International Journal of Minerals, Metallurgy and Materials

International Journal of Minerals, Metallurgy and Materials

Volume 14 | Issue 7 Article 1

June 2007

Cluster-based composition rules for ternary alloy systems

Chuang Dong
State Key Laboratory of Materials Modification, Dalian University of Technology, Dalian 116024, China; International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China

Qing Wang
State Key Laboratory of Materials Modification, Dalian University of Technology, Dalian 116024, China

Weirong Chen
State Key Laboratory of Materials Modification, Dalian University of Technology, Dalian 116024, China

Qingyu Zhang
State Key Laboratory of Materials Modification, Dalian University of Technology, Dalian 116024, China

Jianbing Qiang
State Key Laboratory of Materials Modification, Dalian University of Technology, Dalian 116024, China

See next page for additional authors

Cluster-based composition rules for ternary alloy systems

Authors

Chuang Dong, Qing Wang, Weirong Chen, Qingyu Zhang, Jianbing Qiang, and Yingmin Wang

Journal of University of Science and Technology Beijing
Volume 14, Supplement 1, June 2007, Page 1

Materials

Cluster-based composition rules for ternary alloy systems

Chuang Dong[1,2], *Qing Wang*[1], *Weirong Chen*[1], *Qingyu Zhang*[1], *Jianbing Qiang*[1], *and Yingmin Wang*[1]

1) State Key Laboratory of Materials Modification, Dalian University of Technology, Dalian 116024, China
2) International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China
(Received 2006-06-16)

Abstract: The cluster-based composition rule in ternary alloy systems including quasicrystals, bulk metallic glasses, crystalline phases and Lave phases-related body-centered cubic (BCC) solid solution forming systems was summarized. The so-called cluster line in a ternary phase diagram refers to a straight composition line linking a specific binary cluster to the third element. The composition ranges of quasicrystals and bulk metallic glasses can be determined by the direct use of cluster lines, where two cluster lines intersect at the optimum phase forming composition. Furthermore, the alloys on the cluster line in Laves phase-related BCC solid solution alloy systems have larger hydrogen storage capacities.

Key words: cluster line; composition design; quasicrystals; bulk metallic glasses; hydrogen storage alloys

[*This project was financially supported by the National Natural Science Foundation of China (No.50401020, 50671018 and 50631010).*]

1. Introduction

Composition design is a key step in investigating and developing new multi-component alloy materials with high composition sensitivity, examples being bulk metallic glasses (BMGs) [1] and quasicrystals (QCs) [2]. Their narrow composition ranges usually span less than a few atomic percents.

Recently, a new approach, a cluster line rule for composition design of these materials [3-6], was proposed. In a ternary system, it refers to a straight line linking a binary specific cluster to the third element. Binary clusters are the 1st-shell coordination clusters centered by small atom in the local structure of binary crystalline phases. From topologically closed-packing consideration, a limited number of binary clusters are available: CN12 icosahedrons, CN10 capped Archimedes anti-prisms, and CN6, CN9 and CN11 capped trigonal prisms [3]. The cluster line rule bridges a connection between the ternary system and its binary subsystems. General characteristics of the cluster line rule in quasicrystals, bulk metallic glasses, and Laves phase-related solid solution alloys were summarized in this paper.

2. Al-based quasicrystals

The composition characteristics of all stable Al-based ternary Al-(Cu, Pd, Ni)-TM quasicrystals [3] were comprehensively surveyed. First of all, the constituent elements of these ternary quasicrystal-forming systems were characterized by negative enthalpies of mixing and large atomic size differences. Negative enthalpies of mixing imply a tendency to form clusters consisting of dissimilar atoms, and large atomic size differences favor topological close-packing of clusters. The second and the most important characteristic is that all the experimental quasicrystal composition data can be explained by the cluster line rule. That is to say, a ternary experimental quasicrystal composition is located near the intersection point of two cluster lines, one generally being an icosahedral cluster line. The other cluster line involves a capped Archimedes anti-prism or capped trigonal prism, or another icosahedral cluster. Taking the Al-Cu-Fe system as an example (as shown in Fig. 1), the enthalpies of mixing of constitute elements are respectively $\Delta H_{\text{Al-Fe}}$= −11 kJ/mol, $\Delta H_{\text{Al-Cu}}$= −1 kJ/mol and $\Delta H_{\text{Cu-Fe}}$= 13 kJ/mol [7], and atomic sizes are respectively R_{Al}= 0.143 nm, R_{Cu}= 0.128 nm, and R_{Fe}= 0.127 nm (Goldschmidt atomic radii). Thus two cluster lines, $Al_{10.7}Fe_2$-Cu and Al_8Cu_3-Fe are constructed in this system. Among them, icosahedron $Al_{10.7}Fe_2$ and capped Archimedes anti-prism Al_8Cu_3 are topologically closed-packing clusters derived respectively from Al-Fe and Al-Cu crystalline

Corresponding author: Chuang Dong, **E-mail:** dong@dlut.edu.cn

phases. They intersect at icosahedron quasicrystal $Al_{64}Cu_{24}Fe_{12}$ (=$Al_8Cu_3Fe_{1.5}$=$Al_{64}Cu_{24}Fe_{12}$), quite close to the experimental composition $Al_{62.5}Cu_{24.5}Fe_{13}$ [8].

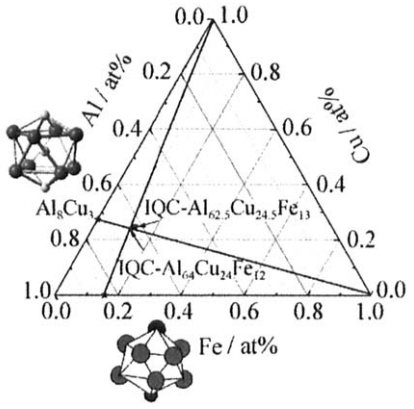

Fig. 1. Schematic composition chart of Al-Cu-Fe. Icosahedral quasicrystal (IQC) is related to icosahedron $Al_{10.7}Fe_2$ and capped Archimedes anti-prism Al_8Cu_3.

3. Bulk metallic glasses

Besides the relatively wide bulk metallic glass-forming ranges, the characteristics of bulk metallic glass-forming systems are similar to those of quasicrystal-forming systems. In the ternary Zr-Al-Ni system [6], Zr-Al and Zr-Ni prefer clustering due to the large negative enthalpies of mixing ($\Delta H_{Ni\text{-}Zr}$= −49 kJ/mol, $\Delta H_{Al\text{-}Zr}$= −44 kJ/mol, and $\Delta H_{Al\text{-}Ni}$= −22 kJ/mol). These clusters centered by Al and Ni respectively are both capped trigonal prisms, which are derived from the corresponding crystalline phases. Several cluster lines are constructed in this system and the bulk metallic glass-forming ranges are determined by use of the cluster lines (Fig. 2). Furthermore, the experimentally known best bulk metallic glass is located at the intersection of close-packing cluster lines Zr_9Ni_3-Al and Zr_9Al_3-Ni [9].

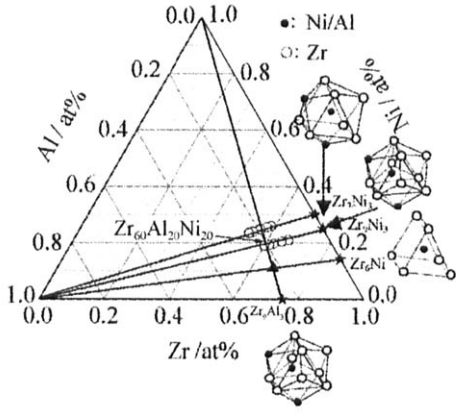

Fig. 2. Composition chart of the Zr-Al-Ni system. Clusters and cluster lines are listed open circles represent bulk metallic glass compositions.

A new series of Cu-based Cu-Zr-TM (TM=Nb, Sn, Ta, Mo, Ag, Al, Ti, and Hf) bulk metallic glasses were also obtained based on icosahedron Cu_8Zr_5-TM cluster lines [4-5]. They can be divided into two classes: one is formed by Cu_8Zr_5 icosahedron glued with the third element atom and the other by minor third element alloying of the Cu_8Zr_5-based Cu-Zr BMG. Therefore, it can be deduced that for the alloy systems with weak glass forming ability such as Fe-based and Co-based systems, where bulk metallic glasses are generally formed in more than quaternary alloy systems [10], the basic ternary compositions can be determined at first by using the cluster line rule and then higher glass forming abilities can be obtained by adding other elements on the basic ternary compositions. A new series of Fe-based and Co-based bulk metallic glasses with good soft magnetism obtained by use of this method will be reported in another paper.

4. Ternary alloy phases

The cluster line rule is not limited to the above quasicrystal and bulk metallic glass forming systems. It is actually based on cluster features, which is common for the systems containing elements with negative enthalpies of mixing. For example, in the Zr-rich corner of a Zr-Al-Ni system, there exists a Zr_6Al_2Ni ternary alloy phase with hP-Mg_2In structure as the competing phase against the amorphous phase. It is exactly located at the intersection of two cluster lines Zr_6Ni-Al and Zr_9Al_3-Ni, as shown in Fig. 2. However, the AlNiZr phase, located in the center of the phase diagram, cannot be directly explained by any cluster lines based on binary clusters. It is highly possible that in cases like this one a ternary cluster should be introduced as the starting point of a cluster line, as already demonstrated *via* the example of glass formation in Sm-Al-Co [11].

5. Laves phase-related body-centered cubic (bcc) solid solution hydrogen storage alloys

In a ternary A-B-C system of Laves phase-related bcc solid solution for storing hydrogen, the enthalpy of mixing between A-B is generally large while those of the other two A-C and B-C are nearly equal to zero. So A-B tends to form an AB_2 Laves while A-C and B-C form solid solutions. The AB_2 Laves phases are a common type of topologically close-packed structure [12] and their local structures can be characterized by an icosahedron B_7A_6 centered by a small B atom, which is similar to the cases in quasicrystal and bulk metallic glass-forming systems [3-6]. Therefore, the cluster line rule also applies to such ternary systems in which only a pair of subsystem has large negative enthalpies of mixing. A typical example is Ti-Cr-V, where the icosahedron Cr_7Ti_6-V cluster line is con-

structed. As shown in Fig. 3, besides the Cr_7Ti_6-V cluster line, the black circles and neighboring numerals represent the Ti-Cr-V alloy compositions and the hydrogen storage capacities of these composition alloys respectively [13]. More importantly, this line traverses exactly the composition range with the largest effective hydrogen storage capacities. Furthermore, the experimental results verified that the alloys on the Cr_7Ti_6-V cluster line have large hydrogen storage capacities.

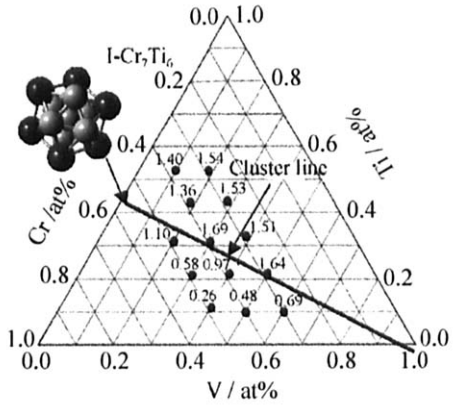

Fig. 3. Composition chart of the Ti-Cr-V ternary system. The cluster line Cr_7Ti_6-V is plotted and the Hydrogen storage capacities of Ti-Cr-V alloys at 303 K [13] are listed.

6. Conclusion

The cluster line rule has successfully directed the composition design of the ternary quasicrystals and bulk metallic glasses, as well as crystalline phases and Laves phase-related BCC solid solution hydrogen storage alloys. It is then a common composition rule for any ternary alloy systems consisting of elements with negative enthalpies of mixing.

References

[1] H.W. Wang, C. Dong, and C.H. Shek, Bulk metallic glasses, *Mater. Sci. Eng. R*, 44(2004), No.2-3, p.45.

[2] S. Ranganathan, K. Chattopadhyay, A. Singh, *et al.*, Decagonal Quasicrystals, *Prog. Mater. Sci.*, 41(1997), No.4, p.195.

[3] C. Dong, J.B. Qiang, Y.M. Wang, *et al.*, Cluster-based composition rule for stable ternary quasicrystals in Al-(Cu, Pd, Ni)-TM systems, *Philos. Mag.*, 86(2006), No.3-5, p.263.

[4] J.H. Xia, J.B. Qiang, Y.M. Wang, *et al.*, Ternary bulk metallic glasses formed by minor alloying of Cu_8Zr_5 icosahedron. *Appl. Phys. Lett.*, 88(2006), No.10, p.101907.

[5] Q. Wang, J.B. Qiang, Y.M. Wang, *et al.*, Formation and optimization of Cu-based Cu-Zr-Al bulk metallic glasses, *Mater. Sci. Forum*, 475-479(2005), No.1, p.3381.

[6] Y.M. Wang, C.H. Shek, J.B. Qiang, *et al.*, The *e/a* criterion for the largest glass-forming abilities of the Zr-Al-Ni(Co) alloys, *Mater. Trans. JIM*, 45(2004), No.4, p.1180.

[7] F.R. de Boer, R. Boom, W.C.M. Mattens, *et al.*, *Cohesion in Metals and Transition Metal Alloys*, Edited by de Boer F R, Pettifor DG North Holland, Amsterdam, 1989. p.1.

[8] D. Gratias, Y. Calvayrac, J. Devaud-Rzepski, *et al.*, Phase diagram and structures of the ternary AlCuFe system in the vicinity of the icosahedral region, *J. Non Cryst. Solids*, 153-154(1993), No.2, p.482.

[9] A. Inoue, T. Zhang, and T. Masumoto, Zr-Al-Ni amorpuous alloys with high glass transition temperature and significant supercooled liquid region. *Mater. Trans. JIM*, 31(1990), No.3, p.177.

[10] A. Inoue, B.L. Shen, and A. Takeuchi, Developments and applications of bulk glassy alloys in late transition metal base system, *Mater. Trans. JIM*, 47(2006), No.5, p.1275.

[11] J. Wu, Q. Wang, J.B. Qiang, *et al.*, Sm-based Sm-Al-Ni ternary bulk metallic glasses, *J. Mater. Res.*, 22(2007), No.3, p.1.

[12] T.B. Massalski, *Physical Metallurgy Part I*, Edited by Cahn R W and Hassen P, North-Holland, New York, 1983, p.190.

[13] S.W. Cho, C.S. Han, C.N. Park, *et al.*, The hydrogen storage characteristics of Ti-Cr-V alloys, *J. Alloys Compd.*, 288(1999), No.1, p.294.