

Effect of the Addition of Large Atomic Size Elements on the Glass Formation of Al-Ca-Ni Amorphous Alloys

Zipan Chen^{1,*}, Xiangqi Xu¹, Huixian Zhang², Shoudong Chen¹ and Jian Su¹

¹School of Mechanical Engineering, Tongling University, 1335 Cuihu four Road, Tongling 244061, China

²China NCS Testing Technology Co., Ltd., Beijing 10008

*Corresponding author e-mail: chenzipan_2004@163.com

Abstract. Effects of different large atomic radius elements (i.e., Na, Eu and Sr) on the glass forming ability (GFA) of Al-Ca-Ni alloy system were systematically investigated. The three doping elements are similar to each other, such as large atomic radius, low melting point and low Pauling's electronegativity. Our results confirmed that addition of 1 at.% Eu and Sr can enhance the crystallization resistance and stabilize the liquid stability, leading to the increment of the GFA. On the contrary, although the addition of Na to the base alloy could lowers the crystallization temperature, but effectively suppresses the competing α -Al crystalline phase and enhance the GFA. Moreover, with the increase of atomic radius of doping elements, the critical thickness for glass formation is gradually increased from 290 to 410 μ m. Therefore, it seemed that their atomic size played a more important role in improving the GFA of Al-Ca-Ni alloy.

1. Introduction

Al-based amorphous alloys have attracted more and more attention since they have a series of excellent physical and chemical properties such as low density, high specific strength and good corrosion resistance [1-3]. For example, Al-based metallic glasses may have yield strength in excess of 1000MPa [4], which are about two times higher than that of conventional high strength aluminum alloys. These favorable material properties allowed a plethora of potential applications in automotive and aerospace industries [5-6]. As a result, there has been a relentless pursuit of Al-rich bulk metallic glasses (BMGs) ever since Al-RE-TM ternary Al-based amorphous alloy have been prepared by Inoue in 1988 [7-9]. Unfortunately, Al-based amorphous alloys have relatively poor glass forming ability (GFA) as compared to other bulk metallic glass (BMG) systems, such as Pd-based and Zr-based amorphous alloys [10-11]. The largest size of Al-based BMG reported so far is only 1.5mm [1-2, 12], which limits its practical application greatly. In addition, most of Al-based metallic glass systems typically contain 3-20 at.% RE (rare-earth) metal elements [13-16], which sacrifices the specific strength because of the high density of the RE elements. Therefore, it is necessary to understand further about glass formation in Al-based alloy systems and to explore potential good glass formers which contain limited contents of RE metals. Mutual substitution of the atoms with similar atomic sizes but different valence electronic structures played an important role in improving the GFA of the alloys such as (Y-Sc)-Co-Al, Mg-(Cu-Ag)-Y and (La-Ce)-Al-(Ni-Cu) [17-19]. This method has also



been applied to Al-based alloys, resulting in the discovery of Al-TM-RE metallic glasses that were cast into 1 mm diameter rods [20]. Based on the periodic table of chemical elements, it is interestingly found that the Ca element has many similar physical and chemical properties with Na, Eu and Sr element, including large atomic radius, low melting point and low Pauling's electronegativity. In this work, we attempt to develop new Al-based light-weight amorphous alloys based on the Al-Ca-Ni system [21]. A series of Al-Ca-Ni (Na, Eu, Sr) alloys were suctioned into wedges under identical preparation conditions to study the effects of mutual substitution of large atomic radius elements (i.e., Ca, Na, Eu and Sr) on the GFA in the Al-Ca-Ni metallic glass system.

2. Experimental Procedure

Master alloys with nominal composition of $\text{Al}_{88}\text{Ca}_7\text{Ni}_5$ and $\text{Al}_{88}\text{Ca}_6\text{Ni}_5\text{M}_1$ ($\text{M} = \text{Na}, \text{Eu}, \text{Sr}$) were prepared by arc-melting a mixture of Al (99.999%), Ni (99.99%) Ca, Sr and Eu (99.5%), Na (99.9%) in a Ti-gettered argon atmosphere. All the ingots were melted at least four times in order to ensure good chemical homogeneity. The weight of each ingot is about 20g. Ribbon samples having a thickness about 50-70 μm and a width about 3-5mm were prepared by remelting the alloys in a quartz tube and subsequently ejecting onto a copper wheel rotating with a surface velocity of 20m/s. In order to detect the critical glass-forming thickness of these alloys, wedge shaped specimens were obtained by injecting the alloy melt into a copper mold with a wedge cavity and as an example, Fig. 1 depicts the outer shape and surface appearance of the as-cast wedge sample and ingot of the $\text{Al}_{88}\text{Ca}_7\text{Ni}_5$ alloy. Structure of the ribbons was investigated by X-ray diffraction (XRD) using Cu K α radiation and high resolution transmission electron microscopy (HRTEM). The TEM samples were first mechanically ground to about 20 μm thickness and then twin-jet electro-polished using a solution mixed in the ratio $\text{HClO}_4\text{:C}_2\text{H}_6\text{OH}=1\text{:}19$. The wedge specimens were grinded and polished, then etched about 10 s using a modified Keller's reagent (i.e., 4mL HNO_3 , 2.5mL HCl , 1.5mL HF and 200mL distilled water). The critical dimension for glass formation of the wedge samples was examined by scanning electron microscopy (SEM). Crystallization behavior of all ribbons was studied by differential scanning calorimetry (DSC) at a heating rate of 20K/min.

3. Results and Discussion

To study the GFA of the alloys containing different large atomic radius elements (i.e., Na, Eu and Sr), wedge-casting of all the alloys has conducted, the wedge samples were first etched about 10s using the modified Keller's reagent, and Figs.2, 3 and 4 show representative SEM images of the wedge-shaped samples of the $\text{Al}_{88}\text{Ca}_7\text{Ni}_5$, $\text{Al}_{88}\text{Ca}_6\text{Ni}_5\text{Na}_1$ and $\text{Al}_{88}\text{Ca}_6\text{Ni}_5\text{Sr}_1$ alloys, respectively. For the base $\text{Al}_{88}\text{Ca}_7\text{Ni}_5$ alloy, a clear structure transition occurs at the width of 280 μm , as shown in Fig.2a. The blowups of the regions A and B shown in Fig.2b and c suggests that the region A is fine equiaxed crystals while the region B is fully coarse dendrites, implying that no any amorphous phase forms in this alloy. Figure 2d shows the corresponding XRD pattern for region A, and as shown, sharp crystalline peaks which correspond to the $\alpha\text{-Al}$ and CaNiAl_9 phase, indicating that region A consists of fully crystalline structure. This result is consistent with the SEM observations.



Figure 1. The outer shape and surface appearance of the as-cast wedge sample and ingot of the $\text{Al}_{88}\text{Ca}_7\text{Ni}_5$ alloy.

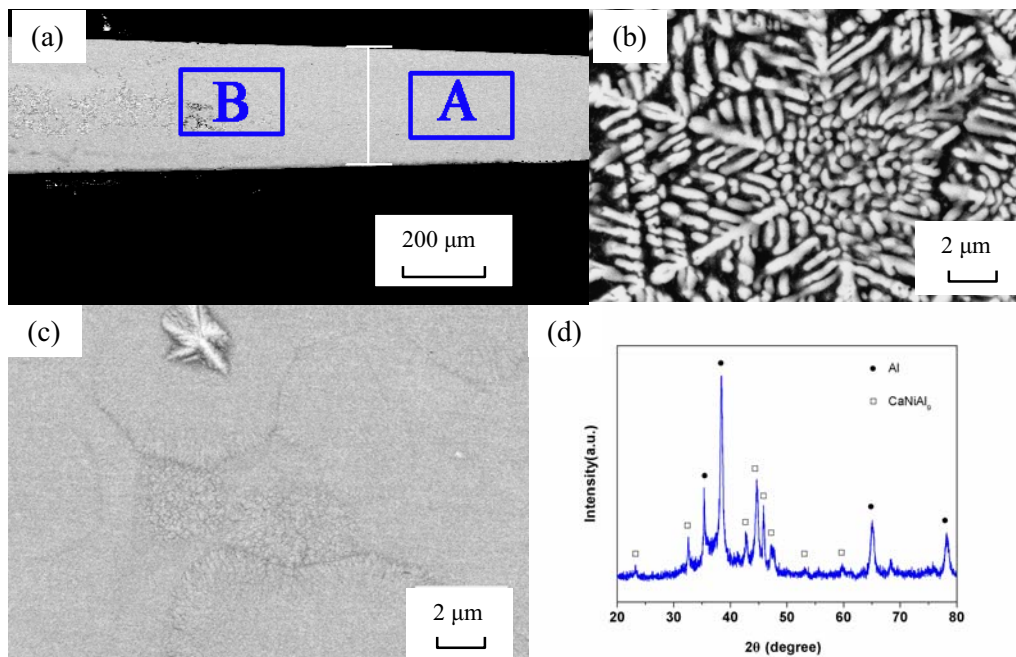


Figure 2. SEM images of the Al88Ca7Ni5 Alloy; (a) macrostructure of the wedge-cast sample, (b) the amplified image of the region B shows the coarse dendrites and (c) the amplified image of the region A shows the fine equiaxed crystals, (d) shows the corresponding XRD patterns of the A region.

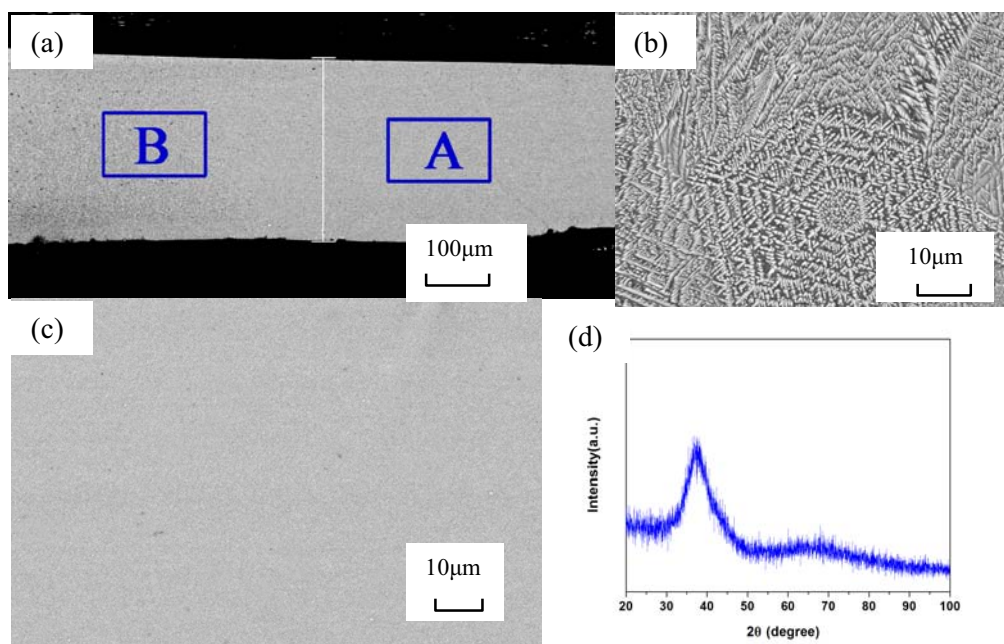


Figure 3. SEM images of the Al88Ca6Ni5Na1 Alloy; (a) macrostructure of the wedge-cast sample, (b) the amplified image of the region B shows the coarse dendrites and (c) the amplified image of the region A shows the fine equiaxed crystals, (d) shows the corresponding XRD patterns of the A region.

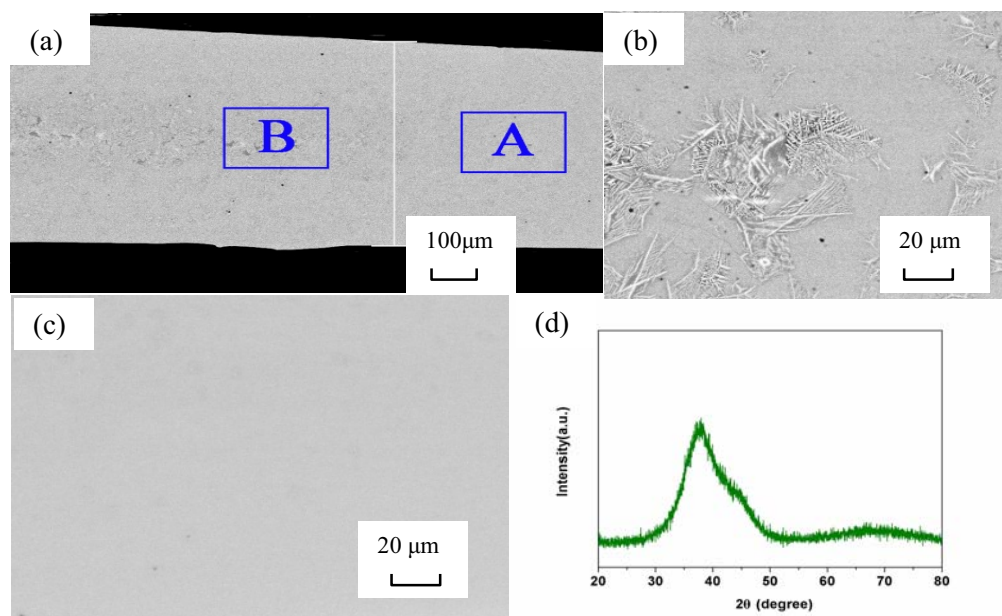


Figure 4. SEM images of the Al₈₈Ca₆Ni₅Sr₁ Alloy; (a) macrostructure of the wedge-cast sample, (b) the amplified image of the region B shows the coarse dendrites and (c) the amplified image of the region A shows the amorphous structure, (d) shows the corresponding XRD patterns of the A region.

For the alloys doped with 1 at.% Na and Sr, typical SEM images of the wedge-shaped samples of the Al₈₈Ca₆Ni₅Na₁ and Al₈₈Ca₆Ni₅Sr₁ alloys are illustrated in Figures 3 and 4, respectively. For the alloy containing 1 at.% Na, the critical glass-forming thickness is about 290 μm, and the clear boundary between amorphous and crystalline structure can be still seen in Fig.3a. In the crystalline region (Fig.3b), the same crystalline phase such as coarse dendrites was present. Moreover, as shown in Fig.3c, it is important to notice that disappearance of the fine equiaxed crystals as observed in Fig 2 was not seen in the alloys doped with Na, implying that the region with a thickness smaller than 290 μm consists of complete amorphous. This result can be further confirmed by the corresponding XRD curve of the region A, as shown in Fig.3d. For the alloy with 1 at.% Sr, the structure transition is observed at the width of 410 μm as shown in Fig.4a. Enlarged images of regions A and B shown in Fig.4b and c, respectively, clearly display the microstructural change from fully amorphous to partially amorphous. Coarse dendrites are homogeneously embedded in the amorphous matrix (region B). Figure 4e shows the corresponding XRD curve for region A, a broad diffuse peak of the amorphous structure is observed. This result further confirms that region A is fully amorphous.

Based on the periodic table of chemical elements, the three doping elements are similar to each other, such as large atomic radius, low melting point and low Pauling's electronegativity. However, their effects on glass formation varied, as demonstrated by the critical thickness shown in Table 1. Due to the addition of Na, Eu or Sr, the GFA can be actually improved and the critical thickness for glass formation ranged from 290 to 410 μm, which is larger than that of the base alloy. To understand effects of these large atomic radius elements (i.e., Na, Eu and Sr) substitutions on glass formation, Crystallization and melting behavior of all the alloys were characterized by DSC at a heating rate of 20K/min and the corresponding results are shown in Fig.5. The various thermal parameters, including Tx (the onset crystallization temperature), Tm (the onset melting temperature), TL (the liquidus temperature) and the GFA parameter γ (Tg was replaced by Tx in the original equation because the glass transition temperature has not been detected [22]) are tabulated in Table 1. As shown, the γ value of all the alloys is less than 0.35, suggesting that these alloys are still not bulk glass formers [23]. In addition, from the DSC curves, it is seen that the devitrification mode of these alloys upon reheating is changed dramatically. The alloy with Na and the base alloy crystalline via two steps while those with

Eu and Sr only shows one single exothermic crystallization peak. The first exothermic crystallization peak for the alloy with Na and the base alloy is related to the crystallization of α -Al while the second one is associated with the crystallization of the eutectic structure. However, for the alloy with 1 at.% Eu and Sr, the first peak completely merged with the eutectic crystallization peak and shifted towards higher temperature.

Table 1. Thermal properties, GFA parameter γ and the critical thickness of the Al₈₈Ca₇Ni₅ and Al₈₈Ca₆Ni₅M₁ (M=Na, Eu, Sr) alloys.

Alloys	T_x (K)	T_m (K)	T_L (K)	$\gamma(=T_x/(T_x+T_L))$	$D_c(\mu\text{m})$
Al ₈₈ Ca ₇ Ni ₅	431	876	983	0.305	70
Al ₈₈ Ca ₆ Ni ₅ Na ₁	422	876	954	0.307	290
Al ₈₈ Ca ₆ Ni ₅ Eu ₁	443	879	938	0.321	370
Al ₈₈ Ca ₆ Ni ₅ Sr ₁	447	879	938	0.323	410

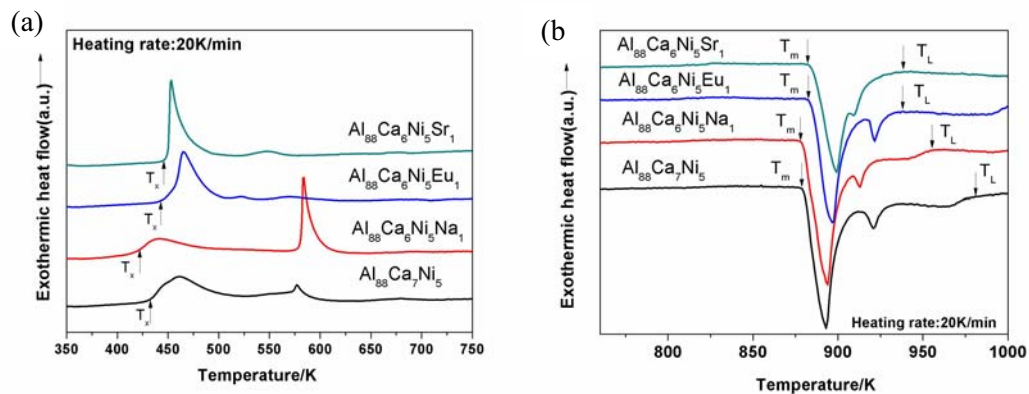


Figure 5. DSC curves of the Al₈₈Ca₇Ni₅ and Al₈₈Ca₆Ni₅M₁ (M=Na, Eu, Sr) samples at a heating rate of 20K/min.

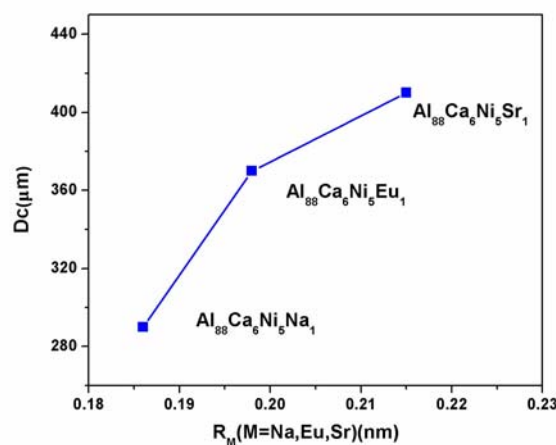


Figure 6. The relation between D_c and atomic size of adding elements in Al₈₈Ca₆Ni₅M₁ (M=Na, Eu, Sr) alloys.

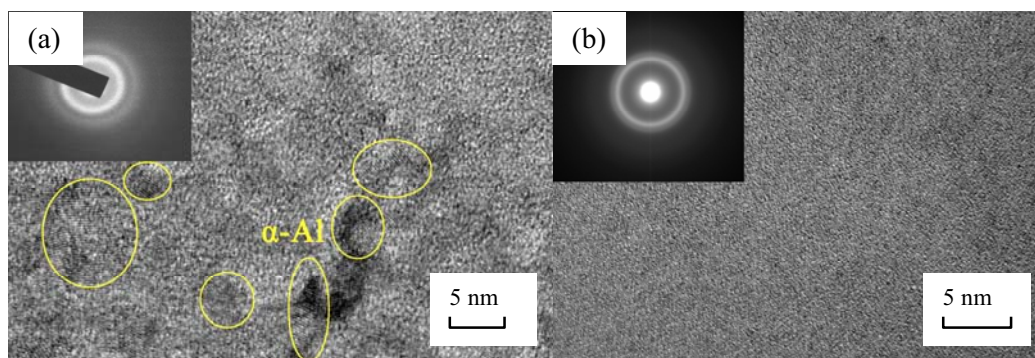


Figure 7. HRTEM images and the corresponding SEAD patterns of the as-spun Al₈₈Ca₇Ni₅ (a) and Al₈₈Ca₆Ni₅Na₁ (b) ribbon.

Generally, glass formation of glass-forming liquids is always related to two aspects, i.e., liquid phase stability and crystallization resistance. The higher the liquid phase stability and the crystallization resistance, the larger GFA of a system should be [24]. Therefore, the effects of these large atomic radius elements on the glass formation in the current Al-based alloys can be twofold.

Firstly, the liquid temperature of all the alloys doped with large atomic radius elements is lower than that of the base Al₈₈Ca₇Ni₅ alloy. As such, additions of Na, Eu and Sr would stabilize the liquid phase stability and favor the glass formation. Such difference in the liquid phase stability could associate with the atomic size of the three large atomic radius elements, as demonstrated in Fig.6 which shows the critical thickness for glass formation as a function of the atomic size of the three doping elements. In addition, as pointed out by Inoue, atomic size difference and the heat of mixing also play important roles in glass formation [25]. The atomic size of all the three doping elements is in the order of Na (0.186 nm) < Eu (0.198 nm) < Sr (0.215 nm). All the three doping have large atomic radius and their additions can cause sequential change in the atomic sizes, as well as the generation of new atomic pairs with large negative heat of mixing. Consequently, the topological and chemical short-range orderings are increased with proper amount of doping elements, thus increasing the packing density of the undercooled liquid with low atomic diffusivity. This can be revealed by the enhanced stability of the liquid phase.

Secondly, the onset crystallization temperature is 443 and 447K for the addition of 1 at.% Eu and Sr, respectively, but decreases to 422K in the alloy doped with 1 at.% Na. Compared with that of the base alloy (i.e., 431K), the onset crystallization temperature actually increased with the additions of 1 at.% Eu or Sr, thus increasing the crystallization resistance and the GFA of the alloys. Sodium is chemically similar to the Eu and Sr, but not only has the lowest melting point but also has the smallest atomic radius among the three doping elements. As shown in Table 1, minor addition of Na element could lower the onset crystallization temperature and reduce the crystallization resistance. But based on our HRTEM studies, addition of 1 at.% Na can suppress the formation of α -Al clusters, which is responsible for the GFA improvement, as shown in Fig.7. As shown in this figure, the glass matrix in the base Al₈₈Ca₇Ni₅ alloy is not fully amorphous and actually contains numerous homogeneously distributed α -Al nano-crystals with a size of about 3-10 nm (Fig.7a). Comparatively, the HRTEM image of the as-spun Al₈₈Ca₆Ni₅Na₁ alloy (Fig.7b) shows a homogeneous featureless contrast and the SEAD pattern is typical for complete amorphous alloys, verifying that the formation of quenching-in nanosized α -Al has been suppressed due to Na addition.

In fact, glass formation is a complex metallurgical phenomenon and both liquid phase stability and crystallization resistance play important roles in the overall GFA [23]. Since all the three doping elements have similar chemical properties, the difference in the liquid stability and crystallization resistance arisen from the atomic size difference may explain why among the three elements, the Sr element is the most effective in enhancement of the GFA.

4. Conclusion

Effects of different large atomic radius elements (i.e., Na, Eu and Sr) on the GFA of the Al-based $\text{Al}_{88}\text{Ca}_7\text{Ni}_5$ alloy were investigated in the study. The results show that 1 at.% Eu and Sr additions is effective to increase GFA and consequently, the critical attainable thickness for glass formation is increased to 370 and 410 μm respectively. The GFA enhancement is found to be associated with the large liquid stability and the higher crystallization resistance due to the doping of Eu and Sr. For the Na-doped alloy, although 1 at.% Na addition lowers the crystallization temperature, but effectively suppresses the competing α -Al crystalline phase, leading to the improvement for the GFA of Al-based alloy.

Acknowledgments

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