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# Tribological behavior of the kinetic sprayed Ni<sub>59</sub>Ti<sub>16</sub>Zr<sub>20</sub>Si<sub>2</sub>Sn<sub>3</sub> bulk metallic glass

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#### Abstract

Gas atomized amorphous  $Ni_{59}Ti_{16}Zr_{20}Si_2Sn_3$  feedstock particles were fed into warm gas dynamics and they were successfully overlaid onto the mild steel substrate. Through the X-ray diffractometry and differential scanning calorimetry, it could be confirmed that thermally activated processes such as crystallization and in-flight particle oxidation were effectively suppressed during the modified kinetic spraying process. In order to evaluate the tribological behavior of the kinetic sprayed  $Ni_{59}Ti_{16}Zr_{20}Si_2Sn_3$  BMG coating, a partially crystallized coating and a fully crystallized coating were prepared by isothermal heat treatments.

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## 1. Introduction

Mechanical failure without plastic deformation of monolithic bulk metallic glass (BMG) is considered to be a main drawback in structural applications in spite of high specific strength and hardness [1]. Furthermore, structural change and crystallization make BMGs brittle. To overcome these brittle natures, material hybridization has been studied [2]. From the viewpoint of material hybridization, coating is a very effective method to make a hybrid material, as for brittle ceramic material on ductile metallic substrates. Meanwhile, BMG unique properties can be used to resist surface attacks such as wear. It is generally known that the abrasion wear resistance is proportional to hardness. If this works for bulk metallic glass coating, the in situ and/or ex situ crystallization makes the BMG coating more resistant to wear. In this study,  $Ni_{59}Ti_{16}Zr_{20}Si_2Sn_3$  BMG coating was overlaid using a modified kinetic spraying system and crystallinity effects on friction and wear were investigated using the scratch wear test.

### 2. Experimental

Inert gas atomized  $Ni_{59}Ti_{16}Zr_{20}Si_2Sn_3$  BMG feedstock was sprayed onto mild steel substrate using a modified kinetic spraying system. Helium gas was used as process gas and gas pressure and temperature were 2.5 MPa and 823 K.

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.08.283 Dissimilar to other conventional kinetic spraying system, the powder carrier gas was also heated to 823 K in this study. Fully amorphous BMG overlay with high density was obtained. In order to evaluate the effects of the crystallinity of the BMG coating on the tribological behavior, scratch test was conducted for the as-sprayed coating, a partially crystallized coating, and a fully crystallized coating: the amorphous phase fraction of the partially crystallized BMG coating is 80 vol.% and the other crystallized coating is fully crystallized according to Ref. [3]. For the scratch test, a diamond tip having a radius of 200 µm was slid onto the specimens at loading speed of  $3.33 \,\mathrm{N \, s^{-1}}$  and at scanning rate of  $0.167 \text{ mm s}^{-1}$ . For the specimens, the accumulated scratch numbers were 1, 2, 5, 10 and 20, respectively, for example, the second scratch is exactly overlapped on the first scratch. During scratching, the tangential force was continuously measured and then the scratch friction coefficient was calculated by dividing the tangential force by the normal force. After scratching, the worn scratch tracks were observed using a scanning electron microscope and the worn crosssectional area was measured using an α-step.

#### 3. Results and discussion

Exact bonding mechanism of the  $Ni_{59}Ti_{16}Zr_{20}Si_2Sn_3$  BMG particle on mild steel has not been clarified. However, the adhesive bonding between the BMG particle and mild steel seems to follow conventional bonding of hard particle on soft substrate: deep impact of hard BMG particle through severe plastic deformation of soft mild steel substrate [4]. On the other hand, the cohesive bonding between BMG particles shows unique features such as shear bands, fracture, and molten particles. From the viewpoint of the impact of the ductile particles on hard substrates, the strain and strain rate hardening is competing with

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the thermal softening [5]. When sufficient amount of heat is accumulated at a localized region around the impacting point due to faster heat generation rate than heat dissipation rate, it reduces the flow stress and thus the adiabatic shear instability intervenes at this localized region. From phenomenological viewpoint, the adiabatic shear instability seems to operate in the deposition of the bulk metallic glass through the abnormally large deformation of BMG particles and further interfacial melting. Vickers microhardness was increased with increase of the crystallinity:  $Hv_{0.3}$  685 for the as-sprayed coating,  $Hv_{0.3}$  715 for partially crystallized coating, and  $Hv_{0.3}$  730 for fully crystallized coating. Variations of both scratch friction coefficient and worn-out cross-sectional area during the repeated scratching test show large dependence on phase composition (Fig. 1). For the scratch coefficient, it gradually increased with the applied normal load and the accumulated scratching number for both the as-sprayed coating and the partially crystallized coating. Meanwhile, the fully crystallized coating showed the highest scratch coefficient and also a large fluctuation. Wear volume can be qualitatively estimated by the worn-out cross-sectional area and the as-sprayed BMG coating shows the best resistance to scratch wear and exponential response to applied normal load. Worst resistance is observed in the fully crystallized coating. Also, cross-sectional area is suddenly increased at a certain applied normal load which is decreased with increase of the repeating number. As a result, the crystallinity of the BMG coating



Fig. 1. Tribological behaviors of as-sprayed coatings and crystallized coating.



(e) Fully crystallized

(f) Fragmentation crack and debris

Fig. 2. Worn scratch tracks of as-sprayed, partially crystallized, and fully crystallized coatings (20th scratch under the normal load of 100 N).

deteriorates the tribological properties. Plane-view morphologies of the worn scratch tracks (after 20th repeated scratching at the normal load of 100 N) are shown in Fig. 2. For the assprayed amorphous coating, the groove with transverse cracks at the central region and with deformed material pile-up along the boundary is the characteristic feature. The transverse crack corresponds to the wear of brittle material under spherical asperity, which results from the maximum tensile stress at the trailing edge of moving asperity and the limitation of plastic strain of the material: it is known that the uniform interval between the transverse cracks is dependent on the load and the fracture toughness of the material [6]. Meanwhile, the material piles up resulting from the ductile deformation of the material. Thus, it seems that the amorphous BMG coating shows both ductile and brittle nature during the scratch test and this is mainly due to the non-uniform distribution of contact pressure and inherently low ductility of the bulk metallic glass. On the other hand, spallation is observed within the scratch groove and along the edge in the partially crystallized coating. Also, additional micro-cutting by

the small particles is evident: fractured small particles seem to act as third body during the scratch test and the micro-fractured particle might result from partial crystallization. Severe fracture and spallation are observed for fully crystallized coating. Fragmented particles showing facet morphologies are easily observed within the spalled region. It is well known that crystallization of BMG materials decreases both fracture strength and fracture strain [7]. As a result, the ductile to brittle transition in the worn track morphology results in the change from mild to severe wear by the increase of the crystallinity of the NiTiZrSiSn BMG coating and this is due to the reduction in the ductility and the tensile strength by crystallization. For applied normal load and repeating scratching effects on the wear of kinetic sprayed BMG coatings, it was observed at the cross-sectional morphologies of worn scratched tracks that the populations of median cracks and lateral cracks were increased with the increases of applied normal load and the repeating number. This corresponds to fatigue wear: damages are concentrated around the defective microstructures by repeated loading. For the kinetic sprayed

BMG coatings, defective microstructures such as pores and splat boundaries and crystalline phases act as stress concentrators.

# 4. Conclusion

Through the kinetic spraying process, a thick  $Ni_{59}Ti_{16}Zr_{20}$ Si<sub>2</sub>Sn<sub>3</sub> bulk metallic glass coating was successfully overlaid onto mild steel substrate without crystallization and the crystallinity effects on the tribological behavior was investigated using the scratch wear test. Crystallization makes the BMG coating harder but it increases both the scratch friction coefficient and the worn-out cross-sectional area. From examination of the scratched wear track microstructure, transition from ductile deformation to brittle deformation in the scratch groove is observed with increase of the crystallinity. This seems to result from loss of the ductility and fracture strength of the crystallized BMG coating.

# References

- [1] T. Gloriant, J. Non-Cryst. Sol. 316 (2003) 96.
- [2] C. Bartuli, T. Valente, M. Tului, Suf. Coat. Technol. 155 (2002) 260.
- [3] J.W. Luster, G.R. Heath, P.A. Kammer, Mater. Manuf. Process. 115 (1996) 855.
- [4] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Acta Mater. 51 (2003) 4379.
  [5] M. Grujicic, C.L. Zhao, W.S. DeRosset, D. Helfritch, Mater. Design 25
- (2004) 681.
- [6] J. Malzbender, Mater. Sci. Eng. R 36 (2002) 47.
- [7] Z.F. Zhang, J. Eckert, L. Schultz, Acta Mater. 51 (2003) 1167.