Dry sliding wear behavior of cold sprayed aluminum amorphous/nanocrystalline alloy coatings

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ABSTRACT

Dry sliding wear behavior of cold sprayed Al amorphous/nanocrystalline alloy coatings in as-sprayed and heat treated conditions is reported. As-sprayed coatings exhibit higher coefficient of friction (COF) and wear volume loss 68% greater than heat treated coatings. Wear mechanism is elucidated in terms of worn surface and subsurface analysis, splat bonding and tribochemical oxidation layer formation. The micro-abrasion and splat delamination resulted in higher wear loss in as-sprayed coatings. Heat treated coatings exhibit lower wear rate due to dense and partially crystallized structure which results in plastic deformation assisted wear. The tribo-chemical layer formation during the wear is studied by energy dispersive spectroscopy (EDS) elemental analysis and supported by thermodynamic computation and flash temperature estimation. The fracture behavior of the splats is investigated using tensile testing of free standing coatings in as-sprayed and heat treated conditions and correlated with the wear mechanism.

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1. Introduction

The development of aluminum based amorphous alloys has made them more attractive to automobile, marine and aerospace industries due to their higher specific strength ratio, better corrosion and wear resistance than conventional counterparts [1–3]. However, the final product size of Al amorphous alloys is largely restricted to thin ribbons, rods, wires and atomized powders due to cooling rate constraints [4,5]. In recent years, conventional techniques like compaction and sintering, and extrusion have been used to generate bulk samples using gas atomized Al amorphous powders. However, the heat involved during the consolidation stage could alter the initial amorphous structure of the powder [4,6–9]. The relatively new technique of cold spraying involves higher kinetic energy and low thermal energy compared to other thermal spray processes and has a great potential to retain initial feedstock’s glassy structure in the deposited coating [10,11]. Cold spraying involves consolidation by solid state deformation and largely prevents phase transformation caused by heating/melting [11]. Hence, Al amorphous alloys can be synthesized as protective coating at a large scale by cold spraying of the similar powder.

We have recently reported the deposition of Al amorphous/nanocrystalline alloy coatings on Al-6061 substrate (gas atomized Al amorphous/nanocrystalline powder (Al-4.4Y–4.3Ni–0.35Sc (at. %))) using cold spray technique [12]. These coatings are a mixture of amorphous and nanocrystalline features/phases in Al based matrix. Cold sprayed Al amorphous/nanocrystalline alloy coating exhibited higher hardness, superior corrosion and wear resistance than Al-6061 substrate [12]. Studies have also been carried out to understand the structure stability of cold sprayed Al amorphous/nanocrystalline alloy coatings by subjecting to thermal treatment just below crystallization temperature and its influence on coating’s scratch resistance [13]. It has been reported that scratch resistance improved after the heat treatment which was attributed to the densification and partial crystallization of the coating during heat treatment [13,14].

As-cast bulk metallic glasses (BMGs) are known for improved tribological properties, but very few studies have been carried out to understand the sliding wear properties of BMGs in the “coating” form [13,15–18]. The wear loss of bulk metallic glasses strongly depends on the structure and the test environment [15,17,18]. Ball-on-disc wear behavior of Cu42Zr41Al17 bulk metallic glass in air, low vacuum and pure nitrogen atmosphere resulted in the oxidation of wear surface. The coefficient of friction (COF), and wear loss increased with the changing atmosphere from air to low vacuum to pure nitrogen and was attributed to the formation of oxide layer [16]. Similarly, wear behavior of as-cast and annealed Zr-based bulk metallic glass was evaluated in air and vacuum [15]. Wear rates were similar for as-cast and annealed Zr-based bulk metallic glasses. The formation of soft mixed amorphous layer due to plastic deformation and transfer of material in both as-cast and annealed condition influenced the sliding wear behavior [15]. Zr-based bulk metallic glasses exhibited extensive plastic deformation and ductility under sliding conditions.
Few studies have reported sliding wear properties of thermal sprayed amorphous alloy coatings synthesized using glass forming Fe, Ni, Cu, Zr and Mo pre-alloyed powders [17–19]. Thermal sprayed amorphous coatings exhibited superior wear properties as compared to conventional crystalline counter parts, carbide/ceramic wear resistance coatings, and substrate materials used for the deposition [17–19]. Cold spray has emerged as the most suitable thermal spray technique for depositing amorphous alloy coatings due to their ability to retain glassy phase from the powder feedstock [5,10,11]. However, there is hardly any study in the literature on cold sprayed Al-based amorphous coatings except our earlier publication [12]. A couple of studies on cold sprayed nano-crystalline aluminum coatings are focused on microstructural evolution and does not report wear behavior [20,21].

In the present study, ball-on-disc sliding wear behavior of cold sprayed Al amorphous/nanocrystalline alloy coating in as-sprayed and heat treated conditions is evaluated. Wear loss and material removal mechanisms of as-sprayed and heat treated coatings are analyzed and related to coating microstructure and properties. The wear scar morphology is examined using SEM and EDS to understand the change in chemical composition and tribochemical film formation. The wear behavior is elucidated in terms of inter-splat bonding in as-sprayed and heat treated microstructure by performing tensile tests on free-standing coatings.

2. Experimental details

Gas atomized Al amorphous/nanocrystalline alloy powder (Al-4.4Y−4.3Ni−0.9Co−0.35Sc (at. %)) was deposited on Al-6061 substrate using cold spray technique to obtain a coating of 250 μm thickness [12]. The structural stability was studied by subjecting as-sprayed coatings to a thermal treatment for 1 h at 300 °C i.e. just below crystallization temperature (~320 °C) [12,13]. The porosity of the coatings was measured using image analysis using Image J software. Low magnification images from metallographically polished cross-sections using Phenom SEM (FEI, Netherlands) were used for image analysis. The phases present in the coatings were analyzed using XRD technique (Siemens D5000 X-ray diffractometer) using Cu-Kα radiation at 40 kV and 40 mA. A scan rate of 1°/min was employed for collecting the XRD data. The microstructure of as-sprayed and heat treated coatings was studied using scanning electron microscope (JEOL-6335, The JEOL Ltd, Japan). Nanoindentation technique (Triboindenter, TI 900, Hysitron Inc., Minneapolis, MN, USA) was used to evaluate hardness and elastic modulus of coatings. More than 50 indents were made in both coatings at two different loads (50 and 200 g) by Vickers indentation to understand the variation in the hardness after thermal treatment.

Sliding wear tests on as-sprayed and heat treated Al amorphous/nanocrystalline alloy coatings were carried out using Ball-on-disc tribometer (NanoVea, CA). Wear tests were carried out at 10 N normal load and 200 rpm. A 3 mm diameter Al2O3 ball was used for the dry sliding tests. Both coatings were polished to a surface roughness ~ 500 nm before the wear tests. Tests were conducted for a period of 60 min using a 6 mm wear track diameter. An average value from at least three tests at each condition is reported. The frictional force between ball and coating was measured by the linear variable differential transformer (LVDT) sensor. The data was acquired at a rate of 1000 data points per minute. The COF values were measured for the entire test duration. Weight loss of coatings was measured using Ohaus digital balance with an accuracy of 10−5 g. The wear track profiles were obtained using optical profiler (Image Metrology A/S, Horsholm, Denmark). Wear volume loss was computed from 3D wear track profiles. SEM analysis (using JEOL JSM-6330F, Japan) of wear tracks was carried out to study worn surface morphology and material removal mechanisms. The elemental analysis of worn and unworn coating surfaces was carried out using EDS system (Thermo Fisher Scientific, Germany) attached to SEM. Sub-surface analysis of wear tracks was carried out using focused ion beam (JEOL Model: JIB-4500; Japan). Initially, a trench 15 × 15 mm was machined across the wear track using high milling rate. Final surface was machined at low milling rate. SEM images were taken from the machined region to understand the sub-surface wear deformation.

Fracture behavior of free-standing cold sprayed Al amorphous/nanocrystalline alloy coatings was carried out using MTS SEMtester1000 micro-load frame (Fig. 1). Free standing dog bone shape tensile samples were fabricated using EDM wire cut from as-sprayed and heat treated coatings (Fig 1). The free-standing tensile samples are very thin (250 μm) and fragile in nature. Hence, a very low crosshead speed (0.005 mm/min) was used for tensile testing. SEM images of fracture surfaces were collected to study the inter-splat bonding behavior. It must be noted that tensile samples from as-sprayed coating were in as-received condition whereas heat treated tensile samples were gently polished to remove surface oxide after the heat treatment.

3. Results

3.1. Coating structure and properties

Microstructure of cold sprayed Al amorphous/nanocrystalline alloy coatings in as-sprayed and heat treated conditions is shown in Fig. 2. Heat treated coating exhibits denser structure with less porosity of

Fig. 1. Digital images showing (a) dog bone shape free standing coatings prepared from coated with Al amorphous coatings using EDM wire cutting and (b) Micro-tensile tester shows the sample fixed between grips before testing.
0.5% due to solid state diffusion during heat treatment as compared to as-sprayed coating having porosity of 2%. XRD analysis (Fig. 3) reveals the presence of α-Al FCC phase and intermetallic phases (Al3Y, Al3Sc, Al4YNi and Al9Co2) in the heat treated coatings. The relative proportion of intermetallic phases (~30%) was evaluated by measuring area under X-ray diffraction peaks in heat treated coatings. As-sprayed coating shows broadened peaks and nano-crystalline α-Al FCC phase peaks. Heat treated coatings exhibited slightly higher nano-hardness of 5.25 ± 0.36 GPa as against 5 ± 0.70 GPa in as-sprayed coatings. A similar trend (3.36 ± 0.11 GPa in as-sprayed and 3.55 ± 0.2 GPa in heat treated coatings) was observed for microhardness measurements. Both nano-hardness and microhardness show a similar trend of increased hardness in heat treated coatings. However, the higher hardness values obtained in the nano-indentation are higher due to small scale effect. Elastic modulus of heat treated coatings (115 ± 6 GPa) improved by 33% than as-sprayed coatings (86 ± 7 GPa). Structure relaxation, high density, partial crystallization and intermetallic phase formation during the heat treatment resulted in higher hardness and elastic modulus. A detailed discussion on the microstructure, phase content and mechanical properties of cold sprayed Al amorphous/nano-crystalline coatings in as-sprayed and heat treated conditions can be found in our earlier works [12,13].

3.2. Ball-on-disc wear

Wear behavior of cold sprayed Al amorphous/nanocrystalline alloy coatings in as-sprayed and heat treated conditions was evaluated using ball-on-disc tribo-system by sliding the coating against stationary Al2O3 ball. Coefficient of friction (COF) during sliding wear as a function of the test time is shown in Fig. 4. As-sprayed coatings exhibited higher steady state COF value of 0.55 as against 0.38 for heat treated coatings. Higher COF value in the initial stages of test in as-sprayed coatings stabilizes after 18 min of sliding test. However, steady state value is achieved immediately at the start of test in heat treated coatings. The higher initial COF value is attributed to run-in wear, where the coating surface adjusts mechanically and chemically to achieve the steady state [19]. Dense and partially crystallized structure of heat treated coatings is more ductile and deforms easily to create a contact between ball and the coatings resulting in steady state COF values at the very beginning of the sliding test. The observed trend in COF values as a function of test time in both coatings is discussed in the following section.

3D wear track profiles of as-sprayed (Fig. 5a) and heat treated coatings (Fig. 5b) as well as 2D line profile across the wear track (Fig. 5c) clearly show higher wear depth in as-sprayed coatings. The wear volume calculated from the track is shown in Fig. 5c. The wear volume loss is 0.37 mm³ and 0.22 mm³ for as-sprayed and heat treated coating, respectively. Wear volume loss is 68% higher in as-sprayed condition. Fig. 5d shows wear weight loss of coatings. The weight loss is nearly one order of magnitude higher (7.6 mg) in as-sprayed coating as compared to heat treated coating (0.8 mg). The weight loss difference between as-sprayed and heat treated coatings is significantly greater than volume loss difference. The observed difference in volume and mass loss is due to combination of crystallization, densification and improved inter-splat bonding in heat treated coatings. The difference also indicates density calculations directly using wear volume and mass loss from the sliding tests should not be made, due to difference in the wear mechanisms between as-sprayed and heat treated coatings.

4. Discussion

4.1. Wear mechanism

In order to understand the wear mechanisms, worn surfaces of both coatings were observed using SEM. Fig. 6 shows worn surfaces of as-sprayed coatings (6a–c) and heat treated coatings (6d–f). The worn surface of as-sprayed coating (Fig. 6a and b) shows rough surface with
mixed regions of delamination and micro-abrasive wear. Heat treated coatings (Fig. 6d,e) exhibit smoother wear surface with reduced wear and delamination. Wear track in heat treated coating also exhibits signs of plastic deformation. Fig. 6c shows wear track edge of as-sprayed coating. Shear band is observed at the track edges in as-sprayed coatings which is attributed to the glassy nature of the coating. Pile-up of material at the track edges in heat treated coating (Fig. 6f) is attributed to a higher degree of plastic deformation due to partial crystallization.

Fig. 7 shows SEM images of the wear debris collected after sliding wear tests on as-sprayed and heat treated coatings. Wear debris consists of larger flakes and finer particles in as-sprayed coatings (Fig. 7a). This indicates micro-abrasion and delamination mechanisms operating simultaneously in as-sprayed coating. In the heat treated condition (Fig. 7b), there is minimal micro-abrasion in the wear debris. Wear occurs largely by the delamination of the splats in combination with the plastic deformation (Fig. 7b). The wear mechanism also strongly depends on the nature of bonding between successive splats. The fracture behavior of the splats was studied by performing tensile testing of free-standing coatings. Fracture strength of as-sprayed and heat treated coatings is found to be 72 ± 7 and 102 ± 5 MPa respectively. SEM images of as-sprayed and heat treated coating fracture surface are shown in Figs. 8–9. Fracture surface of as-sprayed coating (Fig. 8) shows inter-splat cracks, porosity at splat interfaces and pulled out particles corresponds to weaker regions in the coatings. The top (Fig 8b) and bottom surface (Fig 8c) of the tensile sample shows negative and positive features of the fracture surfaces. The particle pull-out and deformation characteristics are clear indicator of weak inter-splat bonding in as-sprayed coating. However, such features are not observed in the fracture surfaces of heat treated coatings (Fig. 9). Heat treated coating shows a more dense and smooth fracture surface suggesting stronger inter-splat region. The dense structure in heat treated coatings reduces splat delamination and the observed lower wear loss in heat treated coatings compared to as-sprayed coatings. SEM images of worn surfaces and debris also support the above phenomenon.

4.2. Flash temperature and tribochemical reaction during wear

The relative motion during sliding wear results in friction, which is converted to heat during the wear process [22]. The maximum temperature which is generated during sliding wear is known as flash...
Fig. 6. SEM images showing wear track surfaces of (a,b) as-sprayed and (d,e) heat treated coatings. The wear track edges of coatings (c) as-prayed and (f) heat treated conditions.

Fig. 7. SEM images of wear debris formed during ball-on-disc wear on cold sprayed Al amorphous/nano-crystalline (a) as-sprayed and (b) heat treated coatings.
temperature. In the present study, the flash temperature developed during sliding wear of both coatings is estimated using Archard’s equation for the material undergoing plastic deformation at very low sliding speeds [22,23]:

\[ T_f = \frac{\mu v (n F_N P_y)^{1/2}}{8k} \]  

(1)

where, \( T_f \) = flash temperature (°C); \( \mu \) = coefficient of friction; \( v \) = velocity (m/s); \( F_N \) = normal force (N); \( P_y \) = yield strength of coating (equal to Hardness) (Pa); and \( k \) = thermal conductivity of coating (W m\(^{-1}\) C\(^{-1}\)). Table 1 lists all variables and their values used to compute flash temperature during wear of as-sprayed and heat treated coatings. Higher flash temperature (312 °C) is estimated for as-sprayed coating as compared to heat treated coatings as compared to the computed value of (255 °C), which is a slight overestimate. The difference in flash temperature in as-sprayed and heat treated coatings can also be explained based on material removal mechanisms during wear process. The wear in as-sprayed coating is dominated by micro-abrasion and debris formation. The smaller debris gets trapped between the coating and alumina ball resulting in three-body wear and hence higher COF and flash temperature is obtained. However, in the case of heat treated coatings, wear is dominated by plastic deformation that leads to lower COF and flash temperature.

The increase in flash temperature in synergy with the surface chemistry of the contact area during wear leads to tribochemical reactions, which also influences the wear mechanism. Elemental X-ray mapping of the wear tracks (Fig. 10) reveals the presence of higher oxygen concentration in the worn region as compared to unworn region in both coatings. This indicates the oxidation of wear surface during sliding of Al amorphous coatings. Semi-quantitative elemental analysis shows the atomic percentage ratio of Al to O\(_2\) is close to 1.5 which is equal to other bulk metallic glasses [24,25]. It is emphasized that heat treated coating is expected to have higher thermal conductivity than as-sprayed coating due to dense and partially crystallized structure [24,25]. Hence, Eq. (1) should result in lower flash temperature for the heat treated coatings as compared to the computed value of (255 °C), which is a slight overestimate. The difference in flash temperature in as-sprayed and heat treated coatings can also be explained based on material removal mechanisms during wear process. The wear in as-sprayed coating is dominated by micro-abrasion and debris formation. The smaller debris gets trapped between the coating and alumina ball resulting in three-body wear and hence higher COF and flash temperature is obtained. However, in the case of heat treated coatings, wear is dominated by plastic deformation that leads to lower COF and flash temperature.

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**Table 1**

Flash temperature calculations of as-sprayed (AS) and heat treated (HT) Al amorphous coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>COF (μ)</th>
<th>v (m/s)</th>
<th>F_N (N)</th>
<th>P_y = H (Pa)</th>
<th>k (W m(^{-1}) C(^{-1}))</th>
<th>T_f (°C)</th>
</tr>
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<tbody>
<tr>
<td>AS</td>
<td>0.5</td>
<td>0.063</td>
<td>10</td>
<td>5 × 10^9</td>
<td>5</td>
<td>312</td>
</tr>
<tr>
<td>HT</td>
<td>0.4</td>
<td>0.063</td>
<td>10</td>
<td>5.25 × 10^9</td>
<td>5</td>
<td>255</td>
</tr>
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stoichiometric ratio for Al₂O₃. Moreover, the Al being the major component in the alloy has a higher probability of reacting with oxygen. The change in Gibbs free energy for the oxidation reaction of each element present in the Al amorphous alloys was computed using FACTSAGE Thermochemistry Software (FACTSAGE Version 5.0, Center for Research in Computational Thermochemistry of the Ecole Polytechnique at the Universite\' de Montre\'al and GTT-Technologies, GmbH, Aachen, Germany, 2001) in the temperature range of 225–325 °C. The temperature range is selected based on the flash temperatures calculated for both coatings. Computed Gibbs free energy for various possible oxides present in coatings with a composition of Al–4.4Y–4.3Ni–0.9Co–0.35Sc (atom %) is presented in Table 2. Oxides of Ni and Co show higher Gibbs free energy among all elements in Al amorphous alloy. The free energy change for aluminum reacting with oxygen is lower and comparable with the free energy changes for Y and Sc reactions with oxygen. Since Y and Sc have a much lower content as compared to Al, the majority of the oxide formed due to tribochemical reaction is Al₂O₃. The elemental mapping (Fig. 10) and thermodynamic calculations support the formation of Al₂O₃ oxide layer formation in both coatings.

The formation of oxide layer was also corroborated by sub-surface analysis of the wear tracks using Focus Ion Beam Milling. Trenches were milled across the wear track and corresponding images are shown in Fig. 11. The formation of thin (1 μm) oxide layer and its delamination can be clearly seen in the sub-surface wear region of as-sprayed coating in Fig. 11a. The delaminated brittle oxide layer gets crushed and trapped between the coating and alumina ball to result in micro-abrasive wear in conjunction with the separation of weaker inter-splat regions. Heat treated coating also shown the formation of oxide layer in Fig. 11b. However, this oxide layer is more adherent

Table 2
Free energy change (ΔG) values of various elements react with oxygen during sliding wear calculated using.

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<tbody>
<tr>
<td>225</td>
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<td>−9.46</td>
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than in the case of as-sprayed coating and hence, restricts micro-abrasive wear. The schematic shown in Fig. 12 summarizes the overall wear mechanisms during dry sliding wear of cold sprayed Al amorphous/nanocrystalline alloy coatings. The oxidative micro-abrasion and delamination of oxide layer and splats is the dominant wear mechanism in as-sprayed coatings. In heat treated coatings, the dominant wear is severe plastic deformation and delamination of deformed layer.

5. Conclusions

Dry sliding wear behavior of as-sprayed and heat treated cold sprayed Al amorphous/nanocrystalline alloy coatings is evaluated. As-sprayed coatings exhibited higher steady state COF value of 0.55 as compared to 0.38 for heat treated coatings. Wear volume loss is 68% higher in as-sprayed condition which is attributed to micro-abrasion and delamination of the weak splats. The tensile testing of free standing coatings reveals the presence of inter splat porosity, and particle pull-out indicating weak inter-splat bonding in as-sprayed coating. The fracture surface of heat treated coatings was more smooth and dense with stronger inter-splat bonding. Both coatings formed Al₂O₃ oxide layer on the surface as a tribochemical layer. A higher flash temperature (312 °C) was estimated for as-sprayed coating, which is attributed to micro-abrasive wear during sliding.

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Fig. 12. Schematic diagram showing the wear mechanisms in as-sprayed and heat treated coatings.