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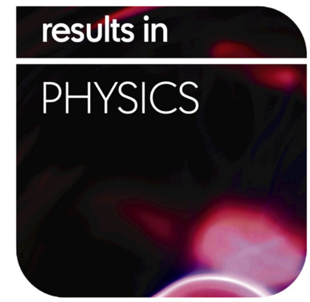

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Glass forming ability, thermal stability and elastic properties of Zr-Ti-Cu-Be-(Fe) bulk metallic glasses

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Abstract. A series of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=0-10) bulk metallic glasses are cast using water-cooled copper mold casting technique. The glass forming ability (GFA) and thermal stability of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys were studied by means of X-ray diffraction and differential scanning calorimetry. It was found that the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=2, 3, 5 and 7, respectively) alloys could be cast into glassy cylindrical rods with a diameters up to 20 mm. However, higher Fe content (x=10) deteriorates the GFA remarkably. The supercooled liquid region (ΔT_x), γ parameter (defined as $T_x/(T_g+T_l)$) and the reduced glass transition temperature T_{rg} (defined as T_g/T_l) are employed to evaluate the GFA in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=0-10) alloys. The results showed that T_{rg} was more effective in gauging the GFA of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloy systems than ΔT_x and γ parameter. In addition, elastic constant (Poisson's ratio) was also employed as a gauge to evaluate the glass forming ability in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys.

1. Introduction

Bulk metallic glasses (BMGs) have received much attention due to their unique mechanical properties such as high fracture strength and hardness, excellent corrosion resistance and fatigue durability [1-3]. Unfortunately, the engineering commercialization of BMGs as structural materials was largely restricted by their limited GFA and "work-softening" behavior under compression or tension [4, 5]. As a result, tremendous efforts have been made in producing centimeter-scale BMGs in different metal-based alloys [6-10]. Minor addition technique, which has been used widely in

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metallurgical fields, is found to be very effective in increasing the GFA and improving the mechanical properties for BMGs [11].

Iron (Fe), which is one of the transitional metals, has been selected as minor alloying element in various systems. For instance, the addition of 6 at% Fe into Ti-Zr-Be system could increase the critical glassy diameter up to 10 mm from the original 5 mm and enlarge the supercooled liquid region ΔT_x from 49 K to 107 K simultaneously [12]. More recently, Tan et al. [13] reported that partially substitution of Co by Fe in the $Zr_{56}Co_{28}Al_{16}$ alloy enhanced the critical fracture strain up to 15.1% in $Zr_{56}Co_{24}Al_{16}Fe_4$. In our present study, Fe is also chosen as the doped element to substitute Zr in the $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy due to (1) a large negative enthalpy of mixing between Fe and the majority constituents [14] and (2) more constituents might help to frustrate the crystallization process and thus favor glass formation based on the confusion principle [15, 16].

In this work, we vary the composition of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ BMGs using a systematic substitution of Zr with Fe (x =0, 1, 2, 3, 5, 7 and 10, respectively). The effects of Fe addition on the GFA，thermal stability and elastic property of the glass forming composition $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ have been studied.

2. Experimental

$Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x = 0, 1, 2, 3, 5, 7, 10 at.%) ingots were prepared by arc melting the high purity (≥ 99.9 wt.%) constituents under a titanium gettered argon atmosphere. Each ingot was remelted at least four times to make sure its chemical homogeneity. Cylindrical alloy rods with a diameter of 3, 4, 15 and 20 mm were prepared by injection casting the remelted ingots into a copper mould under argon atmosphere. The transverse cross-section of the specimens were examined by X-ray diffraction (XRD) with Cu Kα radiation so as to examine the structure of the samples. The thermal properties and melting behavior of the alloys were measured using a Netzsch STA 449C differential scanning calorimetry (DSC) under continuous argon flow at heating rate of 20 K/min. The acoustic velocities were measured at room temperature by using a pulse echo overlap method by a RITEC RAM-5000 ultrasonic system with a measuring sensitivity of 0.5 ns and carry frequency of 10 MHz at room temperature. The samples used for ultrasonic measurement were 4 mm in diameter and 10 mm in length. The density was measured by the Archimedean principle and the accuracy lies within 0.5%. The bulk modulus B, Young's modulus E, shear modulus G and Poisson's ratio v of the BMGs is derived from the acoustic velocities and density [17].

3. Results and discussion

The X-ray diffraction patterns of the as-cast $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy with diameters of 15 mm and 20 mm are presented in Fig.1 (a). It shows that typical broad diffraction maxima without any detectable crystalline Bragg peaks can be seen in the XRD spectrum for the as-cast

$Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy rod of 15 mm in diameter, indicating its glassy nature. While for the alloy rod of 20 mm in diameter, sharp diffraction peaks corresponding to $Cu_{10}Zr_7$ crystalline phase could be observed in the XRD spectra, suggesting that the critical glassy diameter of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy

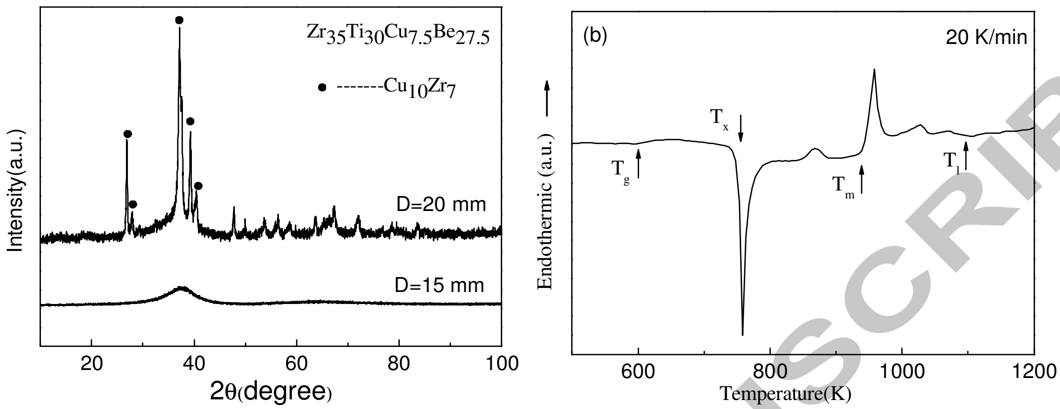

Fig. 1 XRD patterns (a) and DSC curve (b) of the as cast $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy

is larger that 15 mm but much smaller that 20 mm. Fig.1 (b) shows the DSC curve of the $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ glassy alloy with a diameter of 3 mm as recorded using a heating rate of 20 K/min. During the heating process, the samples exhibit a distinct glass transition followed by a supercooled liquid region prior to crystallization. After an exothermic peak due to crystallization events, notable melting events appear.

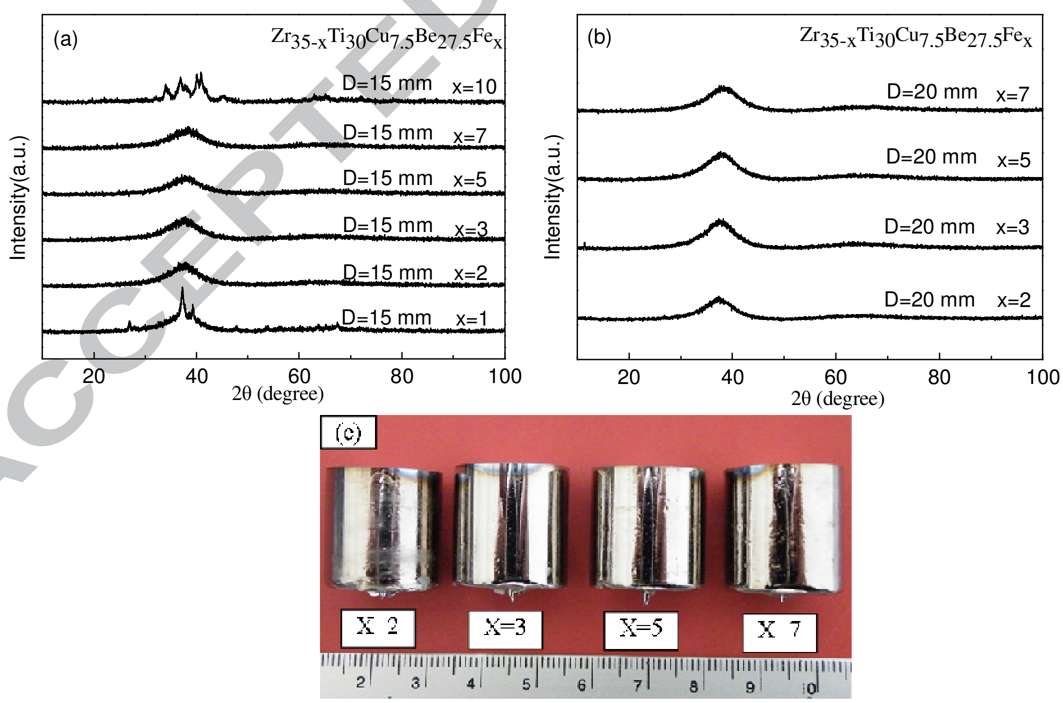

Fig.2 XRD patterns of the as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys with different diameters: (a) D=15 mm, (b) D=20 mm and (c) appearance of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=2, 3, 5 and 7) BMGs with a diameter of 20 mm

Fig.2 shows the XRD patterns of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=1, 2, 3, 5, 7 and 10) with 15 mm (a) and 20 mm (b) in diameter. As shown in Fig.2 (a), the as-cast $Zr_{33}Ti_{30}Cu_{7.5}Be_{27.5}Fe_2$, $Zr_{32}Ti_{30}Cu_{7.5}Be_{27.5}Fe_3$, $Zr_{30}Ti_{30}Cu_{7.5}Be_{27.5}Fe_5$ and $Zr_{28}Ti_{30}Cu_{7.5}Be_{27.5}Fe_7$ rods with 15 mm in diameter possess full glassy structure while the XRD spectrums of the alloys with x=1 and 10 with 15 mm in diameter have a few small Bragg peaks on the broad diffraction halos. The experimental results indicated that the GFA of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy was decreased when replacing Zr by 1 at.% and 10 at.% Fe. Moreover, it is obvious that the intensity of Bragg peaks of $Zr_{25}Ti_{30}Cu_{7.5}Be_{27.5}Fe_{10}$ alloy is much larger than that of the $Zr_{34}Ti_{30}Cu_{7.5}Be_{27.5}Fe_1$ alloy, suggesting that the alloy for x=10 possesses the weakest GFA among these alloys. To further investigate the GFA of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x= 2, 3, 5 and 7) alloy, rods with diameter of 20 mm were prepared by copper mold casting method and the XRD spectrums were shown in Fig.2 (b). It can be seen clearly that except broad diffraction halos no sharp diffraction peaks could be found, confirming the glassy nature of the as-cast rods with 20 mm in diameter. Therefore, it is obvious that replacing Zr by 2 at.%, 3 at.%, 5 at.% and 7 at.% Fe, the critical glassy diameter of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy could be enhanced from 15 mm to at least 20 mm, suggesting that Fe is an effective alloying element for improving the GFA of Zr-Ti-Cu-Be alloys.

Fig. 3 shows DSC curves of as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=1, 2, 3, 5, 7 and 10) glassy alloys at the heating rate of 20 K/min. The specimens for the DSC measurement were cut from the ϕ3 mm glassy rods. The glass transition temperature (T_g), onset crystallization temperature (T_x), onset melting temperature (T_m), liquidus temperature (T_l) and other thermodynamic parameters of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ BMGs are summarized in Table 1. Apparently, the glass transition temperature decreased about 10 ~ 30 K with 1-3 at.% Fe addition and then increased again for about 10 ~ 30 K with progressive Fe addition (x= 5-10 at.%). It can be found that the supercooled liquid region (ΔT_x) increases remarkably from 153 K to 175 K with 1 at.% Fe addition and then monotonously decreases to 80 K with increasing Fe content from 1 to 10 at.%. It should note that the discrepancy between the onset melting temperature and the liquidus temperature for $Zr_{28}Ti_{30}Cu_{7.5}Be_{27.5}Fe_7$ glassy alloy is the smallest, indicating that the composition is much closer to the eutectics and thus facilitates the glass formation.

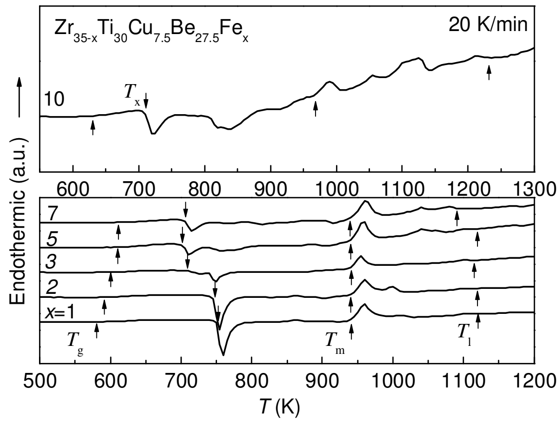

Fig. 3 DSC curves of the as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=1, 2, 3, 5, 7 and 10) glassy alloys with a heating rate of 20 k/min

Table 1 Thermodynamic parameters of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ bulk glassy alloys. D_{max} denotes the maximal accessible glass size in the study.

Samples	T_g/K	T_x/K	T_m/K	T_l/K	ΔT_x/K	T_{rg}	γ	D_{max}/mm
X=0	601	754	940	1097	153	0.548	0.444	15 <D_{max}< 20
X=1	579	754	941	1121	175	0.517	0.444	<15
X=2	589	749	940	1118	160	0.538	0.439	>20
X=3	598	709	941	1115	111	0.537	0.414	>20
X=5	611	702	938	1118	91	0.547	0.406	>20
X=7	610	705	939	1091	95	0.559	0.414	>20
X=10	630	710	968	1228	80	0.513	0.382	<15

In order to understand the reason of beneficial effect of Fe addition on the GFA of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy, the atomic sizes and heats of mixing among the constituents of the alloy have been discussed. The atomic radii size of Fe (1.28 Å) is slightly larger than that of Be (1.12 Å), but smaller than those of Ti (1.46 Å) and Zr (1.58 Å). Moreover, for the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys, there are large negative heats of mixing between Ti and Fe (-17 kJ/mol), Zr and Fe (-25 kJ/mol), Ti and Be (-30 kJ/mol), Zr and Be (-43 kJ/mol) [14], implying the existences of the strong chemical short-range order (SRO) and medium-range order (MRO) which may stabilize the liquid and reduce the atomic mobility during the solidification [18]. On the other hand, the substitution of Zr by Fe in the current $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy might increase the confusion and result in improving the GFA [19, 20].

Previous studies suggested that the glassy alloys with large ΔT_x value could remain stable in a wide temperature range without crystallization and has a high resistance to the nucleation and growth of crystalline phases. ΔT_x value basically serves as a measure of the GFA of a specific material. Waniuk et al. [21] reported that the reduced glass transition temperature T_{rg} (T_g/T_l) correlated well with GFA in Zr–Ti–Cu–Ni–Be alloys whereas the supercooled liquid region ΔT_x has no relationship with GFA in the least. However, Lu *et al* pointed out that it was inappropriate to utilize ΔT_x alone as a gauge of GFA for BMGs and proposed a new criterion γ defined as $T_x/(T_g+T_l)$ which proves to work out with success [22]. In our present study, the T_{rg}, ΔT_x and γ parameter were used as the thermal criteria to evaluate the GFA of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys. Fig.4 shows the composition dependence of the T_{rg}, ΔT_x, and γ parameter in the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ BMGs. As shown in Fig.4, although ΔT_x and γ parameter show the same tendency with Fe contents varying from 0 to 10, they did correlate nearly contrasting trend versus GFA in the current $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys. Compared to ΔT_x and γ parameter, the reduced glass transition temperature T_{rg} is more effective in evaluating the GFA of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys. According to the results of XRD and DSC measurements, the largest (0.559) and least (0.513) value of T_{rg} are corresponding the best (x=7) and worst (x=10) GFA of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloys, respectively. Inoue et al [23] also proved that the GFA is more closely associated with T_g/T_l values in Cu-Zr-Ti and Cu-Hf-Ti ternary systems rather than ΔT_x.

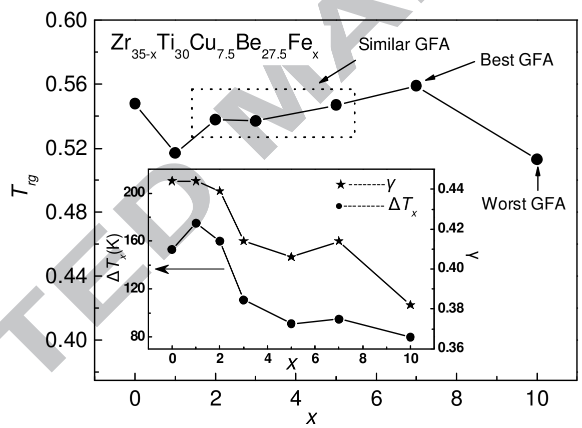

Fig. 4 Composition dependence of the T_{rg}, ΔT_x and γ (shown in the inset) in the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ BMGs

Recently, a few works emphasized the glass transition dependence of elastic properties such as shear modulus G and Poisson ratio ν, and elastic criteria is developed by using G/B or Poisson ratio to judge GFA [24, 25]. The ratio of shear modulus G to bulk modulus B or Poisson's ratio was reported to correlate with the critical cooling rate (Rc) on the basis of experimental observation that the glass with high values in G/B (or low value in Poisson's ratio) roughly correspond to high GFA of the system [26]. A small ν means that atoms or molecules can hardly rearrange themselves to shear strains without a drastic disturbance in bonding configurations, and the large v indicates the ease of atomic rearrangement. Therefore, glass-forming systems with relative low ν may exhibit high GFA. However, in this study, it can be seen that the Poisson's ratio (as shown in Figure 5) were not effective in evaluating the glass forming ability of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ BMGs. Additionally, in our recent

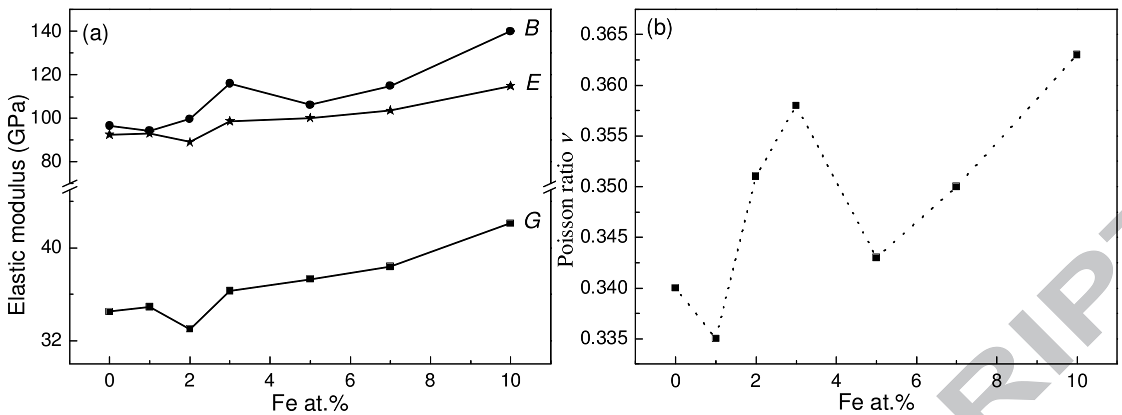

Figure 5 Composition dependences of elastic moduli (a) and poisson ratio ν (b) of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ BMGs

publication [27], we studied the effect of Al addition on the GFA of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloys and the *G/B* also show an inverse correlation with GFA. Therefore, the discrepancy between Poisson's ratio and thermal parameters in judging the GFA emphasizes that the explanation of GFA asks for comprehensive consideration.

Generally, ΔT_x is a quantitative measure of glass stability which is defined as the resistance of glasses towards devitrification upon reheating above T_g and GFA is specified as the ease by which melts can be cooled to form amorphous alloys without any crystal formation. As mentioned previously, GFA and glass thermal stability were related but independent properties. It is certain that GFA concerns thermodynamic, kinetic and structural aspects, but few studies are done to identify the correlation among them. And up to now, the explanation of glass forming ability of various substances has been remained unsolved and still an open question.

4. Conclusion

In conclusion, the glass forming ability (GFA) of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ (x=0-10) bulk metallic glasses is studied with XRD and DSC measurements. Bulk metallic glasses with critical diameter of larger than 20 mm are successfully prepared by water cooled copper mold casting technique. Finally, the reduced glass transition temperature T_{rg}, supercooled liquid region ΔT_x and γ parameter are employed to evaluate the GFA of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Fe_x$ alloy systems and the results show that T_{rg} is more effective in evaluating the GFA than ΔT_x , γ parameter and Poisson's ratio *v*.

Acknowledgements

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