FORMABILITY OF INTERMEDIATE COMPOUNDS IN OXIDE SYSTEMS OF M_2O_3-M'_2O_3 TYPE①

Wu Zhu, Li Chonghe, Deng Hongmei and Chen Nianyi
Shanghai Institute of Metallurgy,
Chinese Academy of Sciences, Shanghai 200050, P. R. China
Wu Ping
National Supercomputing Research Center of Singapore,
National University of Singapore, 89 Science Park Drive, Singapore 118261

ABSTRACT By atomic parameters and pattern recognition method, the regularities of the formability of intermediate compounds in M_2O_3-M'_2O_3 oxide systems were studied, and the criteria were obtained. It was found that the formation and its chemical formula of complex oxide are chiefly determined by the positive ionic radii of its constituent elements. The predicted results of six M_2O_3-M'_2O_3 systems were in agreement with the experiments.

Key words oxide system calculation of phase diagram complex oxide

1 INTRODUCTION

Phase diagrams of oxide systems provide important basic knowledge of ceramics, cement, metallurgical slag and rock mineralogy. In the oxide systems, there are a large number of intermediate compounds which are of interest to industry and mineralogy research. In fact many functional materials are complex oxides. If phase relations of unknown oxide systems can be predicted with confidence, the phase relations so obtained will be used to guide the phase diagram measurement and to aid the materials design process.

Phase diagram calculation based on thermodynamics principles has been progressed rapidly. This method is, however, limited by the accuracy and availability of thermodynamic data of the system. Also thermodynamics calculation is not expected to determine whether an intermediate compound is formed in the system[1].

Pattern recognition and atomic bond parameter method had been found to be useful in predicting phase diagrams of alloys[2]. The CAD expert system based on pattern recognition method has been applied to alloy steel design[3]. It is also used in the study of the phase diagram of rock mineralogy[4, 5]. Some good results have been achieved.

2 THEORETICAL MODEL AND METHOD

It is well known that Gibbs free energy dominates whether a compound is stable or not:

$$G = H - TS \quad (1)$$

$$G = U + PV + hW/2 - TS \quad (2)$$

For solid materials, at low temperatures, $G \approx U$. The Born-Mayer's formula can be used for the estimation of U:

$$U = \left(1 - \frac{1}{n}\right) \frac{NAe^2Z^2}{r_0} \quad (3)$$

Where r_0 is the equilibrium interatomic distance.

When the numbers of ionic charge are constant, the lattice energy of simple oxide or complex oxide is chiefly determined by the ionic radi-

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i. Since the complex oxides in M_2O_3-M'_2O_3 system are ionic compounds, and the radius of anion is constant, the cationic radii should determine the Gibbs free energy and whether the intermediate compound is formed or not. It is reasonable to use the cationic radii as the parameters to study the formability of the intermediate compounds in M_2O_3-M'_2O_3 systems.

3 RESULT AND DISCUSSION

3.1 Regularity and criterion of formability of intermediate compound in M_2O_3-M'_2O_3 oxide systems

The phase diagrams of 174 oxide systems are found in literature[6, 7], in which 92 oxide systems are complex-oxide-forming. A two-dimensional diagram with cationic radii as coordinate is used to study the regularity of formability of intermediate compound in M_2O_3-M'_2O_3 oxide systems. It can be seen from Fig. 1 that the systems with complex oxide formation and the systems without complex oxide formation distribute into different regions.

3.2 Regularity and criterion of formability of $MM'O_3$ type intermediate compounds in M_2O_3-M'_2O_3 oxide systems

The phase diagrams of 174 oxide systems (Al_2O_3-La_2O_3, Cr_2O_3-Yb_2O_3, Ga_2O_3-In_2O_3 etc) can be classified into two classes: 89 oxide systems which can form $MM'O_3$ type complex oxides are classified as first class, the other 85 oxide systems which can not form $MM'O_3$ type complex oxide are classified as second class. The regularity of $MM'O_3$ type compound formability can be also studied by using a diagram plotted by cationic radii, as shown in Fig. 2. Fig. 2 can be used to predict the formation of some previous unknown complex oxides. For example, the formation of $MM'O_3$ type compound of six systems (Ga_2O_3-Gd_2O_3, Al_2O_3-Pm_2O_3, Cr_2O_3-V_2O_3, Al_2O_3-Tb_2O_3, Y_2O_3-Bi_2O_3, Al_2O_3-Tm_2O_3) is predicted by this way. The results are in agreement with the newly published experimental results and some prediction results by Wu and Pelton[8]. Some complex oxides of other stoichiometry type can be studied in the same methods.

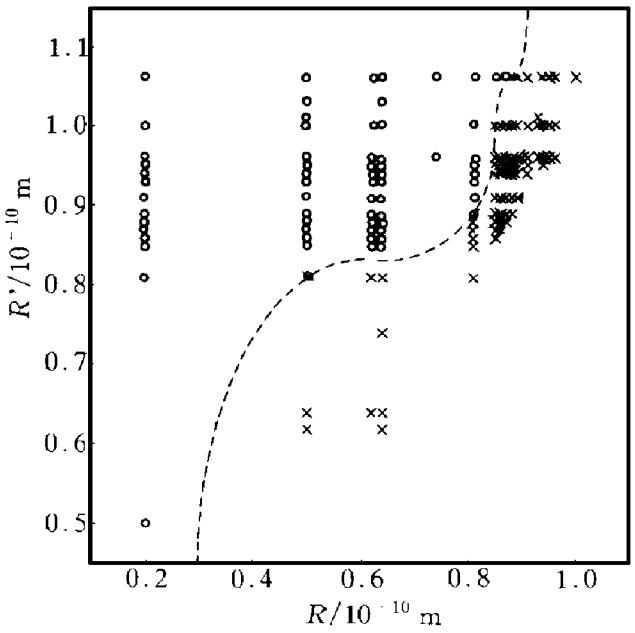

Fig. 1 Classification of forming complex oxide in M_2O_3-M'_2O_3 system

○—Complex oxide forming;
× —Without complex oxide formation

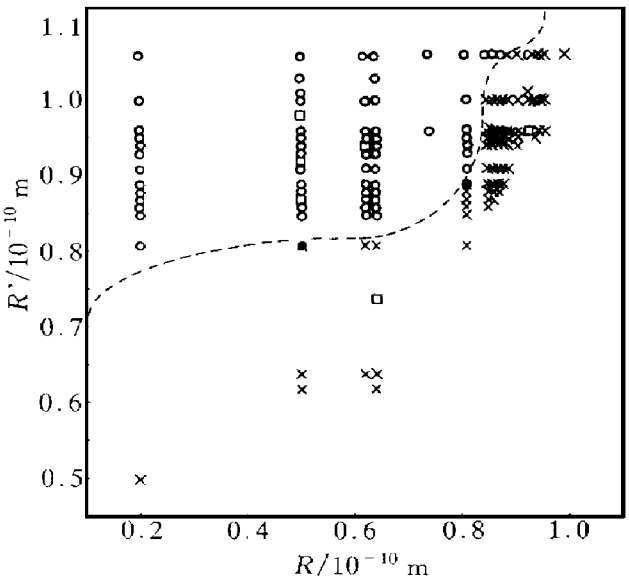

Fig. 2 Classification of forming $MM'O_3$ in M_2O_3-M'_2O_3 system

○—$MM'O_3$ forming;
× —Without $MM'O_3$ formation;
□ —Predicted

It is interesting to note that the cationic radii of rare earth elements dominate the stability of $LnAlO_3$ type compounds. According to the metal ionic radii we can see in Fig. 2 that, for the lanthanide complex oxide (from $LaAlO_3$ to $LuAlO_3$), as the radius decrease, the stability of $MM'O_3$ type compounds decrease. In Fig. 2 it shows that the complex oxide is gradually close to the boundary curves.

REFERENCES

1 Okamoto H. J of Phase Equilibria, 1991, 12(6): 623

2 Chen Nianyi, Xie Leiming and Shi Tiansheng. Scientia Sinica, 1981, 24: 1527.

3 Chen Yu, Chen Nianyi, Peng Pin *et al*. Acta Metallurgica Sinica, (in Chinese), 1992, 28: B471.

4 Li Ming, Yan Liuming and Chen Nianyi. Journal of the Chinese Ceramic Society, (in Chinese), 1993, 21(6): 534- 539.

5 Kang Deshan, Wang Xueye, Yao Shuwen *et al*. Trans Nonferrous Met Soc China, 1995, 5(2): 23- 25.

6 Ernest M L *et al* eds. Phase Diagrams for Ceramists (I- X). Westerville, Ohio 43081: The American Ceramic Society, 1958- 1994.

7 Muller O and Roy R. The Major Ternary Structural Families. Berlin/Heidelberg/New York: Springer-Verlag, 1974.

8 Wu Ping and Arthur D P. J of Alloy and Compounds, 1992, 179: 259- 287.

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