

THE TRIBOLOGICAL BEHAVIOR OF BLENDED NiTiZrSiSn BULK METALLIC GLASS MATRIX COMPOSITE SPRAY COATING

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Abstract. In this study, the newly designed [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating was deposited by atmospheric plasma spraying and then compared with a [BMG]-Cr₂O₃ coating in view of the wear properties and the effect of solid lubricant addition in regards to tribological behavior or friction. The tribological behavior of the BMG base blended coating was evaluated by a rig test which simulated real service conditions in the turbo-machinery components and tests were conducted at both room temperature and high temperature [350 °C]. The results showed that, the [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating had a considerably lower friction and excellent wear depth at RT and high temperature due to tribofilm of solid lubricant. However, the friction current of the [BMG]-Cr₂O₃ was slightly higher due to the crystalline phase transformation that occurred on the worn surface. As the temperature increased, the worn surface of the [BMG]-Cr₂O₃ displayed plastic deformation and a crystallized layer indicating that temperature wearing on the interface lead to a temperature higher than the glass transition temperature (T_g).

1. INTRODUCTION

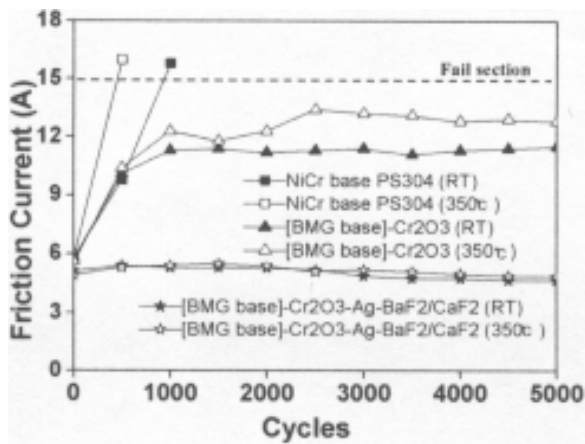
A NiCr-Cr₂O₃-Ag-BaF₂/CaF₂ feedstock (PS304) has been developed by NASA [1,2] in order to improve efficiency without a loss of wear and friction in the foil bearing component. The PS304 feedstock is a blended mixture containing four components: 60 wt.% NiCr as a binder component, 20 wt.% Cr₂O₃ as a component of high wear resistance, high chemical stability and high oxidation-resistance over a wide temperature range, 10 wt.% Ag as a low temperature solid lubricant, and 10 wt.% BaF₂/CaF₂ eutectic phases as a high temperature solid lubricant. NiCr base PS304 had experienced wearing and galling damage problems between journal (coatings on SCM440) and foil (Inconel 718) of air foil bearings in harsh environ-

ments. In order to solve this problem, we designed a NiTiZrSiSn bulk metallic glass [BMG] to replace the NiCr matrix component of the PS304 feedstock because the BMG shows relatively good mechanical properties and excellent wear resistance/ friction coefficient [3]. Therefore, in this study, a BMG powder including the Cr₂O₃, Ag and BaF₂/CaF₂ eutectic powder feedstock were deposited by atmospheric plasma spraying (APS) and then compared with the microstructures and tribological properties of the [BMG]-Cr₂O₃ feedstock. Furthermore, the tribological behavior of the [BMG]-Cr₂O₃ and [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coatings both at room and high [350 °C] temperatures using a rig tester to simulate actual service conditions were compared.

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Table 1. Results of the rig tests of blended and nanostructured composite coatings.

Coating	Test Temp.	Accumulated rig cycles	Friction current	Wear depth
NiCr base PS304	RT	48	Final 16 A	5 μm
NiCr base PS304	350 °C	880	Final 16 A	> 30 μm
[BMG]-Cr ₂ O ₃	RT	> 5,000	10~12 A	< 5 μm
[BMG]-Cr ₂ O ₃	350 °C	> 5,000	11~13 A	< 6 μm
[BMG]-Cr ₂ O ₃ -Ag- BaF ₂ /CaF ₂	RT	> 5,000	4~5A	< 0.2 μm
[BMG]-Cr ₂ O ₃ -Ag- BaF ₂ /CaF ₂	350 °C	> 5,000	4~5A	< 0.5 μm

**Fig. 1.** Friction current of the NiCr base PS304 and [BMG]-Cr₂O₃ and [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coatings during rig test cycling at RT and 350 °C.

2. EXPERIMENTS

The Ni-base bulk metallic glass [BMG] powder feedstocks (60 wt.%) blended with Cr₂O₃ (20 wt.%), Ag (10 wt.%) and eutectic BaF₂/CaF₂ (10 wt.%) was deposited on the surface of a rotating journal (SCM440) after NiCr bond coating by an atmospheric plasma spray system (Sulzer Metco 9 MB). 75 wt.% [BMG]-25 wt.% Cr₂O₃ blended powder feedstock was also deposited in the same coating conditions. The wear behavior of the coatings was evaluated with a rig test to simulate actual application conditions. All tests were conducted at ambient temperature and 350 °C. Cycling experiments

were carried out up to 5,000 cycles. The maximum sliding speed was 15.7 m/s (6000 rpm) and the journal was pressed with a total load of 25.48 N against the foil counterpart. The frictional torque for the calculation of tangential load between the journal and the foil was obtained from the power loss and the friction force. Then the friction current was automatically calculated from the data by computerize acquisition system. During repeated cycles, the rig tester was set to stop automatically if the friction current steadily increased above 15 A. The weight loss was also calculated from the wear depth of the journal. It was measured after each 500 cycles and the rotating journal was stopped when the wear depth of the journal was greater than 30 μm . After the wear test, the microstructure and phase fraction were observed using scanning electron microscopy (SEM) and energy dispersion spectrometry (EDS). Phase identification in the as-sprayed coating and feedstock material was performed by X-ray diffraction (XRD). The amorphous phase fraction of the as-sprayed coating was calculated using differential scanning calorimetry (DSC) according to J. W. Luster *et al.*'s methods [4].

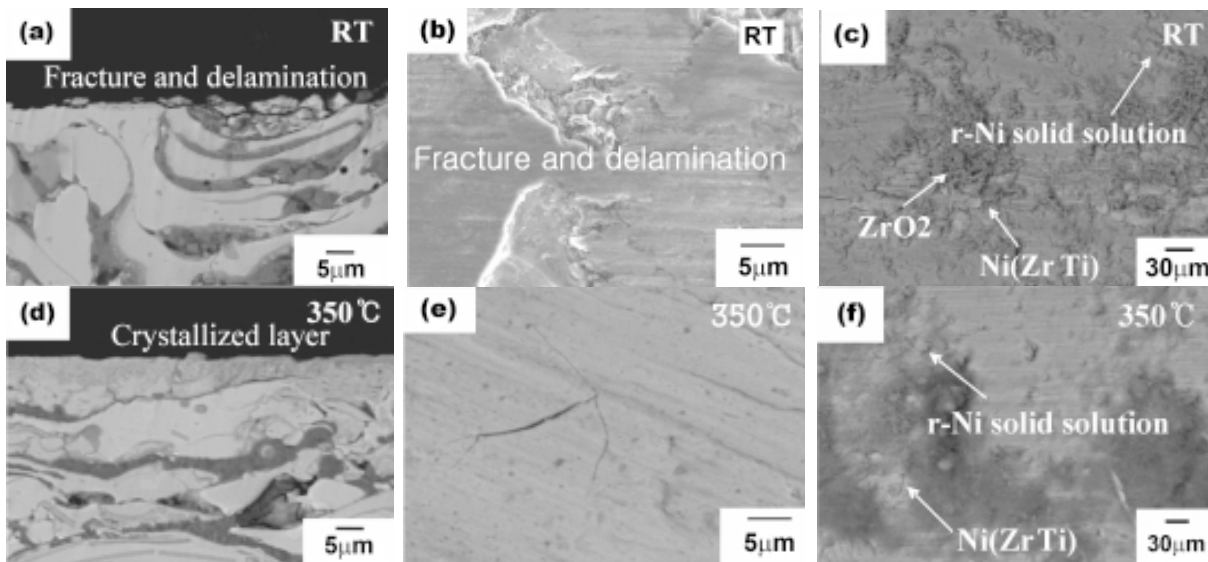
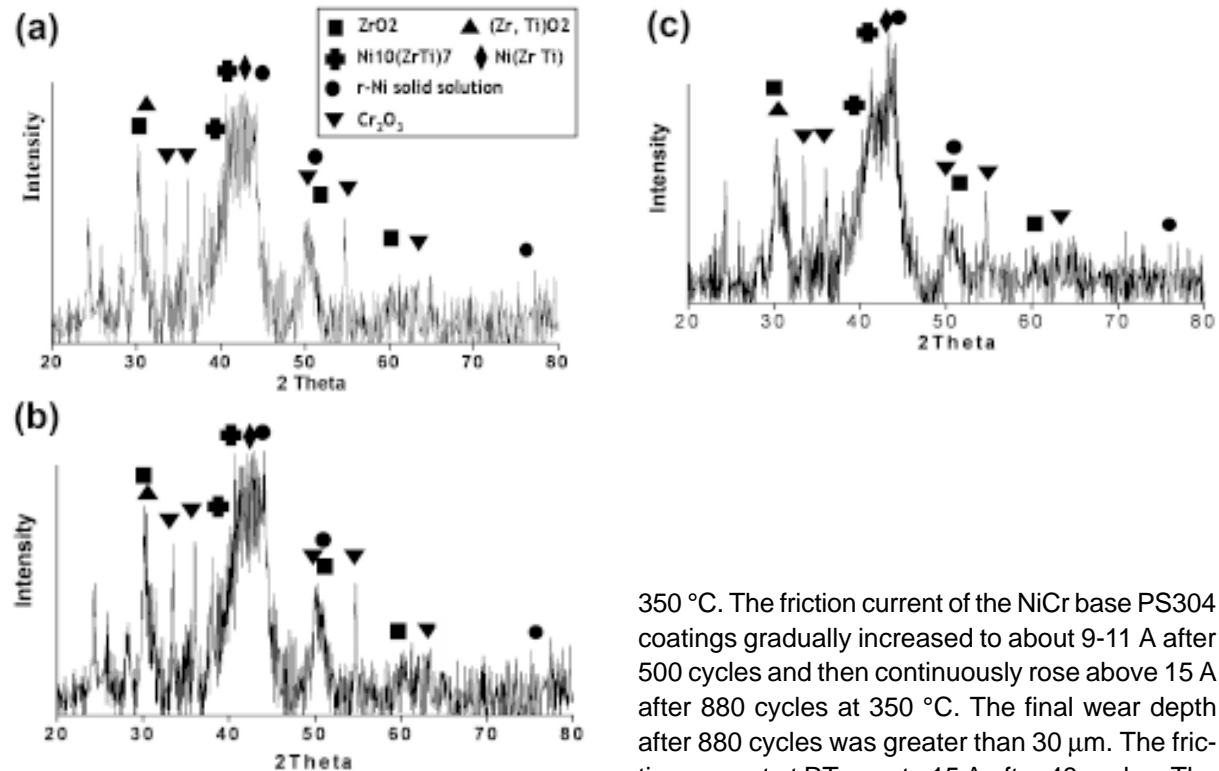
3. RESULTS & DISCUSSIONS

3.1. Friction and wear loss

Rig tests evaluate the friction stability between the rotating journal and the foil for up to 5,000 cycles through repeated start-up and shut-down cycling. The results of rig tests are summarized in Table 1 and Fig. 1 which show the friction current variation of the NiCr base PS304 coating, [BMG]-Cr₂O₃ and [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coatings at RT and

Table 2. Amorphous phase fraction in [BMG]-Cr₂O₃ coating.

Coating	powder	As-coating	RT	350 °C
ΔH , J/g	23.4	18.53	18.31	16.47
Amorphous phase fraction, %	75	53.9	51.7	43.6

**Fig. 2.** Cross sections of BMG-Cr₂O₃ coatings on (a, d) journal and worn surfaces of (b, e) journal and (c, f) foil after rig test at room temperature and 350 °C, respectively.**Fig. 3.** XRD patterns of BMG-Cr₂O₃ coatings, (a) as coated and after rig test at (b) room temperature and (c) 350 °C respectively.

350 °C. The friction current of the NiCr base PS304 coatings gradually increased to about 9-11 A after 500 cycles and then continuously rose above 15 A after 880 cycles at 350 °C. The final wear depth after 880 cycles was greater than 30 μm. The friction current at RT rose to 15 A after 48 cycles. The NiCr base PS304 coating was assumed to have failed because the friction current was higher than the specified criterion of 15 A and also the wear

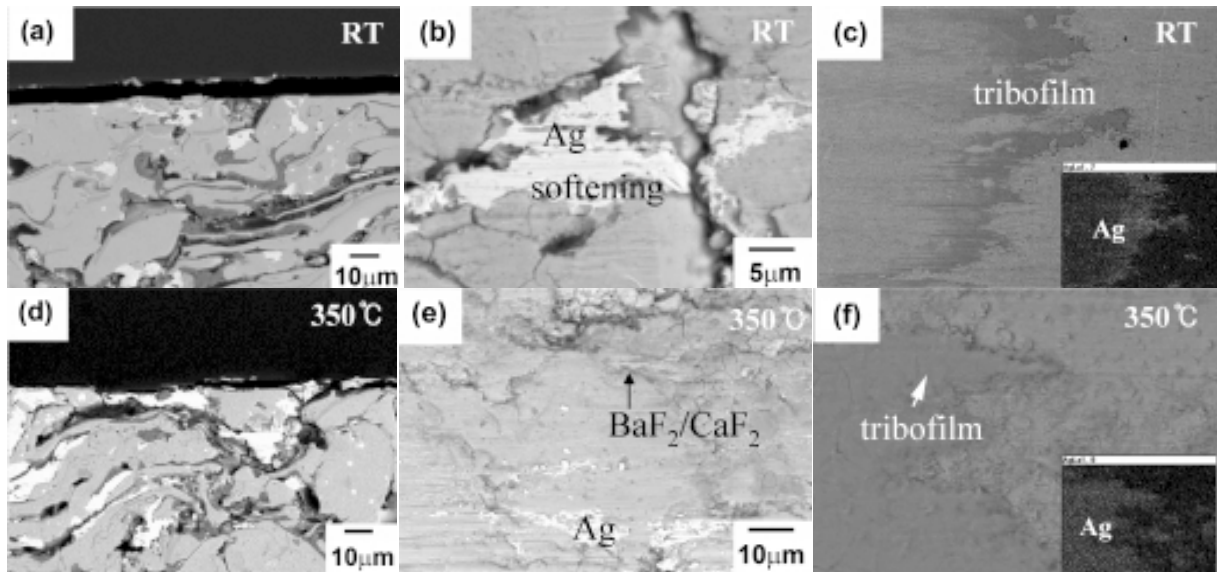


Fig. 4. Cross sections of BMG-Cr₂O₃-Ag-(Ba,Ca)F₂ coatings on (a, d) journal and worn surfaces of (b, e) journal and (c, f) foil after rig test at room temperature and 350 °C respectively. (insets in (c) and (f) for Ag mapping).

depth was greater than the limiting value of 30 μm . The [BMG]-Cr₂O₃ coating passed through 5,000 cycles with a lower 10-13 A friction current and a small wear depth 5-6 μm , regardless of test temperature. However, the [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating, passed 5,000 cycles with a very low friction current 4.5-5.5 A and a small wear depth 0.1-0.3 μm irregardless of test temperature. The friction current and wear depth of the [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating were determined to be superior to the other blended coatings.

3.2. Tribological behaviors of [BMG]

Fig. 2 shows the sliding surface morphology, cross-section of the [BMG]-Cr₂O₃ coating (journal) and of the foil counterpart Inconel 718, after rig tests at RT and 350 °C. According to the respective temperatures, different tribological behaviors can be seen from the morphology differences apparent on the wear track. The SEM observations of the worn surface of the journal revealed a relatively rougher surface at RT, as is shown in Figs. 2a and 2b. During the high speed rotation test, fracture and delamination occurred preferentially at the weakest boundaries such as oxide phases or crystalline phases which lead to the formation of debris on the worn

surface. In particular, ZrO₂, ZrTiO₂ oxide and Ni(Ti, Zr), and γ -Ni solid solution crystalline phases easily fractured and pulled-out at room temperature, and transferred to the counterpart as shown in Fig. 2c due to the repeated friction force and heat of friction. The ZrO₂, ZrTiO₂, Ni(Ti, Zr), and γ -Ni solid solution phase may provide the preferential propagation paths for surface cracks and thus, increase the propensity of the wear loss. However, an amorphous phase with high hardness and low friction combined with the high wear resistance of the Cr₂O₃ phase could resist splat pull-out. Therefore, in comparison with our previous experience with NiCr base PS304, the [BMG]-Cr₂O₃ coating had a lower friction current of 10-12 A and a small wear depth of 5 μm after 5000 cycles.

A smooth surface layer seemed to cover the worn surface by extensive plastic deformation in the sample tested at 350 °C as shown in Figs. 2d and 2e. Depending on the sliding condition, a higher surface temperature induced by the frictional heat as well as from high environment temperature can reach the supercooled liquid temperature range between the glass formation temperature (T_g) and crystallization temperature (T_x) or increased above the crystallization temperature. In order to verify

the thermomechanical properties of NiTiZrSiSn bulk metallic glass [5], the Vickers microhardness was measured as a function of indentation temperature using a normal load of 400 g. The Vickers microhardness decreased with increasing indentation temperature and a sharp decrease was observed at temperature near the transition temperature. Consequently, high plastic deformation could be induced during wear if the temperature of the friction surface rose above the glass formation temperature (T_g). Fig. 2e shows the layer plastically deformed. Through the X-ray diffraction as shown in Fig. 3, a phase evolution according to wear temperature could be observed. Ni(Ti, Zr) and g-Ni solid solution peaks were increased at 350 °C as compared to test of RT. The amorphous phase fraction was calculated from DSC data following the Ref. [4]. During the 350 °C wear test, the amorphous phase fraction was decreased to about 8% as shown in Table. 2. The worn surface consisted mainly of the Ni(Ti, Zr) and r-Ni solid solution crystalline phase together with the amorphous phase. As a result, during the 350 °C wear test, friction current was slightly higher and unstable compared to RT wear test as shown in Fig. 1 due to the increase of the crystalline phase.

3.3. Effects of solid lubricant

Fig. 4 shows the cross-section and sliding surface morphology of the [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating after 5000 cycle rig test at RT and at 350 °C. The [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating both at RT and 350 °C showed a smooth worn surface and plastic shear of the Ag solid lubricant along the sliding direction. The [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating showed a wide Ag distribution, and on evidence of fracture or delamination could be observed on the worn surface unlike in case of the [BMG]-Cr₂O₃ coating. The tribofilm was generated locally and provided a lubricant thin film between two contact surfaces during wear testing. The counterpart surface of the [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating in Fig. 4c shows a dispersed and continuous distribution of the Ag tribofilm. Tribofilm formation is dependant on the adhesion and wettability of the Ag lubricant to the counterpart. The [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating had a superior friction current and wear depth during rotating wear cycles compared to the [BMG]-Cr₂O₃ coating as shown in Fig. 1. XRD patterns after wear tests shown in Fig. 5 indicate that there were no detectable changes in the phase composition, especially in the amorphous phase fraction, when compared

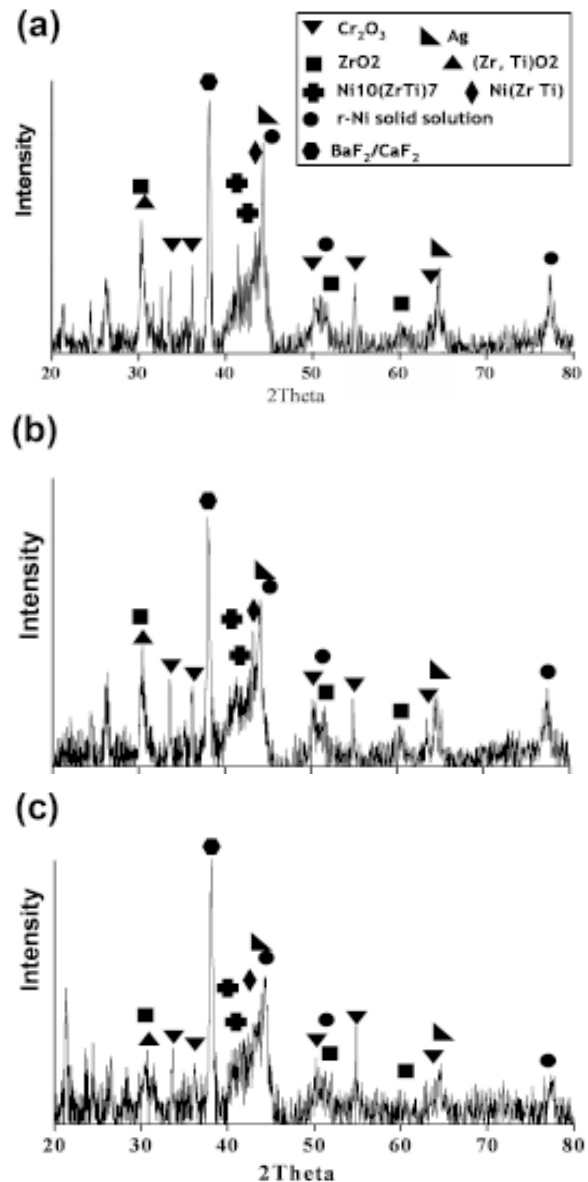


Fig. 5. XRD patterns of BMG-Cr₂O₃-Ag-(Ba,Ca)F₂ coatings, (a) as coated and after rig test at (b) room temperature and (c) 350 °C respectively.

the as coated layer. The absence of changes in the phase fraction may mean that the sliding surface temperature has not reached the glass transition temperature.

4. CONCLUSIONS

- (1) The BMG base blended feedstock coating showed better wear behavior compared to the metallic base feedstock coating.

- (2) A phase transformation from the amorphous to crystalline phase could be a result of the increased sliding surface temperature above the glass transition temperature. However, the addition of a solid lubricant could reduce the possibility of transformation through the formation of a soft tribofilm.
- (3) By adding solid lubricants, the [BMG]-Cr₂O₃-Ag-BaF₂/CaF₂ coating exhibited enhanced wear-resistance and friction current resulting from the formation of a tribofilm in addition to the low friction coefficient of the BMG phase.

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