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A Brief Review of High Entropy Alloys and Serration Behavior and Flow Units

Yong ZHANG[1], Jun-wei QIAO[2], Peter K. LIAW[3]

(1. State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China; 2. Laboratory of Applied Physics and Mechanics of Advanced Materials, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China; 3. Department of Materials Science and Engineering, University of Tennessee, Knoxville 37996, Tennessee, USA)

Abstract: Multicomponent alloys with high entropy of mixing, e. g., high entropy alloys (HEAs) and/or multiprincipal-element alloys (MEAs), are attracting increasing attentions, because the materials with novel properties are being developed, based on the design strategy of the equiatomic ratio, multicomponent, and high entropy of mixing in their liquid or random solution state. Recently, HEAs with the ultrahigh strength and fracture toughness, excellent magnetic properties, high fatigue, wear and corrosion resistance, great phase stability/high resistance to heat-softening behavior, sluggish diffusion effects, and potential superconductivity, etc., were developed. The HEAs can even have very high irradiation resistance and may have some self-healing effects, and can potentially be used as the first wall and nuclear fuel cladding materials. Serration behaviors and flow units are powerful methods to understand the plastic deformation or fracture of materials. The methods have been successfully used to study the plasticity of amorphous alloys (also bulk metallic glasses, BMGs). The flow units are proposed as: free volumes, shear transition zones (STZs), tension-transition zones (TTZs), liquid-like regions, soft regions or soft spots, etc. The flow units in the crystalline alloys are usually dislocations, which may interact with the solute atoms, interstitial types, or substitution types. Moreover, the flow units often change with the testing temperatures and loading strain rates, e. g., at the low temperature and high strain rate, plastic deformation will be carried out by the flow unit of twinning, and at high temperatures, the grain boundary will be the weak area, and play as the flow unit. The serration shapes are related to the types of flow units, and the serration behavior can be analyzed using the power law and modified power law.

Key words: high entropy alloy; bulk metallic glass; serration behavior; flow unit

Recently, much attention has been focused on the topic of multicomponent alloys, also called high-entropy alloys (HEAs). This kind of alloys usually have high entropy of mixing in their liquid or random solution states[1-7]. The high entropy (HE) of alloys may intend to stabilize the disordered solid solution (DSS) and amorphous phase also bulk metallic glass (BMG) rather than intermetallic ordered phases (IOP).

In 1990′s, many scientists worked hard to look for multicomponent alloys with the high glass forming ability (GFA). Greer[8] proposed that the more elements involved, the lower the chance that the alloy can select variable crystal structures, and the greater the chance of glass formation, which is also called the confusion principle. According to the confusion principle, Takeuchi et al.[9] reported that the PdPtCuNiP equiatomic ratio alloy can form BMGs with a critical size of 10 mm. Gong et al.[10] reported that the TiZrHfCuNiBe equiatomic ratio alloy can form BMGs with a critical size of 20 mm. However, the equiatomic ratio alloys, CuCoNiCrFe and CrCoMnNiFe, form the face-centered cubic (FCC) DSS phase, and AlCoCrFeNi form the body-centered cubic (BCC) DSS phase. The confusion principle breaks down for forming the DSS phase rather than the BMG phase. This trend may result from the fact that the viscosity of the equiatomic alloys may not be always high enough to suppress the crystallization process. Up to now, the HE DSS alloys may have

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Biography: Yong ZHANG, Doctor, Professor; **E-mail**: drzhangy@ustb.edu.cn; **Received Date**: September 9, 2015

five characteristics: high entropy effects, sluggish diffusion, severe lattice distortion, cocktail effects, and high phase stability at high temperature.

Thermodynamically, Gibbs-free energy can be expressed by enthalpy and entropy as Eq. (1):

$$G = H - TS \tag{1}$$

where, G is the Gibbs-free energy; H is the enthalpy; S is the entropy, and T is the absolute temperature. From Eq. (1), HE results in the low G, especially at high temperatures. The lower the G is, the more stable the phases are. The high phase stability of HEAs was also verified by Senkov et al.[11] using the neutron study of NbMoTaW or NbMoTaWV equiatomic alloys. It was found that even annealing at 1400 ℃ for 19 h, no phase structure changes can be observed by neutron diffraction.

1 Numbers of Components

According to the confusion principle, the GFA will be increased with more elements involved in the alloy, and almost no pure single metal can be made into the glass. Only recently, the single metal of refractory elements, such as Ta, Mo, V, and Nb, can be made into glass in nanoscale, by using very high cooling rate, 10^{14} K/s[12]. Pure Zr and pure Ti were vitrified into glasses at very high pressures. However, the results are not repeatable, and the papers were then retracted. Binary alloy systems can be vitrified into glasses in a bulk form. This trend means that binary BMGs, at relatively slow cooling rates, were extensively reported[13,14]. The most mentioned composition is the CuZr binary BMG, which was firstly reported by Wang et al.[13] and Yu et al.[14], respectively. Chi and Jiang[15] studied the GFA with a number of elements in alloy systems, and found that GFA increases with increasing the constitute numbers of elements up to five, and then the GFA has no obvious change with increasing the elements number. Fig. 1 shows the critical size t_{max} of the amorphous phase as a function of the number of elements N in the alloy systems.

For forming the DSS phase, the content of HEAs is extending from the ZrNbHf three-element by Guo et al.[16], up to four-element NbMoTaW by Senkov et al.[11], five-element CoCrCuFeNi by Yeh et al.[1], CrCoMnFeNi by Cantor et al.[17], AlCoCrFeNi by Zhang et al.[18], 8-element CuCoNiCrAlFeTiV by Yeh et al.[19], and even to 16 to 20 elements alloys[17].

Inoue[20] proposed three empirical rules for the prediction of glass formation, which are very similar to the DSS-phase formation: (1) the confusion principle, as containing at least three elements or more; (2) atomic-size mismatch, which will lead to the dense atomic packing and the atomic-level stress; (3) enthalpy, in which case the negative heat of mixing is needed.

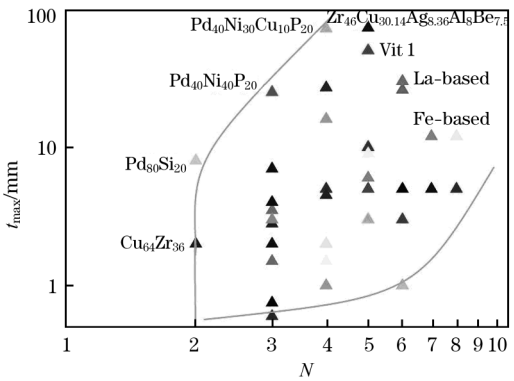

Fig. 1 Critical sizes of BMGs as a function of elements number in alloys

The mixing of Gibbs-free energy can be expressed by Eq. (2):

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2}$$

where, ΔG_m is the Gibbs-free energy of mixing; ΔH_m is the enthalpy of mixing; and ΔS_m is the entropy of mixing. The part of the enthalpy of mixing may play a rather weak role in the alloy system above the melting temperature, and the entropy of mixing will play a very important role in forming phases, which will a bit like a soft-matter state. Thus, a parameter[21] may be defined as:

$$\Omega = \frac{T_l \Delta S_m}{\Delta H_m} \tag{3}$$

where, T_l is the liquidus temperature for an alloy system; and Ω can be a HE parameter. When Ω is larger than 1, this case means that the entropy effect will overcome the effect of the enthalpy at the melting point. The enthalpy can be positive or negative: when it is positive, the elements intend to be repulsive away, and the phase separation occurs in the alloys; while when it is negative, the intermetallic ordered phase (IOP) forms. The entropy effect intends to make the elements distributed uniformly without any phase separation or forming of IOP. Fig. 2 shows the HE parameter Ω as a function of the element number in alloy systems.

2 Entropy and Enthalpy Effects

When the phase formation during the solidification process was considered, viscosity should also be considered. This process is closely related to the mobility of the atoms when the liquid phase transits