this paper. So in the

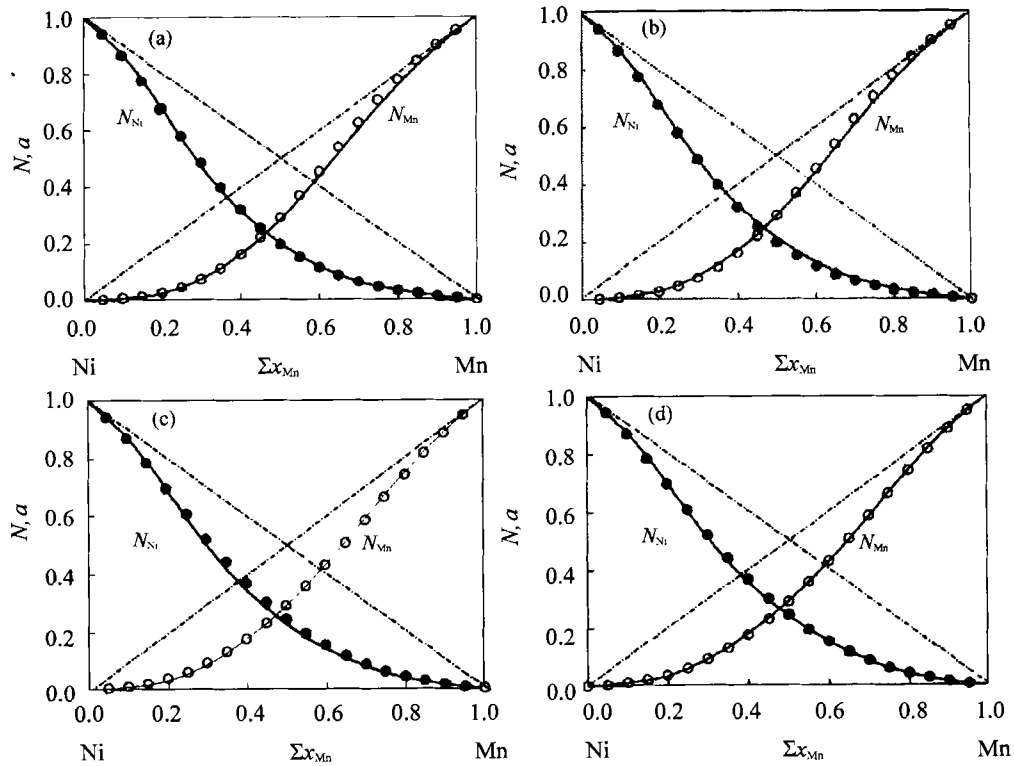

Figure 1 Comparisons of the calculated N_{Ni} and N_{Mn} (—) with the measured activities a_{Ni} and a_{Mn} (● and O) respectively at (a) 1 743, (b) 1 793, (c) 1 843, and (d) 1 893 K.

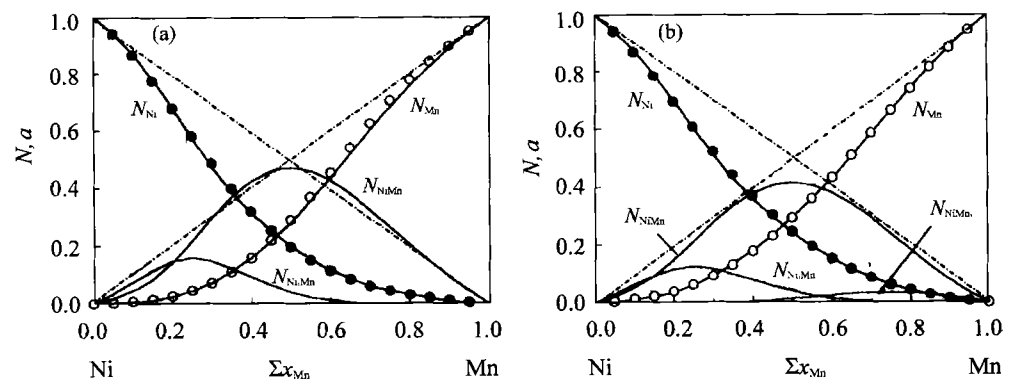

Figure 2 Variations of the calculated mass action concentrations of different structural units with Σx_{Mn} at (a) 1 743, and (b) 1 793 K.

course of the calculating model formulation, multifarious and repeated examination of different models in combination with the phase diagram is indispensable. In so doing, it is possible to reduce unreasonable determinations of the structural units.

2.2 Co-Mn melts

In accordance with equations (17), (18), (20) and (21), the calculated N_{Co} and N_{Mn} at different temperatures are compared respectively with the measured activities a_{Co} and a_{Mn} from reference [6] as showing in **figure 3**. The agreement between the calculated and practical values at different compositions and temperatures is considerably good, confirming that the aforementioned model can reflect the structural reality of the melts. **Figure 4** is an illustration of the variation of calculated mass action concentrations of all structural units with Σx_{Mn} for Co-Mn melts at 1 893 K.

3 Conclusions

(1) Based on the phase diagrams, measured activities as well as the coexistence theory of metallic melts structure involving compound formation, the calculating models of mass action concentrations for Ni-Mn and Co-Mn melts are formulated and their thermodynamic parameters are optimized. Moreover, these models can reflect the structural characteristics of both Ni-Mn and Co-Mn melts.

(2) The optimized thermodynamic parameters are

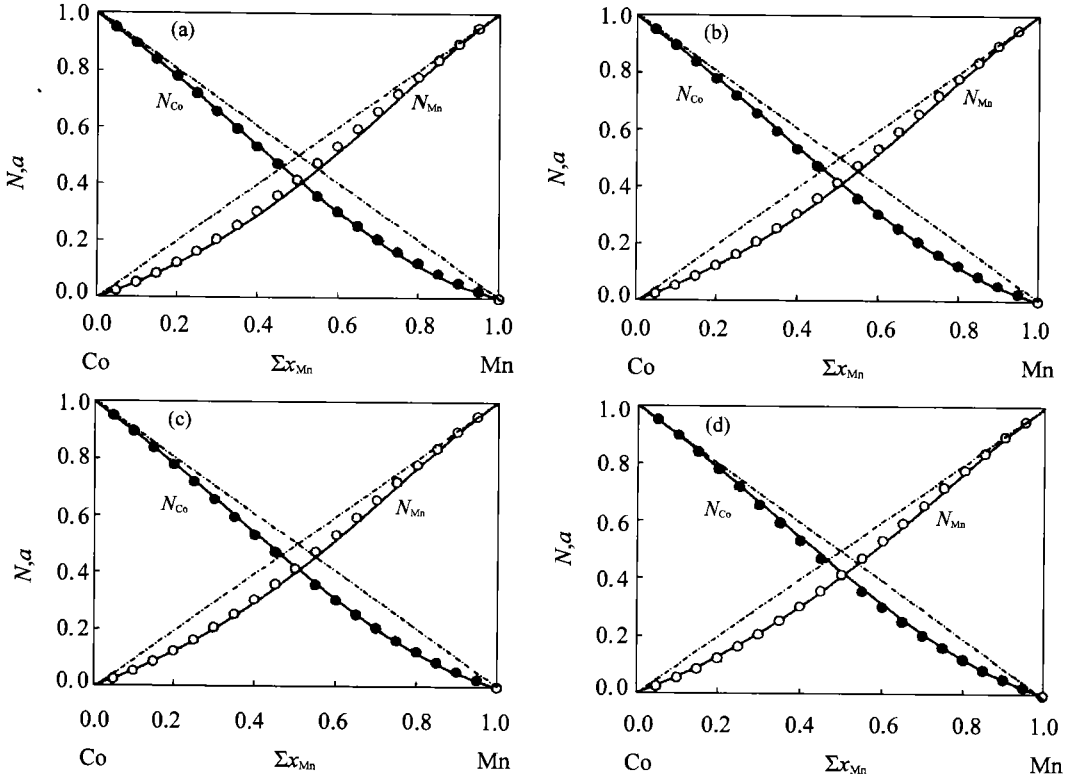

Figure 3 Comparisons of the calculated N_{Co} and N_{Mn} (—) with the measured activities a_{Co} and a_{Mn} (●, O) respectively at (a) 1 743, (b)1 793, (c) 1 843, and (d) 1 893 K.

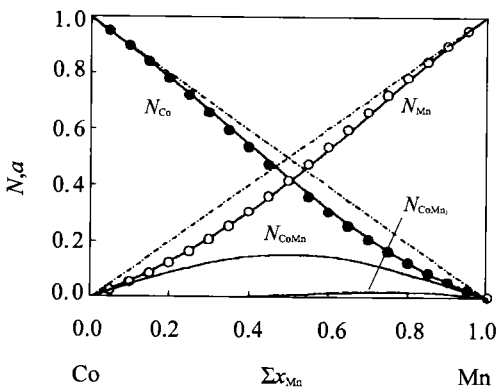

Figure 4 Variations of the calculated mass action concentrations of different structural units with Σx_{Mn} for Co-Mn melts at 1 893 K.

listed as follows.

For Ni-Mn melts:

T=1 743–1 893 K,

$\Delta G^{\ominus}_{NiMn}$=−122 694.57+46.224$T$ (J/mol);

T=1 743–1 893 K,

$\Delta G^{\ominus}_{NiMn}$=−65 312.09+19.84$T$ (J/mol);

T=1 799.45–1 893 K,

$\Delta G^{\ominus}_{NiMn_3}$=207 351−115.23$T$ (J/mol).

For Co-Mn melts:

T=1 050–1 893 K,

$\Delta G^{\ominus}_{CoMn}$=−37 178.907+20.665$T$ (J/mol);

T=1 050–1 893 K,

$\Delta G^{\ominus}_{CoMn_3}$=−51 501.545+36.06$T$ (J/mol).

References

[1] M. Hansen, K. Anderko: *Constitution of Binary Alloys*. McGraw-Hill, 1958, p.480; p.939.

[2] R. Hultgren, P. D. Desai, D.T. Hawkins, *et al.*: *Selected Values of the Thermodynamic Properties of Binary Alloys*. American Society for Metals, Metals Park, Ohio, 1973, pp. 1132–1138.

[3] T. B. Massalski, T. L. Murry, L. N. Bennet, *et al.*: *Binary Alloy Phase Diagrams, Vol.2*. American Society of Metals, Metals Park, Ohio, 1986, p.1573.

[4] H. Baker, H. Okamoto, S. D. Henry, *et al.*: *ASM Handbook, Vol. 3, Alloy Phase Diagrams*. The Materials Information Socety, Materials Park, Ohio, 1992, pp.2143-2286.

[5] Mukai Kusuhiro, Wasai Yoshimi, Funatsu Koji, *et al.*: *Japan Inst. Metals*, 46(1982), No.9, p.870.

[6] Mukai Kusuhiro, Funatsu Koji, Wasai Kyoko *et al.*: *Japan Inst. Metals*, 46(1982), No.9, p.863.

[7] M Venkataraman, J. P. Hajra: *Scripta Metallurgica*, 16(1982), No.9, p.1043.

[8] J. Zhang. *Special Steel* (in Chinese), 15(1994), No.6, p.43.

[9] I. S. Kulikov: [in] *Proceedings of 5th Conference of Phsycochemical Principles of Steelmaking*. Press Academy of Sciences of SSSR, Mosco, 1961, pp.5–10.