SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE Co-Cr COATINGS BY PLASMA SPRAYING

M.L. Lau, E. Strock*, A. Fabel*, C.J. Lavernia** and E.J. Lavernia

Department of Chemical and Biochemical Engineering and Materials Science
University of California, Irvine, Irvine, CA 92697-2575
*Englehard Surface Technologies, East Windsor, CT 06088
**Department of Orthopedics and Biomedical Engineering
University of Miami, Miami, FL 33101

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Abstract—The present paper describes the synthesis and characterization of nanocrystalline Co-Cr (ASTM F75) coating produced by plasma spraying for possible surgical implant applications. The feedstock powders were synthesized by mechanical milling to produce irregular agglomerates with an average grain size of less than 100 nm. The powders were then introduced into an argon plasma spray to successfully produce a nanocrystalline coating. Scanning electron microscopy and transmission electron microscopy were used to study the morphology of the nanometric particles and the resultant sprayed coatings. Microhardness and porosity measurements were performed on the conventional and the nanocrystalline coatings to characterize and compare the physical and mechanical properties. ©1998 Acta Metallurgica Inc.

INTRODUCTION

Thermally sprayed coatings in medical applications typically involve orthopedic and dental prostheses (1-4). Significant research has been focused on the assessment of compatibility of bioinert materials for surgical implants and the effect of these materials on muscle and bone tissue (1-5). Conventional prostheses are made of bioinert materials such as low carbon steel, Ti-6Al-4V alloys or CoCr type alloys such as ASTM designated F75 alloys (1). Thermally sprayed coatings lead to improvements in the contact surface, diminishing the wear provided by prosthetic devices. (3-4). The coatings must have a high porosity (20-40%) and good adhesion to the prosthesis (1). Furthermore, thermally sprayed coatings must be biocompatible and maintain mechanical integrity following implantation (1). More recently, thermal spraying of nanocrystalline coatings (defined hereafter as having a grain size smaller than 100 nm) using nanocrystalline powder feedstock prepared by mechanical alloying/milling or chemical synthesis has attracted considerable interest for many industrial applications. This interest stems from the reported property improvements in the physical properties of the nanostructured coatings (6-12). For instance, in...
a recent study, nanocrystalline 316-stainless steel powders prepared by mechanical milling were thermally sprayed using HVOF (high velocity oxy-fuel) to produce nanocrystalline coatings with an average grain size of less than 100 nm. The resultant coating exhibited a 48% increase in microhardness over that of the conventional stainless steel coating, while the porosity of the nanocrystalline coating was higher than that of the conventional counterpart (10). The combination of increased hardness and porosity associated with the nanocrystalline coatings may provide potential benefits for implant applications such as increased surface area and improved wear properties. The objectives of the present study are: first, to investigate the feasibility of preparing a nanostructured Co-Cr (ASTM F75) coating by mechanical milling and plasma spraying: and second, to provide preliminary results on the microstructure and the physical properties of the as-sprayed nanocrystalline Co-Cr coating for potential implant applications.

**EXPERIMENTAL PROCEDURE**

Inert gas atomized ASTM F75 Co based superalloy powders (Cr-28.55 wt.%, Mo-5.95%, Si-0.53%, C-0.30%, Fe-0.27%, Ni-0.13%, Mn-0.09%, balance Co, Starmet Corp.) with a nominal particle size range of 149 + 44 μm with an average particle size of 88 μm were chosen for the study. The powders were mechanical milled in a modified Union Process 01-ST attritor mill with a grinding tank capacity of 0.0057 m³ in a methanol environment. Stainless steel balls with 0.635 cm in diameter were used as the grinding media and the powder to ball mass ratio was 1:20. The drive shaft operated at 180 rpm. A Microtrac Standard Range Particle Analyzer (Leeds-Northrop 93-100 series) was employed to determine the particle size distributions of the milled powders. The milled powders were thermally sprayed by an argon plasma flame (Sulzer Metco 7M spray system) onto Ti substrates. The powders were fed at a rate of 1.81 kg/hr and the spray distance was 10.16 cm. The average velocity of the plasma jet reached 1,500 m/s with the nominal flame temperature at the exit of the plasma torch of approximately 10,000 K to produce a coating with a nominal thickness of 0.254 mm.

The porosity of the as-sprayed coatings was measured following the ASTM No. B328 guidelines (13). Microscopy observations were performed in a Philips XL30 FESEM scanning electron microscope equipped with EDAX analysis. The milled powders and the as-sprayed coatings were mounted in a conductive mold and mechanically ground to provide a polished surface. The milled powder particles to be analyzed by transmission electron microscopy (TEM) were dispersed in methanol, deposited on carbon grid substrates and allowed to dry in air. Preliminary TEM studies to determine the grain size of the milled powders were performed in a Philips CM20 transmission electron microscope operated at 200 keV. Microhardness measurements were performed on the cross-section of the coatings, which had been mechanically polished. A Buehler microhardness tester with a diamond indentor and a 300 g load was used and at least thirty measurements were taken and the average value was reported for each coating sample.

**RESULTS AND DISCUSSION**

X-ray diffraction analysis was performed on the as-received and mechanically milled powders. After 10 hrs. of milling, the broadening of characteristic Co peaks was observed, as shown in Figure 1. Furthermore, the presence of the characteristic Co₃Mo peaks indicated the
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Figure 1. X-ray Diffraction patterns for (a) as-received Co-Cr powders, (b) methanol milled powders for 10 hrs., (c) conventional plasma sprayed Co-Cr coating, (d) methanol milled Co-Cr coating.

Figure 2. Methanol milled Co-Cr powders for 10 hrs.

Figure 3. Dark field TEM image of methanol milled Co-Cr powders.
formation of an intermetallic phase in the milled powders. Mechanical milling of the as-received Co-Cr spherical powders lead to the formation of irregular and flake-shaped agglomerates, as shown in the secondary electron image (Figure 2) attained from the SEM analysis. The formation of irregular flake-shaped agglomerates is attributed to the continuous welding and fracturing of the powder particles during the mechanical milling process (14). The particle size range of the as-milled powders determined by Microtrac Standard Range Particle Analyzer (Insitec Measurement Systems) was \(-164 + 68 \mu m\) with the average particle size of \(106 \mu m\). Transmission electron analysis was performed on the milled powders. Backscattered electron image shown in Figure 3 revealed regions of nanocrystalline grains. The average grain size of the milled powders was 12 nm, as shown in the grain size distribution in Figure 4. Furthermore, selected area diffraction patterns indicated the presence of cubic \(Co_3O_4\), which also may have been formed during the mechanical milling process.

Backscattered electron images were obtained from SEM analysis performed on the as-sprayed nanocrystalline coatings and the conventional coatings processed using identical spraying parameters, as shown in Figure 5a-b. Energy dispersive analysis performed on the coatings indicated that the oxygen concentration at the grain boundary region is approximately four times higher than that of the coating. It is speculated that the oxides are formed with the constituents of
the Co-Cr such as Cr₂O₃ (ΔH₂⁹₈K = -1130.4 kJ/mol) and Co₃O₄ (ΔH₂⁹₈K = -905.6 kJ/mol) (15) along the grain boundaries during rapid cooling. Table 1 lists the microstructural characteristics of methanol milled Co-Cr coating for 10 hrs., which include porosity and microhardness, as determined on cross-sectional areas. The results of the present study indicate that the microhardness and the porosity of the methanol milled Co-Cr coatings are marginally higher than those obtained from the conventional Co-Cr coating with the same spraying parameters. Although the underlying mechanism for the cause of the increase associated with the nanocrystalline coating is not clearly understood, several investigators have reported enhanced hardness values for nanocrystalline metals, based on the rationale of refined grain size and associated grain-boundary strengthening (16-19). In addition, since the agglomerate size of the nanocrystalline Co-Cr is higher than that of the conventional spherical powders, it is expected that the chemical reactivity of nanocrystalline Co-Cr powders will increase due to the increased surface area. Therefore, it is speculated that the marginal increase in microhardness of the nanocrystalline Co-Cr coatings may be due to the presence of an increased proportion of oxide phases throughout the grains.

### Table 1

Properties of Plasma Sprayed Co-Cr Coatings

<table>
<thead>
<tr>
<th>Material</th>
<th>Porosity (%)</th>
<th>Microhardness 300g load (DPH)</th>
<th>Increase in hardness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>conventional</td>
<td>4.53</td>
<td>363 ± 36</td>
<td>not applicable</td>
</tr>
<tr>
<td>nanocrystalline</td>
<td>9.62</td>
<td>392 ± 77</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Figure 5a. Conventional Co-Cr coating by plasma spraying.

Figure 5b: Methanol milled Co-Cr coating by plasma spraying.
Microscopy was performed on the methanol milled Co-Cr coating. Regions of nanocrystalline grains with an average grain size of 21 nm were observed in the dark field imaging, as shown in Figure 6. However, regions of large grains (>80 nm) were also observed. Figure 7 shows the grain size distribution of the methanol milled CoCr coating. These preliminary findings show promising results of utilizing nanocrystalline coating for potential implant applications due to the increased surface area and microhardness associated with the nanocrystalline coatings. Further studies are underway to determine the erosion properties of the coatings.
CONCLUSION

ASTM specified Co-Cr F75 powders have been mechanically milled in methanol environment for 10 hrs. to produce nanocrystalline powders with an average grain size of 12 nm, determined by TEM dark field imaging. The feedstock powders were plasma sprayed onto Ti substrate and the resultant coating remained nanocrystalline with an average grain size of 21 nm. Furthermore, the microhardness and porosity of the nanocrystalline Co-Cr coating are found to be higher than those from the conventional Co-Cr coating, indicating that nanocrystalline coatings may be potential coating candidates for implant applications.

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REFERENCES