# Effects of Trace Additions of Sn and Nb on the Thermal Stability and Plasticity of Zr-Cu-Fe-Al Bulk Metallic Glasses (Postprint)

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## Abstract

Amorphous alloy rods of Zr61.5Cu21.5-xFe5Al11Sn1Nbx (x=0, 1, 2, at. %) and Zr61.5Cu21.5Fe5Al12 with diameters of 2 and 3 mm were fabricated using copper mold casting. The results indicate that Sn and Nb microalloying slightly reduces the glass-forming ability of Zr-Cu-Fe-Al amorphous alloys. The Zr61.5Cu19.5Fe5Al11Sn1Nb2 amorphous alloy exhibits excellent compressive plasticity and demonstrates a "strain hardening" phenomenon. High-resolution transmission electron microscopy (HRTEM) observations reveal that both Zr61.5Cu19.5Fe5Al11Sn1Nb2 and Zr61.5Cu21.5Fe5Al12 alloys are fully amorphous, and the atomic packing within the alloy becomes denser after Sn and Nb microalloying. Positron annihilation spectroscopy (PAS) analysis results show that, compared with the Zr61.5Cu21.5Fe5Al12 amorphous alloy, the Zr61.5Cu19.5Fe5Al11Sn1Nb2 amorphous alloy exhibits decreased size but increased total amount of atomic dense-packed interstices and structural free volume. The large amount of homogeneously distributed free volume facilitates the formation, branching, and interaction of shear bands in the Zr61.5Cu19.5Fe5Al11Sn1Nb2 amorphous alloy, ultimately improving its plasticity.

## Full Text

## Effect of Minor Sn and Nb Additions on the Thermal Stability and Compressive Plasticity of Zr-Cu-Fe-Al Bulk Metallic Glass

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## Abstract

New Ni-free Zr61.5Cu21.5-xFe5Al11Sn1Nbx (x=0, 1, 2, atomic fraction, %) and Zr61.5Cu21.5Fe5Al12 bulk metallic glass (BMG) rods with diameters of 2 and 3 mm were fabricated by copper mold casting. In order to improve the plasticity of the Zr61.5Cu21.5Fe5Al12 BMG, minor Sn and Nb with lower thermal neutron cross-sections were added into the Zr-Cu-Fe-Al alloy. The experimental results showed that the glass-forming abilities of the BMGs with Sn and Nb elements were reduced slightly. Among them, however, Zr61.5Cu19.5Fe5Al11Sn1Nb2 BMG exhibits high compressive strength, high ductility together with extensive "work hardening." HRTEM study verifies the glassy states of both Zr61.5Cu19.5Fe5Al11Sn1Nb2 and Zr61.5Cu21.5Fe5Al12 alloy samples. The difference between the microstructures of the BMG samples with and without Sn and Nb elements is that the atomic arrangement in Zr61.5Cu19.5Fe5Al11Sn1Nb2 BMG is more closely packed than that in Zr61.5Cu21.5Fe5Al12 BMG. Positron annihilation lifetime spectroscopy study showed further that the Zr61.5Cu19.5Fe5Al11Sn1Nb2 BMG has more closely packed atomic arrangement than the Zr61.5Cu21.5Fe5Al12 BMG. The structural free-volume size of the former BMG is smaller than that of the latter BMG, and the total free-volume amount of the former BMG is obviously higher than that of the latter BMG. Uniformly distributed free volume is beneficial to improve the shear band formation, branching, and interactions of the Zr61.5Cu19.5Fe5Al11Sn1Nb2 BMG, which increases finally the compressive ductility of the BMG.

**KEY WORDS** minor Sn and Nb additions, Zr-Cu-Fe-Al bulk metallic glass, thermal stability, plasticity

## Introduction

Developed Zr-based bulk metallic glass systems mainly contain elements such as Zr, Cu, Al, Ni, Ti, Fe, Be, and Co, including Zr-Al-Ni(Fe)-Cu [?], Zr-(Ti, Nb)-Al-

Ni-Cu [?], Zr-Cu-Al-Ag [?, ?], Zr-(Pd, Ni)-Cu-Al-Ag [?], and Zr-Ti-Ni-Cu-Be [?], with critical sizes reaching the centimeter scale. Among these, Zr-Al-Ni-Cu and Zr-Al-Fe-Cu are two Zr-based bulk metallic glass systems with strong glass-forming ability. Studies [?, ?] have shown that Ni in Zr alloys increases hydrogen absorption, leading to hydrogen embrittlement. Based on existing amorphous alloy composition design theories, this work selected the Zr-Cu-Fe-Al system with high glass-forming ability as the research object. Our previous work [?] demonstrated that the prepared Zr61.5Cu21.5Fe5Al12 (abbreviated as Z1) bulk metallic glass possesses high glass-forming ability and thermal stability but exhibits typical brittle fracture behavior [?].

Microalloying can effectively improve the plasticity of Zr-based bulk metallic glasses [?, ?], but there are few reports on simultaneously adding Sn and Nb as alloying elements to Zr-based amorphous alloys to improve their comprehensive properties (plasticity, corrosion resistance, etc.) [?]. In nuclear fuel assembly zirconium alloys, the main alloying elements are Sn (0.65 b) and Nb (1.1 b) with small thermal neutron absorption cross-sections. For example, Zr-2 and Zr-4 alloys contain 1.2%~1.5% Sn (mass fraction), Zr-1Nb alloy contains about 1% Nb, Zr-2.5Nb alloy contains about 2.5% Nb, and new zirconium alloys such as ZIRLO and E635 are Zr-Sn-Nb series alloys containing approximately 1% each of Sn and Nb. Adding small amounts of Sn and Nb to pure Zr can substantially improve the mechanical properties and corrosion resistance of the alloy [?]. This work adopts the microalloying approach of Sn and Nb (substituting for some Al and Cu atoms in the Zr61.5Cu21.5Fe5Al12 amorphous alloy) to design a series of Zr61.5Cu21.5-xFe5Al11Sn1Nbx (x=0, 1, 2, atomic fraction, %) alloys, investigating the thermal stability and plasticity of Zr-Cu-Fe-Al-Sn-Nb bulk metallic glasses.

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## 1 Experimental Methods

High-purity metals Zr (99.9%), Cu (99.98%), Fe (99.9%), Al (99.99%), Sn (99.99%), and Nb (99.9%) were placed in a WKDHL-2 high-vacuum arc furnace and melted according to the composition ratios. The melting atmosphere was high-purity Ar (99.999%) after titanium gettering. Each alloy ingot was remelted four times to ensure compositional homogeneity. Rod-shaped alloy samples with diameters of 2 and 3 mm were prepared by differential pressure suction casting.

X-ray diffraction confirmed that the obtained rod samples were fully amorphous. The amorphous rods were cut into 1 mm thick discs using a low-speed precision cutting machine, then ground with sandpaper, polished, ultrasonically cleaned, and dried for storage.

The phase composition of the 3 mm diameter rods was examined using a D/MAX-RB X-ray diffractometer (XRD). A NETZSCH STA 449 C/CD differential scanning calorimeter (DSC) was used to determine the glass transition temperature Tg and crystallization onset temperature Tx. Compressive mechanical properties were tested using a CMT4305 electronic universal testing machine. Compression specimens were cylindrical samples with a diameter of 2 mm and height of 4 mm, tested at a strain rate of 4$×$10-4 s-1. Three specimens were tested to ensure reliability. Fracture morphologies of the compressed amorphous alloy specimens were observed using a SUPRA55 field emission scanning electron microscope (SEM). The structure and selected area electron diffraction (SAED) patterns of the amorphous alloy samples were examined using a JEM 2010 high-resolution transmission electron microscope (HRTEM) at an accelerating voltage of 200 kV. Positron annihilation lifetime spectroscopy (custom-built by the Institute of High Energy Physics, Chinese Academy of Sciences, with EG&G ORTEC NIM modules as the core) was used to analyze the free volume inside the amorphous alloys. The positron annihilation lifetime spectra were measured using a fast-slow coincidence spectrometer with a resolution of 196.6 ps. Each spectrum accumulated 2 million counts to ensure good statistics, and the fitting software was the standard LT9.0 package.

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## 2.1 Effect of Minor Sn and Nb Additions on Thermal Stability of Zr-Cu-Fe-Al Amorphous Alloys

Figure 1 [Figure 1: see original paper] shows the XRD patterns of the Zr61.5Cu21.5-xFe5Al11Sn1Nbx series alloys and the Z1 amorphous alloy. Only the Zr61.5Cu19.5Fe5Al11Sn1Nb2 (abbreviated as Z2) alloy exhibits a fully amorphous structure. The patterns reveal that adding 1% Sn (atomic fraction) to the Zr-Cu-Fe-Al amorphous alloy results in the appearance of AlZr2, AlZr3, Al3Zr, and ZrCu phases. As the Nb content increases, the intensity of crystalline phase peaks weakens. When the Nb content increases to 2% (atomic fraction), the Z2 alloy possesses a complete amorphous structure.

Figure 2 [Figure 2: see original paper] presents the DSC curves of the Z2 and Z1 amorphous alloys. Minor additions of Sn and Nb transform the primary crystallization behavior from single-stage to two-stage. The thermodynamic parameters and thermal neutron absorption cross-section data for both amorphous alloys are listed in Table 1 . Compared with the Z1 amorphous alloy, the primary crystallization temperature Tx1 of the Z2 amorphous alloy decreases by 12 K, the supercooled liquid region $\Delta$Tx decreases by 10 K, and the reduced glass transition temperature Trg (Trg=Tg/Tl, where Tl is the liquidus temperature) and $\gamma$ parameter ($\gamma$=Tx/(Tg+Tl)) decrease slightly. These results indicate that Sn and Nb microalloying slightly reduces the glass-forming ability of the Zr-Cu-Fe-Al amorphous alloy, while Tg, melting temperature Tm, and Tl remain almost unchanged. Table 1 also shows that the thermal neutron absorption cross-section ($\sigma$a) of the Z2 amorphous alloy is smaller than that of the Z1 amorphous alloy, which is beneficial for developing new Zr-based amorphous alloys for irradiation-resistant applications.

Figure 3 [Figure 3: see original paper] shows the DSC curves of the Z2 amorphous alloy at different heating rates. The Kissinger plots constructed from the Tg, Tx, first crystallization peak temperature Tp1, and second crystallization peak temperature Tp2 at various heating rates are presented in Figure 4 [Figure 4: see original paper]. The apparent activation energies at each characteristic temperature for the Z2 amorphous alloy were calculated from the slopes and are listed in Table 2 , along with the corresponding values for the Z1 amorphous alloy [?]. Table 2 indicates that both Z2 and Z1 amorphous alloys possess good resistance to crystallization and high thermal stability. The apparent activation energy for glass transition Eg and for crystallization onset Ex1 of the Z2 amorphous alloy are slightly lower than those of the Z1 amorphous alloy, suggesting that minor Sn and Nb additions slightly decrease the crystallization resistance of the amorphous alloy.

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## 2.2 Effect of Minor Sn and Nb Additions on Plasticity of Zr-Cu-Fe-Al Amorphous Alloys

Figure 5 [Figure 5: see original paper] shows the engineering stress-strain curves of the Z2 and Z1 amorphous alloys at a strain rate of 4$×$10-4 s-1. The Z1 amorphous alloy exhibits brittle fracture behavior, whereas the Z2 amorphous alloy demonstrates excellent compressive plasticity and shows a "strain hardening" phenomenon.

Table 3 lists the compressive mechanical properties of the Z2 and Z1 amorphous alloys. The maximum compressive stress $\sigma$max and fracture strain f of the Z2 amorphous alloy are significantly higher than those of the Z1 amorphous alloy, while the elastic modulus E and yield strength $\sigma$y are slightly lower. Notably, the $\sigma$max of the Z2 amorphous alloy far exceeds its yield strength $\sigma$y, exhibiting a "strain hardening" phenomenon that is very rare in bulk metallic glasses [?].

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## 3 Analysis and Discussion

The effective suppression of AlZr3, AlZr2, Al3Zr, and ZrCu phase precipitation by Nb addition can be explained by the negative mixing enthalpies of Nb-Al, Nb-Fe, and Nb-Sn pairs, which are -16, -18, and -1 kJ/mol, respectively. According to Inoue' s empirical rules for amorphous formation [?], adding Nb to the Zr-Cu-Fe-Al-Sn alloy is favorable for obtaining an amorphous structure.

Most previously reported bulk metallic glasses show stress softening with shear band propagation during plastic deformation, without obvious strain hardening [?]. In 2005, Das et al. [?] first discovered obvious "work hardening" in a Cu47.5Zr47.5Al5 bulk metallic glass, attributing it to atomic-scale heterogeneity in the amorphous structure that leads to massive shear band formation and strong interactions. Figures 6a [Figure 6: see original paper] and 6c show the

HRTEM images and corresponding SAED patterns of the Z2 and Z1 amorphous alloys, respectively. The Sn and Nb microalloyed alloy maintains a fully amorphous structure. Figures 6b and 6d reveal that compared with the Z1 amorphous alloy, the Z2 amorphous alloy has more closely packed atomic arrangement with more short-range ordered atomic configurations.

Figure 7 [Figure 7: see original paper] presents the fracture morphologies of the compressed Z2 and Z1 amorphous alloys. The Z2 amorphous alloy shows shear bands and their intersections (Figure 7a). This occurs because adding relatively large Sn and Nb atoms helps hinder the diffusion of smaller atoms like Cu and Fe, making the free volume distribution more uniform, increasing shear band nucleation sites, and promoting shear band multiplication. Figure 7b shows numerous shear bands piled up in region B and propagating in region C, similar to dislocation pile-up and intersection phenomena in crystalline metals during deformation. The Z1 amorphous alloy exhibits highly localized shear fracture with a fracture plane angle of approximately 43° to the stress axis (Figure 7c). Figure 7d shows the typical vein pattern fracture morphology of the Z1 amorphous alloy.

It is well known that the "work hardening" phenomenon in crystalline metals arises from the presence of numerous grain boundaries and second-phase particles, where dislocation slip easily piles up, causing dislocation intersections that increase deformation resistance. However, bulk metallic glasses lack grain boundaries, and Figure 6 shows no second-phase particles after Sn and Nb microalloying. Therefore, this plastic deformation behavior accompanied by "work hardening"may be related to randomly distributed free volume in the amorphous alloy [**?**, **?**].

Literature [**?**] indicates that structural relaxation and glass transition phenomena in DSC curves can be explained by the free volume model. The average free volume per atom Δvf is proportional to the relaxation enthalpy ΔH, i.e., ΔH = bΔvf, where b is a constant for a specific alloy. Slipenyuk and Eckert [**?**] confirmed the linear relationship between Δvf and ΔH by measuring the density of Zr55Cu30Al10Ni5 amorphous alloy at different annealing degrees. Accordingly, the relative magnitude of structural relaxation energy can be used to characterize the trend of free volume change [**?**].

The DSC curves of the Z2 and Z1 amorphous alloys are shown in Figure 8 [Figure 8: see original paper]. Both curves exhibit exothermic peaks characteristic of structural relaxation, and the glass transition temperatures are similar (Table 1). The inset of Figure 8 shows that the area of the relaxation exothermic peak for the Z2 amorphous alloy is significantly larger than that for the Z1 amorphous alloy, indicating that the energy released during structural relaxation is higher in the Z2 amorphous alloy, suggesting it contains more free volume. However, DSC results only demonstrate an increase in the total free volume in the Z2 amorphous alloy and cannot provide information on the morphology and distribution of various vacancy types, requiring further analysis by positron annihilation techniques.

Three different types of vacancies exist in amorphous alloys [**?**]: atomic dense-packing interstices, structural free volume, and nanovoids. Structural free volume and atomic dense-packing interstices are the two main types. Structural free volume consists of Bernal vacancies remaining after random atomic packing or defects caused by structural flow in the amorphous state, with relatively large sizes and thus longer positron annihilation lifetimes $\tau$i. Atomic dense-packing interstices mainly exist in the ordered atomic structure of amorphous alloys with relatively small sizes and thus shorter positron annihilation lifetimes.

Table 4 presents the three-lifetime component fitting results of positron annihilation spectroscopy for the Z2 and Z1 amorphous alloys [**?**]. The $\tau$3 lifetime corresponds to nanovoids, but its intensity I3 is small and shows little difference between the two alloys, so it is neglected in this work. The $\tau$2 lifetime, greater than the positron annihilation lifetime at lattice vacancies in pure Fe (165 ps), is considered as annihilation at relatively large structural free volume. The $\tau$1 lifetime with smaller values is attributed to annihilation at relatively small atomic dense-packing interstices.

After Sn and Nb microalloying, the positron annihilation lifetime of the Z2 amorphous alloy decreases, indicating that both structural free volume and atomic dense-packing interstice sizes are reduced. To further illustrate changes in free volume size and quantity after Sn and Nb microalloying, two-lifetime fitting was performed on the positron annihilation lifetime spectroscopy data to obtain the average lifetime $\tau$m and intensity of positrons annihilating in free volume (Table 5 ). The $\tau$m value reflects changes in overall free volume size, while its intensity variation reflects changes in overall free volume quantity. Table 5 shows that after Sn and Nb microalloying, $\tau$m decreases from 176.4 ps to 168.3 ps, while its intensity increases from 98.68% to 98.77%.

Comparing the two sets of lifetime values in Table 4 for the Z2 and Z1 amorphous alloys, the $\tau$1 and $\tau$2 lifetimes of the Z1 amorphous alloy are both larger than those of the Z2 amorphous alloy, indicating relatively larger atomic spacing and more sparse atomic arrangement in the Z1 amorphous alloy, with larger structural free volume and atomic dense-packing interstice sizes. Comparing the lifetime intensities in Table 5, Sn and Nb microalloying increases Im and decreases Iv in the amorphous alloy, indicating that Sn and Nb microalloying increases the quantity of structural free volume while reducing its size, meaning the structural free volume distribution in the Z2 amorphous alloy becomes more dispersed. Evidently, a large amount of uniformly distributed free volume is beneficial for shear band formation, branching, and interaction, ultimately improving the plasticity of the amorphous alloy.

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## 4 Conclusions

1. The Zr61.5Cu19.5Fe5Al11Sn1Nb2 amorphous alloy has slightly lower crystallization resistance than the Zr61.5Cu21.5Fe5Al12 amorphous alloy.

2. Compared with the Zr61.5Cu21.5Fe5Al12 amorphous alloy, the Zr61.5Cu19.5Fe5Al11Sn1Nb2 amorphous alloy has smaller atomic dense-packing interstices, reduced structural free volume size, and increased total free volume amount.
3. After minor Sn and Nb additions, the large amount of uniformly distributed free volume facilitates shear band formation, branching, and interaction, ultimately enhancing the plasticity of the Zr-Cu-Fe-Al amorphous alloy.

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