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Preparation of diamond reinforced metal powders as thermal spray feedstock using ball milling

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ABSTRACT

This investigation envisages the preparation of diamond reinforced bronze and Mo powders as thermal spray feedstock via ball milling route. The metal powders with 10 wt.% micro-sized mono-crystalline diamond have been ball milled for up to 48 h. The powders have been characterised to get their crystal structure and stability of diamond using XRD and Raman spectroscopy. Substantial peak broadening of both powders has been observed, indicating a reduction in crystallite size. The bronze powder has turned flaky and shown cold welding of flakes. The Mo powder, on the other hand, exhibited brittle characteristics. Raman spectrum of the bronze-diamond powder indicates some changes in the sp^3 hybridised structure while the D-band has been protected. The Mo-diamond powder retained the sharp D-band up to 42 h of ball milling. After 48 h of milling, a substantial decrease in the intensity of D-band and a significant growth of G-band has been observed for this powder.

1. Introduction

Thermal spraying is one of the most important technologies for surface protection. Depending on the variety of feedstocks, thermally sprayed coatings can be used in a number of applications, like wear resistance [1–2], corrosion resistance [3–4], and thermal barrier coatings [5–6].

Thermal spray feedstocks are produced using several routes, e.g., crushing and grinding, air atomising, and water atomising. Ball milling is also used to grind larger powders to a size range suitable for thermal spraying [7]. This technique can also be utilised to mix two or more constituent powders into a so-called 'mechanically alloyed' powder [7–8]. Bearing surfaces are frequently used in machine building. Lathe bed, machine tool guide ways, lathe centres are examples of bearing surfaces. These surfaces are finished to close tolerance, and expected to possess good friction and wear characteristics. Wear results in loss of shape of the bearing surface and this in turn produces inaccuracy of slide movement. Typical examples of bearing surface materials are Babbitt metal, bearing steel and bronze. Owing to the superior structural property and high load capacity, tin bronze alloys are often employed in high-load, low-speed applications like trunnion bearings, gear bushings, and rolling mill bearings. Having an excellent level of lubricity and wear characteristics, bronze also finds its application in IC engine components, like connecting-rod bearings, valve guides, and starters [9]. Refractory property and lubricity of molybdenum allows it to be used in high temperature and highly corrosive environment like marine crankshafts, compressor vanes, automobile components like piston ring [10].

One limitation of bronze is its limited wear resistance. The wear characteristics of bronze can be enhanced considerably by incorporating small hard reinforcing particles in the bronze matrix [11]. Similarly, wear properties of molybdenum coatings are also expected to be improved upon reinforcement. In this context it may be noted that molybdenum itself is much harder than bronze [10,12]. Small sized diamond particles can serve as reinforcement. These can be incorporated in the metal by long term ball milling. The powder feedstock thus prepared can be utilised to fabricate a diamond reinforced coating using thermal spraying technique [13].

Preparation of particulate reinforced thermal spray feedstock by ball milling has been seldom reported in the literature. In one such rare report, Wielage et al. [8] discussed the preparation of SiC reinforced Ni and Co based self-fluxing alloy powder feedstock by ball milling. Subsequently, this powder was sprayed using high velocity oxy-fuel (HVOF) technique to produce excellent wear resistant coatings. Performances of the SiC reinforced Ni-based alloy coatings under oscillating wear test were comparable to WC–Co, which is a well known benchmark amongst tribo-coating.

In a separate investigation, Wilden et al. [14] attempted the preparation of TiB_2 reinforced Ni/Ni–Cr alloy powders by the ball milling route. The coatings were deposited using HVOF technique and tested under Taber-abrasive wear test. The TiB_2 reinforced coatings have shown excellent wear resistance and mechanical properties.

Some reports are available in the literature dealing with incorporation of micron size diamond particulates in a thermal spray feedstock and its effect on the performance of corresponding coatings. Tillmann

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et al. [15] sprayed bronze impregnated micron size diamond particle (180–300 μm) on steel substrate for grinding applications using a detonation gun (D-gun). The wear performance of the D-gun sprayed coatings containing 3 vol.% diamonds was comparable to that of the sintered composite having 10 vol.% diamonds. This was attributed to a very dense coating structure achieved by D-gun spraying. It was also shown that thermo-chemical deterioration of diamond is of lesser concern in such cases as the flame-particle interaction time is considerably small in high speed deposition processes like HVOF, and cold gas spraying.

Richardson et al. [16] have studied the effect of inclusion of diamond into Ni-based hard facing alloy coatings on stainless steel substrate. Introduction of diamond grits (size 270–325 μm) in the coatings resulted in an increase in the micro-hardness. A diamond concentration beyond 20 wt.%, however, resulted in an increase in porosity and reduction in hardness. Abrasion resistance of the coatings was found to improve with a rise in diamond concentration up to 20 wt.%. Ni-coated diamond particles were observed to be more compatible with the Ni-based matrix.

Diamond has very rarely been used as a constituent of ball milled thermal spray feedstock. In one such report, Woo et al. [13] described the performance of nano-diamond reinforced aluminium coatings, deposited using the cold spray technique. Micro-size aluminium (40–45 μm) powder and nano-scaled diamond were ground together to prepare the feedstock, and were subsequently deposited using cold spray technique. It has been observed that an increase in diamond concentration resulted in a reduction in average particle size upon ball milling. A rise in lattice strain and a reduction in crystallite size were reported up on increase in the BPR and milling time. Raman spectroscopy revealed traces of graphitization of diamond particulate upon prolonged ball milling. Crystal refinement and dispersion strengthening offered by the nano-diamond particulates were attributed as reasons for increase in coating hardness up on diamond concentration.

The objective of this work is to produce and characterise a diamond impregnated metal powder by ball milling. The final goal is to use these powders as thermal spray feedstock to deposit a highly durable bearing surface. The coating properties would be reported in a following publication. To the knowledge of the authors, no similar work has been reported in the literature.

2. Experimental

2.1. Sample preparation

The constituent powders used to produce thermal spray feedstock by ball milling are listed in Table 1.

10 wt.% of the mono-crystalline diamond powder was mixed with bronze or molybdenum powder. The powder mixture was milled for 48 h at 500 rpm in an asymmetrically moved planetary ball mill (FRITSCH PULVERISETTE 6.0, Ider, Oberstien, Germany). SiAlON bowl and balls were used for ball milling purpose. Toluene served as grinding media. The ball-to-powder weight ratio was kept as 5:1. Powder samples were collected at an interval of 6 h starting from 12 h of milling till the end of milling process that continued up to 48 h.

2.2. Characterisation of samples

Both the as-received and ball milled powder samples were characterised using a ZEISS EVO 60 Scanning Electron Microscope with Oxford EDS Detector (Carl ZEISS SMT, Germany), PAnalytical High Resolution PW 3040/60 X-ray diffractometer (XRD) (Philips Analytical, Netherlands) and a micro-Raman spectrometer equipped with a 488 nm argon ion laser. The spectrometer consisted of an optical microscope (Model BX 41, Olympus, Japan), a single monochromator (Model TRIAX550, JY, Horiba, France), an edge filter, and a Peltier cooled CCD detector. X-ray diffraction data was analysed using the X'Pert HighScore Plus (Philips Analytical B.V., Netherlands; version 2.1.0) software.

To do the necessary background correction, removal of Kα_2 signals and identification of phases, X'Pert HighScore Plus software was used. The XRD analysis method assumes that the overall broadening of XRD peaks comprises of three effects: one arising from the small coherent grain size, another from the errors present in the instruments and a third for the atomic level micro-strain. The instrumental broadening correction factor was measured from the X-ray diffraction of a standard Si (single crystal) sample. This correction factor was incorporated in the X-ray diffraction data of the ball milled powder. Full-width-half-maxima (FWHM) is a measure of the broadening of peaks in XRD patterns. The values of FWHM for peaks at different angles (2θ) were measured and plotted to observe the effect of ball milling on different peaks, i.e. in different crystallographic directions.

3. Results and discussion

3.1. Bronze matrix

The SEM micrographs of metal powders in as-received condition are presented in Fig. 1a–b. The gas atomised powders for both metal powders had a spherical morphology in as-received condition. The SEM images of bronze powders mixed with 10 wt.% diamond powder, and milled for different time durations are presented in Fig. 2. The morphology of the milled powder was like platelets. A flaky appearance has been observed in the first stage of milling (12 h). Owing to high ductility, the level of strain accumulation as well as deformation was very high in bronze particles, leading to flaky structures of particles after ball milling. Upon further milling, at the end of 18 h of ball milling the flakes were seen to be locally welded to give a lumpy appearance. On further milling, large platelets of very low thickness were produced. This speaks of strain accumulation in the particles. After this stage, breakage of flakes started to take place. The phenomenon of local welding and breakage of flakes seemed to balance each other at around 36 h, as the morphological features seemed to be same upon milling afterwards. A similar phenomenon has been predicted by Maurice and Courtney in their study on the deformation behaviour of milling charge under the ball milling environment [17]. Copper–chromium alloy powders produced by ball milling route [18] also followed the same regime of deformation and particle fragmentation that was observed using scanning electron microscopy. The series of phenomenon observed during ball milling of bronze can be easily categorised as a response of a ductile material with low melting point subjected to hertzian pressure of high magnitude, exerted during the collision of the balls during ball milling.

The X-ray diffraction pattern of bronze–diamond powder after 36 h of milling is presented in Fig. 3. The XRD pattern shows the presence of $Cu_{0.85}Sn_{0.15}$ and Cu_2O peaks. Most of the peaks found in this powder belong to the δ phase of bronze. In addition, Cu_2O has also been found. A small amount of oxygen and silicon has been detected in the energy

Table 1
Details of constituent powders used for ball milling.

Name	Size	Composition	Type	Manufacturer
Diamond	−100 + 5 μm	99.5% pure diamond	Synthetic diamond powders	Element Six Ltd. Shannon, Ireland
Bronze	−50 + 5 μm	Cu 85% Sn 15%	Gas atomised, spherical	MEPCO, India
Molybdenum	−75 + 38 μm	99.5% pure Mo	Agglomerated and densified	Sulzer Metco, Westbury, NY, USA