



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 sub-surface 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–0.9Co–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 Cu₄₅Zr₄₈Al₇ 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.

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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 $^{\circ}\text{C}$ i.e. just below crystallization temperature (~ 320 $^{\circ}\text{C}$) [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-K α radiation at 40 kV and 40 mA. A scan rate of 1 $^{\circ}$ /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 “within splat” and “inter-splat” regions to obtain an average value. Coating hardness was also evaluated at higher loads (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 Al $_2$ O $_3$ 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 \times 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 MTI 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

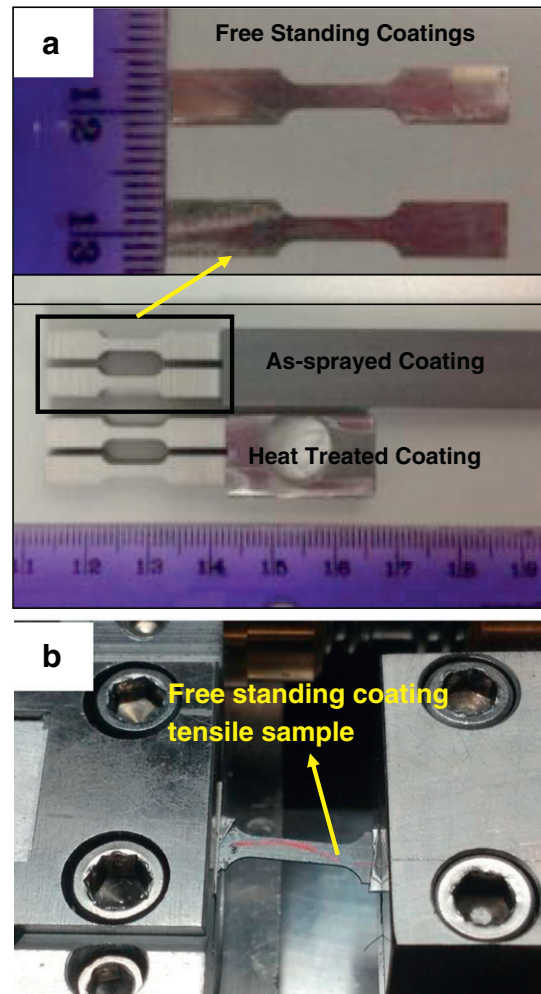


Fig. 1. Digital images showing (a) dog bone shape free standing coatings prepared from coated with Al amorphous coatings using EDM wire cutting and (b) Micro-tensile tester shows the sample fixed between grips before testing.

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