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Amorphous Forming Ability, Thermal Stability, Viscosity and Thermoplastic Formability of $(Cu_{43}Zr_{48}Al_9)_{100-x}RE_x$ (x=0-4, RE: Y,Gd) Alloy

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Abstract. The width, deformation and viscosity change of super cooled liquid region of $(Cu_{43}Zr_{48}Al_9)_{100-x}RE_x$(x=0-4, RE: Y, Gd) bulk metallic glasses in super cooled liquid region are systemically investigated by thermoanalysis tests. By analyzing the width, deformation and viscosity of super cooled liquid region, the amorphous forming ability, thermal stability and thermoplastic forming ability of $(Cu_{43}Zr_{48}Al_9)_{100-x}RE_x$ (x=0-4, RE: Y, Gd) in the super cooled liquid region were obtained. It was found that the addition of rare earth elements Y and Gd improved amorphous forming ability, thermal stability, viscosity and deformation, however, by adding rare earth Y, Gd, viscosity and ΔT was no obvious connection. With the increase of Y content, the thermal stability first increases and then decreases, the viscosity decreases firstly, then increases and decreases finally, the deformation increases firstly and then decreases, it preliminary reveals the relationship between viscosity and amorphous forming ability. $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$ amorphous alloy has better thermal stability and thermoplastic formability by adding a small amount of Y.

Introduction

The material needs to be processed into a shape required by society to be used, but the amorphous alloys have some disadvantages such as brittleness and high strength at room temperature[1-6], and it is not easily processed into a desired shape, the thermoplastics of the amorphous alloy is in a super cooled liquid allow the researchers to see the hope, the width of the super cooled liquid region is an important factor for the formation of amorphous alloys and thermoplastic molding[7]. Amorphous alloys of different compositions change its properties[8-10] during the transition of the state, such as changes in thermal stability, viscosity and deformation. The study of effect of rare earth elements on the formation ability and thermal stability of amorphous alloys is now deep. Li Zhengkun [11] found that the addition of Y has greatly improved the amorphous forming ability and thermal stability of the alloy, but Fan Xinhui [12] found that excessive addition of Y reduced its amorphous forming ability and thermal stability. However, the influence of the content of Y on the viscosity of amorphous alloys is not known, most scholars study the viscosity on the influence of temperature and strain. Fan [13] uses TMA three-point bending and parallel plates to study the viscosity of $Pd_{43}Cu_{20}Ni_{20}P_{17}$ bulk amorphous alloy in the super cooled liquid region, according to the proposed cluster model, The viscosity data of $Ni_{20}P_{17}$ bulk amorphous alloy was fitted and a good fitting effect was obtained. They[14] measured the viscosity of the Zr-based bulk amorphous alloy system in the super cooled liquid region at different heating rates. The calculated activation energy of the viscous flow to the bulk amorphous alloy indicates the possibility of internal clusters of the bulk amorphous alloy. Zhang Meng[15] conducted a preliminary study on the effect of amorphous alloys on the viscosity of different systems. It was found that the viscosity of strong super cooled liquids decreased slowly, while the viscosity of brittle and super cooled liquids decreased rapidly. However, the effect of different elements on the viscosity of amorphous alloys has not been studied.

This paper takes $(Cu_{43}Zr_{48}Al_9)_{100-x}RE_x$(x=0-4, RE: Y, Gd) amorphous alloys were studied. The amorphous forming ability, thermal stability and viscosity of different rare earth elements and different contents of rare earth elements were studied. And the influence of the amount of deformation, and analysis of the relationship between the thermal stability, viscosity, deformation and thermoplastic molding of the amorphous alloy, find the composition of the amorphous alloy suitable for thermoplastic molding, using the amorphous alloy in the super cooled liquid region thermoplastic molding, promote the development of precision forming technology and the application of amorphous alloys in daily life.

Experimention

Cu, Zr, Al, Y, Gd with a purity of 99.99 % (mass fraction) are used as raw materials, the accuracy of mass weighing is controlled with 0.002g, the total mass of the sample is 20 g, which is protected in a high-purity Ar atmosphere. The alloy ingot was repeatedly smelted 6 times to ensure the uniformity of the alloy composition. A rod sample of Φ 3×2 mm was prepared by a copper mold suction casting method, and a Shimadzu 6000 X-ray diffractometer (XRD, Cu-Kα, $\lambda = 1.54056$ nm), the phase angle of the rod sample was identified by the diffraction angle of 20°~80° and the step size was 0.02°. The thermodynamic parameters of the rod sample were measured by DSC823e type (high purity argon gas protection), the heating rate was 20 K/min. The parameters were analyzed to obtain the thermal stability and amorphous forming ability of the sample. The TME/SDTA 840 thermomechanical analyzer (TMA) was used to measure the softening point and stress/strain of the sample in the super cooled liquid region. The static load was 0.6 N, the heating rate was 10 K/min, and the viscosity value was calculated. Further, the viscosity curve is further fitted, the variation characteristics of the viscosity are analyzed and the law is summarized.

Experimental Result

Effect of Different Rare Earth Elements on the Amorphous Forming Ability and Thermal Stability of Amorphous Alloys

Table 1. Thermodynamic parameters of Cu-Zr-Al amorphous samples prepared by different rare earth elements.

Amorphous alloy	T_g /K	T_x / K	ΔT / K
$Cu_{43}Zr_{48}Al_9$	701.54	768.07	66.53
$(Cu_{43}Zr_{48}Al_9)_{98}Y_2$	690.55	772.59	82.04
$(Cu_{43}Zr_{48}Al_9)_{98}Gd_2$	676.87	760.79	83.92

Figure 1 is XRD pattern and DSC curve of three kinds of amorphous samples. For the XRD pattern analysis, amorphous samples with different rare earth elements have a typical amorphous diffraction near 38°, The peak indicates that the alloys of the three components are all amorphous. From the DSC curve, the glass transition temperature Tg, the crystallization start temperature Tx, and the super cooled liquid region temperature ΔT characterizing the thermal stability of the amorphous alloy can be obtained. As shown in Table 1, the width of the cold liquid phase of the rare earth element Y and Gd is obviously increased. Because of the width of the super cooled liquid region is closely related to the thermal stability of the amorphous alloy, the larger the width, the better the thermal stability, so the addition of Y and Gd The thermal stability of the amorphous alloy is enhanced.

Effect of Different Rare Earth Elements on the Viscosity and Deformation of Amorphous Alloys

Figure 2 is $Cu_{43}Zr_{48}Al_9$, $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$, $(Cu_{43}Zr_{48}Al_9)_{98}$ Gd_2 amorphous sample strain curve (a) and viscosity fit curve (b) in the super cooled liquid region. It can be seen from Figure 2(a) that when the temperature is low, the three samples exhibit similar deformation behavior. As the temperature increases, the strain value becomes negative, the strain increases, the sample begins to soften. At this time, the temperature has reached the glass transition temperature of the three amorphous alloys, the sample enters the super cooled liquid region and begins to glass transition. At this time, the three alloys have different deformation amounts, indicating that the addition of different rare earth elements can be changed the nature of super cooled liquids. When the temperature continues to rise, the samples stop deforming, indicating that the temperature has risen to the crystallization temperature, the crystallization begins to cause strain hardening of the alloy, making the plastic deformation of the sample difficult to continue.

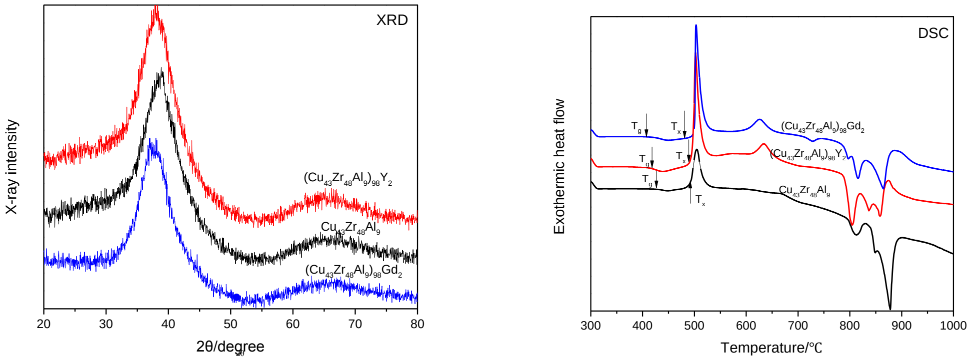

Figure 1. XRD pattern and DSC curve of Cu-Zr-Al amorphous samples with different rare earth elements.

It can be seen from Figure 2(b) that when the current temperature is T_g, the viscosity of the amorphous alloy added with Y and Gd in the super cooled liquid region is 10^{10} Pa·s. The viscosity of $Cu_{43}Zr_{48}Al_9$ amorphous sample without added rare earth element is only 5×10^9 Pa·s, the state of amorphous alloy with Y and Gd added is shown similar solid-state behavior, the viscosity decreases by 2~3 orders of magnitude with increasing temperature, $Cu_{43}Zr_{48}Al_9$ amorphous alloy have lower viscosity values than $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$ and $(Cu_{43}Zr_{48}Al_9)_{98}Gd_2$ amorphous alloys , and the viscosity values of three amorphous alloys decrease trend corresponds to the softening of the sample of Figure 2(a), indicating that Y and Gd increase the fluidity of the amorphous alloy in the super cooled liquid region. When the temperature rises to the crystallization temperature, the viscosity of the three samples begins to increase. Comparing the three curves, it can be seen that the viscosity change trend is consistent near the T_g temperature. In general, $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$ has the largest deformation, while the minimum viscosity of the three alloys is not much different, indicating that the addition of different rare earth elements will affects the deformation amount and viscosity of the amorphous alloy in the super cooled liquid region, thus affects the plastic forming of the amorphous alloy in the super cooled liquid region.

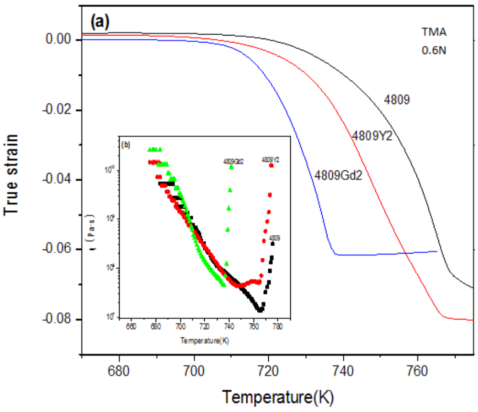

Figure 2. $Cu_{43}Zr_{48}Al_9$, $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$, $(Cu_{43}Zr_{48}Al_9)_{98}Gd_2$ amorphous sample strain curve (a) and viscosity fitting curve in the super cooled liquid region (b).

Effect of Rare Earth Element Y on Viscosity and Deformation of Amorphous Alloy

Figure 3 shows the true strain as a function of temperature after adding different contents of Y to the Cu-Zr-Al alloy. It can be seen that when the temperature is low, the deformation behavior is basically the same. As the temperature increases, the strain increases significantly. When the temperature reaches the respective glass transition temperature, the sample softens and enters the super cooled liquid region, the four alloys exhibit different deformation amounts, the true strain of x=1 and x=3 is 0.01 and 0.08. when x=2, and the true strain without adding Y element is 0.07. When the temperature rises to the crystallization temperature, the curve appears on the platform, the crystallization starts and causes the strain to harden, the deformation stops. When x=2, the deformation amount is the largest, and the softening of the sample is most obvious.

Figure 3(b) is a plot of the viscosity of the amorphous sample in the super cooled liquid region after adding different contents of Y in the Cu-Zr-Al alloy. When x=0 and x=2, the temperature is Tg, the viscosity values are 10^{10} Pa·s. When x=1 and x=3, the viscosity values are 5.9×10^{9} Pa·s, the viscosity of the amorphous alloy without Y added is lower, when the temperature rises, the viscosity begins to decrease by 2~3 orders of magnitude. It is obvious from Figure 3(b) that the viscosity of $Cu_{43}Zr_{48}Al_{9}$ amorphous alloy is higher than that of Y-added amorphous alloy, its drop is much, and the decrease in the viscosity value corresponds to the amount of deformation in Figure 3(a).When the temperature rises to the crystallization temperature, crystallization begins and the viscosity of the sample begins to increase. Comparing the four curves, it can be seen that the viscosity change trend is almost uniform near the Tg , the Y content is not as good as possible. In general, the addition of Y increases the viscosity and deformation of the super cooled liquid region. The plastic deformation ability firstly increases and then decreases.

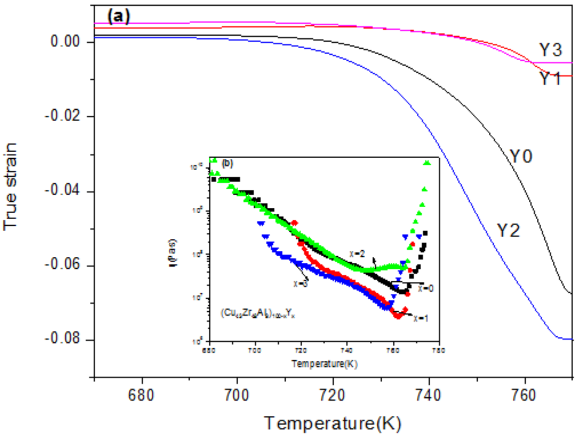

Figure 3. Strain curve (a) and viscosity fitting curve of amorphous sample with different content of rare earth element Y in the super cooled liquid region (b).

Results and Analysis

Effect of Rare Earth Elements on the Forming Ability, Thermal Stability and Viscosity of Amorphous Alloys

It can be seen from the DSC curve in Figure 1 that the addition of different rare earth elements Y and Gd can increase the width of the super cooled liquid region, the area of the crystallization peak becomes larger after the addition of Y and Gd, indicating that after adding Y and Gd, The volume fraction of crystallization in the amorphous alloy matrix is reduced. In addition, with the addition of Y and Gd, the relaxation peak before the glass transition increases, indicating that the free volume of the amorphous alloy added with rare earth elements increases, the addition of Y and Gd enhances the amorphous forming ability and thermal stability of the amorphous alloy.

The oxygen in the alloy melt will affect its amorphous forming ability, and the enthalpy of formation of the oxides of the three elements in the Cu-Zr-Al amorphous alloy is 157.3 kJ/mol 1102.3 kJ/mol and 1675.7 kJ/mol, respectively, the enthalpy of formation of oxides of Y and Gd are 1905.3 kJ/mol and 1819.6 kJ/mol, respectively, which is much higher than that of Cu, Zr and Al, so Y and Gd are more likely to react with oxygen. Therefore, the addition of Y and Gd can effectively eliminate the oxygen in the experiment and the matrix, and the oxides of Y and Gd are not mixed with the melt, so the rare earth elements Y and Gd can increase the amorphous forming ability of the alloy. .

In addition, the difference in atomic size is also an important factor affecting the ability of alloy amorphous formation. The atomic sizes of Cu, Zr, Al, Y and Gd are 0.157, 0.216, 0.182, 0.227 and 0.254 nm, respectively. It can be seen that atomic size of the different elements have a large difference, which makes the structure of the alloy melt more chaotic, the bulk density between the atoms is greater, the diffusion between atoms becomes more difficult, which reduces the energy of the entire system. The viscosity of the super cooled liquid region increases, which is consistent with the results of the viscosity changes in Figure 2(b) and 3(b), so the addition of rare earth elements increases the viscosity of the super cooled liquid region, and the viscosity increases the complexity of overall system. The formation of nucleation in the alloy requires large composition fluctuations and energy fluctuations, increasing the crystallization resistance, so it improves the amorphous forming ability of the alloy and the thermal stability in the super cooled liquid region.

Finally, the negative mixing enthalpy between different elements is another factor that affects the ability of the alloy to form amorphous. In the alloy system , Cu-Y and Cu-Gd: -22 kJ/mol; Al-Y and Al-Gd: -38 kJ/mol and -39 kJ/mol; Cu-Zr: -23 kJ/mol. The larger the negative mixing between different atoms, the stronger the interaction between atoms, promoting the short-range order of the alloy melt and inhibiting the long-range diffusion of the atomic clusters, thus facilitating the formation of amorphous alloys.

Effect of the Content of Rare Earth Element Y on the Viscosity and Deformation of Amorphous alloy in the Super cooled Liquid Region

In 1965, the Adam-Gibbs relationship was proposed. Since the temperature in the super cooled liquid state determines the minimum size of the recombinable atomic clusters, these recombinable atomic clusters are independent of the other clusters in the alloy system. The viscous flow is accomplished by mutual coordination and recombination of several atomic clusters with other atomic clusters. Therefore, we introduce configuration entropy and link the two thermodynamic factors of entropy and temperature with viscosity. The closer the temperature is to the glass transition temperature, the more the structure type in the alloy system will be reduced, the ideal glass state will be achieved finally. At this time, the configuration entropy is zero, and the temperature at this time is the ideal glass. transition temperature.

In addition, it can be seen from Figure 3 that the viscosity of the amorphous alloy of each component in the super cooled liquid phase varies greatly with temperature, which indicates that the viscosity of the super cooled melt is extremely sensitive to temperature changes, different contents of Y of the amorphous alloy has different viscosities in the super cooled liquid region, and the viscosity decreases with increasing temperature before the crystallization temperature. Therefore, the viscosity is not only related to temperature, but the alloying elements are also important factors for viscosity. It is known from the chaos principle that the more the alloy components, the higher the configuration entropy, the better the glass-forming ability. The Adam-Gibbs relationship shows that the larger the configuration entropy, the viscosity is lower. On the one hand, as the Y content increases, the number of configurations present in the alloy increases, the configuration entropy increases, the viscosity decreases. In addition, the relationship between the viscosity of the liquid and the effective diffusion coefficient is described according to the Stokes-Einstein relationship. It can be seen that as the temperature increases and the viscosity decreases, the atomic diffusion accelerates, and the chance of nucleation and growth increases, which leads to the transition of the amorphous state to the crystalline state. On the other hand, the content of Y is more, the better the formation of a higher density atomic packing structure, resulting in an increase in the viscosity of the amorphous alloy in the super cooled liquid region, which is detrimental to the long-range diffusion motion and migration of the atom, it is not conducive to deformation, combining these two factors plus the temperature range of the minimum viscosity retention, we see the result of Figure 3, Although the viscosity of $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ is not the smallest, the amount of deformation is the largest, so $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ is the best plastic deformation in the super cooled liquid region. It can also be seen from Figure 3 that the super cooled liquid region of $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ is wider than other components, so the content of Y also affects the thermal stability of the crystalline alloy in the super cooled liquid region, $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ has the best thermal stability.

Temperature, Viscosity, Thermal Stability, Deformation and Thermoplastic Molding

It is analyzed from Figure 3 that the viscosity decreases with increasing temperature in the super cooled liquid region, because the size of the atomic clusters in the alloy system is continuously decreasing as the temperature increases. The average distance between adjacent clusters increases continuously. The larger distance means that the interaction between atoms becomes weaker, the activation energy required for atomic migration decreases, the resistance also decreases, resulting in the viscosity of the amorphous alloy in the super cooled liquid region gradually becomes smaller, so the metallic glass tends to balance the structural relaxation phenomenon of the super cooled liquid under thermodynamic driving. However, this process is not so easy to implement in terms of kinetics, because the time scale of the localized rearrangement of the glassy state is very long, and each step toward the super cooled liquid state is closer, the barrier to the next rearrangement will become higher, the time required will be longer, the time to reach equilibrium will increase exponentially. Therefore, for the thermoplastic molding of amorphous alloys, it is necessary to ensure the processing temperature and the processing time, and also to obtain a suitable viscosity and thermal stability in the super cooled liquid region.

Schroers[16] pointed out that the thermoplastic forming ability of amorphous alloys is related to the brittleness coefficient and the glass transition temperature. The brittleness coefficient refers to the degree of change of the viscosity of the amorphous alloy as the temperature changes. The smaller the viscosity, the more brittle it is, which is advantageous for thermoplastic molding. When the brittleness coefficient is constant, the easier control of thermoplastic molding requires a lower glass transition temperature. The lower the temperature, the slower the transition from amorphous to crystalline, the greater the thermal stability of the amorphous alloy. It also prevents the conversion of the amorphous state to the crystalline state. In addition, the amount of deformation is also an important factor affecting thermoplastic molding. Different amorphous alloy systems have different deformation amounts in the super cooled liquid region, the deformation amount is too small, so it is not worthy of thermoplastic molding, so the thermoplastic molding requires a suitable amount of deformation, the deformation amount of $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ is the largest among several amorphous alloy compositions, and $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ has better amorphous forming ability and thermal stability, lower glass transition temperature and wider super cooled liquid region, so thermoplastic molding can be selected $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ amorphous alloy.

Conclusion

(1) The addition of Y and Gd increases the amorphous forming ability of the alloy and improves its thermal stability. With the increase of Y content, the thermal stability of the amorphous alloy increases firstly and then decreases. $(Cu_{43}Zr_{48}Al_{9})_{98}Y_{2}$ has the largest width of the super cooled liquid region and the thermal stability.

(2) As the heating rate increases, the viscosity decreases, but the decrease is not obvious. The addition of different rare earth elements Y and Gd will enhance the fluidity of the amorphous alloy in the super cooled liquid region, but the content of rare earth element Y is not as good as possible, when x=2 Amorphous viscosity values are the most informative.

(3) According to $(Cu_{43}Zr_{48}Al_9)_{100-x}Y_x$ Comprehensive analysis of amorphous forming ability, thermal stability, viscosity and deformation in the super cooled liquid region, $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$ The glass transition temperature is low, and it is found that $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$ has the best thermoplastic molding ability, so it is the best amorphous alloy composition suitable for thermoplastic molding. It is $(Cu_{43}Zr_{48}Al_9)_{98}Y_2$.

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