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Journal of Alloys and Compounds 234 (1996) 125–129

Journal of ALLOYS AND COMPOUNDS

Regularities of melting behavior of some binary alloy phases. Part 1. Criteria for congruent and incongruent melting

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Received 10 November 1994; in final form 2 May 1995

Abstract

Regularities of lattice stability and melting type (congruent or incongruent melting) of Laves phase, CsCl-type and $AuCu_3$-type alloy phases are investigated by the pattern recognition method using atomic parameters. It has been found that the congruent and incongruent melting alloy phases are distributed in different regions of a four-dimensional space spanned by R_A/R_B, Z_A, Z_B and $X_B - X_A$, or its subspaces. Based on the regularities found, the criteria for the melting types of the above-mentioned alloy phases have been obtained.

Keywords: Melting types; Alloy phases; Pattern recognition

1. Introduction

Although the prediction of phase diagrams of alloy systems is a very difficult problem, considerable progress towards this goal has been made by some semi-empiricial methods. Miedema's model enables us to predict binary compound formation between metallic elements [1]. Villar proposed some criteria for the classification of alloy phase diagrams [2]. Hulliger and Villars [3] and Chelikowsky and Anderson [4] have found some regularities in the melting points of alloy phases. The present authors have investigated the regularities of crystal-type alloy phases by the pattern recognition method using Z_A, Z_B (number of valence electrons per atom of the constituent elements), R_A, R_B (metallic radii of constituent elements), X_A, X_B (electronegativities of the elements), or ϕ_A, ϕ_B (the work functions of constituent elements, which are approximately linear functions of electronegativities of elements) or their functions as features, and found that every kind of crystal-type alloy phase is distributed in a definite region (the so-called formability region of this crystal-type) in some multi-dimensional space spanned by the above-mentioned atomic parameters or their functions. Using the regularity found, a series of new alloy phases ($EuNi_2$, $EuFe_2$, $LaPd_5$, etc.) have been predicted and synthesized [5,6].

There are, however, several difficult problems still unsolved by phase diagram prediction. Among them is the prediction of melting behavior. The prediction of the melting type (congruent or incongruent melting) and the melting point of alloy phases is of paramount importance.

In this work, some important crystal types (Laves phase, CsCl-type, $AuCu_3$-type) of binary alloy phases have been selected in order to find the regularities of melting types.

2. Model and method of computation

The incongruent melting process (or peritectic reaction) involves the transformation of one crystal lattice into another crystal lattice and a liquid phase. The relative stabilities of these two lattices (or the difference between the lattice energies) should have a great influence on the occurrence of incongruent melting. It is well known that there are three factors affecting the lattice energy of alloy phases: the energy band factor (depending on the numbers of valence electrons, Z_A, Z_B); the charge-transfer factor (depending on the difference between the electronegativities of the constituent elements, $(X_B - X_A)$); and the geometrical factor (depending on the ratio of metallic radii of elements, (R_A/R_B)). So, it is reasonable to use the atomic parameters R_A/R_B, Z_A, Z_B and $X_B - X_A$ in

SSDI 0925-8388(95)01962-6

order to find the criteria for the melting types of alloy phases. In this work we use these parameters to span a four-dimensional space, and find semi-empirical rules from known experimental data by pattern recognition in this space. The semi-empirical rules found can be used for computerized prediction. The pattern recognition methods used here are computational methods mapping the patterns in multi-dimensional space to two-dimensional figures, along with some technique for mapping the two-dimensional figures back to original multi-dimensional space [7]. Sometimes, certain subspaces can be also used to find regularities. For example, a (R_A/R_B)-$(X_B - X_A)$ diagram is often useful for the study of some regularities chiefly related to the geometrical factors.

All data of crystal types and melting behavior of alloy phases used in this paper are quoted from the handbook *Binary Alloy Phase Diagrams*, edited by Massalski [8]. The electronegativity data used are Pauling scale values; the metallic radii data are Teatum's values [9].

3. Phase stability and melting types of Laves phases

As is well known, the geometrical factor plays an important role in the lattice stability and formability of Laves phases. Based on purely geometrical considerations the optimal R_A/R_B (making the closest packing and the higest lattice stability) should be 1.225. But this argument neglects the fact that charge transfer (dominated by electronegativity difference) may change the effective radii of the atoms of the constituent elements. So the optimal R_A/R_B (where R_A and R_B are unchanged metallic radii) should deviate from 1.225 for the alloy phases which $|X_B - X_A| \gg 0$. Fig. 1 illustrates the distribution of known Laves phases in the (R_A/R_B)-$(X_B - X_A)$ diagram. It can be seen that the formability region of Laves phases is located near $R_A/R_B = 1.225$ at $X_B - X_A = 0$, but shifts to higher R_A/R_B values at $X_B \gg X_A$.

Laves phases include three intimately related crystal-types, i.e. C14 ($MgZn_2$-type), C15 ($MgCu_2$-type) and C36 ($MgNi_2$-type). The (R_A/R_B)-$(X_B - X_A)$ diagram does not succeed in classifying these three types of crystal, since their relative stabilities are strongly dependent on the number of valence electrons Z_A and Z_B. However, these three crystal-types can be differentiated by pattern recognition in the four-dimensional space spanned by Z_{avg}, $|\Delta Z|$, R_A/R_B and $X_B - X_A$ (where $Z_{avg} = (Z_A + Z_B)/2$; $|\Delta Z| = |Z_A - Z_B|$). For example, Fig. 2 illustrates a linear mapping of the distribution of C15 and C14 Laves phases formed by two transition elements in the above-mentioned multi-dimensional space by the PLS (Partial Least Squares Regression) method. It can be seen that C14 phases are distributed in a band-like region located between two regions of C15 phases. The criterion for C14 phase formation is: $21.25 < 8.04(R_A/R_B) + 2.22Z_{avg} + 0.30|\Delta Z| + 0.37X_B/X_A < 23.40$.

It is found that the transition between C15 and C14 is strongly dependent on Z_A and Z_B. This may be the result of a Fermi-surface–energy-zone interaction effect, as proposed by Wallace and Craig [10].

The melting type of Laves phases (congruent or incongruent melting) can be investigated in the (R_A/R_B)-$(X_B - X_A)$ diagram or in the four-dimentional space spanned by (R_A/R_B), $(X_B - X_A)$, Z_A and Z_B. For example, Fig. 3 illustrates some (R_A/R_B)-$(X_B - X_A)$

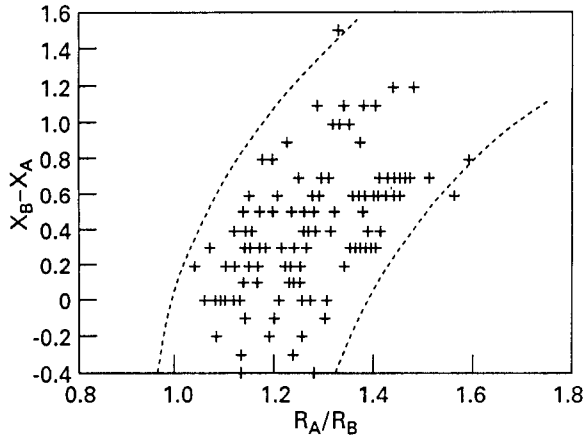

Fig. 1. The formability region of Laves phases in the (R_A/R_B)-$(X_B - X_A)$ diagram.

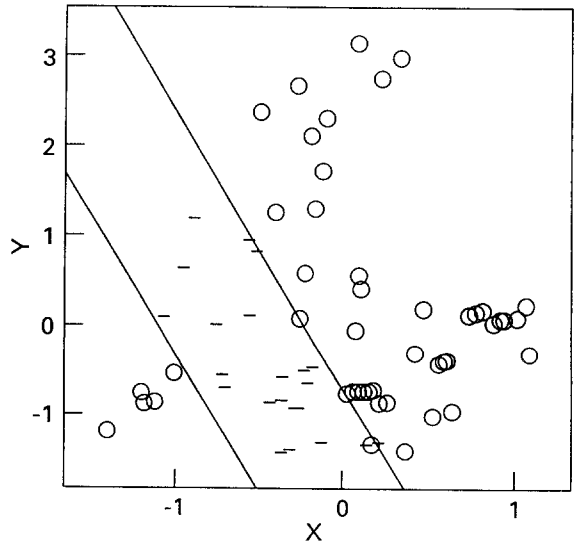

Fig. 2. Distribution of C14 and C15 phases formed between two transition elements: — C14 Laves phases; ○ C15 Laves phase. $X = 4.52(R_A/R_B) + 0.67Z_{avg} + 1.04(X_B - X_A) + 0.26|\Delta Z| - 11.7$; $Y = 0.82(R_A/R_B) + 1.15Z_{avg} - 1.29(X_B - X_A) - 0.13|\Delta Z| - 6.76$.

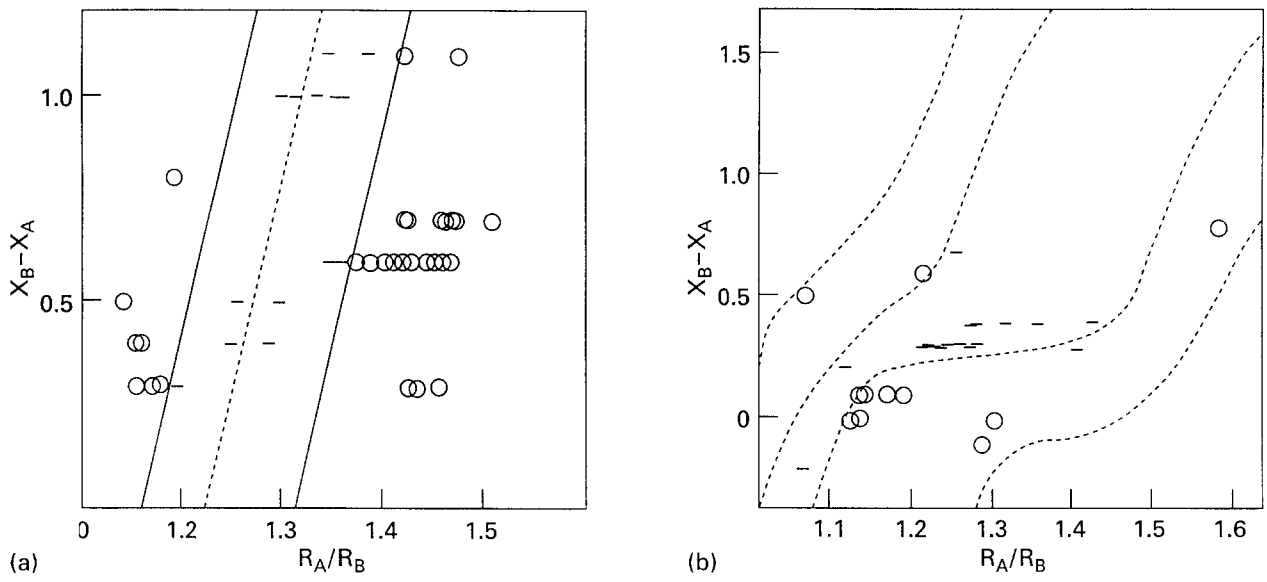

Fig. 3. Classification of Laves phases according to their melting type by the (R_A/R_B)–$(X_B - X_A)$ diagram: — congruently melted; ○ incongruently melted. (a) C15 phases formed with two transition elements; (b) C15 phases formed with one transtion and one non-transtion element.

diagrams for the classification of C15 Laves phase according to their melting types, and Fig. 4 gives an example of the classfication of Laves phases according to their melting type by the PCA (Principal Component Analysis) method in four-dimensional space.

Based on the regularities found in Figs. 3 and 4, the criteria for the congruent and incongruent melting types can be obtained. For example, the criterion for congruent melting C15 phases formed with two transition elements is as follows: $12.6 < 10.9(R_A/R_B)-(X_B - X_A) < 14.3$.

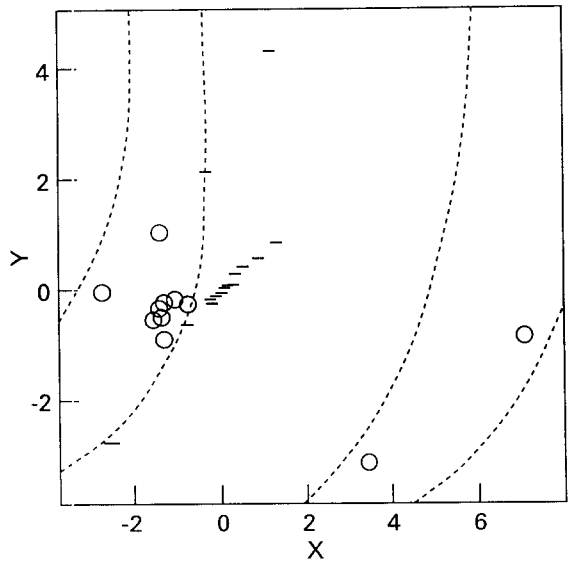

Fig. 4. Classification of C15 Laves phases between transition and non-transition elements in four-dimensional space (linear mapping by PCA method): — congruently melted; ○ incongruently melted. $X = 0.547(R_A/R_B) + 0.244(X_B - X_A) - 0.342Z_A + 0.724Z_B$; $Y = 0.321(R_A/R_B) + 0.615(X_B - X_A) - 0.364Z_A - 0.622Z_B$.

It can be seen from Figs. 3 and 4 that the incongruent melting Laves phases usually distribute near the borders of the formability region of Laves phases, while the congruent melting phases distribute near the middle line (or curve) in the formability region. This is easily understandable since the middle curve may correspond to the optimal radius ratio by which the Laves phases can fit the ideal lattice without significant internal strain, thereby exhibiting a higher melting point and congruent melting; however, the Laves phases distributed far from the optimal curve can not fit the ideal lattice without significant internal strain and show a tendency to remove this strain, exhibiting a lower melting point and peritectic decomposition if the neighboring region contains some highly stable crystal-type alloy phase.

Fig. 5 illustrates the relation between neighboring regions of some stable crystal-types and the occurrence of incongruent C15 phases in a linear mapped $(Z_B - Z_A)$–(R_A/R_B) diagram. With R_A/R_B increasing from 1.3 to 1.5 the Laves phases become unstable, melt incongruently, and finally break down; the AB_3-type phase is the stable one.

If the deviation of the melting point from the linear average of the melting points of constituent elements, ΔT, is used as a criterion of lattice stability against melting, the distribution of high positive ΔT alloy phases is also instructive. The C15 phases with high positive ΔT are distributed in the central part of the

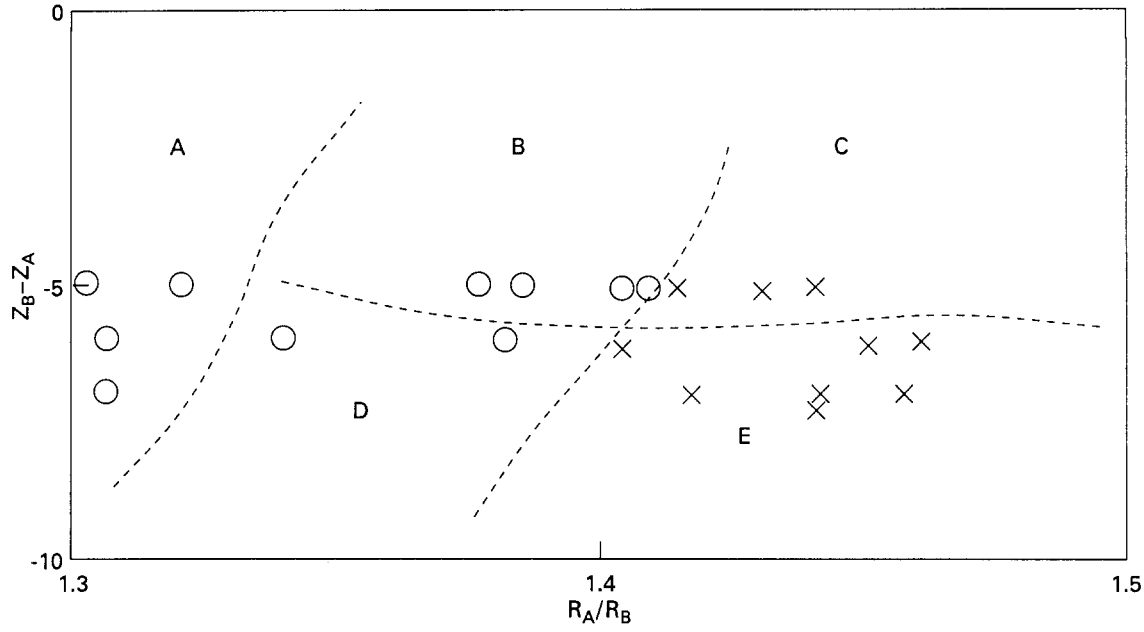

Fig. 5. The relationship between melting behaviors of C15-type phases and neighboring $NbBe_3$-type or $PuNi_3$-type phases regions. ○ congruently melted; × incongruently melted. (A) only congruently melted C15 phases; (B) congruently melted C15 phases and incongruently melted $PuNi_3$-type phases; (C) incongruently melted C15 phases and congruently melted $PuNi_3$-type phases; (D) congruently melted C15 phases and incongruently melted $NbBe_3$-type phases; (E) incongruently melted C15 phases and congruently melted $NbBe_3$-type phases.

formability region of C15 phases, while those with low or negative ΔT are distributed near the border of the formability region.

4. Melting types of $AuCu_3$-type and CsCl-type alloy phases

The same four-dimensional space spanned by R_A/R_B, $(X_B - X_A)$, Z_A and Z_B in the form of a (R_A/R_B)–$(X_B - X_A)$ diagram can also be used for the classification of CsCl and $AuCu_3$-type alloy phases according to their melting types. Fig. 6 illustrates such a classification. It can be seen that the separation of congruent and incongruent melting phases is clear-cut, but the distribution regularity of CsCl-type alloy phases is very different from that of Laves phases. The incongruent melting CsCl-type phases are distributed in the region where $(X_B - X_A)$ is almost zero, while the congruent melting CsCl-type phases are found in the region with large $|X_B - X_A|$. These facts can be explained as follows: the geometrical factor does not have a strong

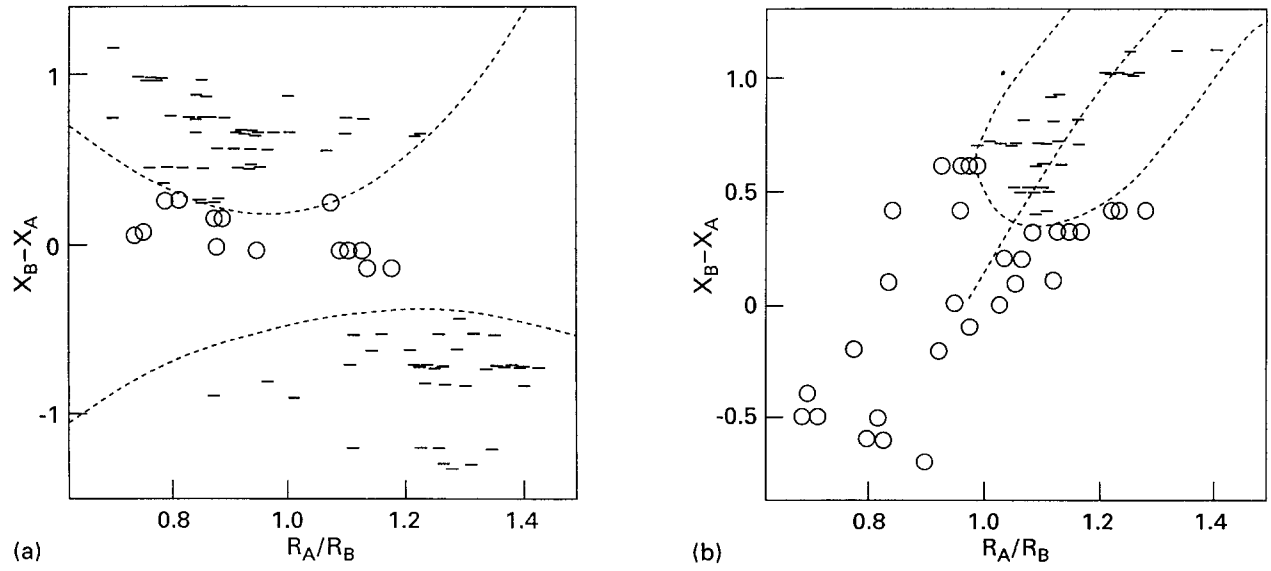

Fig. 6. classification of CsCl and $AuCu_3$-type alloy phases according to their melting types in the (R_A/R_B)–$(X_B - X_A)$ diagram: — congruently melted; ○ incongruently melted. (a) CsCl-type alloy phase; (b) $AuCu_3$-type alloy phases.

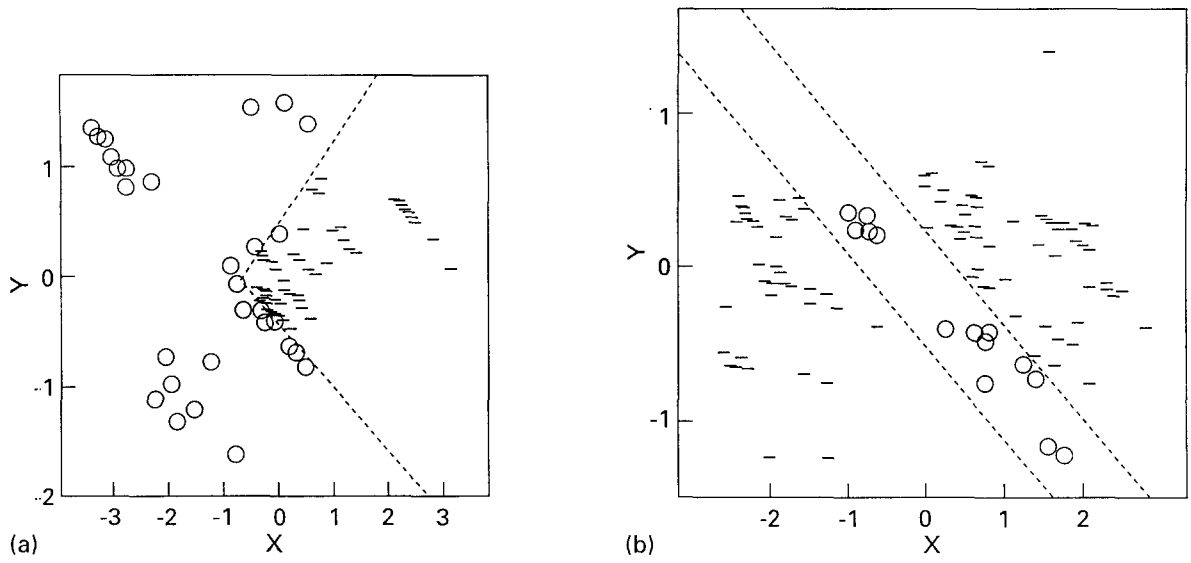

Fig. 7. Classification of CsCl-type and $AuCu_3$-type phases according to their melting types in four-dimensional space (linear mapping by PCA method): — congruently melted; ○ incongruently melted. (a) $AuCu_3$-type phases; $X = 4.02(R_A/R_B) + 1.47(X_B - X_A) - 0.12Z_A - 0.15Z_B - 5.54$, $Y = -2.98(R_A/R_B) - 0.45\ (X_B - X_A) - 0.56Z_A + 0.23Z_B + 4.08$. (b) CsCl-type phases; $X = -2.95(R_A/R_B) + 0.85(X_B - X_A) + 0.15Z_A + 0.09Z_B + 2.1$, $Y = -2.96(R_A/R_B) + 1.09\ (X_B - X_A) - 0.06Z_A + 0.22Z_B - 3.7$.

influence, the charge transfer factor dominating the lattice stability for this type of phase. Therefore, the formability region of CsCl-type phases covers a wide range of R_A/R_B, and the phases with large $|X_B - X_A|$ exhibit higher lattice stability and congruent melting.

Fig. 7 illustrates the results of the linear mapping of the classification of these two types of phase according to their melting type in the four-dimensional space. Based on the regularities found in Figs. 6 and 7, the criteria for melting type may be obtained. For example, the criterion for incongruent CsCl-type phases can be expressed as follows: $2.0 < 1.22(R_A/R_B) + 1.59(X_B - X_A) + 0.03Z_A + 0.27Z_B < 2.6$

The criterion of the congruently melting $AuCu_3$-type phases is the following: $-5.774(R_A/R_B) - 1.502(X_B - X_A) - 0.467Z_A + 0.121Z_B + 7.697 < 0$ and $-0.818(R_A/R_B) + 0.306(X_B - X_A) - 0.618Z_A + 0.312Z_B + 1.685 > 0$

References

[1] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema and A.K. Niessen, in F.R. de Boer and D.G. Pettifor (eds), *Cohesion and Structure*, Vol. 1, North-Holland, Amsterdam, 1988, pp. 1–101.

[2] P. Villars, *J. Less-Common Met., 92* (1983) 215.

[3] F. Hulliger and P. Villars, *J. Alloys Comp., 197* (1993) 197.

[4] J.R. Chelikowsky and K.E. Anderson, *J. Phys. Chem. Solids, 48* (1987) 197.

[5] Chen Nianyi, *Anal. Chim. Acta, 210* (1988) 175.

[6] Ning Yuantao, Zhou Xinmin and Chen Nianyi, *J. Less-Common Met., 167* (1988) 197. [7] O. Strouf, *Chemical Pattern Recognition*, Reserach Studies Press, Letchworth, Hertfordshire, UK, 1986, pp. 13–104.

[8] T.B. Massalski, *Binary Alloy Phase Diagrams, American Society for Metals*, Metal Park, 1986.

[9] W.B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, New York, 1972.

[10] W.E., Wallace and R.S. Craig, in R.S. Rudman and J. Stringer (eds.), *Phase Stability in Metals and Alloys*, McGraw-Hill, New York, 1967, p. 25.