ON THE STABILITY OF LAVES PHASES①

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ABSTRACT The regularities of the crystal-types and melting behaviours (congruent or incongruent melting) of Laves phases have been investigated by artificial neural networks or pattern recognition methods using chemical bond parameters as inputs or features. And the corresponding criteria based on chemical bond parameters have been obtained.

Key words Laves phases Crystal-type criterion melting behaviour

1 INTRODUCTION

Laves phase is one of the most important alloy phases, including three crystal-type of alloy phases intimately resemble to each other, i. e., C14-type ($MgZn_2$), C15-type ($MgCu_2$) and C36-type ($MgNi_2$). In previous works, we have studied the formability of Laves phases by pattern recognition method, but the problem of the classification of C14, C15 and C36 crystal-types is still to be solved[1]. Dwight has studied the formability of C14 or C15 type Laves phases between transition elements, but no crystal-type criterion has been obtained[2]. In recent years, we have used pattern recognition and artificial neural network with chemical bond parameters as features or inputs to find the regularities relating to the crystal-type or melting behaviours (congruent or incongruent melting) of some intermediate phases[3]. In this work, similar techniques were used to study the regularities of the crystal-type or melting behaviour of Laves phases.

2 REGULARITIES OF CRYSTAL-TYPE OF LAVES PHASES

Fig. 1 illustrates the classification of the C14 and C15 types of Laves phases formed between transition elements. It is the linear mapping (PCA method) from a four-dimensional space spanned by R_A/R_B (ratio of metallic radii of two elements), Z' (average valence electron number of constituent elements), ΔZ (difference of valence electron numbers of constituent elements) and ΔX (electronegativity difference of constituent elements). [R_A and R_B are Pauling's metallic radii modified by Teatum, and ΔX are the difference of Pauling's electronegativity[7, 8].] It can be seen from Fig. 1 that C14-type phases distribute in a band-like region and C15-type phases distribute in both sides. The normal vector r of the border lines is nearly equal to $5.61(R_A/R_B)+17.5Z'+8.27\Delta X-9.75\Delta Z$. Therefore, Z', ΔZ are the dominating factors affecting the classification between C14 and C15 phases, while the Laves phases with constituent elements having large ΔX tend to form C15 crystal-type. This is to say, the electronic structure is the chief factor determining C14 and C15 crystal-type. Dweight and Wallace have noted that C15 phases distribute in both sides of C14 region[2, 4]. Their conclusion is in agreement with our result.

Similar method is also applied to the crystal-type classification of Laves phases formed with a transition metal and a non-transition metal. Fig. 2 illustrates the distribution of C14 and C15-type phases. Three-layered artificial neural network or PCA method is used to predict the crystal-types of $DyMg_2$, YMg_2, $BaPt_2$, $LuAl_2$, $EuAl_2$ and $NdMg_2$. YMg_2 and

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$DyMg_2$ are predicted to be C14 type, others are C15 type. These results of prediction are in agreement with experimental results.

The crystal-type of Laves phases between non - transition metals are determined chiefly by Z' and ΔZ. This criterion is

$$f(Z) = 3Z' - 0.5\Delta Z - 42$$

C15 type forms as $f(Z) > 0$, while C14 type forms as $f(Z) < 0$ (upto now no C36 type phase between non-transition metals has been discovered).

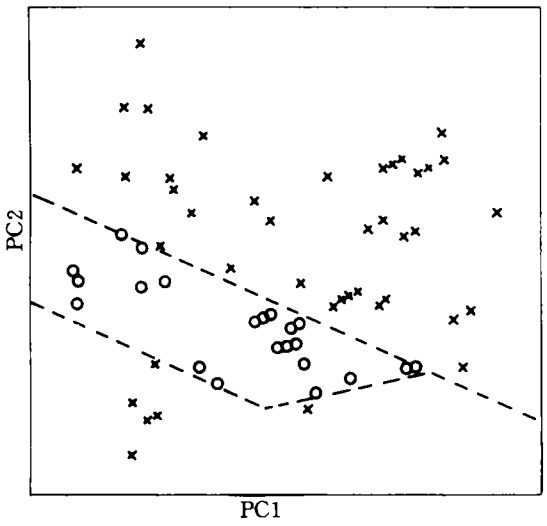

Fig. 1 Distribution of C14 and C15 phases formed between transition and transition elements
o—C14 Laves Phases; ×—C15 Laves phase

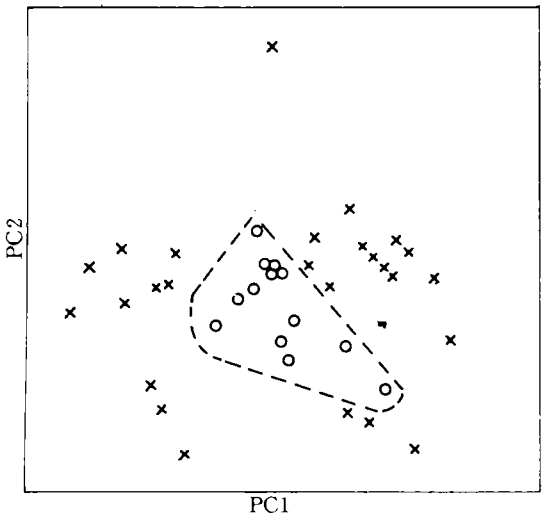

Fig. 2 Distribution of C14 and C15 phases formed between transition and non-transition elements
o—C14 Laves Phases; ×—C15 Laves phase

3 MELTING BEHAVIOURS OF LAVES PHASES (REGULARITIES ABOUT CONGRUENT OR INCONGRUENT MELTING)

Some Laves phases melt congruently, while others melt incongruently. This can be also considered as a behaviour related to lattice stability. As well-known, Laves phases are one kind of alloy phases dominated by geometrical closest packing. The ideal lattice of Laves phases requires $R_A/R_B = 1.225$. But in real cases the atomic radii of A and B change in compound formation due to the charge transfer between A and B atoms. In our previous work, it has been conformed that Laves phases indeed distributed near the point of $R_A/R_B = 1.225$ when ΔX (or $\Delta\varphi$) equals to zero. But when ΔX is larger than zero, the best R_A/R_B value changes continuously and Laves phases distribute in a band region around best R_A/R_B value. It is interesting that the congruently melted Laves phases usually distribute near the central part of the band, while incongruently melted Laves phases distribute near the boundary curves of the band, just as shown in Fig. 3. These facts imply that the best close-packed structure favors the stability of Laves phases, and highly stabilized lattices should melt congruently, i. e., without decomposition before melting.

The regularities of the melting behaviours of the Laves phases discovered before 1990 have been found by artificial neural network or PCA method. Then 12 newly discovered Laves phases (discovered after 1990) are predicted by the trained artificial neural network or mathematical model found by PCA. It has been predicted that $LuAl_2$, $DyIr_2$, $SmRu_2$ and YIr_2 are melted congruently, while $DyMg_2$,

YMg_2 , $NdMg_2$, $HoNi_2$, YCo_2 , $NdRu_2$ and $LaRh_2$ are melted incongruently. All these results of prediction have been conformed by expertimental results.

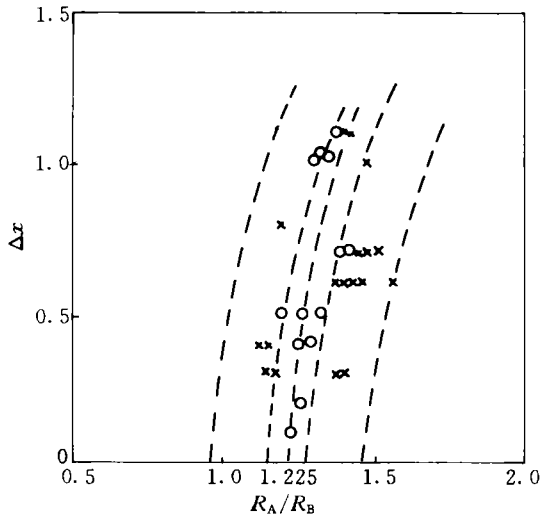

Fig. 3 Melting behaviours of Laves phases formed with two transition metals (Regularities of congruent or incongruent melting)

o—congruent melting; ×—incongruent melting

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(*From page 33*) the central site in the octahedron, and then the others (if there are more to left) accompany with iron atoms to joint with sulphur. Experimental results of electric and magnatic tests show that there are delocalized unpaired electrons in $(Ni, Fe)_9S_8$, which is similar to character of π_4^6 in NO_3^-, and these two materials have matching symmetry, and closed energy level, so they can react easily.

4 CONCLUSIONS

(1) The calculation results show that HNO_3 has much more larger thermodynamic tendency than $FeCl_3$ to oxidate copper, nickel and iron sulphides in original ore. HNO_3 can oxidate the intermadiate product β-NiS, which resists the further leaching reaction in $FeCl_3$ solution, so good results can be got with HNO_3.

(2) The reason why the leached fraction of nickel is higher than that of copper is explained with the theory of gavanic cell.

(3) The frontline orbits theory confirms that NO_3^- reacts with nickel and iron sulphides more easily than Fe^{3+}, so HNO_3 has high leaching efficiency.

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