Enhancement of Strength and Corrosion Resistance of Copper Wires by Metallic Glass Coating

P. Yu¹, K. C. Chan¹,* L. Xia¹, H. B. Yu² and H. Y. Bai²

¹Advanced Manufacturing Technology Research Centre, Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hong Kong, P. R. China
²Institute of Physics, Chinese Academy of Sciences, Beijing, P. R. China

Metallic glass was coated on copper (Cu) wires for enhancing their strength and corrosion resistance. The metallic glass coating has strong cohesion to the copper, and can effectively protect the wires from external forces and corrosive environments. Compared with bare Cu wires, the yield strength and the elastic strain limit of the coated wires have been significantly increased. The excellent corrosion resistance of the metallic glass coating has also provided essential shielding of the wires from chloride-containing electrolyte environments. The experimental results present a new technique for strengthening and enhancing the corrosion resistance of copper wires. [doi:10.2320/matertrans.M2009157]

(Received May 1, 2009; Accepted July 6, 2009; Published September 25, 2009)

Keywords: coating, metallic glass, copper wires, corrosion resistance

1. Introduction

As a new class in the field of materials science, metallic glasses have attracted intense attention because of their outstanding mechanical, physical, and chemical performances.¹–³ The disordered atomic structure of metallic glasses generates ultrahigh strength, lower Young’s moduli, and high elastic strain limits leading to comprehensive applications as a structural and functional material.⁴–⁷ However, the weaknesses of metallic glasses, such as the disappointing plasticity at room temperature and the low forming ability which limits the size to the millimeter level, seriously hinders the practical applications.⁸–¹² With the development of multi-component metallic glass systems, many bulk metallic glass (BMG) systems with excellent glass forming ability (GFA) have been developed.¹³–¹⁵ The Pd- and Zr-based alloys even have the very low critical cooling rate of 1 K/s, which makes thermal shaping and fabrication of large size BMG specimens very convenient.¹³,¹⁴

At present, the applications of BMGs are mainly focused on magnetic devices, fuel-cell separators, sporting goods, precision optical parts, and so on.⁴,¹⁶,¹⁷ Most of them, however, are still limited to prototypes because of the economic cost and the limitations of the process technology. Some metallic glasses exhibit excellent abradability, high hardness and good corrosion resistance, which also provide promising application potentials as coating materials.¹⁸–²⁰ The excellent anticorrosion behavior of metallic glasses derives from two sources.²¹,²² Firstly, the amorphous structure leads to a particularly homogeneous passive film with no underlying defects to serve as pitting sites. Secondly, the surface of a glassy alloy has a higher free energy than the surface of the corresponding crystalline solid leading to more aggressive passivation. But, more research and development work is needed to make use of the advantages of BMGs.

In industry, the development of coatings on Cu wires is an issue of great importance for the durability and efficiency of practical applications in complex environments. There are several techniques for the deposition of coatings on metal wires, including physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical deposition, plasma spraying, and sol-gel process.²³–²⁵ Although these techniques and coating materials are well developed, new coating materials and techniques have yet to be explored for enhancing the performance of Cu wires. In this study, a Zr-based metallic glass was coated on Cu wires by rapid solidification, and their mechanical properties and corrosion resistance were examined and compared with bare Cu wires.

2. Experimental

The selection of Zr₄₁.₅T₆₁₃.₇₅Ni₁₀Cu₁₂.₅Be₁₂₂.₅ (Vit1) metallic glass for the present study is based on its outstanding glass forming ability and excellent viscous flow characteristics in the supercooled liquid region.¹¹,²⁰ The ingots of Vit1 were prepared, firstly, by producing the pre-alloyed material by arc melting the pure elements in an argon atmosphere. Secondly, the pre-alloyed ingot was remelted five times and kept in a liquid state. Then, a Cu wire of 1 mm diameter was drawn through the liquid Vit1 melt at a rate of 5 m/s, to achieve the metallic glass coating. The structure of the coatings was characterized by X-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu Kα radiation, and a differential scanning calorimeter (DSC) of Perkin Elmer DSC-7. Cylindrical specimens of aspect ratios 2:1 were cut from the prepared wires and tested under a uniaxial compressive deformation, at room temperature using an Instron 5500R1186 machine with a loading strain rate of 5 × 10⁻⁴ s⁻¹. The specimens and the fracture surfaces after failure were investigated by scanning electron microscopy (SEM) using a Philips XL 30 SEM. The corrosion behavior of the coatings was characterized by immersion testing and potentiodynamic polarization measurement in 3% NaCl solutions, open to air. Electrochemical measurements were conducted in a three-electrode cell using a saturated calomel reference electrode (SCE), U (SCE) = 241 mV, and graphite counter electrodes. Potentiodynamic polarization curves

*Corresponding author, E-mail: mfkcchan@inet.polyu.edu.hk
were measured at a potential sweep rate of 50 mV·min⁻¹ along the anodic direction after open circuit immersion in an electrolyte for about 30 mins, in order to attain the steady free corrosion potential.

3. Results and Discussions

In this study, the coating process heavily relies on the glass forming ability (GFA) of the selected BMG material. The Vit1 alloy, which has high GFA, only requires a low cooling rate of 1 K/s, which reduces the requirements of the cooling conditions. The entire coating process is operated in an argon gas environment of 0.6 atm. The Cu wires were treated by sanding and cleaned by hydrochloric acid before coating. A clean and rough surface is important to ensure a good interface between the coating and the Cu wire. After surface treatment, the Cu wires were drawn through the liquid melt of the Vit1 alloy at a rate of 5 m/s, thereby coating the metallic glass on the Cu wires. The prepared coatings had an average thickness of 0.16 mm.

Figure 1(a) shows the SEM photos of the coated Cu wire. The coating surface is smooth and lustrous reflecting the quality of the coating process. The insets of Fig. 1(a) and Fig. 1(b) show the cross section of the coated Cu wire. The interface is distinctly shown and has a flexural dividing line, with no visible gaps at the interface. Figure 2 shows the XRD pattern of the coating material stripped from the coated specimen. The XRD pattern exhibits smooth diffraction maxima indicating the amorphous structure of the coating. The inset of Fig. 2 presents the DSC trace for the coating. The glass transition temperature \(T_g\) and the three crystallization temperatures \(T_{x1}, T_{x2}, T_{x3}\) of the coating pointed out with arrows in the figure are 629 K, 710 K, 752 K, and 799 K respectively. They are in good agreement with that reported for \(\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}\) bulk metallic glass by other researchers. Both the XRD and DSC confirm the fully glassy structure of the coating layer.

Uniaxial compression tests were carried out to examine the mechanical strength and elastic deformation of the coated Cu wire. Figure 3 shows the uniaxial compressive stress-strain curves of the coated Cu wire and the one without the coating. The data are summarized in Table 1. The elastic limit, the yield stress \(\sigma_y\), maximum compression stress \(\sigma_{\text{max}}\), and plastic strain \(\varepsilon_f\) for coated and bare Cu wires.

![Fig. 1](image1.png)  
**Fig. 1** (a) shows a lateral SEM picture of a coated Cu wire; the inset picture is a cutting of the prepared sample; (b) shows a cross-section photograph of a coated Cu wire.

![Fig. 2](image2.png)  
**Fig. 2** The XRD pattern of coating material. The inset shows the DSC curve of the coating material.

![Fig. 3](image3.png)  
**Fig. 3** The uniaxial compressive stress-strain curve of the coated and uncoated specimens.

<table>
<thead>
<tr>
<th>Cu wires</th>
<th>(E) (GPa)</th>
<th>(\varepsilon_e)</th>
<th>(\sigma_y) (MPa)</th>
<th>(\sigma_{\text{max}}) (MPa)</th>
<th>(\varepsilon_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating</td>
<td>57</td>
<td>1.8%</td>
<td>1031</td>
<td>1040</td>
<td>&gt; 30%</td>
</tr>
<tr>
<td>No coating</td>
<td>122</td>
<td>0.1%</td>
<td>125</td>
<td>360</td>
<td>&gt; 30%</td>
</tr>
</tbody>
</table>
coated Cu wires exhibited a significant increase in the yield stress and the elastic strain limit, which is attributed to the enhanced properties of the metallic glass coating. After yielding, the strength of the coated specimen obviously decreases because of the poor plasticity of the metallic glass coating at room temperature. However, the elastic modulus of the coated Cu wire (57 GPa) is significantly smaller than approximately 90-110 GPa of Zr based BMGs or 122 GPa of the bare Cu wire. Figure 3 shows that the deformation of the bare Cu wire after the strain of 0.1% will no longer exhibit elastic behavior, and its stress only increases from about 125 MPa to about 170 MPa when the strain increases from 0.1 to 1.8%. Due to such inelastic deformation of the bare Cu wire, the elastic modulus of the coated Cu wire is significantly reduced and lower than that of the Zr-based BMG or the bare Cu wire.

Actually, the coated Cu wire behaves like a sleeve-wrapped composite in uniaxial compression. Thus, for a metallic glass confined Cu wire, the yield strength can be predicted by the empirical equation:

\[ \sigma_y = \sigma_W V_W + \sigma_C V_C \]  

where \( \sigma_W \) and \( \sigma_C \) denote the yield strengths for wire and coating material, and \( V_W \) and \( V_C \) are the volume percentages of the two materials. The values of \( \sigma_W \) and \( \sigma_C \) are 125 MPa and 1940 MPa, respectively. By using this equation, the predicted \( \sigma_y \) is about 900 MPa, which is slightly lower than that of the experimental result. The higher experimental strength indicates that Cu wire is confined tightly by the metallic glass coating in compression, and the coating has a strong cohesion with the Cu substance.

The deformation process of the coated specimen can be divided into two stages: elastic deformation (stage 1) and plastic deformation (stage 2), as shown in Fig. 3. The coated specimen exhibits large elasticity, which mainly comes from the mechanical properties of metallic glass in stage 1. With the gradual damage of the coating, the strength of coated specimen drops significantly from 1000 MPa to \( \sim 500 \) MPa (in stage 2), as shown in Fig. 3. The curve then exhibits a wavy pattern, and the minimum strength is \( \sim 400 \) MPa. In spite of the damage to the coating, the specimen still achieves a good plasticity. Therefore, these results indicate that the metallic glass coating is remarkably useful in improving the elasticity and strength (load-carrying capacity) of Cu wire for practical applications.

Figure 4(a) shows the transversal surface of the deformed coated Cu wire after 25% compressive strain. It can be clearly seen that the metallic glass coating has partially detached from the Cu wire. Because the Cu and Vit1 metallic glass have different elastic moduli, strength, and plastic deformation ability, the detachment phenomenon can be predicted by mechanical analysis. Figure 4(b) reveals that a portion of the coating which is still adhered to the wire after compressive plastic deformation. Because the coatings are formed during the thermal solidification process, the high temperature induces mutual diffusion in the interface of the Cu and Vit1 metallic glass. The mutual diffusion leads to chemical bonding and a stronger coating. Figure 4(c) shows the crack captured by the metallic glass coating. The dashed line in Fig. 4(c) indicates the flexural interface of the coating and Cu. Vit1 metallic glass has a higher strength and hardness than those of Cu wire, so when a crack propagates through the Cu wire and reaches the interface, the coating will prevent it. This result reveals that the metallic glass coating can effectively protect Cu wire from damage under the action of external stress.

The corrosion behavior of coated Cu wires in a chloride-containing environment is studied in this work. Figure 5 shows the anodic potentiodynamic polarization curves for the coated Cu wire in a 3% NaCl solution, and the curve for bare Cu wire is also presented for comparison. Cu wire exhibits high sensitivity to the chloride medium corresponding to an immediate breakdown of the passive film. The glass coated wire was spontaneously passivated in a wide passive region, with a low passive current density of about \( 5 \times 10^{-3} \) A m\(^{-2} \) in the solution. The passive film is very stable even in an aggressive chloride-containing electrolyte. This indicates the formation of a barrier-type passive film covering the whole sample surface. The metallic glass coating of Vit1 contains a large number of different sized atoms, which makes the
atoms difficult to move, and thus results in high corrosion and wear resistance.\textsuperscript{27} Those results prove that a metallic glass coating can effectively enhance the corrosion resistance in a chloride-containing environment, which is of great significance for the application of Cu wire in oceanic and coastal environments.

4. Conclusions

Metallic glass coatings on Cu wires were prepared by a simple thermal solidification technique. Using the excellent GFA of Vit1 metallic glass, the Cu wires can be coated with metallic glass by drawing the wire through a glass-forming alloy melt. The metallic glass coating can effectively enhance the strength of Cu wires and protect them from damage under external stress. Furthermore, the metallic glass coating can effectively increase the corrosion resistance in a chloride-containing electrolyte environment, which is of great significance for the application of Cu wire in oceanic and coastal environments. The results demonstrate a simple technique for strengthening and enhancing the corrosion resistance of copper wires. Such coatings could be exploited in other metal wires, allowing these materials to be used in a more reliable way, and in more demanding environments.

Acknowledgements

The work described in the paper was supported by the Research Committee of The Hong Kong Polytechnic University (under the project code:G-YX2H) and the NSF of China (Grant No.: 50671117). We are also grateful to J. X. Lu and J. L. Zhang for the experimental support.

REFERENCES