

Plasticity enhancement of a Zr-based bulk metallic glass by an electroplated Cu/Ni bilayered coating

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Abstract

In this study, the effect of a Cu/Ni bilayered coating on the shear banding behavior and compressive plasticity of a Zr-based bulk metallic glass (BMG) was investigated. As compared to a mono-layered Cu or Ni coating, the Cu/Ni bilayered coating has provided a better geometric confinement effect. Through a detailed comparative analysis among coated BMG samples with different plasticity, the correlation between the macroscopic plastic deformation behavior and the serrated flow characteristics is studied from the potential energy landscape point of view. The comparatively longer hanging time and larger elastic energy density in the Cu/Ni coated BMG in the serrated plastic regime result in an increased global plastic strain of ~11.2%. The enhanced plasticity is attributed to the thin soft Cu layer acting as a buffer zone for absorbing the elastic energy upon loading, and the strong outer Ni coating exerting a high confining stress upon loading, which impede the rapid propagation of the shear

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bands. In addition, the strong Cu-Ni interface is also believed to contribute to the enhanced plasticity.

Keywords: bulk metallic glass; electroplating; Cu/Ni bilayered coating; mechanical properties; shear bands

1. Introduction

Due to the lack of strain hardening, plastic deformation of most monolithic bulk metallic glasses (BMGs) at high stresses and low temperatures (e.g., room temperature) is usually localized into nano-scale shear bands, which propagate rapidly such that many BMGs can only experience limited plastic deformation before catastrophic failure [1, 2]. Among various strategies to circumvent this problem, Cu or Ni plating has been successfully adopted to enhance the compressive plastic strain of BMGs [3-6]. The findings suggested that electroplated metal coatings can help inhibit the propagation of shear bands and boost the proliferation of multiple shear bands via radial geometric constraints.

To interpret the mechanism of plasticity enhancement by electroplated coatings, it is worth noting that Choi *et al.* [3] proposed a schematic "crack buffer zone" model to explain the plastic deformation region in the soft Cu metal coating layer. This localized plastic deformation region or "crack buffer zone" (of the order of $\sim 20\ \mu\text{m}$ in width) immediately adjacent to the BMGs is able to absorb the strain as well as the elastic energy released from the deformation induced surface steps, thereby effectively suppressing the crack formation and delaying the final fracture [3]. From this standpoint, the coating layer should be sufficiently ductile to translate the shear band propagation energy into its own plastic deformation. On the other hand, a layer with a high strength coating, such as Ni, has been shown to be quite critical in guaranteeing pronounced geometric confinement during loading [5, 7]. Therefore, it is of great interest to synthesize a coating exhibiting both the above two mechanisms to further enhance the plasticity of BMGs. Electroplating is featured as a unique way for obtaining predetermined mechanical properties from a particular metal, and a wide range of properties are attainable for most metal electrodeposits by means of tuning the special characteristics (e.g., electrolyte solutions) of the electrodeposition process [8, 9]. In the present work, a two-stage electrodeposition process is adopted to deposit

a Cu/Ni bilayered coating on a BMG, and the effects on the mechanical properties of the BMG are investigated and compared to those with mono-layered Cu or Ni coatings.

Macroscopically, the compressive curves of BMGs usually exhibit numerous flow serrations associated with intermittent bursts of plastic strain after yielding, analogous to the well-known Portevin-Le Châtelier (PLC) effect in crystalline solids [10, 11]. Although it has been recognized that the serration events correspond to the emission or propagation of individual shear bands during deformation, the correlation between the serrated flow behavior in the plastic regime and the global plasticity of BMGs is still not fully understood. In the present study, a comparative analysis of the serration flow characteristics of different coated BMGs is further investigated. The findings are able to help understand not only how the different coating confinements affect the plastic flow of BMGs, but also the correlation between the serration characteristics and the plasticity of BMGs.

2. Experimental Procedure

Cylindrical $Zr_{57}Al_{10}Ni_8Cu_{20}Ti_5$ (at. %) BMG ingots of 2 mm in diameter were prepared by arc melting the pure elements together in a titanium-gettered Ar atmosphere, followed by copper mold casting. The amorphous structure of the BMGs was checked by X-ray diffraction (XRD), which showed no evidence of crystalline diffraction peaks.

A common acid sulphate solution was used for the Cu plating. Typically Cu electrodeposits obtained from this type of bath exhibit considerable ductility (11% ~ 16% tensile elongation) with a relatively low yield strength of 120 ~ 150 MPa [9]. On the other hand, the Ni coating was electroplated from a Hard Watts electrolyte (containing ammonia ions) at room temperature, which is able to produce a strong coating layer of Ni with a tensile strength as high as around 1000 MPa, but with

limited ductility [8]. The details of the BMG pre-treatment and plating process have been introduced previously [4, 5]. For the mono-layered Cu coated BMG, electroplating proceeded for 160 min, compared to 480 mins for the mono-layered Ni coated BMG. In the case of the Cu/Ni bilayered coating, Cu and Ni plating was undertaken for 60 min and 360 min, respectively, using the conceptually simple dual bath technique [12]. The thicknesses of the different coatings (Cu, Ni, Cu/Ni) on the BMGs were measured by optical microscopy (OM), equipped with length scale measuring tools.

Room-temperature compression tests were undertaken for different specimens, all with a nominal aspect ratio of 2:1 at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$, on a Materials Testing System (MTS) equipped with an extensometer. Before testing, the two ends of the test specimens were carefully polished to ensure parallelism and perpendicularity. The fracture morphologies of the failed samples were examined by scanning electron microscopy (SEM).

3. Results and Discussions

The cross-sections of the Zr-based BMG with different coatings are shown in Fig. 1. Due to the continuous agitation of the electroplating solution and the rotation of the BMG rods, the coatings are all evenly distributed around the BMGs. The thicknesses of all the mono-layer and bi-layer coatings are maintained at around 80 μm in order to minimize its effect on the compressive behavior.

Fig. 2 shows the representative engineering stress-strain curves of the various samples. The as-cast specimen is found to yield at 1807 MPa with a limited plastic strain of 1.3% before failure. The pure Cu coated BMG yields at a lower strength of 1580 MPa, followed by a plastic strain of 4.6%. In contrast, the pure Ni coated specimen and the bilayered Cu/Ni coated sample yield at 1705 MPa and 1637 MPa with improved plastic strains up to 7.0% and 11.2 %, respectively. It is worthwhile mentioning that

the measured yield strengths of the coated BMGs agree well with the predictions based on the "rule of mixtures" in composite materials mechanics [13].

The serrated flow on the stress-strain curves illustrates the characteristic feature of the plastic flow behavior of BMGs, manifested as repeated elastic loading (stress increase) and sudden unloading (stress drop) processes accommodated by plastic strain release. This feature is more clearly revealed in Fig. 3 which shows the representative magnified plastic flow region of 2.5% ~ 4.5% for the Cu-coated specimen. The sudden stress drop during each serration event can be clearly observed as the corresponding "peak" in the derivative of stress versus time, i.e., the $|d\sigma/dt|$ trace (see Fig. 3). It is important to realize that some small peaks that correspond to stress drops with magnitude smaller than 12 MPa are caused by vibration of the machine instead of the serrations [14]. From the $|d\sigma/dt|$ plot, one can see that the elastic loading time is much larger than the unloading time, which suggests that the internal relaxation rate under external loading by the release of stored elastic energy is much lower than the elastic energy storage rate. The time taken during each serration event can be roughly estimated by the elastic loading hanging time $t_n = T_{n+1} - T_n$ for the n^{th} serration as shown in Fig. 3, where T_{n+1} and T_n are two successive onset times of serration. The corresponding elastic energy density involved in this serration event can be calculated as:

$$E_n = \frac{1}{2} \Delta\sigma_n \Delta\varepsilon_n \quad (1)$$

where $\Delta\sigma_n$ and $\Delta\varepsilon_n$ respectively denote the elastic stress and elastic strain increments in the serration. By carefully observing the compressive stress-strain curves of all the specimens, one can note that the hanging time and elastic energy density are inhomogeneous, varying from serration to serration, and from sample to sample. Here, two parameters are defined to characterize the serration events in the plastic regime for different coated BMG samples, the mean hanging time t_m and the mean elastic energy density E_m . Supposing there are totally i serration events in the plastic regime,

the mean hanging time t_m and the mean elastic energy density E_m can then be obtained as:

$$\begin{aligned} t_m &= (t_1 + t_2 + \dots + t_i)/i \\ E_m &= (E_1 + E_2 + \dots + E_i)/i \end{aligned} \quad (2)$$

The t_m and E_m values, together with the mechanical properties for different BMG samples are summarized in Table 1. When statistically calculating t_m and E_m values, the small serrations originating from vibration of the MTS machine should not be counted. It is interesting to notice that t_m and E_m increase monotonously with the improvement of the plasticity by different electroplated coatings, indicating some correlations between the macroscopic plasticity and the microscopic serrated flow behavior may exist. Recently, a detailed statistical analysis of the magnitude and the time scale (or the hanging time herein) of the stress-flow serrations within the plastic flow regime of a Zr-based BMG disclosed that the jerky flow behavior of BMGs is very sensitive to strain rate and there exist some interlinks between the jerky flow kinetics in BMGs and the temperature rise during adiabatic shear localization [15, 16]. In fact, BMGs are usually in thermodynamically metastable states at room temperature. Upon external loading, the elastic energy stored within a BMG during each serration event behaves as a driving force to propel the BMG from one metastable state to another more stable metastable state in terms of potential energy landscapes, overcoming the potential energy barrier in this transition [17]. In this regard, the mean elastic energy density E_m for the serration events is proportional to the mean energy barrier E_b over the transitions of potential energy from the initial state to the final state [17, 18]. In other words, the higher the E_b , the higher the required mean stored elastic energy E_m (achieved by external mechanical work) to balance E_b . Therefore, the variation in E_m listed in Table 1 for different samples reflects a variation in the required mechanical work during serrated flow to overcome the different E_b values for the different BMG samples. From Table 1, instructively, E_m for the uncoated as-cast sample is much lower than for the coated ones, suggesting

that the E_b is smaller in the as-cast BMG and the required amount of mechanical work E_m is lower in operating and finishing the serrated flow events. Meanwhile, the transitions among different metastable potential energy states are associated with atomistic rearrangements with discrete bursts of plastic strain by consuming the stored mechanical work. Thus, a lower average mechanical work input yields a lower burst of plastic strain. Compared with the as-cast sample that has an E_m value of 5.664 kJ/m^3 , all the coated samples show higher E_m values (with the highest E_m up to 7.141 kJ/m^3 for the Cu/Ni coated sample). This increased E_m implies that more mechanical work is demanded to overcome the increased mean energy barrier E_b to accomplish the serrated flow process and reach the more "preferred" metastable state. As a result, more plastic strain is involved with the increase in mechanical work. On the other hand, under the same fixed strain rate loading condition, it is imaginable that the increase in mean stored mechanical work for the serration events requires longer time to overcome the increased energy barrier E_b and to fulfill the energetic transition. This explains the variation in mean hanging time t_m for the BMG samples with different global plasticity.

It is well appreciated the successive serration events (or the stress fluctuation) correspond to the emission of new shear bands or progression of existing shear bands. While the stress drop in a serration event can be considered as a consequence of the propagation of the shear bands or sliding on the shear plane, the stress increase is believed to stem from the blunting of the shear bands or micro-cracks. It is obvious that the number of serrations monotonously increases with the increase of plasticity. Experimental observations of the shear band traces on the various deformed BMGs after compression also reveal that the increase in the number of serrations is accompanied with the increase in the shear band density. Fig. 4 shows that few shear bands can be seen on the as-cast specimen, illustrating that the main shear band, after activation, propagates rapidly throughout the whole BMG. On the Cu coated BMG, a couple of sparse parallel shear bands can be detected [Fig. 4(b)]. In contrast, a large

number of shear bands appear on the pure Ni coated BMG and the Cu/Ni coated BMG. From Fig. 4(c), it can be clearly seen, that for the Ni coated BMG, besides a few shear bands in the horizontal direction, there are mainly two groups of parallel shear bands that are perpendicular to each other, having an angle of nearly 45° to the loading direction. On the other hand, strikingly more dense shear bands are observed on the Cu/Ni coated sample as shown in Fig. 4(d). These shear bands, compared with those on the pure Ni coated sample, appear to be somewhat randomly arranged in orientation. An enormous number of tenuous branched shear bands eradiate from the primary shear bands. This concurrent emission of multiple shear bands is responsible for the numerous minor serrations and the large plastic deformation strain, as revealed in the compressive curve.

In order to elucidate the differences between the effects of the different coatings, the mechanisms for the enhancement of plasticity are discussed in terms of residual stress, confining stress and the Cu/Ni interface strength. It has been reported in the literature that the electrodeposition process can bring about residual compressive stress on the surface of BMGs, which helps arrest the shear banding or cracking behavior [4]. Usually the Cu coating obtained from acid sulfate baths is stress-free or contains negligible residual stress [9], whereas the residual compressive stress involved in the Ni plating process from the Hard Watts baths can reach up to 280 ~ 340 MPa [8]. On the other hand, the radial confining stress σ_c exerted on the BMG is linearly proportional to the yield strength of the coating σ_y , as indicated in the following expression [7]:

$$\sigma_c = \sigma_y \ln \frac{b}{a} \quad (3)$$

where b denotes the outer diameter of the BMG/coating composite and a represents the diameter of the bare BMG. This confinement pressure will not be released until the following criterion:

$$(\nu_c - \nu_B)\varepsilon \geq \frac{\sigma_y}{E_c} \quad (4)$$

is satisfied [19], where ε represents the axial strain for the BMG sample; E_c refers to Young's modulus of the coating, ν_B and ν_c are the respective Poisson's ratios of the BMG and the coating. The Ni coating and the Cu coating are assumed to yield at 1000 MPa [8], and 135 MPa [9], with Young's modulus of 207 GPa [20], and 117 GPa [21], respectively. It is assumed that ν_B is 0.30 for the present BMG, and Poisson's ratio is roughly estimated to be 0.36 for the Ni coating [20] and 0.33 for the Cu coating [22]. For the Cu/Ni bilayered coating, the "rule of mixtures" is employed to estimate the yield strength, Young's modulus and Poisson's ratio. If one substitutes these values into equation (4), the axial strain ε can be estimated to be 5.77%, 9.66%, 10.06% for the Cu-coated, the Ni-coated and the Cu/Ni coated samples, respectively. These results show that the duration of the lateral confinement pressure exerted by the Cu/Ni coating is the longest when the axial strain of the coated BMG reaches 10.06%. It is also in line with the findings that the Cu/Ni coating is more effective in enhancing the plasticity of the BMG.

Furthermore, as far as the Cu/Ni coated BMG is concerned, the 53.7 μm Ni layer plating can produce almost an equivalent residual compressive stress to that of a pure 76.6 μm Ni plating layer, since this residual stress in Ni plating is highly dependent on the deposition rate, and it remains constant in thicknesses in excess of 50 μm [23]. Apart from this Ni plating induced residual stress, the inner Cu layer in the Cu/Ni bilayer, being more ductile in comparison with the relatively brittle Ni coating, can be regarded as an effective shear strain and elastic deformation energy storage area that adequately absorb the shear banding energy and crack propagation energy by means of its strong deformability through dislocation operations without the premature formation of micro-cracks, which may otherwise take place if localized in the brittle Ni coating.

In addition, if the stress at which the interface obstacle to this bilayered coating system can be overcome is defined as the "blocking strength", this blocking strength has been roughly estimated through atomic simulation to be of the order of ~ 1.24 GPa, based on the modulus mismatch (Koehler barrier), the slip plane mismatch, and the lattice parameter mismatch between the Cu and the Ni layer [24]. Such a substantial high blocking strength is inevitably beneficial for the creation of a large external confining stress, upon loading, and is indirectly verified by the fracture profile of the post-failed sample, shown in Fig. 5, where it is seen that most of the Cu-Ni interface is still intact and remains bonded after failure. This robust confining effect helps to retard the shear band movements or micro-crack propagation and the initiation of multiple shear bands, thereby improving the macroscopic plastic deformation.

4. Conclusions

The mechanical behavior of a Zr-based BMG with different coatings, i.e., a mono-layered Cu coating, a mono-layered Ni coating and a Cu/Ni bilayered coating was compared. It has been demonstrated that the bilayered Cu/Ni coated BMG can sustain more plastic strain than the Cu coated or the Ni coated one. The correlation between the macroscopic plastic deformation behavior and the serrated flow characteristic has been analyzed and it is shown that the increase in mean holding time and mean elastic energy density during the serration events gives rise to the improved plasticity from the perspective of the potential energy landscape. Besides, the thin soft Cu layer in the Cu/Ni coating serves as a strain buffer zone to absorb elastic deformation energy, while the stronger outer Ni layer ensures a substantial confining stress during deformation of the BMG. In addition to these, the large blocking strength of the Cu/Ni interface also helps to hinder the rapid propagation of the shear bands. This two-step Cu/Ni coating electrodeposition technique has provided a new insight into the enhancement of plasticity of BMGs.

Acknowledgements

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Figures and Table captions

Figure 1. The cross-sections of Zr-based BMGs with different coatings: a) 80.09 μm Cu coating; b) 76.56 μm Ni coating; c) Cu/Ni coatings (24.23 μm Cu coating, plus 53.73 μm Ni coating)

Figure 2. The uniaxial compressive stress-strain curves of different samples: a) As-cast; b) Cu coated; c) Ni coated; d) Cu/Ni coated.

Figure 3. The representative magnified plastic flow region (strain 2.5% ~ 4.5%) for the Cu-coated specimen.

Figure 4. The fracture morphologies of different specimens after failure: a) As-cast; b) Cu coated; c) Ni coated; d) Cu/Ni coated.

Figure 5. (a) The post-failure fracture profile of Cu/Ni coated sample; (b) The tightly bonded Cu-Ni interface after fracture.

Table 1. The summarized mechanical properties, mean hanging time and mean elastic energy density for different specimens.

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where $\Delta\sigma_n$ and $\Delta\varepsilon_n$ respectively denote the elastic stress and elastic strain increments in the serration. By carefully observing the compressive stress-strain curves of all the specimens, one can note that the hanging time and elastic energy density are inhomogeneous, varying from serration to serration, and from sample to sample. Here, two parameters are defined to characterize the serration events in the plastic regime for different coated BMG samples, the mean hanging time t_m and the mean elastic energy density E_m . Supposing there are totally i serration events in the plastic regime,

the mean hanging time t_m and the mean elastic energy density E_m can then be obtained as:

$$\begin{aligned} t_m &= (t_1 + t_2 + \dots + t_i)/i \\ E_m &= (E_1 + E_2 + \dots + E_i)/i \end{aligned} \quad (2)$$

The t_m and E_m values, together with the mechanical properties for different BMG samples are summarized in Table 1. When statistically calculating t_m and E_m values, the small serrations originating from vibration of the MTS machine should not be counted. It is interesting to notice that t_m and E_m increase monotonously with the improvement of the plasticity by different electroplated coatings, indicating some correlations between the macroscopic plasticity and the microscopic serrated flow behavior may exist. Recently, a detailed statistical analysis of the magnitude and the time scale (or the hanging time herein) of the stress-flow serrations within the plastic flow regime of a Zr-based BMG disclosed that the jerky flow behavior of BMGs is very sensitive to strain rate and there exist some interlinks between the jerky flow kinetics in BMGs and the temperature rise during adiabatic shear localization [15, 16]. In fact, BMGs are usually in thermodynamically metastable states at room temperature. Upon external loading, the elastic energy stored within a BMG during each serration event behaves as a driving force to propel the BMG from one metastable state to another more stable metastable state in terms of potential energy landscapes, overcoming the potential energy barrier in this transition [17]. In this regard, the mean elastic energy density E_m for the serration events is proportional to the mean energy barrier E_b over the transitions of potential energy from the initial state to the final state [17, 18]. In other words, the higher the E_b , the higher the required mean stored elastic energy E_m (achieved by external mechanical work) to balance E_b . Therefore, the variation in E_m listed in Table 1 for different samples reflects a variation in the required mechanical work during serrated flow to overcome the different E_b values for the different BMG samples. From Table 1, instructively, E_m for the uncoated as-cast sample is much lower than for the coated ones, suggesting

that the E_b is smaller in the as-cast BMG and the required amount of mechanical work E_m is lower in operating and finishing the serrated flow events. Meanwhile, the transitions among different metastable potential energy states are associated with atomistic rearrangements with discrete bursts of plastic strain by consuming the stored mechanical work. Thus, a lower average mechanical work input yields a lower burst of plastic strain. Compared with the as-cast sample that has an E_m value of 5.664 kJ/m^3 , all the coated samples show higher E_m values (with the highest E_m up to 7.141 kJ/m^3 for the Cu/Ni coated sample). This increased E_m implies that more mechanical work is demanded to overcome the increased mean energy barrier E_b to accomplish the serrated flow process and reach the more "preferred" metastable state. As a result, more plastic strain is involved with the increase in mechanical work. On the other hand, under the same fixed strain rate loading condition, it is imaginable that the increase in mean stored mechanical work for the serration events requires longer time to overcome the increased energy barrier E_b and to fulfill the energetic transition. This explains the variation in mean hanging time t_m for the BMG samples with different global plasticity.

It is well appreciated the successive serration events (or the stress fluctuation) correspond to the emission of new shear bands or progression of existing shear bands. While the stress drop in a serration event can be considered as a consequence of the propagation of the shear bands or sliding on the shear plane, the stress increase is believed to stem from the blunting of the shear bands or micro-cracks. It is obvious that the number of serrations monotonously increases with the increase of plasticity. Experimental observations of the shear band traces on the various deformed BMGs after compression also reveal that the increase in the number of serrations is accompanied with the increase in the shear band density. Fig. 4 shows that few shear bands can be seen on the as-cast specimen, illustrating that the main shear band, after activation, propagates rapidly throughout the whole BMG. On the Cu coated BMG, a couple of sparse parallel shear bands can be detected [Fig. 4(b)]. In contrast, a large

number of shear bands appear on the pure Ni coated BMG and the Cu/Ni coated BMG. From Fig. 4(c), it can be clearly seen, that for the Ni coated BMG, besides a few shear bands in the horizontal direction, there are mainly two groups of parallel shear bands that are perpendicular to each other, having an angle of nearly 45° to the loading direction. On the other hand, strikingly more dense shear bands are observed on the Cu/Ni coated sample as shown in Fig. 4(d). These shear bands, compared with those on the pure Ni coated sample, appear to be somewhat randomly arranged in orientation. An enormous number of tenuous branched shear bands eradiate from the primary shear bands. This concurrent emission of multiple shear bands is responsible for the numerous minor serrations and the large plastic deformation strain, as revealed in the compressive curve.

In order to elucidate the differences between the effects of the different coatings, the mechanisms for the enhancement of plasticity are discussed in terms of residual stress, confining stress and the Cu/Ni interface strength. It has been reported in the literature that the electrodeposition process can bring about residual compressive stress on the surface of BMGs, which helps arrest the shear banding or cracking behavior [4]. Usually the Cu coating obtained from acid sulfate baths is stress-free or contains negligible residual stress [9], whereas the residual compressive stress involved in the Ni plating process from the Hard Watts baths can reach up to 280 ~ 340 MPa [8]. On the other hand, the radial confining stress σ_c exerted on the BMG is linearly proportional to the yield strength of the coating σ_y , as indicated in the following expression [7]:

$$\sigma_c = \sigma_y \ln \frac{b}{a} \quad (3)$$

where b denotes the outer diameter of the BMG/coating composite and a represents the diameter of the bare BMG. This confinement pressure will not be released until the following criterion:

$$(\nu_c - \nu_B)\varepsilon \geq \frac{\sigma_y}{E_c} \quad (4)$$

is satisfied [19], where ε represents the axial strain for the BMG sample; E_c refers to Young's modulus of the coating, ν_B and ν_c are the respective Poisson's ratios of the BMG and the coating. The Ni coating and the Cu coating are assumed to yield at 1000 MPa [8], and 135 MPa [9], with Young's modulus of 207 GPa [20], and 117 GPa [21], respectively. It is assumed that ν_B is 0.30 for the present BMG, and Poisson's ratio is roughly estimated to be 0.36 for the Ni coating [20] and 0.33 for the Cu coating [22]. For the Cu/Ni bilayered coating, the "rule of mixtures" is employed to estimate the yield strength, Young's modulus and Poisson's ratio. If one substitutes these values into equation (4), the axial strain ε can be estimated to be 5.77%, 9.66%, 10.06% for the Cu-coated, the Ni-coated and the Cu/Ni coated samples, respectively. These results show that the duration of the lateral confinement pressure exerted by the Cu/Ni coating is the longest when the axial strain of the coated BMG reaches 10.06%. It is also in line with the findings that the Cu/Ni coating is more effective in enhancing the plasticity of the BMG.

Furthermore, as far as the Cu/Ni coated BMG is concerned, the 53.7 μm Ni layer plating can produce almost an equivalent residual compressive stress to that of a pure 76.6 μm Ni plating layer, since this residual stress in Ni plating is highly dependent on the deposition rate, and it remains constant in thicknesses in excess of 50 μm [23]. Apart from this Ni plating induced residual stress, the inner Cu layer in the Cu/Ni bilayer, being more ductile in comparison with the relatively brittle Ni coating, can be regarded as an effective shear strain and elastic deformation energy storage area that adequately absorb the shear banding energy and crack propagation energy by means of its strong deformability through dislocation operations without the premature formation of micro-cracks, which may otherwise take place if localized in the brittle Ni coating.

In addition, if the stress at which the interface obstacle to this bilayered coating system can be overcome is defined as the "blocking strength", this blocking strength has been roughly estimated through atomic simulation to be of the order of ~ 1.24 GPa, based on the modulus mismatch (Koehler barrier), the slip plane mismatch, and the lattice parameter mismatch between the Cu and the Ni layer [24]. Such a substantial high blocking strength is inevitably beneficial for the creation of a large external confining stress, upon loading, and is indirectly verified by the fracture profile of the post-failed sample, shown in Fig. 5, where it is seen that most of the Cu-Ni interface is still intact and remains bonded after failure. This robust confining effect helps to retard the shear band movements or micro-crack propagation and the initiation of multiple shear bands, thereby improving the macroscopic plastic deformation.

4. Conclusions

The mechanical behavior of a Zr-based BMG with different coatings, i.e., a mono-layered Cu coating, a mono-layered Ni coating and a Cu/Ni bilayered coating was compared. It has been demonstrated that the bilayered Cu/Ni coated BMG can sustain more plastic strain than the Cu coated or the Ni coated one. The correlation between the macroscopic plastic deformation behavior and the serrated flow characteristic has been analyzed and it is shown that the increase in mean holding time and mean elastic energy density during the serration events gives rise to the improved plasticity from the perspective of the potential energy landscape. Besides, the thin soft Cu layer in the Cu/Ni coating serves as a strain buffer zone to absorb elastic deformation energy, while the stronger outer Ni layer ensures a substantial confining stress during deformation of the BMG. In addition to these, the large blocking strength of the Cu/Ni interface also helps to hinder the rapid propagation of the shear bands. This two-step Cu/Ni coating electrodeposition technique has provided a new insight into the enhancement of plasticity of BMGs.

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Figures and Table captions

Figure 1. The cross-sections of Zr-based BMGs with different coatings: a) 80.09 μm Cu coating; b) 76.56 μm Ni coating; c) Cu/Ni coatings (24.23 μm Cu coating, plus 53.73 μm Ni coating)

Figure 2. The uniaxial compressive stress-strain curves of different samples: a) As-cast; b) Cu coated; c) Ni coated; d) Cu/Ni coated.

Figure 3. The representative magnified plastic flow region (strain 2.5% ~ 4.5%) for the Cu-coated specimen.

Figure 4. The fracture morphologies of different specimens after failure: a) As-cast; b) Cu coated; c) Ni coated; d) Cu/Ni coated.

Figure 5. (a) The post-failure fracture profile of Cu/Ni coated sample; (b) The tightly bonded Cu-Ni interface after fracture.

Table 1. The summarized mechanical properties, mean hanging time and mean elastic energy density for different specimens.

Fig. 1

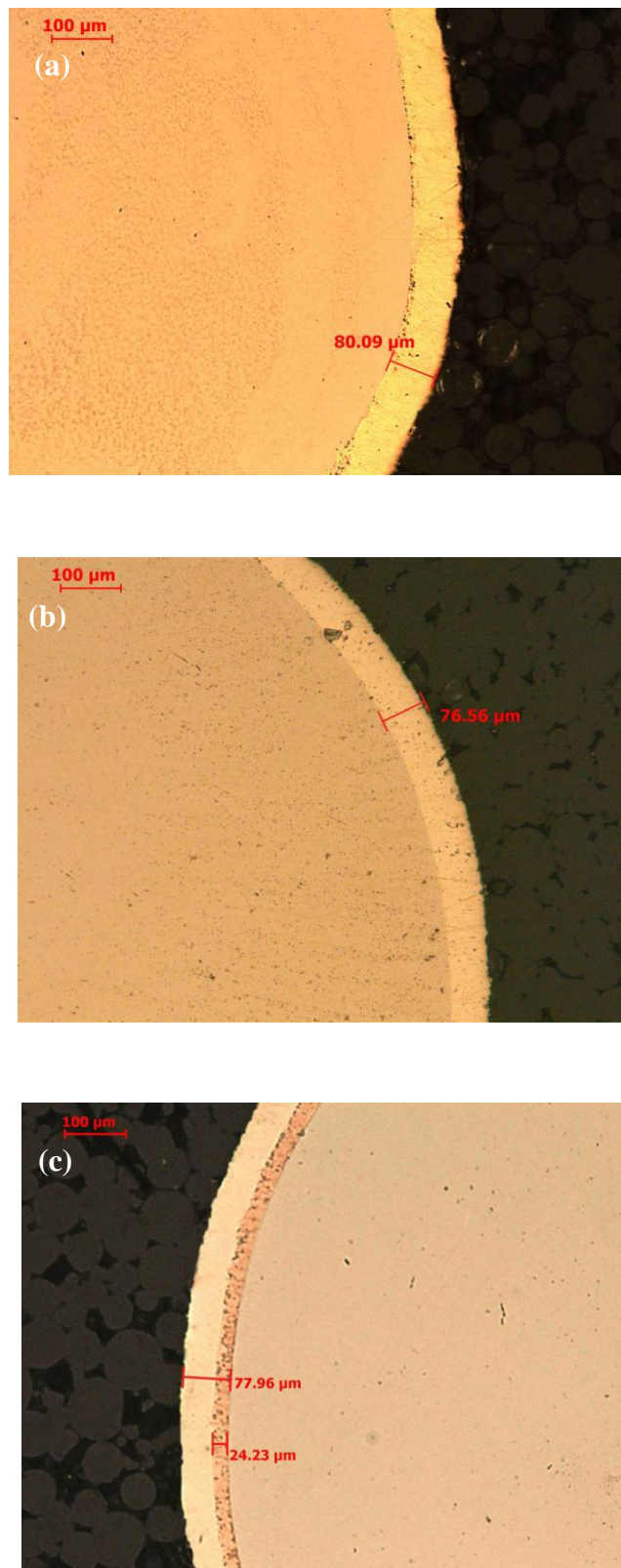


Fig. 1 The cross-sections of Zr-based BMGs with different coatings: a) 80.09 μm Cu coating; b) 76.56 μm Ni coating; c) Cu/Ni coatings (24.23 μm Cu coating, plus 53.73 μm Ni coating)

Fig. 2

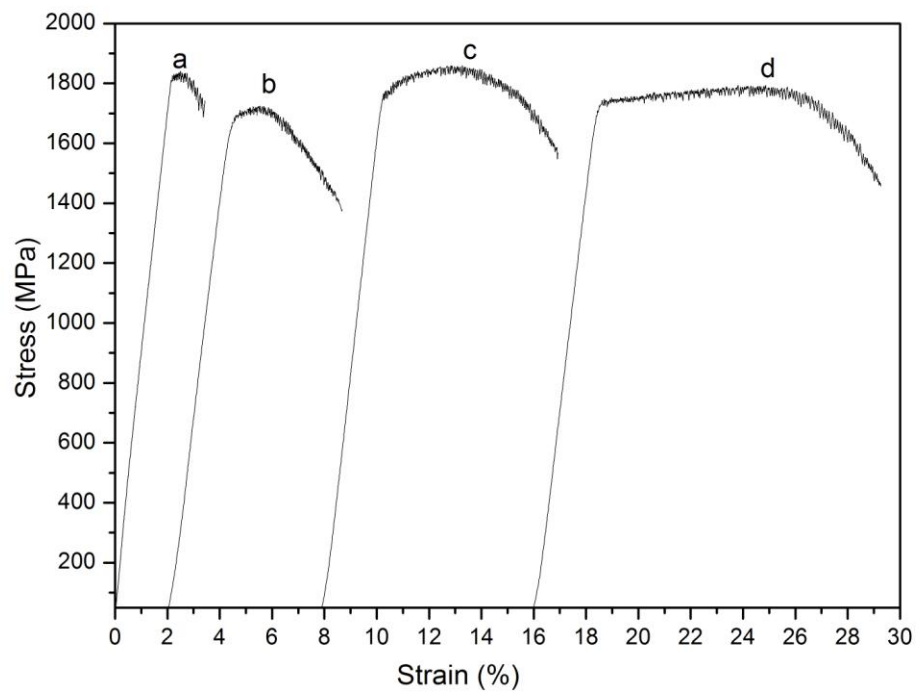


Fig. 2 The uniaxial compressive stress-strain curves of different samples: a) As-cast; b) Cu coated; c) Ni coated; d) Cu/Ni coated.

Fig. 3

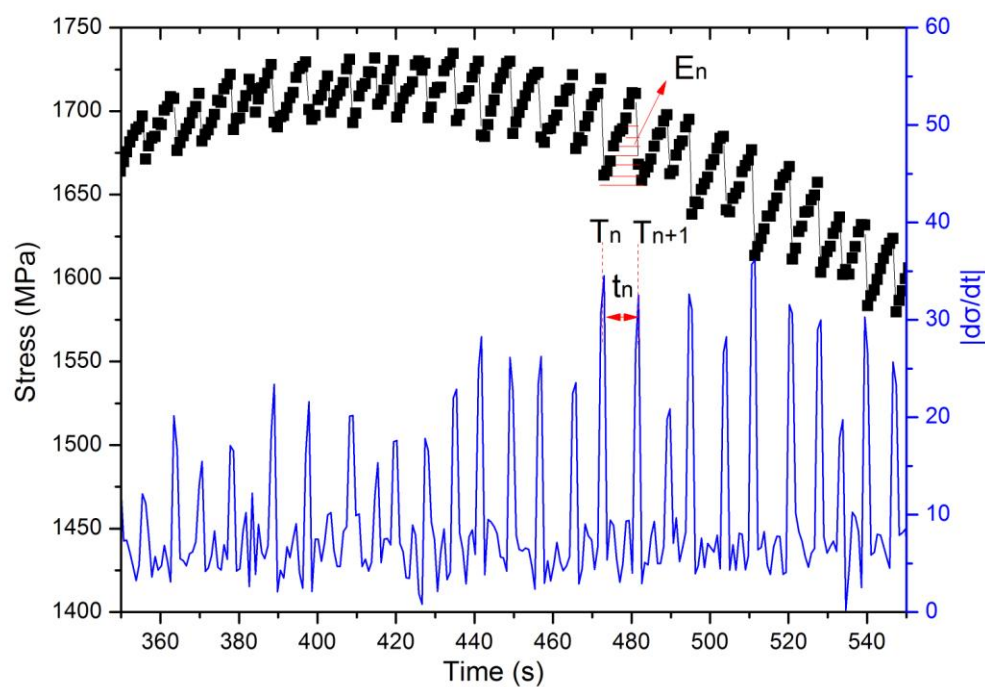
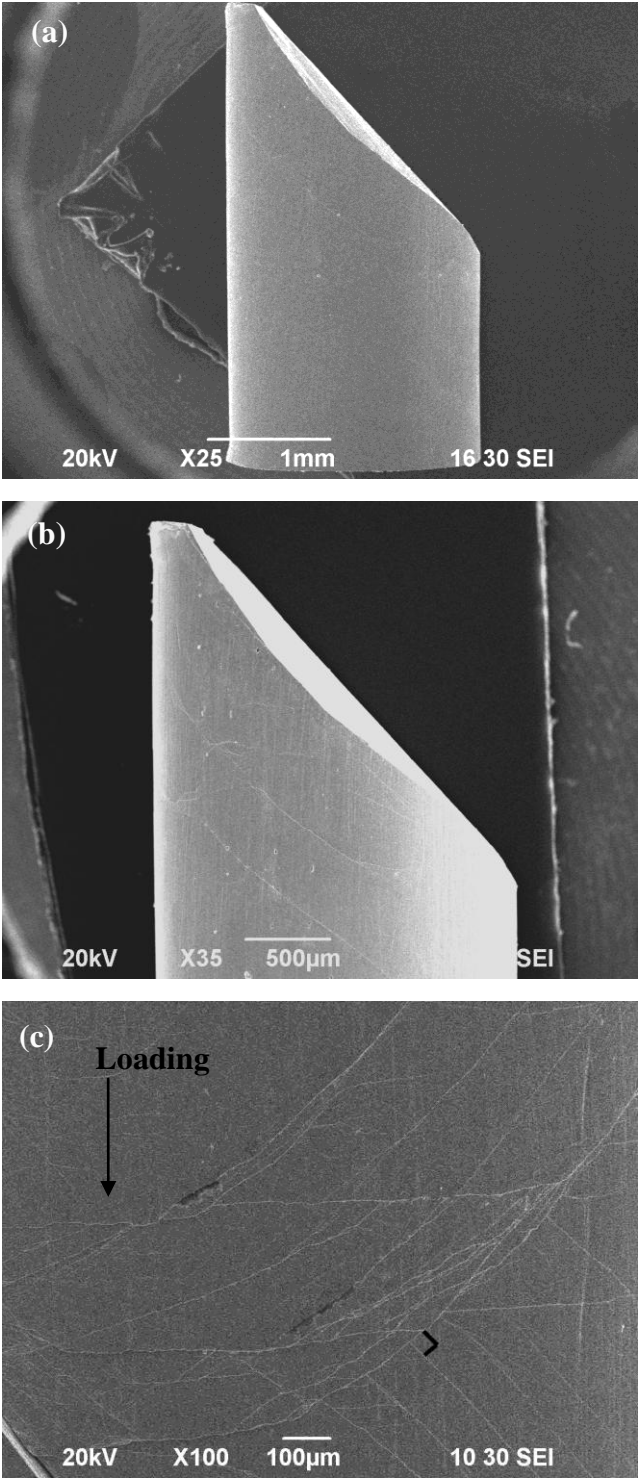


Fig. 3 The representative magnified plastic flow region (strain 2.5% ~ 4.5%) for the Cu-coated specimen.

Fig. 4



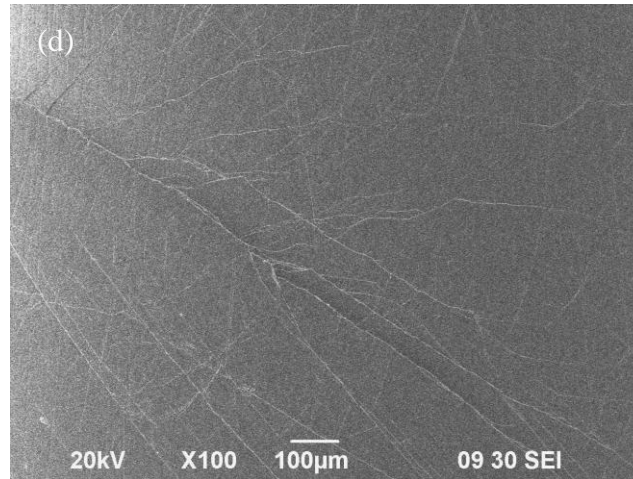


Figure 4. The fracture morphologies of different specimens after failure: a) As-cast; b) Cu coated; c) Ni coated; d) Cu/Ni coated.

Fig. 5

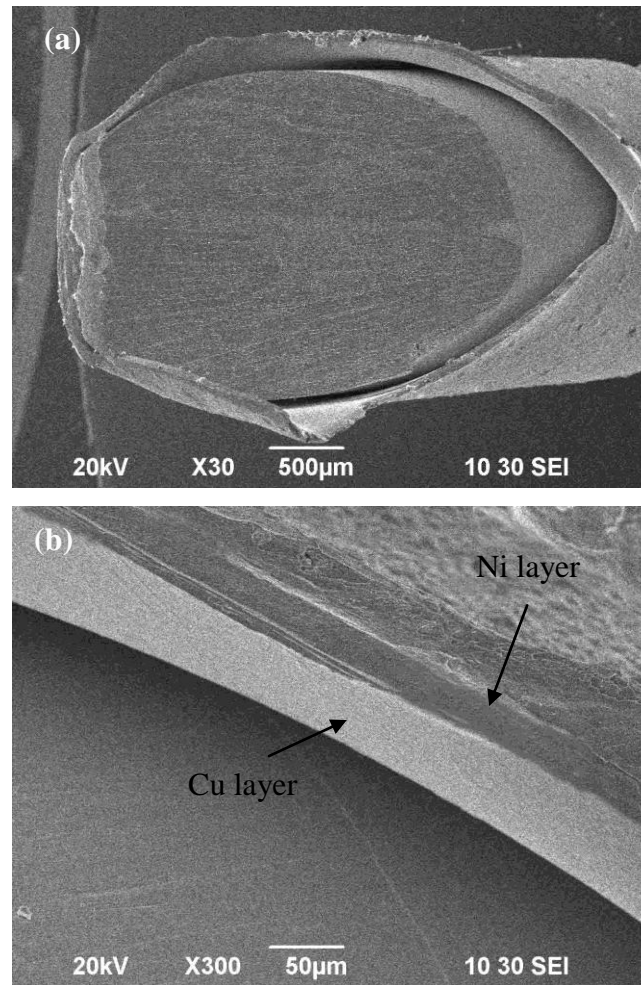


Figure 5. (a) The post-failure fracture profile of Cu/Ni coated sample; (b) The tightly bonded Cu-Ni interface after fracture.

Table 1. The summarized mechanical properties, mean hanging time and mean elastic energy density for different specimens.

Specimens	Yield strength σ_y (MPa)	Plastic strain ϵ_p (%)	Mean hanging time t_m (s)	Mean elastic energy density E_m (kJ/m ³)
As-cast	1807	1.3	5.816	5.664
Cu-coated	1580	4.6	6.384	6.376
Ni-coated	1705	7.0	6.957	6.548
Cu/Ni-coated	1637	11.2	7.839	7.141