Synthesis, characterization and tribological studies of Chromium-Nano diamond composite coating

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Abstract—Nano composite coatings are a new forms of materials containing hard phase particles to enhance the hardness and wear resistance, among which diamond in terms of feasibility and cost, is the best combination for chromium. In this study, electrolytic coating of pure chromium and Cr-ND (nano diamond) composite coatings were applied on pre-alloy metal powder metallurgy specimens. The effects of the ND particles on tribological behavior of the chromium coatings were investigated. Characterization tests were carried out using an optical microscope, SEM, EDS, XRD and AFM. The dry sliding wear behavior of the specimens was carried out using pin on plate configuration. The hardness and wear resistance of the Cr-ND coated samples were compared with pure chromium coated and non-coated specimens. The results demonstrated that the embedding of the ND particles in the chromium matrix led to a significant improvement on the hardness and wear behavior of the Cr-ND coatings than pure chromium coatings and non-coated specimens.

Keywords—Nano Composite, electrolytic coating, tribology, SEM (scanning electron microscope), EDS (Energy-dispersive X-ray spectroscopy), XRD (X-ray diffraction), AFM (Atomic Force Microscope)

I. INTRODUCTION

Being a precise method, PM has the capability of forming parts with near net shape and complex geometries in acceptable dimensional precision with no need for machining. The mentioned characteristics of PM makes it irresistible in aerospace, mining, automotive and weaponry industries. However, certain problems are arisen in the powder metallurgy parts when they contain pre-existing porosity and voids associated with property degradation [1, 12]. The existence of porosities results in large decreases in both strength and ductility. Porous substrates show less resistance to corrosive agents, reduced mechanical properties, and deleteriously influenced density, electrical properties and diffusion characteristics [1, 2, 12]. To avoid the problems mentioned above, industries are highly inclined to make bigger demands for improved performance. Therefore, it seems that the development of near- perfect surface coatings with higher wear and corrosion resistance is imperative [1, 2]. One useful technique to produce nano composites by deposition of dispersed nano particles (metallic, non-metallic or polymeric) in the matrix solution to fulfil the uniformity of the external layer of a part is electrolytic coating [2, 6]. Diamond, the frequently studied and applied [5, 13] for its high hardness, good oxidation resistance, chemical stability and wear resistance [12], is a common particulate material to be used for reinforcement in the field of composite coating. The type, shape, size and properties of particles affect the final properties of the composite coatings. So far, most studies have been concentrated on the micro sized particles. However, the application of nano particles is quite a new field for their mechanical, magnetical and optical properties.

Juneghani et. al [8] coated AISI 1020 with pure Cr and Cr-SiC nano composite. They reported that the hardness value of the nanocomposite coating is higher than that of pure chromium coating and with the increasing amount of SiC added to the solution, the hardness value of the coating and the corrosion resistance have improved. Yousefpour et al. [7] studied the wear and corrosion behavior of Ck 75 steel Coated with TiO₂, Al₂O₃ and SiO₂ particles reinforced chromium matrix and reported an increase in wear, corrosion resistance and microhardness. Gidikova et al. [5] coated the carbon steel C45 with electrochemical nano diamond reinforced chromium in acid solution of CrO₃ and they found evolution in the hardness values by increasing nano diamond particle concentration. Isakov et al. [13], studied the surface properties of nano diamond reinforced chromium on stainless steel. The main goal of this study was to investigate the influences of ND particles on the surface morphology, phase structure, grain and crystal sizes, hardness, wear resistance within a chromium matrix on a sintered pre-alloy powder substrate.

II. EXPERIMENTAL PROCEDURES

A. Press and sintering:

The pre-alloy metal powder, supplied by the Toz Metal A. Ş. with the chemical properties as in Table 1 was pressed at 550 MPa in a biaxial die into $31.7 \times 12.7 \times 7.9$ mm. The sintering of pressed specimens took place at 1120 °C for 25 minutes in %0.6

carbon potential atmosphere $(CH_4+C_3H_8)$ where the total sintering process time was 150 minutes.

TABLE I
THE CHEMICAL PROPERTIES OF THE USED METAL POWDER

Composition	wt. %
AHC.100.29	96.8
Cu	1.5
Graphite F10	0.2
Graphite KS44	0.2
MnS	0.5
Lube E	0.8

B. Deposition of Chromium and Chromium-Nanodiamond coatings

A reduction in H_2 at 950 °C for 45 minutes followed by degreasing in 1.2 dichloroethane solution for 10 minutes were done on the specimen to perish the oxide layer on the surface prior to the coating. The galvanic electrodeposition bath based on the Hull-Cell method was taken advantage of to do the chromium and the nano diamond coatings. Lead was used to be anode, and the distance between anode and cathode was 50-60 mm.

 TABLE II

 ELECTRODEPOSITION BATH COMPOSITION AND PARAMETERS [4]

Electrodeposition bath	Valua	
composition and parameters	value	
CrO ₃	220 g/l	
H_2SO_4	2.2 g/l	
ND concentration	0 and 25	
Current density	45 A/dm ²	
Temperature	50° C	
Stirring rate	100 rpm	
pH	5.5-5.8	
Average ND size	6 nm	

C. Characterization of the materials

The densities of the sintered and coated specimens were calculated with Archimedes principle. The porosity percent, coating thickness of the coated and non-coated specimens were calculated from the average value of the taken pictures of the cross section by optical microscope using ImageJ software.

D. Microstructure and surface morphology tests

The surface morphologies of electrodeposited Cr-ND composite coatings were investigated using scanning electron microscope (SEM). The chemical composition of coatings analysed by Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The grain and crystal size of the coating were calculated using Intercept method and Scherrer formula.

E. Hardness tests

The macro hardness tests of the sintered specimens were carried out using 100 Kg. The micro hardness of coatings and non-coated samples was measured using Vickers diamond indenter by a load of 50 g for a loading time of 15 sec. The average of ten repeated measurements has been reported.

F. Wear tests

The dry wear tests of the non-coated and Cr-ND coated specimens were carried out in pin on plate configuration under 1.4 MPa, 20 mm/s at room temperature. The weight loss of the specimens was calculated at 10, 40 and 90 meters of sliding distance after ultrasonic cleaning for 10 minutes in distilled water. The surface roughness and their distribution have been measured before and after every sliding.

III. RESULTS AND DISCUSSION

The sintered specimens' density was measured at 6.90 g/cm³. The total porosity rate of the non-coated samples was %11.751 where the average surface porosity rate was %10.870. Due to the low melting point of copper, increased porosity was brought about during the sintering process [12]. Fig. 1a and b are representative of the microstructures of sintered specimens prior to and following the coating process by chromium.



Fig. 14 The surface porosities of the samples before coating; a)100X, b)500X



Fig. 2 The SEM images of the surfaces of the coated salipies, a) environment, b)

Fig. 2 a and b demonstrate the microstructures of coated specimens. The average grain size of the Cr-ND coating was calculated 14.28 μ m, however this value was 39.68 μ m for pure Cr. The average thickness of the pure chromium and Cr-ND coated samples were 17,26 and 19,02 μ m, respectively. It is worth noting that the chromium yield noticeably increased [5, 13] to %1.55 by enhancing the ND particles in the bath for the 25 g.l⁻¹ concentration while this value was %1.13 for the pure

chromium. The more ND particles in the bath are, the higher the chromium yield becomes. This behavior is justified by the incorporation of the nano particles into the metal coating according to the Gugliemli model [6, 7]. The Guglielmi Model is mainly a two-step process [3, 4]. Initially, the particles approach the cathode and are weakly absorbed onto the cathode surface. The ion cloud surrounds the weakly bound particles. In the second stage, the particles leave the ion cloud surrounding them due to the chemical reaction and are absorbed more strongly on the cathodic surface. Additionally, the increase in particle concentration in the electrolyte also increases the absorption on the cathode surface, according to the two-step model. As a result, there is an increase in the coating's particle content.

The average macro hardness of the sintered parts was 56.38 HRB. Fig 3 shows the average micro hardness values of the specimens.



Fig. 3 The average micro hardness of the specimens

The mechanisms for the strengthening of metals and alloys can be explained as follows: a) Strain hardening b) Grainboundary strengthening and grain-size reduction c) Dispersion strengthening d) Dilute atoms and solid solution strengthening e) Crystal orientation (f) precipitation hardening.

Thus, when considering nano composite coatings, hardness is achieved through mechanisms b and c. The equation below describes grain size reduction and grain boundary strengthening from the Hall-Petch contribution to strengthening.

 $\sigma_{v} = \sigma_{0} + kd^{1/2}$

where σ_y is the yield stress, σ_o a friction stress, d the average grain size in diameter and k is a constant [8]. In grain-boundary strengthening, the grain boundaries act as pinning points impeding further dislocation propagation. Since the lattice structure of adjacent grains differs in orientation, it requires more energy for a dislocation to change directions and move into the adjacent grain. The grain boundary is also much more disordered than inside the grain, which also prevents the dislocation movement will hinder the onset of plasticity and hence increase the yield strength of the material. The dispersion strengthening by Orowan mechanism suggests the yield stress of an alloy/composite containing a dispersion of fine particles is determined by the shear stress required to force a dislocation line between two particles separated by a distance 2r [9]. The dislocation line between the particles turn into a semicircle. The resulting semicircle can be calculated by:

$$r = \frac{D - d}{2}; \ \sigma_y = \frac{Gb}{r}; \ \tau_0 = \frac{Gb}{2r}$$

where G shear modulus of the matrix, b the Burger's vector of the dislocation and τ_0 the shear stress required to move dislocation between the blocks in the microstructure obstacles (Cr-ND), D the distance between the centres of two particles and d refers to the diameter of a particle.



Fig. 4 Schematic view of Orowan dispersion hardening mechanism [8]

In Fig. 4. line 1 exhibits a straight dislocation line approaching two particles separated by a distance 2r. The line began to bend in the 2nd, the critical bend in the 3rd. Dislocation, without reduction in the radius of the curve, it can be carried forward until it encounters the oppositely marked dislocation. Dislocations in opposite directions in the 4th grade meet each other and destroy each other. Then to continue the original dislocation movement free [9].

For pure chromium G and b are supposed 115 GPa and 0.2884 nm respectively [8]. Restriction occurs in the growth of the chromium grains, crystals and the plastic deformation of the matrix under a loading by way of grain size reduction, dispersive strengthening and crystal orientation effects, and the hardness of Cr-ND composite coatings enhances due to the distribution of ND particles in the Cr matrix. The contribution from the dispersion strengthening is largely due to the uniform distribution of ND particles in the coatings in the case of nanocomposite coatings. Such particles possess a fine grain size. The inclusion of nano diamond particles activates the hardening mechanism of the second phase barrier. When the material flow is hindered by distributed hard nanometer diamond particles as a barrier to dislocation movement, the plastic deformation of the depositions would be more difficult. The hardness would also be improved by achieving a better distribution of nanometer particles within the chromium deposition matrix. Results are confirmed by the SEM and XRD analysis.

The electro-deposited Cr-ND coating is composed of a solid solution in a mono-phase matrix, as confirmed by the XRD pattern shown in Fig. 5. The peaks corresponding to the [111] peaks of nano diamond in the coatings are shown in the graphs, implying that the nano diamond particles have been embedded in the chromium matrix.



Diffraction lines are exhibited by pure chromium deposit [110], [200] and [211]. The intensity of the diffraction peaks of the chromium in the nano composite coating is lower and the peak width is broader than that of the pure chromium coating. The peak of Cr [200] in pure Cr is sharper and higher than that of the Cr-ND coating. With respect to the peak of pure chromium, the Cr [200] and [211] peaks occurring at 20 angle of the samples differed somewhat in the Bragg angle. The fact that the lattice distance of chromium is restricted by the incorporated ND particles is due to the physical effect of the composite coating process. No diffraction peaks of any unexpected substance arose due to chemical reactions, as demonstrated in the graphs. The crystal sizes of the chromium have decreased with the incorporation of ND particles in chromium with respect to pure chromium coating [6, 10, 11].

The EDS analyses expressed the composition of the electrodeposited Cr–ND coating in which the weight percent of Cr is 84.94 wt.% and that of ND is 5.05 wt.% form EDS as shown in Fig. 6.



Fig 7. shows the mass loss during wear test, Fig 8. shows the total mass loss and wear rate. It is found that the Cr-ND composite coating shows higher wear resistance than the pure chromium coating. The influences of ND particles in the amendment of the tribological properties of Cr-ND composite coatings is due to the incorporation of the ball-shaped and ultrahard ND particles in the coatings refined grain sizes [8, 9]. The increase microhardness of Cr-ND composite coatings can improve the wear resistance remarkably.



Fig 9. shows the average surface roughness and its distribution during the wear tests of the specimens. With increasing the sliding distance, the surface roughness and its distribution of the non-coated specimen increases, whereas these the opposite is valid for the Cr and Cr-ND coated specimens. The increasing surface roughness and its distribution of the non-coated specimen can be attributed to the adhesive and abrasive wear [14].



Fig. 10, Fig. 11 and Fig. 12 demonstrate the worn surfaces of the non-coated, pure Cr and Cr-ND coating. The parallel lines on the surface are indicative of abrasive wear. Adhesive

wear is also noticeable on the non-coated specimen as well as abrasive wear.



Fig 10. The SEM image of the worn Non-coated sample



Fig 11. The SEM image of the worn pure Cr coated sample



Fig 12. The SEM image of the worn Cr-ND coated sample

The 3D surface topography of the surfaces was taken from a $1{\times}1~\mu m^2$ area by AFM of the samples. The 3-D surface

topography of the Cr-ND coating is shown Fig. The Ra surface roughness, RMS surface roughness distribution values were calculated. The surface roughness and its distribution values of Cr-ND are less than both pure Cr and non-coated surfaces. This can be attributed to the contribution of ND particles which created a more compact and smoother surface.



Fig 11. The AFM image of the Cr-ND coated sample

TABLE III

THE 3D SURFACE TOPOGRAPHY RESULTS OF THE SPECIMENS

Sample	R _a (nm)	RMS (nm)
Non-coated	5.04	6.62
Pure Cr	2.86	3.81
Cr-ND	2.12	2.65

IV. CONCLUSIONS

X-ray diffraction analyses performed a successful mono phase nanocomposite coating process on pre-alloy metal powder substrates by electrolytic coating process.

The incorporation of ND particles during electrochemical deposition of chromium enhances of the chromium yield and the thickness of the coating.

The embedding of ND particles in the chromium matrix resulted in a layer with smaller crystallite and grain sizes and more compact and smoother surface than those of pure Cr deposits.

It could be observed from the SEM micrographs of the worn sample surfaces in the dry wear tests that abrasion was the main wear mechanism. Furthermore, a little adhesion occurred on the worn surface of the substrate, especially on the non-coated samples.

The embedding of ND particles in the chromium matrix enhances the hardness, wear behavior.

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