Chromium-Ceria Electrocomposite Coatings

R. Narayanan & S.K. Seshadri

Chromium-ceria electrocomposite coatings were produced from four different levels of addition of ceria powder to the bath. Properties of the coatings, such as incorporation of the ceramic particles in the chromium metal matrix, hardness, specific wear rate and Archard wear coefficient were determined and compared with those of plain chromium coatings. In all baths used, tetraethylenepentamine (TEPA) was added as a promoting agent and a ratio of ceria:TEPA was maintained at 10:1. The coatings produced from the baths containing high content of ceria powder show high hardness and good resistance to wear.

Electroforming as a technique for the manufacture of metal matrix composites has several advantages, such as no heat or pressure needed, does not require elaborate and expensive equipment, does not deform the components, etc.

Chromium was deposited from a hexavalent bath and used to provide wear resistance and low coefficient of friction. Such coatings find applications on hydraulic pistons and cylinders, piston rings, wearing parts in machines, aircraft engine parts and various parts of nuclear reactors where galling is of particular concern.

Electrodeposited Chromium Composite Coating

To further improve the various properties of chromium deposits, hard particles such as oxides, carbides and borides, as well as lubricating particles, were codeposited with chromium.[1] The amount of codeposition in most chromium-ceramic electrodeposition systems is small and, in some cases, has not been successful. The reasons could be the result of (a) the corrosive nature of chromium acid causing chemical deterioration of particles such as MgO, ZrB_2, etc.; (b) low cathode efficiency of the process; (c) copious hydrogen evolution; and (d) high surface tension of the electrolyte.

Improvement in the incorporation level of ceramics and the properties of chromium composite coatings can be achieved by addition of monovalent cations such as Ca^+, Na^+, Tl^+ and NH_4^+ in the chromic acid bath.[2] Another option available for increasing particle incorporation is to add suitable surface modifying agents to the bath.[3] The effect of adding rare earth elements in the case of SiC codeposition from a chromium bath has been studied and the influence of this additive was found to be more pronounced at higher concentrations of SiC particles.[4] Sunke-Ning reported that the weight loss of chromium-alumina coatings containing rare earth elements was decreased by a factor of 2 to 6, compared with a plain chromium coating.[5]

Chromium Ceria Electro-codeposition System

Only a limited amount of work has been done on chromium-ceria codeposition systems. Kamat[6] reported that addition of a small amount of tetraethylenepentamine (TEPA) as promoter to a chromic acid bath containing 2 g/L ceria, increases the hardness of the coating. Much larger concentrations of the dispersoid and the promoter were found necessary to codeposit an appreciable amount of particulate matter with copper and nickel.[6] Accordingly, it is expected that a higher level of dispersoid (ceria) addition to the chromium bath would increase the codeposition and, consequently, enhance the properties of the coating. This study involved addition of higher levels of ceria to the bath, while maintaining a ratio of ceria:TEPA at 10:1. The aim of this study was to investigate the wear characteristics of the coatings thus produced. Table 1 lists the properties of ceria used.

Table 1
Properties of Ceria
(Adapted from Ryshktewich, 1960)

a. Color	: off-white
b. Melting point, °C	: 2750
c. Crystal structure	: Fluorite (at random)
d. Free energy of formation, MJ/mol	: 1.026
e. Specific heat, cal/g, °C	: 0.10
f. Coefficient of thermal expansion	: 8.6 x 10^{-6}/°C
g. Specific resistivity in air	
at 500 °C	: 5 x 10^7 ohm-cm
at 1200 °C	: 240 ohm-cm
h. Molar heat capacity	: 15.8 cal/°C
i. Molar heat of formation	: 224.6 kcal
j. Density, g/cc	: 7.13

Experimental Procedure

Mild steel coupons 30 mm in diameter and 5 mm thick were used for preparation of the coatings. Table 2 lists the composition of the coupons.

The electrolytic bath contained 200 g/L chromic acid, catalyzed by 2 g/L sulfuric acid and maintained at pH 2. Pb-9%Sb alloy was used as anode. Five sets of coatings, namely, plain chromium (Bath 1), as well as coatings from baths to which were added 25 g/L ceria (Bath 2), 50 g/L ceria (Bath 3), 75 g/L ceria (Bath 4) and 100 g/L ceria (Bath 5). Baths 2-5 contained ceria and TEPA in the ratio of 10:1. The samples were coated at a current density of 40 to 60 A/dm^2 for four hr at 50°C and stirred magnetically. The anode-to-cathode area ratio was maintained at 2:1.

The steel substrates were treated in an alkaline solution to remove oil, grease, dirt, etc., then rinsed with water. They were then etched in a solution containing 150 g/L CrO_3 and 2 g/L sulfuric acid at a cathode current density of 25 A/dm^2 for not more than two min.[7] This produced the necessary microscopic etch for good adherent chromium coatings. The

Table 2
Composition of Mild Steel

Element	C	Si	Mn	S	P	Cr	Mo	Ni
% wt	0.229	0.07	0.676	0.022	0.53	0.001	0.0001	0.004

Table 3
Percent Concentration of Ceria

From	Pct in Coating
Bath 2	0.104
Bath 3	0.142
Bath 4	0.165
Bath 5	0.216

Table 4
Hardness of Coatings

From	Hardness (VHN), 50-g load
Bath 1	874
Bath 2	810
Bath 3	866
Bath 4	927
Bath 5	946

Table 5
Specific Wear Rate W_s

From	Wear loss in kg (x 10^{-6})	Load (N)	Sliding distance m x 10^3	W_s kg/Nm (x 10^{-9})
Bath 1	45	---	0.0468	65.41
Bath 2	37	14.7	0.0470	53.55
Bath 3	34	14.7	0.0470	49.21
Bath 4	30	14.7	0.0470	43.42
Bath 5	26	14.7	0.0468	37.70

Table 6
Archard Coefficient K

From	Wear loss in kg (x 10^{-6})	Load (N)	Sliding distance m x 10^3	K
Bath 1	45	---	0.0468	0.039
Bath 2	37	14.7	0.0470	0.030
Bath 3	34	14.7	0.0470	0.029
Bath 4	30	14.7	0.0470	0.028
Bath 5	26	14.7	0.0468	0.025

coated substrates were then rinsed in cold water to remove any chromium stain, then treated with methanol and dried.

The samples were then studied for X-ray diffraction patterns using a Cu source and K_d radiation at 1.5418 Å in a microprocessor-controlled X-ray diffractometer. This was done to identify the phases present in the coatings.

The incorporaion level of ceria in the coatings was determined by stripping them in a solution of 150 g/L NaOH at a current density of 4-8 A/dm^2 for about five hr. The solution was then filtered, and the filter paper burned at 1000 °C to yield a residue of ceria. The weight of the residue indicated the level of incorporation. Care was taken to see that the base metal was not attacked by the NaOH.

The coatings were tested for hardness using a 50-g load in a microhardness tester. Wear tests were conducted using a disc-on-disc type machine. The coating was held in position and pushed against a titanium nitride counterface disc and tested at 1000 rpm against a load of 14.7 N for one hr. The weight loss was used to calculate the specific wear rate, W_s (expressed in kg/Nm) and the Archard coefficient.

Results & Discussion

X-ray diffraction studies indicated the presence of ceria in the composite chromium coatings. With increased concentration of ceria in the electrolyte, the intensity of the ceria peak increased. Table 3 shows the percentage incorporation of ceria in the coatings produced from all four baths containing it.

In any coating system, the impingement factor and holding time are two important considerations in controlling the process. The impingement factor is influenced by the concentration of second-phase particles in the solution. In the chromium electrodeposition system, the time of holding of particles in the vicinity of the cathode is very short because of copious hydrogen evolution and, consequently, a high level of incorporation of ceramic particles in the matrix is not possible, even if the impingement factor is quite favorable. Even a very high level of second-phase particles in the bath produces only a small percentage of incorporation.[5] Yang observed deposition of only 0.8 to 1.5 wt-pct of graphite in an electrodeposited chromium composite coating.[8]

When tests were made with addition of one mg/L TEPA to an acidified $CuSO_4$ bath containing $BaSO_4$ powder, excellent codeposition on vertical surfaces was obtained.[9] Very little TEPA was adsorbed on the crystallite powder, so it is not a prime factor in codeposition. It is in the cathode film that TEPA exerts its effect in promoting codeposition of the dispersoid. Adsorption effects and complexing effects in the cathode film are perhaps involved in the electro-osmotic process that makes it possible for the particles to cling to the surface, resulting in increased incorporation.[9] TEPA is suspected to cause this via modification of the surfaces of the ceria particles. The higher level of incorporation in Baths 4 and 5 is the result of the synergistic effect of increased impingement factor and increased holding time.

Table 4 lists the hardness measurements made. Hardness depends on the number and properties of the embedded particles.[8] Because ceria particles are relatively soft, composite coatings from Baths 2 and 3 show hardness lower than that of plain chromium, as was observed for chromium-graphite codeposition.[8]

Table 5 shows the results of wear study. A reasonable assumption is that the load acts at the center point of the radius of the sample. Sliding distance is the distance traveled by a point at the center of the radius during the test (one hr at 1000 rpm).

Specific wear rate is defined as the ratio of wear loss to the product of applied load and sliding distance. With increased ceria content, the wear loss and specific wear rate are reduced. A high level of incorporation of uniformly distributed ceria particles causes lower wear loss.

The use of ceramic particles in the coatings tends to cause serious abrasive wear of the opposing sliding surface and may even transfer the wear problem to the counterface.[10] Knowing the density, D, of chromium (7200 kg/m^3), weight loss W during the wear test, hardness of the coating, H, sliding distance, S, and the applied load, L, it is possible to calculate the Archard coefficient, A, as:

$$A = WH/DSL$$

For abrasive wear, the Archard coefficient should lie between 10^{-4} and 1. Table 6 gives the Archard coefficient values for the coatings tested at 1,000 rpm for one hr against the titanium nitride counterface. It can be seen that these values lie in the acceptable range; accordingly, the wear is the abrasive type. It could be deduced from Table 5 that coatings containing large amounts of ceria show good wear resistance compared to coatings containing small amounts.

Findings

To promote the codeposition of ceria along with chromium, TEPA was added. This enhanced incorporation of second-phase ceria, resulting in increased hardness and wear resistance.

Editor's Note: *Manuscript received July 1999.*

References

1. V.K. William Grips & Indira Rajagopal, *Seminar on Advances in Plating and Coating Technology*, 67, HAL, Bangalore, India (1989).
2. J.P Young, *Plat. and Surf. Fin.*, **62**, 348 (April 1975).
3. O. Berkh, S. Eskin & J. Zahavi, *Plat. and Surf. Fin.*, **81**, 62 (March 1994).
4. Xin-Guo Hu, *Proc. 2nd Asian Metal Fin. Forum,* 125, Tokyo (1985).
5. Sunke-Ning, Xin-Guo Hu, Zi-Hai Zhang & Ji-Ren Wang, *Proc. Asia Pacific Interfinish*, 6.1, Singapore (1990).
6. G.R. Kamat, *Plat. and Surf. Fin.*, **66**, 56 (June 1979).
7. Raj Narayanan & Surjit Singh, *Metal Fin.*, **81**, 45 (March 1983).
8. D. Yang & C. Jiang, *Plat. and Surf. Fin.*, **85**, 111 (Jan. 1998).
9. T.W. Tomaszewski, L.C. Tomaszewski & H. Brown, *Plating*, **56**, 1234 (Nov. 1969).
10. D.T. Gawne & U. Ma, *Surf. Engineering*, **4**(3), 239 (1988).

About the Authors

R. Narayanan is a doctoral candidate in the Department of Metallurgical Engineering of the Indian Institute of Technology (ITT), Madras, India. He holds an M.Tech from IIT. His areas of research include electrodeposition, biomaterials and nanocrystalline materials.

Dr. S.K. Seshadri is an associate professor in the Department of Metallurgical Engineering, Indian Institute of Technology, Madras, 600 036, India. He received a BE from the University of Poona and ME from the Indian Institute of Science, Bangalore. He obtained his PhD from the Imperial College of Science and Technology, University of London. His research interests include surface technology, chemical metallurgy and utilization of renewable agricultural resources.*

** To whom correspondence should be addressed.*