Properties of Ni-WC Electrocomposites

By M. Pushpavanam, S.R. Natarajan & K. Balakrishnan

A significant increase in hardness and wear resistance was observed by incorporation of WC particles in nickel deposits. These properties were not drastically altered, even after annealing up to 800 °C, unlike nickel deposits. This has been attributed to Ni-W solid solution formation. Also, the oxidation resistance of the composite was found to be better than that of pure nickel deposits.

The wear and tear of industrial plants and equipment has long been accepted as a fact of industrial practice, but it is the cause of large expenditure necessitated by replacement or reclamation of worn-out parts.

Developments in the methods of reducing wear include improved design, lubrication and highly wear-resistant coatings. Electrodeposition is one of the best methods adopted for producing a large number of wear-resistant coatings for varied applications. It is well known that dispersion-strengthened electro-deposits can be produced by incorporating inert particles of an oxide, carbide, nitride or boride in suitable metal matrices.[1-4] Although electrodeposited composites containing WC particles are frequently mentioned in the literature, details about them are seldom available.[5] This paper deals with evaluation of the physico-mechanical properties of WC dispersion-strengthened nickel deposits produced from a Watts nickel electrolyte.

Experimental Procedure

The composites were produced using a conventional Watts-type nickel electrolyte containing 0.1 g/L sodium lauryl sulfate, tungsten carbide powder (99.9 percent) having particle size in the range of 5-6 μm. Preparation of the suspension was similar to methods described earlier.[6] The particles were kept in suspension by mechanically stirring the electrolyte at a rate of 350 rpm; solution temperature was controlled thermostatically at 55 °C. Deposits prepared on etched 316 stainless steel substrates of 6.25 cm^2 area were analyzed gravimetrically after dissolving the deposit in 30-percent v/v sulfuric acid anodically at 10 A/dm^2, using a nickel cathode.

On the basis of the analytical data, the optimum conditions for co-deposition were standardized. Deposits produced on stainless steel panels were used for testing hardness and wear resistance, with varying amounts of incorporated tungsten carbide. Similar samples were also used for studying oxidation resistance and for structural analysis.[7] Specimens of varying thicknesses prepared on steel substrates were used for assessing porosity.

Microhardness of the deposits was determined by Knoop indentation, with a load of 50 g. The wear resistance of the deposits was tested by Taber abraser, using a CS-10 calibrase wheel at a load of 1 kg for two cycles, the average being taken as the wear index.[7] Oxidation resistance of the cermet coatings was estimated by exposing them to a current of air at 700 and 800 °C in a furnace.[8] Deposits were also heat treated in a current of hydrogen, then tested for wear resistance and hardness.

Porosity of the samples produced on steel substrates was assessed, using the standard Ferroxyl test.[9] It was estimated from the area and the number of pores, then calculating the percent defect per unit area. Structural analysis of the deposits was carried out by means of a scanning electron microscope before and after heat treatment, as well as after testing for their oxidation resistance. The deposits were also examined by XRD with Cu Kα radiation.

Results and Discussion

Figure 1 shows the variation of volume percent of particle incorporation with particle concentration in the electrolyte.

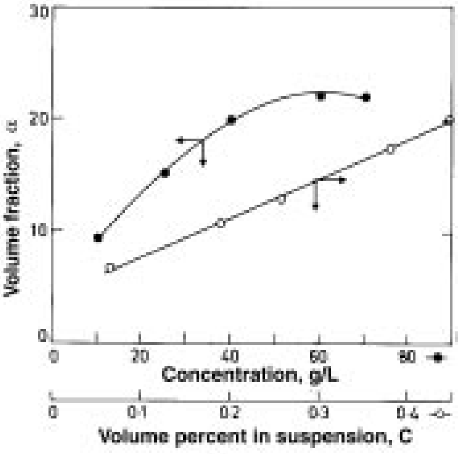

Fig. 1—Variation of volume percent incorporation with concentration of WC in suspension.

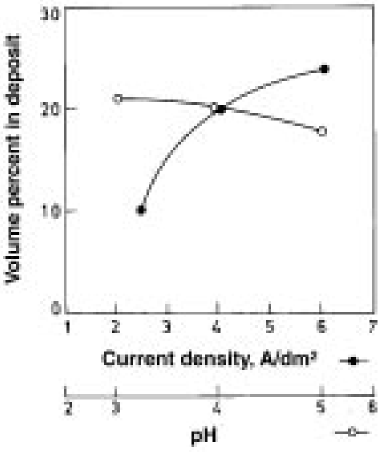

Fig. 2—Effect of parametric variables on volume percent in deposit, with 40 g/L WC in solution; pH 4, 60 °C, 4 A/dm^2.

Table 1
Effect of WC on Deposit Microhardness & Wear Resistance

Volume % WC	Microhardness KHN	Wear Index
0	265	45.5
9.0	430	35.0
15.3	445	30.0
19.9	480	32.0
22.0	490	35.0

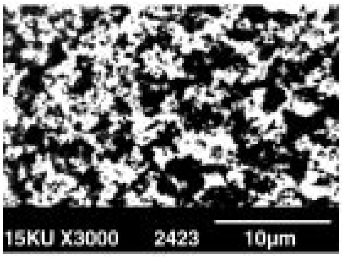

Fig. 3—SEM micrograph of Ni-WC composite before annealing.

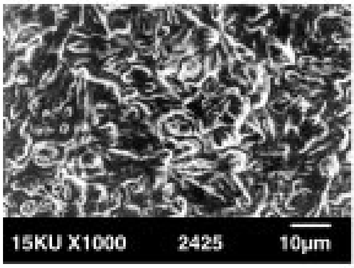

Fig. 4—SEM micrograph of Ni-WC after annealing.

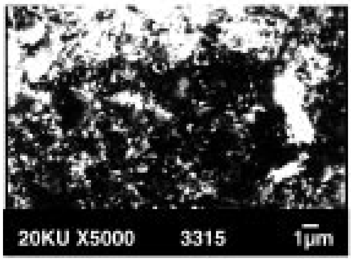

Fig. 5—SEM micrograph of Ni after oxidation.

Table 2
Effect of Heat Treatment on Composite Microhardness & Wear Resistance

Deposit	Temp. °C	Micro-Hardness KHN	Wear Index	% Reduction	
				Micro-Hardness	Wear Index
Ni-WC (15.34%)	600	400	31.0	10.10	3.30
Ni-WC	800	390	32.0	12.30	6.60
Ni	600	175	51.4	33.96	12.96
Ni	800	100	65.1	62.20	43.10

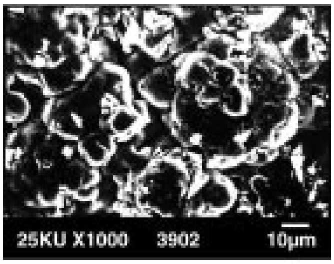

Fig. 6—SEM micrograph of Ni-WC (15.34%) after oxidation, 700 °C.

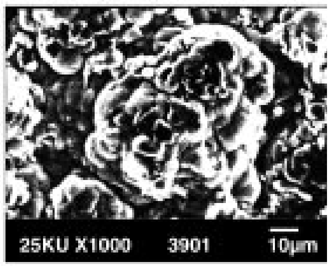

Fig. 7—SEM micrograph of Ni-WC (15.34%) after oxidation, 800 °C.

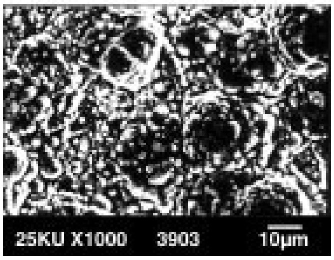

Fig. 8—SEM micrograph of Ni-WC (19.9%) after oxidation, 800 °C.

The curve shows a non-linear dependence at higher concentrations. When C/alpha values are plotted, however, C being the volume percent of particles in suspension and alpha their volume fraction, a straight line is obtained, indicating that the process is governed by a two-step adsorption.[7-9]

The variation in the percentage incorporation of the particles with pH and current density are depicted in Fig. 2. The deposits became rough at high pH levels (>4.5) and high current densities (>50 A/m^2) and with high loadings (>50 g/L) in solution, making estimates and handling very difficult.

Table 1 compares the microhardness and the wear index of nickel and Ni-WC composites. There is a significant increase in both the values by incorporation of the abrasive, up to 15.3 percent. Above this limit, the measurements were highly inconsistent because of very great roughness of the deposits. Particles of still smaller size might solve this problem and permit use of higher bath loadings.

The microhardness and wear resistance of the composites are not significantly altered on annealing up to 800 °C, unlike pure nickel deposits. In composites, recrystallization of the deposit upon heat treatment is prevalent if the particles do not undergo any marked decomposition. A structural analysis (Figs. 3 & 4) shows, however, that there is a distinct change after annealing.

As indicated in the literature, WC particles might have undergone decomposition at higher temperature, especially in the presence of hydrogen.[10] The remarkable retention of microhardness and wear resistance of the composite coat-

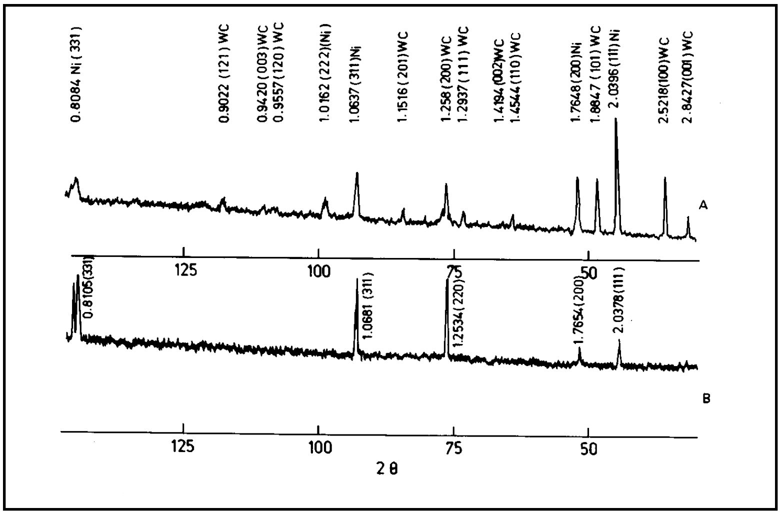

Fig. 9—X-ray diffraction pattern of Ni-WC (15.3%): (A) before and (B) after heat treatment at 800 °C.

ings can therefore be attributed to the formation of Ni-W solid solution, as indicated by Hansen.[11] This solid solution formation retains the microhardness of the electrodeposited Ni-W alloy upon heat treatment.[12]

With regard to high-temperature oxidation, the studies indicate poor oxidation resistance of the composite, compared to Ni-TiO_2 and Ni-Al_2O_3 composites, although better than pure nickel. This can be attributed to the oxidation of WC to WO_3 and the result of rupture of the oxide film by the CO_2 generated.[13] The results are confirmed by SEM micrographs, as shown in Figs. 5-8.

The composites exhibit considerably less porosity over the entire range of thickness studied (4.0-12.5 µm).[9] This may be a result of more even distribution of tiny pores on a composite coating, unlike the localized, isolated and larger pores in nickel deposits that cause substrate-oriented deep pits.

Figure 9 shows the XRD patterns of Ni-WC composites before and after annealing at 800 °C. From Fig. 9a, it can be inferred that Ni and WC exist as individual phases, confirming that the coating is only a mechanical mixture of cubic structure and alpha-WC of hexagonal close packed structure. On heating at 800 °C, noticeable changes occur in the XRD pattern (Fig. 9b). The peak heights of the (111) and (200) planes of nickel are reduced and those of (220), (311) and (331) planes increase. The (222) nickel plane is absent. Many of the peaks corresponding to WC are absent, but the lattice parameters show a considerable increase (Tables 3 & 4). It has been reported that the diffraction pattern of Ni-W is that of a solid solution.[14,15] Because no tungsten peak is present and only nickel peaks are shifted in the direction expected for a solid solution of tungsten in nickel, it is probable that on heating, the deposit forms alpha phase NI-W alloy with cubic structure.

Table 3
Results of X-Ray Diffraction Studies on Ni-WC Composite

2θ degrees	d nm	Peak Identified	% Relative Intensity	hkl
35.576	2.520	WC	110	100
44.385	2.034	Ni	100	111
48.254	1.884	WC	100	101
51.765	1.764	Ni	41	200
63.970	1.454	WC	49	110
65.744	1.419	WC	42	002
73.095	1.293	WC	32	111
76.281	1.247	Ni	40	220
83.970	1.151	WC	3	201
92.815	1.060	Ni	42	311
98.594	1.016	Ni	28	222
109.74	0.942	WC	63	003
117.28	0.902	WC	68	121
144.459	0.809	Ni	34	331

Table 4
Results of X-Ray Diffraction Studies on Ni-WC Composite

After Heat Treatment

2θ deg	d nm	Peak Height cps	a°, Ni_4W nm	a°, Ni Before Annealing nm
44.460	2.0378	294	3.5295	3.552
51.782	1.7654	245	3.5308	3.528
75.915	1.2534	489	3.5451	3.5281
92.400	1.0681	573	3.5425	3.5156
144.000	0.8105	741	3.5328	3.5263

Conclusion

The excellent retention of microhardness and wear resistance exhibited by Ni-WC composites on heating at around 800 °C can be attributed to Ni-W alloy formation.

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References

1. J.R. Roos, J.P. Celis, J. Fransaer and C. Buelens, *J. Metals,* **42**, 60 (1990).
2. H. Matsuda, V. Kiyano, M. Nishira and O. Takano, *Trans. Inst. Met. Fin.,* **72**(5), 55 (1994).
3. E.P. Rajiv and S.K. Seshadri, *Plat. & Surf. Fin.,* **80**, 66 (Oct. 1993).
4. C.S. Ramesh, S.K. Seshadri and J.L. Iyer, *Surf. Eng.,* **7**, 216 (1991).
5. R.N. Bunshah, *Handbook of Deposition Technologies for Films and Coatings,* 2nd Ed., Noyes Publications, NJ, 1994; p. 633.
6. Malathy Pushpavanam and B.A. Shenoy, *Metal Fin.,* **75**(1), 37, (1977).
7. Malathy Pushpavanam, K. Balakrishnan, S.R. Natarajan and L.R. Sharama, *Proc. Int'l Symp. on Industrial Metal Finishing,* Karaikudi, India (1989).
8. Malathy Pushpavanam, K. Balakrishnan, S.R. Natarajan and L.R. Sharma, *Bull. Electrochem.,* **5**, 161 (1989).
9. Malathy Pushpavanam, K. Balakrishnan and L.R. Sharma, *Proc. 10th Int'l Cong. on Metallic Corrosion,* Vol. II, 1343 (1987).
10. E.K. Storms, *The Refractory Carbides,* Academic Press, New York, NY, 1967; p. 147.
11. M. Hanson, *Constitution of Binary Alloys,* McGraw-Hill Book Co., London, 1958; p. 1058.
12. A. Brenner, *Electrodeposition of Alloys,* Principles and Practice, Vol. II, Academic Press, New York, NY, 1963; p. 390.
13. T. Ya. Nosolapova, *Carbides—Properties and Applications,* Plenum Press, New York, NY, 1970; p. 242.
14. J.S. Sallo and R.D. Fisher, *J. Electrochem. Soc.,* **107**, 277 (1960).
15. K.I. Vasu and T.L. Ramachar, *Met. Finish. J.,* **13**(1), 5 (1967).

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