FORMABILITY AND CRYSTAL TYPES OF RARE EARTH-SILICON CONTAINING TERNARY COMPOUNDS①

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ABSTRACT

By pattern recognition-chemical bond parameter method, the formability of $NaZn_{13}$ type and $BaCd_{11}$ type ternary compounds in RE-M-Si (RE = La - Lu, M is any metallic element) systems has been investigated. And the existence of unknown ternary compounds is predicted by the pattern recognition method.

Key words: RE-M-Si system ternary compounds crystal type

1 INTRODUCTION

In recent years, the investigation on the ternary compounds in RE-M-X systems (RE is rare earth element, M is any metallic element, X is metalloid) becomes rather active due to the potentiality of these compounds (such as $Nd_2Fe_{14}B$) used as functional materials. By pattern recognition-chemical bond parameter method[1, 2], it may be possible to predict the formability of these compounds, useful for new functional materials exploration. In this paper, results of the investigation about the formability of ternary compounds with $NaZn_{13}$ and that with $BaCd_{11}$ crystal-type are described and discussed.

2 PATTERN RECOGNITION-CHEMICAL BOND PARAMETER METHOD

Pattern recognition- chemical bond parameter method, proposed in our previous works[1, 2], is especially suitable for the computerized prediction of the crystal-type of intermetallic compounds[3]. It has been found that if a multi-dimensional space spanned by the parameters Z_1, Z_2 (valence electron numbers), R_1, R_2 (metallic radii) and X_1, X_2 (electronegativities) or their functions, then all the intermetallic compound with a definite crystal-type and valence-type distribute within a special region in this space. Based on this regularity, an expert system has been built in our work, and has been successfully applied to predict the existence and crystal-type of a series of unknown intermetallic compounds. Some rare earth intermetallic compounds have been synthesized and discovered by this prediction[3, 4]. In order to extend the application of this method and make it more reliable, we have modified this method in the following ways.

(1) To apply this method to predict the ternary compounds in the RE-M-Si systems. Here Si is a fixed component, so that only the parameters Z, R and X (electronegativity difference) of RE and M are used. Since the valency of RE is 3, only four chemical bond parameters Z_M, R_{RE}, R_M and ΔX are used to span the multi-dimensional space for pattern recognition.

(2) In our previous works, it is usual to use one figure of projection having best

① Financilly Supported by the National Natural Science Foundation of China; Manuscript received November 20, 1992

separation to predict unknown compound, without accounting the distortion in dimension reduction. In this work, we use several figures in PCA method (the number of coordinates equals the dimension of the original space) together to determine the formability of an unknown compound. If a ternary system locates in the regions with compound formation (or without compound formation) in all figures, it can be concluded that this compound is existent or nonexistent. In some ambiguous cases, KNN method is used to predict with lower reliability.

3 COMPUTATION RESULT

Fig. 1 are the projections of multi-dimensional space for prediction of the formability of $NaZn_{13}$ type compounds. It can be seen that each projection figure has the region of formation of $NaZn_{13}$ type compounds. If the region of formation can be considered as hypervolumes and transform the parameters Z_M, ΔX, R_M and R_{RE} as follows.

$$x_1 = (Z_M - 9.00) / 1.50$$
$$x_2 = (\Delta X - 0.70) / 0.25$$
$$x_3 = (R_M - 1.29) / 0.06$$
$$x_4 = (R_{RE} - 1.79) / 0.05$$

So the region can be described by simultaneous equations of non-equality.

$$\left.\begin{array}{l} -1.15 \leqslant 0.25x_1 + 0.69x_2 + 0.55x_3 + 0.39x_4 \leqslant 0.70 \\ 0.61 < 0.88x_1 + 0.13x_2 - 0.41x_3 - 0.21x_4 \leqslant 1.21 \\ 0.25 \leqslant -0.11x_2 - 0.48x_3 + 0.87x_4 < 0.99 \\ -0.20 < 0.40x_1 - 0.70x_2 + 0.55x_3 + 0.21x_4 < 0.51 \end{array}\right\} \quad (1)$$

We have used Ce-Co-Si, Ce-Ni-Si, Dy-Ni-Si, Er-Ni-Si, Eu-Ni-Si, Cd-Ni-Si, La-Co-Si ··· ($NaZn_{13}$ type forming systems) and Ce-Cu-Si, Ce-Fe-Si, Y-Co-Si, Sc-Ni-Si, Ce-Al-Si ··· ($NaZn_{13}$ type not formed) as training set. All these ternary systems are reported in literatures before 1990. Based on the regularity found, the compound unknown before 1990 can be "predicted". For example, all projection figures in Fig. 1 indicate that Ho- Al- Si system is located outside of the regions of formability, and its chemical bond parameters can not satisfy the constraints of Equation (1), therefore it can be predicted that no compound of $NaZn_{13}$ type in this system.

Fig. 2 illustrates the projection figures with the formation regions for $BaCd_{11}$ type compound in RE-M-Si systems. The formation region can be described by the following simultaneous equations of inequality.

$$\left.\begin{array}{l} -0.89 < 0.19x_1 + 0.68x_2 + 0.54x_3 + 0.45x_4 < 0.17 \\ 0.13 < 0.87x_1 + 0.16x_2 - 0.45x_3 - 0.07x_4 < 0.91 \\ -0.34 < -0.14x_1 - 0.17x_2 - 0.46x_3 + 0.86x_4 < 0.69 \\ -0.24 < 0.42x_1 - 0.69x_2 - 0.54x_3 - 0.23x_4 < 0.20 \end{array}\right\} \quad (2)$$

where
$$x_1 = (Z_M - 8.91) / 1.41$$
$$x_2 = (\Delta X - 0.68) / 0.23$$
$$x_3 = (R_M - 1.28) / 0.06$$
$$x_4 = (R_{RE} - 1.79) / 0.05$$

The training set includes Ce-Ni-Si, Eu-Co-Si ··· ($BaCd_{11}$ type compound forming) and Sc-Mn-Si, Lu-Co-Si, Ho-Fe-Si···

Fig. 3(a)~(b) are the projection fig-

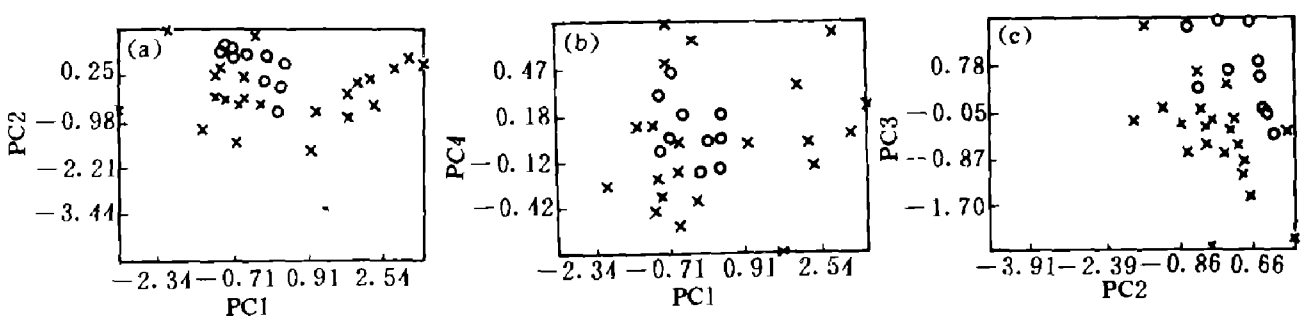

Fig. 1 The distribution of ternary compounds with $NaZn_{13}$ crystal type (PCA)
o—$NaZn_{13}$ type forming systems; x—$NaZn_{13}$ type not formed

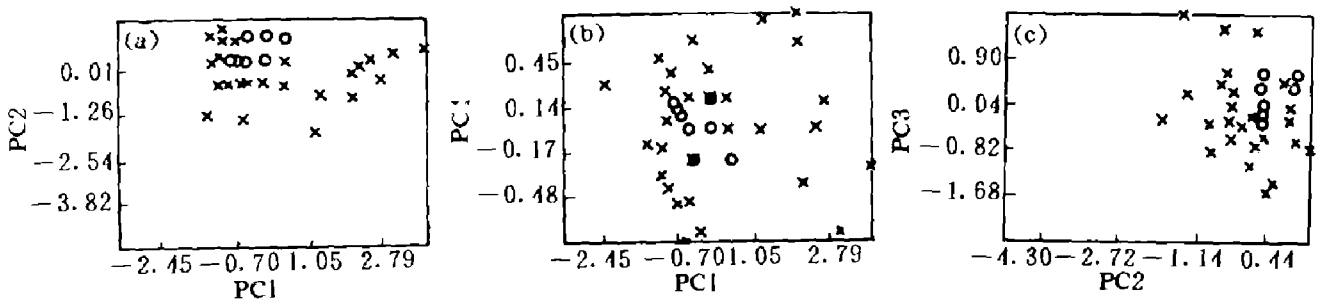

Fig. 2 The distribution of ternary compounds with $BaCd_{11}$ crystal type (PCA)
o—$BaCd_{11}$ type forming systems; x—$BaCd_{11}$ type not formed

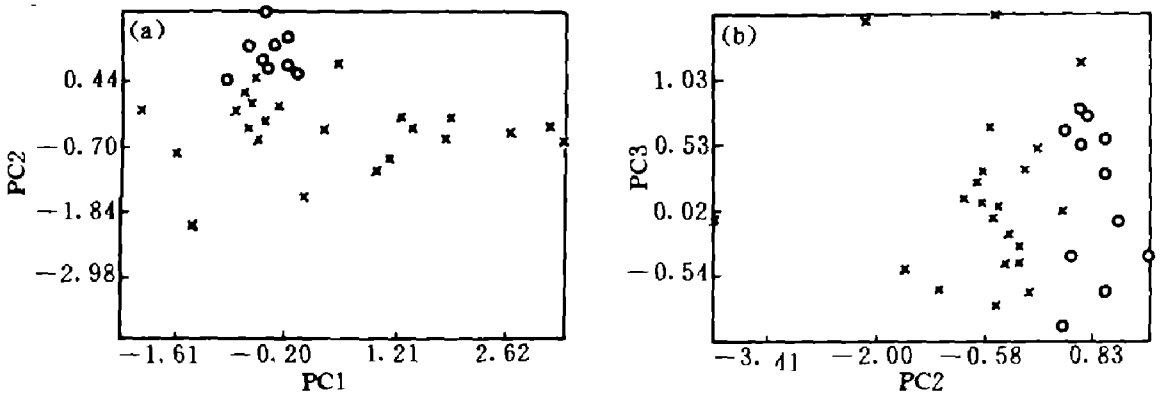

Fig. 3 Geometrical factors influencing the formation of $NaZn_{13}$ type compounds
o—$NaZn_{13}$ type forming systems; x—$NaZn_{13}$ type not formed

ures of PCA method for formability of $NaZn_{13}$ type in RE-M-Si systems, like Fig. 1, but replace R_{RE} and R_M by R_{RE}/R_M, and to span a three-dimensional space. It can be seen that the second principal component is the dominating factors for $NaZn_{13}$ type compound formation, and the eigenvector of this principal component is

$$[\,0.68 \quad -0.01 \quad 0.73\,]^T$$

It can be seen that the third parameter R_{RE}/R_M is the most important factor to the formation of $NaZn_{13}$ type lattice.

4 DISCUSSION

$NaZn_{13}$ type and $BaCd_{11}$ type are common crystal types for binary intermetallic compounds. It is interesting to note that the ternary compounds with $NaZn_{13}$ (or $BaCd_{11}$) type usually have no corresponding binary $NaZn_{13}$ (or $BaCd_{11}$) type compounds, so it is obvious that the presence of silicon stabilize the crystal structure of these types. From geometrical point of view, we find that the radius-ratio R_{RE}/R_M of these ternary compounds is too low for the $NaZn_{13}$ or $BaCd_{11}$ type binary compounds formation. Perhaps quantum chemical factor or electronic factor might give explanation of these facts.

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