ADVANCED
ENGINEERING
MATERIALS

DOI: 10.1002/adem.200700240

Solid-Solution Phase Formation Rules for Multi-component Alloys**

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Multi-component high-entropy alloys (MHAs) are expected to be one of the emerging structural materials, which are designed by the strategy of equal/near-equal atomic ratio and high entropy of mixing, (ΔS_{mix}).[1–3] MHAs generally have at least five principal elements with the concentrations of each of them being between 5 and 35 at.%. Their particular microstructure and properties offer many potential applications, such as tools, molds, and mechanical parts, etc.[4]

Many kinds of MHAs have been studied on their microstructure and properties since the concept was first proposed.[5] Some MHAs have complex microstructures including many intermetallic compounds as its main phases, which makes them brittle and difficult in processing and analyses.[6] However, for some other MHAs, only body-centered cubic (BCC) or face- centered cubic (FCC) solid-solution phase forms rather than intermetallics, and the total number of phases is well below the maximum equilibrium number allowed by the Gibbs phase rule.[2,4,5,7–9] This kind of particular microstructure makes them possess excellent properties, such as high strength, high plasticity, and so on.[2,4,8,9] Thus, for the MHAs, solid solution phase formation rules remain a common interesting scientific problem.

Up to now, the existing solid-solution-formation rules are mainly based on alloys with one or two principal components, and there are no any detailed solid-solution formation rules for the MHAs. The purpose of this paper is, by summarizing the microstructure characteristics of the reported MHAs in terms of their atomic-size difference and enthalpy of mixing, to predict the solid-solution formation in various MHAs.

From the thermodynamics of materials, solid solution generally forms at the terminal side of the phase diagram, while the ordered intermediate-phase forms at the center of the phase diagram. According to the Hume-Rothery rules for high degree of solubility in binary alloy systems,[10] two factors are mentioned, which would affect the formation of the solid solution in alloys. The first is the size effects of component atoms. For alloys whose component atomic-size differences are over 15 %, it's most improbable to form a substitution solid solution. The second is the chemical compatibility between components, i.e., the electro-negativity difference, or the enthalpy of mixing. The larger the electro-negativity difference (or the more negative of the enthalpy of mixing), the more likely the alloys form compounds rather than solid solutions.

In MHAs, however, the case is quite different. As there are many more principal components than common alloys, the component atoms have the same probability to occupy the

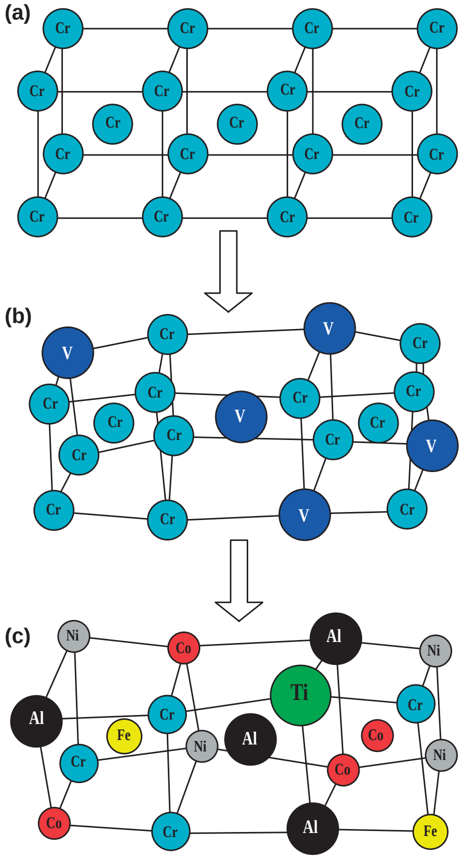

Fig. 1. Schematic illustration of BCC crystal structure: (a) perfect lattice (take Cr as example); (b) distorted lattice caused by additional one component with different atomic radius (take Cr-V solid solution as example); (c) serious distorted lattice caused by many kinds of different-sized atoms randomly distributed in the crystal lattice with the same probability to occupy the lattice sites in multi-component solid solutions (take AlCoCrFeNiTi$_{0.5}$ [2] as example)

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[**] *The financial support by the National Natural Science Foundation of China under the granted No. 50571018, and Program for New Century Excellent Talents in University (NCET-05-0/05) is greatly acknowledged. The authors are grateful to G. J. Hao, W. J. Peng, and Y. Xu for providing technical assistance.*

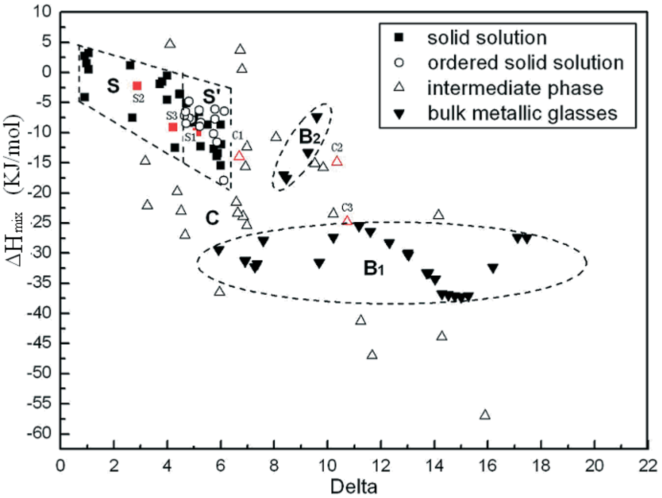

Fig. 2. Relationship between Delta and ΔH_{mix} for MHAs and typical multicomponent bulk metallic glasses (Refs. [2,4,5,7–9,15–42])(NOTE TO THE SYMBOL: "solid solution" indicates the alloy contains only solid solution, "ordered solid solution" indicates minor ordered solid solution precipitate besides solid solution, and "intermediate phase" indicates there is precipitation of intermediate phases like intermetallics in HEAs. Red sign represents the alloys designed to verify the phase formation rules for multi-component HEAs)

lattice sites to form solid solution. Therefore, each component element could be regarded as a solute atom, together with the serious lattice distortion caused by a large atomic radius difference between so many components, which make the structure of the solid solution in MHAs is distinctive from that of pure metal and common alloys, as shown in Figure 1. Here, the parameter *Delta* is adopted to describe the comprehensive effect of the atomic-size difference in multi-component alloys as follows:[11]

$$Delta = \sqrt{\sum_{i=1}^{N} c_i(1 - r_i/\bar{r})^2} \qquad (1)$$

Here N is the number of the components in an alloy system, c_i is the atomic percentage of the ith component, $\bar{r}(=\sum_{i=1}^{n} c_i r_i)$ is the average atomic radius, and r_i is the atomic radius which can be obtained in Reference.[12]

The other parameter, i.e., the mixing enthalpy, is used to characterize the chemical compatibility among the many principal components in MHAs. Based on the regular melt model,[13,14] the mixing enthalpy of a solid solution ΔH_{mix} (kJ/mol) is determined as:

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \qquad (2)$$

Where $\Omega_{ij}(=4\ \Delta H^{mix}{}_{AB})$ is the regular melt-interaction parameter between ith and jth elements, and $\Delta H^{mix}{}_{AB}$ is the mixing enthalpy of binary liquid alloys, the values can be obtained in Ref.[13] The calibration value of $\Delta H^{mix}{}_{AB}$ is used as $\Delta H^{mix(cali)}{}_{AB}=\Delta H^{mix}{}_{AB}-\Delta H^{trans}/2$ for that of containing one non-transition metal (NTM), and $\Delta H^{mix(cali)}{}_{AB}=(\Delta H^{trans}{}_{i}+\Delta H^{trans}{}_{i})/2$ for containing two NTMs. ΔH^{trans} are 100, 30, 180, 310, 34, 17, and 25 kJ/mol for containing H, B, C, N, Si, P, and Ge, respectively.

By summarizing the *Delta* (here *Delta* is amplified by 100 times for convenience) and ΔH_{mix} of MHAs reported, their relationship is shown in Figure 2. For comparison, the corresponding parameters of the typical multi-component bulk metallic glasses (MBMGs) are also calculated.

In the zone marked by S, only solid solution will form. In this zone, as the component atomic-size difference is relative small, the component atoms easily substitute for each other and have the similar probability to occupy the lattice sites to form solid solution. At the same time, ΔH_{mix} is not negative enough for alloys to form a compound.

While in the zone marked by S', MHAs still have solid solution as its main phases. But for some MHAs, a small amount of the ordered solid solution precipitates. Compared with zone S, *Delta* increases so as to deepen the extent of ordering of MHAs. ΔH_{mix} also becomes relative negative to bring about the precipitation of ordered phases in certain MHAs systems.

The MBMGs are located in two zones marked as B_1 and B_2. The zone B_2 contains Mg and Cu based bulk metallic glasses, while the zone B_1 contains the other kind of bulk metallic glasses, such as Zr based bulk metallic glasses. Clearly, compared with MHAs, MBMGs have larger *Delta* and more negative ΔH_{mix}.

The other zone in Figure 2 is marked by C, in which many intermediate phases will form for MHAs.

Following Boltzmann's hypotheses, the entropy of mixing (ΔS_{mix}) of an N-element regular liquid can be expressed as Equation 3, and would reach the maximum when the alloy is of equi-atomic ratio (Eq. 4), as shown in Figure 3. Thus,

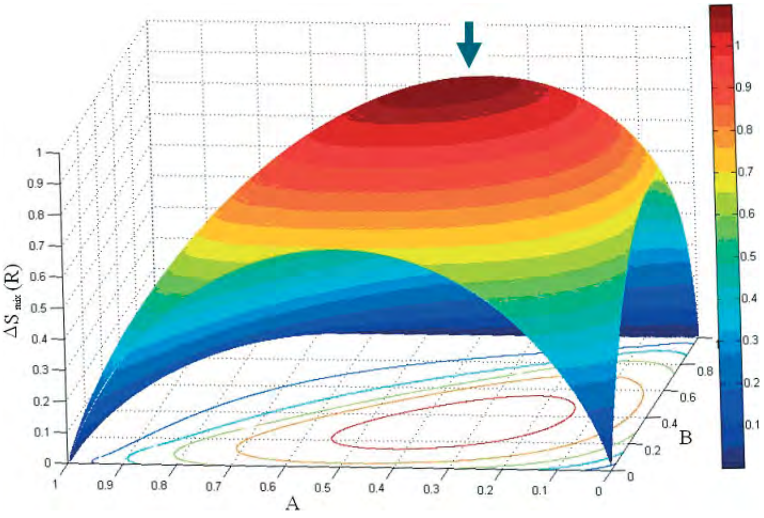

Fig. 3. Illustration of the ΔS_{mix} for ternary alloy system.

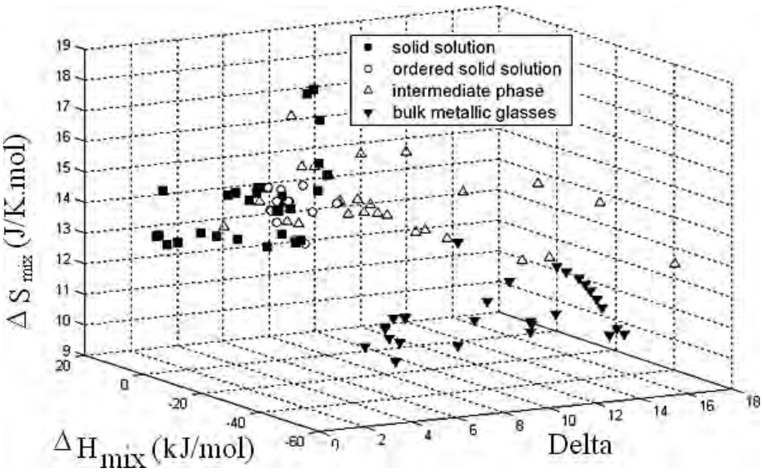

Fig. 4. The Effect of ΔS_{mix} on the phase formation of the MHAs and typical multicomponent bulk metallic glasses.

MHAs, which have at least five similar-content principal components, have much higher ΔS_{mix} than common alloys.

$$\Delta S_{mix} = -R\sum_{i=1}^{N} c_i Ln\, c_i \tag{3}$$

$$\Delta S_{mix} = RLnN \tag{4}$$

Here *R* is the gas constant.

Below is the formula of the Gibbs free energy (ΔG_{mix}):

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{5}$$

Here T is the absolute temperature.

According to Equation 5, the high δS_{mix} can significantly lower the free energy, thus lowering the tendency to order and segregate, which consequently makes solid solution more easily form and more stable than intermetallics or other ordered phases during the solidification in alloys.[43,44] Thus for some MHAs, attributed to the effect of high ΔS_{mix}, solid-solution phases are prior to intermetallics to form, and the total number of phases is well below the maximum equilibrium number allowed by the Gibbs phase rule.

To compare the effect of ΔS_{mix}, Figure 2 was replotted in three dimensions by adding an axis of entropy of mixing as shown Figure 4. It is apparent that all the MHAs studied have a higher level of ΔS_{mix} than that of the bulk metallic glasses as marked by (▼). The MHAs forming solid solution phase marked as (■) have ΔS_{mix} in the range of 12–17.5 J/K.mol, and with smaller values of *Delta*. While the intermetallic phases form at a larger value of *Delta*, but with the ΔS_{mix} in the range of 11 to 16.5 kJ/ K.mol. There is a transition zone marked as (○) between the solid solution phase zone and the intermetallic compound zone, which contains ordered solid solution phases.

The Adam-Gibbs equation connects the viscosity with the configuration entropy S_c (mainly related to the ΔS_{mix}):[45]

$$\eta = \eta_0 \cdot \exp[\frac{C}{TS_c(T)}] \tag{6}$$

Here, *C* is a free enthalpy barrier to cooperative rearrangements.

According to Equation 6, high δS_{mix} will lead to low viscosity, and a high mobility of the atoms in the liquid, thus a lower glass forming ability. This may be the reason why the

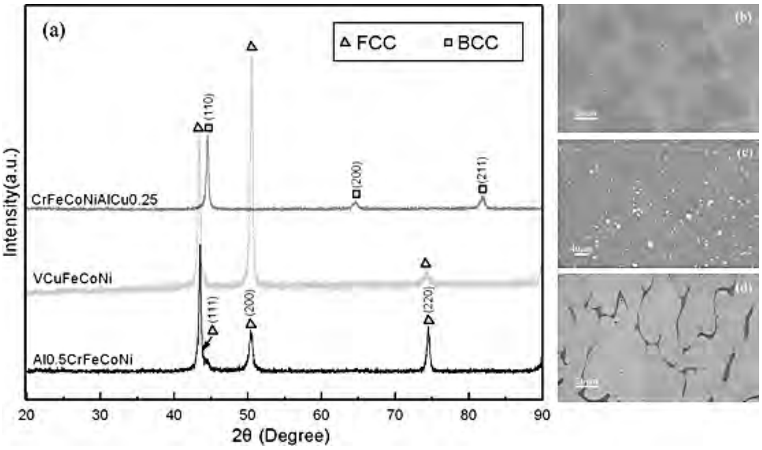

Fig. 5. XRD patterns of as-cast alloy samples forming solid solution (a), and their corresponding SEM back-scattered electron images: (b) $CrFeCoNiAlCu_{0.25}$; (c) VCuFeCoNi; (d) $Al_{0.5}CrFeCoNi$.

Table 1. Delta and ΔH_{mix} (kJ/mol) of $CrFeCoNiAlCu_{0.25}$, VCuFeCoNi, $Al_{0.5}CrFeCoNi$, $Ti_2CrCuFeCoNi$, AlTiVYZr, and ZrTiVCuNiBe MHAs, and their corresponding microstructures.

Alloys	$CrFeCoNiAlCu_{0.25}$	VCuFeCoNi	$Al_{0.5}CrFeCoNi$	$Ti_2CrCuFeCoNi$	AlTiVYZr	ZrTiVCuNiBe
Markes	S1	S2	S3	C1	C2	C3
Delta	5.13	2.88	4.22	6.69	10.35	11.27
ΔH_{mix}	–9.94	–2.24	–9.09	–14.00	–14.88	–24.89
Microstructure	BCC	FCC	FCC	Compound	Compound	Compound

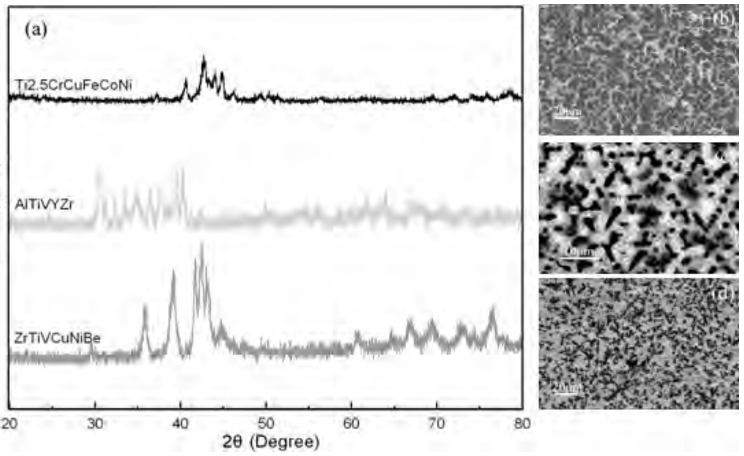

Fig. 6. XRD patterns of as-cast alloy samples forming intermediate phases (a), and their corresponding SEM back-scattered electron images: (b) $Ti_{2.5}CrCuFeCoNi$; (c) AlTiVYZr; (d) ZrTiVCuNiBe.

atomic ratio of the bulk metallic glass forming alloys generally is not equal. However, this conclusion may be in some contradiction to the confusion principle.[6]

To verify the phase-formation zones in Figure 2 and 4, six MHAs of $CrFeCoNiAlCu_{0.25}$, VCuFeCoNi, $Al_{0.5}CrFeCoNi$, $Ti_2CrCuFeCoNi$, ZrTiVCuNiBe, and AlTiVYZr with different *Delta* and ΔH_{mix} were designed. The *Delta* and ΔH_{mix} of the above six MHAs are listed in Table 1, and their locations are indicated by S1, S2, S3, C1, C2, and C3 in Figure 2, respectively. Their microstructure and the morphology are shown in Figure 5 and 6. Just as predicted, the three alloys of $CrFeCoNiAlCu_{0.25}$ (S1), VCuFeCoNi (S2), and $Al_{0.5}CrFeCoNi$ (S3), located in Zone S and S', are composed of solid solution like FCC or BCC. While the other three alloys of $Ti_2CrCuFeCoNi$ (C1), ZrTiVCuNiBe (C2), and AlTiVYZr (C3), located in Zone C contain complex structures of many intermetallics. Thus, the experiment results are in good agreement with the solid-solution formation rules for multi-component MHAs above.

Experimental

Alloy ingots with nominal composition of $CrFeCoNiAlCu_{0.25}$, VCuFeCoNi, $Al_{0.5}CrFeCoNi$, $Ti_2CrCuFeCoNi$, ZrTiVCuNiBe, and AlTiVYZr (the subscript denotes molar ratio) were prepared by arc melting mixtures of commercial-purity metals (purity better than 99.5 wt.%) in a Ti-gettered high-purity argon atmosphere. The alloys were remelted at least four times to improve homogeneity. The ingots were then remelted under high vacuum (10^{-3} Pa) and injection cast into a water-cooled copper mould to obtain cylindrical rods with the diameter of 5 mm.

The structure of cross-section rod samples was characterized by X-ray diffraction using a diffractometer with CuKα radiation. The morphology and composition were examined by the scanning electron microscope (SEM) with energy dispersive spectrometry (EDS).

The weight losses of the six alloys after arc melting and casting were lower than 0.2 wt.% because no volatile element was used for the alloy preparation, which ensures the homogeneity of the six alloys. This fact was also verified by EDS results of SEM (not shown in this article).

Received: September 19, 2007
Final version: November 30, 2007

[1] S. Ranganathan, *Curr. Sci.* **2003**, *85*, 1404.
[2] Y. J. Zhou, Y. Zhang, Y. L. Wang, G. L. Chen, *Appl. Phys. Lett.* **2007**, *90*, 181904.
[3] A. Pichon, *Alloys: six of one.* doi:10.1038/nchina. **2007**, 83.
[4] C. J. Tong, Y. L. Chen, S. K. Chen, J. W. Yeh, T. T. Shun, C. H. Tsau, S. J. Lin, S. Y. Chang, *Met. Mater. Trans. A.* **2005**, *36A*, 881.
[5] J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau, S. Y. Chang, *Adv. Eng. Mater.* **2004**, *6*, 299.
[6] A. L. Greer, *Nature.* **1993**, *366*, 303.
[7] B. Cantor, I. T. H. Chang, P. Knight, A. J. Vincent, *Mater. Sci. Eng. A.* **2004**, *375*, 213.
[8] X. F. Wang, Y. Zhang, Y. Qiao, G. L. Chen, *Intermetallics.* **2007**, *15*, 357.
[9] Y. J. Zhou, Y. Zhang, Y. L. Wang, G. L. Chen, *Mater. Sci. Eng. A* **2007**, *454–455*, 260.
[10] R. E. Reed-Hill, R. Abbaschian, in *Phys. Metall. Principles*, 3rd ed., PWS Publishing Company, Boston, MA, **1994**, 272.
[11] S. S. Fang, X. S. Xiao, L. Xia, W. H. Li, Y. D. Dong, *J. Non-Cryst. Solids* **2003**, *321*, 120.
[12] C. Kittel, in *Int. to Solid State Phys.* 6th ed., John Wiley&-Songs, Inc., New York, NY, **1980**, 26
[13] A. Takeuchi, A. Inoue, *Mater. Sci. Eng. A* **2001**, *304–306*, 446
[14] A. R. Miedema, P. F. de Chatel, F. R. de Boer, *Phys. B* **1980**, *100*, 1.
[15] H. Y. Chen, C. W. Tsai, C. C. Tung, J. W. Yeh, T. T. Shun, C. C. Yang, S. K. Chen, *Ann. de Chim.-Sci. des Matériaux* **2006**, *31 (6)*, 685.
[16] J. W. Yeh, S. K. Chen, J. Y. Gan, S. J. Lin, T. S. Chin, T. T. Shun, C. H. Tsau, S. Y. Chang, *Met. Mater. Trans A* **2004**, *35*, 2533.
[17] L. Q. Ma, L. M. Wang, T. Zhang, A. Inoue, *Mater. Trans., JIM* **2002**, *43 (2)*, 277.
[18] G. Y. Ke, S. K. Chen, T. Hsu, J. W. Yeh, *Ann. de Chim.-Sci. des Matériaux* **2006**, *31 (6)*, 669.
[19] C. Y. Hsu, J. W. Yeh, S. K. Chen, T. T. Shun, *Met. Mater. Trans. A* **2004**, *35*, 1465.
[20] Y. Y. Chen, T. Duval, U. D. Hung, J. W. Yeh, H. C. Shih. *Corros. Sci.* **2005**, *47*, 2257
[21] Y. Y. Chen, U. T. Hong, J. W, Yeh, H. C. Shih, *Appl. Phys. Lett.* **2005**, *87*, 261918.
[22] J. W. Yeh, S. Y. Chang, Y. D. Hong, S. K. Chen, S. J. Lin. *Mater. Chem. Phys.* **2007**, *103* 41.
[23] U. S. Hsu, U. D. Hung, J. W. Yeh, S. K. Chen, Y. S. Huang, C. C. Yang, *Mater. Sci. Eng. A* **2007**, *460–461*, 403.
[24] C. C. Tung, J. W. Yeh, T. T. Shun. S. K. Chen, Y. S. Huang, H. C. Chen, *Mater. Lett.* **2007** *61*, 1.
[25] Y. J. Hsu, W. C. Chiang, J. K. Wu, *Mater. Chem. Phys.* **2005**, *92*, 112.
[26] Z. P. Lu, H. Tan, Y. Li, S. C. Ng, *Scr. Mater.* **2000**, *42*, 667.

[27] Z. P. Lu, Y. Li, S. C. Ng, *J. Non-Cryst. Solids* **2000**, *270*, 103.
[28] T. A. Waniuk, J. Schroers, W. L. Johnson, *Appl. Phys. Lett.* **2001**, *78*, 1213.
[29] T. Zhang, A. Inoue, *Mater. Sci. Eng. A* **2001**, *304–306*, 771.
[30] K. Amiya, A. Inoue, *Mater. Trans. JIM* **2000**, *41*, 1460.
[31] A. Inoue, A. Kato, T. Zhang, S. G. Kim, T. Masumoto, *Mater. Trans. JIM* **1991**, *32*, 609.
[32] H. G. Kang, E. S. Park, W. T. Kim, D. H. Kim, H. K. Cho, *Mater. Trans. JIM* **2000**, *41*, 846.
[33] H. Men, Z. Q. Hu, J. Xu, *Scr. Mater.* **2002**, *46*, 699.
[34] H. Ma, J. Xu, E. Ma, *Appl. Phy. Lett.* **2003**, *83 (14)*, 2793
[35] H. Men, W. T. Kim, D. H. Kim, *Mater. Trans. JIM* **2003**, *44*, 2141.
[36] Z. P. Lu, C. T. Liu, *Acta Mater.* **2002**, *50*, 3501.
[37] J. M. Park, Y. C. Kim, W. T. Kim, D. H. Kim, *Mater. Trans. JIM* **2004**, *45*, 595.
[38] Y. C. Kim, W. T. Kim, D. H. Kim, *Mater. Sci. Eng. A* **2004**, *375–377*, 127.
[39] E. S. Park, H. K. Lim, H. K. Kim, W. T. Kim, D. H. Kim, *J. Non-Cryst. Solids* **2002**, *298*, 15.
[40] Z. P. Lu, C. T. Liu, W. D. Porter, *Appl. Phys. Lett.* **2003**, *83*, 2581.
[41] J. Schroers, B. Lohwongwatana, W. L. Johnson, A. Peker, *Appl. Phys. Lett.* **2005**, *87*, 061912.
[42] W. H. Wang, *J. Appl. Phys.* **2006**, *99*, 093506.
[43] K. A. Porter, K. E. Easterling, in *Phase Transformation in Met. and Alloys*, Chapman& Hall, New York, **1981**, 308.
[44] F. R. de Boer, in *Cohesion in Met. Trans. Met. Alloys. 1*, North-Holland, Amsterdam, **1988**, 9.
[45] R. Busch, J. Schroers, W. H. Wang, *MRS Bulletin* **2007**, *32*, 620.