Co-W Alloys for Replacement Of Conventional Hard Chromium

By S. Eskin, O. Berkh, G. Rogalsky & J. Zahavi

The influence of deposition conditions on bath stability and some coating properties was investigated. Using the Rochelle salt-ammonium chloride bath electroplating, with the soluble tungsten anode, was possible only at elevated temperatures of about 90 °C and resulted in current efficiency at 92 to 96 percent. With an inert platinum anode, deposition temperature could be reduced to 50 °C, but with significant decrease in current efficiency and much faster deterioration of the bath. Deposits obtained from the bath with the tungsten anode were fine-grained, with crystallite size 90 to 150 Å, while plating at 50 °C with an inert platinum anode yielded nanocrystalline coatings. Thermal treatment of deposits at 400 to 500 °C in air led to the formation of a Co_3O_4 surface layer, 3-5 µm thick. The oxide coating was distinguished by good protective characteristics, capable of enhancing corrosion resistance substantially. Properties of alloy deposits are compared with those of conventional hexavalent chromium.

Replacement of hard chromium coatings can now be considered as a problem of foremost significance. The reasons for the search for alternative processes are explained by recent fundamental investigations, according to which chromates have been recognized over the past 10 years as both highly toxic and carcinogenic chemicals.[1] The level of emissions of 0.015-0.03 mg/dm^3 for hard Cr shops is regulated by the Environmental Protection Agency.[2] Accordingly, the use of hexavalent chromates will require special waste disposal and the introduction of expensive breathing apparatus and exhaust systems. Consequently, investigation and development of alternative technologies may prove more promising.

The goal of the current investigation was deposition of coatings that could replace conventional Cr at high temperatures. Accordingly, refractory metal-based coatings, and particularly electroplating of Co-W alloys[3,4] were of primary concern.

Analysis of basic electrolytes for deposition of Co alloys with refractory metals allowed identification of the Rochelle salt-ammonium chloride bath[5-9] as more compatible with industrial operation for obtaining thick coatings. In the course of our investigation, bath stability was examined. Some significant properties of as-plated and heat-treated CoW deposits were studied in comparison with those of conventionally electroplated chromium deposits.

Experimental Procedure

Electrodeposition of Co-W coatings was carried out using the electrolyte formulation and conditions shown in Table 1.

As the substrate, low-carbon and mild barrel steel were used. The anodes were either soluble (W-rods) or insoluble and inert (Ti grid coated with Pt). The electrolyte was purified by activated carbon and pretreated under the low current density of 0.5 A/dm^2 for several hours. Cathodic potential was measured vs. a calomel reference electrode. Thermal threatment was conducted by oven heating of deposits in air with a slow cooling rate: ~1 °C/min. Electron dispersive spectroscopy (EDS) analysis and Auger electron spectroscopy (AES) were used for determination of chemical composition in deposits, the latter mainly for measurement of light element content. By the AES-aided technique, elemental composition was measured at a depth ≥ 1.2 µm, after Ar sputtering of the surface layer.

Morphology was examined under optical and scanning electron microscopes. Structural examination was carried out by X-ray analysis, using an automatic diffractometer, and a goniometer with a long-focus Cu K_α tube. Microhardness was measured on the deposit cross section by a Vickers microhardness tester under 100-g load. The wear resistance was examined by dry wheel abrasive test at a rotational speed of the (CS-17) wheel of 50 rpm and load of 850 g. The linear wear rate was calculated as the ratio of weight loss to sliding distance. The complete test covered a total sliding distance of 40 m (2000 cycles) and was interrupted every 4 m for specimen weighing. Adhesion of deposits was evaluated by standard bend testing.[10]

For study of the corrosion behavior, a salt spray test[11] was used for 60 hr, with the temperature of the exposed zone at 35 °C. Also, potentiodynamic polarization tests were carried out with 0.5 M NaCl solution at pH 7.0 ±0.1. Tests were run at room temperature from the initial potential, -0.9 V vs. the standard calomel reference electrode, at a rate 0.2 mV/sec. Additionally, examination of coatings from the above solution was made by the method of electrochemical impedance spectroscopy (EIS). The measurements covered a frequency range between 100 and 0.01 Hz. The impedance data were displayed as Nyquist, Bode and Randles plots for determination of basic coating characteristics.

Results

Bath Stability

Current efficiency, cathode potential, composition and structure of CoW deposits, as well as absorbance spectra of the electrolyte were studied as a function of electric charge

Table 1
Bath Composition & Deposition Conditions for Co-W Alloys

Bath Composition		Conditions	
Component	**Concentration**	**g/LParameter**	**Value**
$CoSO_4\_7H_2O$	100	Temperature	50 or 90°C
$Na_2WO_4\_2H_2O$	40	pH	9.0
Rochelle salt	360	Current density	5 A/dm^2
NH_4Cl	50	Agitation	No

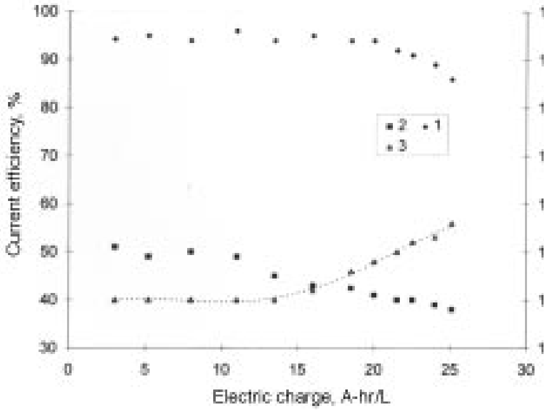

Fig. 1—Current efficiency (1,2) and cathode potential(3) as a function of bath operation time. Deposition with the W-anode at 90 °C (1,3) and Pt-anode at 50 °C (2).

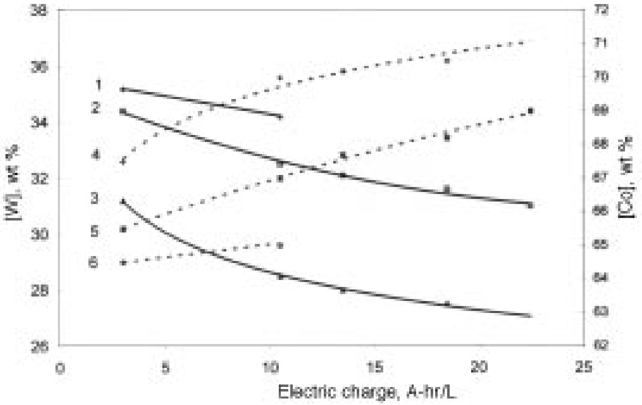

Fig. 2—Concentration of W (1,2,3) and Co (4,5,6) in the deposit vs. the electric charge passed through the bath with the W-anode at 90 °C (2,5) and the Pt-anode (1,3,4,6) at 90 °C (1,6) and 50°C (3,4).

consumption. The [Co]/[W] ratio in the electrolyte was maintained during these trials at 0.9.

Long-term operation of the bath was accompanied by the following phenomena: decrease of current efficiency and increase of cathodic potential (Fig. 1), increase of Co content in deposits (Fig. 2), accumulation of O and C in deposits (Fig. 3), and changes in their structure (Figs. 4 and 5). These tendencies were revealed in operation with soluble W and inert Pt anodes at 90 °C, as well as with Pt anodes at 50 °C. Degradation of the bath and deposits was accelerated in the case of inert anodes, however, especially at low temperature.

Long-term operation at 90 °C, with soluble W anodes, led to refining the structure (Fig. 4a, b), but deposits still appeared dull and matte. They were shown by X-ray analysis to remain a solid solution on the basis of α-Co with a c.p. hexagonal structure (Fig. 6a). Routine analysis of the (1011) peak (single-line analysis), as well as of both reflections $(10\bar{1}1)$ and $(20\bar{2}1)$ simultaneously, showed that line broadening can be attributed mainly to the small crystallite size: 90-150 Å. Texture coefficients calculated for the peaks available in the spectrum are plotted in Fig. 7 as a function of the electric charge. The texture coefficient for the $(10\bar{1}1)$ reflection slightly increased within the range of 2.2 to 2.8 with the time of bath operation.

In the long-term deposition with the inert Pt anode at 90 °C, deposits became degraded in appearance and surface morphology differed greatly (Fig. 5a) despite close values of current efficiency, deposition potential and Co content in deposits. Operation of the bath with a tungsten anode at temperatures lower than 90 °C was impossible because of anode passivation. Mechanical and ultrasound solution agitation proved insufficient to change the character of anode passivation. Only the use of an insoluble anode allowed the temperature to be reduced significantly, but current efficiency decreased as well. It was about 50 percent at 50 °C and the electrolyte performed stably not more than 10-13 A-hr/L with further monotonic degradation (Fig. 1). More intensive hydrogen evolution produced a slight drop in pH to about 8.8-8.9 after one hr bath operation, while pH dropped to 8.6-8.7 and to 8.35-8.45 after one hr plating at 90 °C with the soluble and inert anodes, respectively.

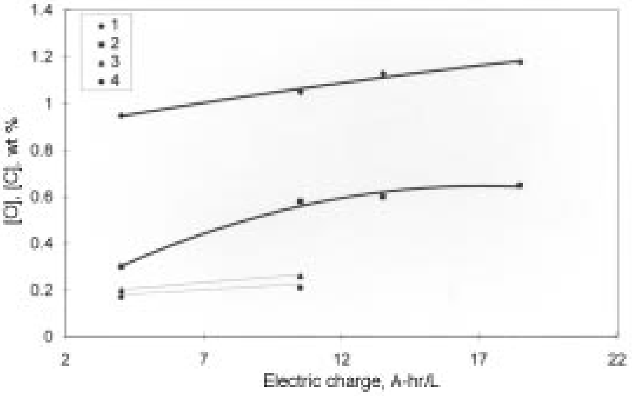

Fig. 3—Concentration of O (1,3) and C (2,4) in the deposit vs. the electric charge. Deposition with the Pt-anode at 50 °C (1,2) and 90 °C (3,4).

Long operation with the inert Pt anode at 50 °C was accompanied by strong change in coating appearance. A dull gray coating was converted to semi-bright or bright with fine-grained structure as revealed by microscope. Morphology examination (Fig. 5b) indicated formation of a network of

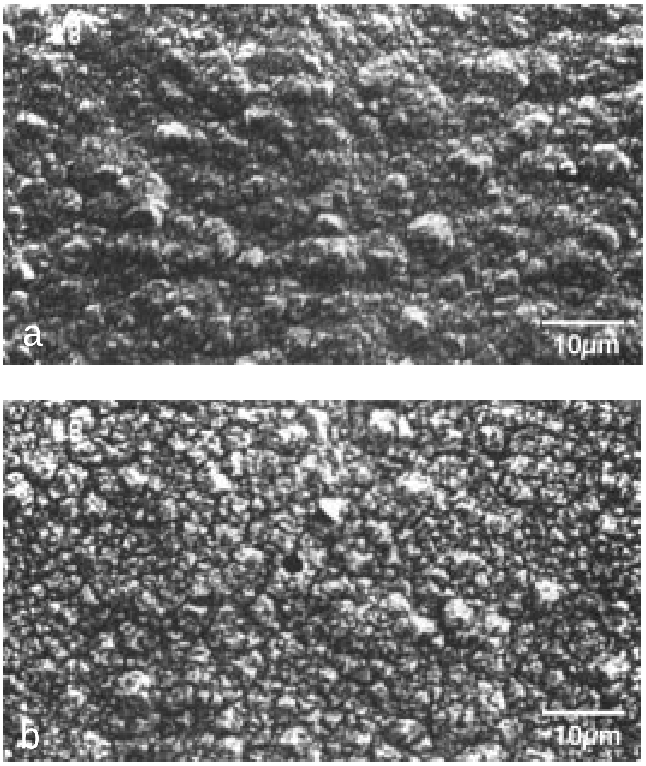

Fig. 4—Morphology of the Co-W alloy deposited at 90 °C from the bath with the W-anode after 4 (a) and 22 A-hr/L (b).

cracks unlike deposits obtained at 90 °C. This was probably caused by enhanced hydrogen content and stresses in deposits owing to low current efficiency and intensive hydrogen evolution during the process.

Table 2
Wear Resistance of Cr- & Co-W Deposits
Obtained Under Various Conditions

Deposit	Conditions of deposition		Conditions of thermal treatment		Wear rate, mg/m
	Anode	Temp, °C	Temp, °C	Time, hr	
Co-W	W	90	untreated		0.14
	Pt	50	untreated		0.13
	W	90	500	1	0.14
	Pt	90	500	1	0.135
	Pt	90	400	1	0.12
	W	90	200	3	0.1
	Pt	50	200	3	0.1
	Pt	90	150	4	0.11
Cr	Pb	55	untreated		0.06

X-ray spectra of coatings deposited at 50 °C exhibited only one wide peak of the (0002) line (Fig. 6b). The peak position and shape did not change with the time of bath operation. According to the analysis, data line broadening was ascribed only to very small crystallite sizes of 10-20 Å.

The content of oxygen and carbon in the coatings steadily increased with the time of bath operation as deposition occurred with the inert anode at both 50 and 90 °C (Fig. 3). Much higher content of these contaminants was obtained, however, at 50 °C. Electroplating with the tungsten anode yielded, by contrast, a practically unidentifiable content of oxygen and carbon in the deposits.

Adhesion, Hardness & Wear Resistance

Coatings adhered to the steel substrate up to 400 °C, irrespective of the anode and plating temperature. Heating at 500 °C led to the appearance of cracks; above 600 °C, deposits peeled from the substrate, while a Cr deposit was retained. According to EDS data, a black layer formed on the deposit surface at 400-500 °C was the cobalt oxide, Co_3O_4. Layer thickness amounted to about 2-3 and 4-5 µm after one hr of treatment at 400 and 500 °C, respectively.

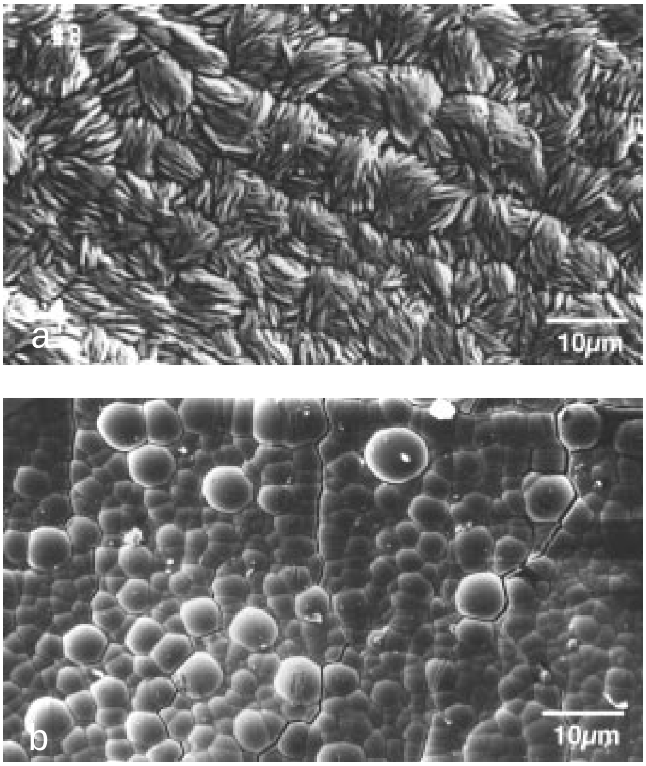

Fig. 5—Morphology of the Co-W alloy deposited at 90 °C (a) and 50 °C (b) from bath with the Pt anode after 4 A-hr/L.

The effect of thermal treatment on the hardness of Co-W alloys is shown in Fig. 8. The hardness of specimens without annealing was in the range, HV 420-470 and, at 500 °C, it reached about HV 650, but was still 1.4 to 1.5 times lower than that of conventional Cr. Increase in the hardness after thermal treatment resulted from the well-known phenomenon of precipitation hardening of Co-W alloys and formation of the Co_3W phase.[12,13] Wear resistance of deposits is given in Table 2.

Although the hardness of coatings after heating at 400-500 °C was well beyond the range of the untreated alloys, the wear rate was practically the same. This is attributed to a rather soft oxide layer on the surface, inasmuch as its removal after the first 400-700 cycles yielded a subsequent rise in the wear resistance. That is why the lowest wear rate was obtained after heating at 150-200 °C. According to the X-ray evidence, treatment at these temperatures yielded formation of the Co_3W phase which, although it only slightly affected the hardness, enhanced the resistance to wear. Compared to Cr coatings, the wear rate obtained for Co-W deposits was about 1.7 times higher.

Corrosion Resistance

Results of corrosion tests by methods of potentiodynamic polarization and EIS are shown in Table 3. Nyquist, Bode and Randles plots and equivalent circuits for the metal coated with a protective dielectric layer[14-16] were used for the calculation of R_p, R_t and C_c values listed in Table 3, where it can be seen that more positive values of E_o, lower I_{corr} and m correspond to specimens oxidized at 500 °C. The values of m for them were about 2 and 1.6 times lower than those for Cr and for the as-deposited coatings, respectively.

R_t and R_p values markedly increased as a result of heat treatment at 500 °C, while C_c dropped. These data, as well as the results of potentiodynamic tests, indicate protective properties of the oxide layer formed at 500 °C on the surface of CoW deposits.

Results of salt spray testing were in good agreement with those of the electrochemical corrosion tests. Untreated de-

Table 3
Electrochemical Corrosion Tests

Deposition conditions		Annealing conditions		Data of corrosion tests					
				EIS			Potentiodynamic		
Anode	**Temp, °C**	**Temp, °C**	**Time, hr**	**R_t, kOhm**	**R_p, kΩ**	**C_c, μF**	**E_o, mV**	**$I_{corr} \cdot 10^6$, A/cm^2**	**m, mpy**
Pt	55	untreated		1.6			-650	3.2	1.0
W	90	untreated		0.6			-620	25	8.1
Pt	90	320	2	1.4	3.6	500			
W	90	320	2				-645	7.8	2.5
W	90	500	1	9	9	75	-480	1.6	0.52
Pt	90	500	1	10	8	100	-505	1.4	0.46

R_p—the pore resistance of the dielectric coating (in this study, oxide coating)
R_t—the charge-transfer resistance at the electorde/solution interface
C_c—coating capacitance
m—corrosion rate
I_{corr}—corrosion current
E_o—open-circuit potential

posits, or those heated at 150 or 200 °C, were almost completely corroded after 60 hr testing. For such specimens, only some small regions observable under the microscope appeared unaffected by the corrosion attack. The surface of deposits after treatment at 320 °C was greatly pitted, but for alloys annealed at 400-500 °C, and for conventional Cr, only some small pits were seen.

Discussion

Degradation of CoW deposits in long-term operation with inert anodes seems to be associated with accumulation of nonmetallics (O and C) in the deposits because of anodic conversion of Rochelle salt. Obviously, this part of the process is increased when the anode is insoluble. Peeling of the Co-W coating after annealing at temperatures greater than 500 °C can be associated with the stress appearing to result from distinction between the thermal expansion coefficients of the substrate and the deposit, and its poor adhesion to the substrate. The thermal stress for a Cr deposit on the steel substrate was evaluated, using reference data,[17,18] as much higher than that of the Co-W coating. Accordingly, retention of the Cr deposit points to incomparably better adhesive properties. To provide better adhesion of the alloy coating with the steel substrate, electroplating the underlayer, such as Cu or Ni, may prove useful.

The surface oxide coating is capable of withstanding corrosion attack, but unfortunately is insufficiently resistant to wear. Thermal treatment in vacuum or inert atmosphere at 400-500 °C to obtain rather high hardness and at the same time prevent surface oxidation could substantially enhance the wear resistance. Of course, it would be acceptable for alloy deposits not intended for operation in strongly corrosive media.

The service temperature of the Co-W alloy was found to be < 500 °C to avoid peeling the deposit from the steel substrate. Such a coating can hardly replace conventional Cr on parts

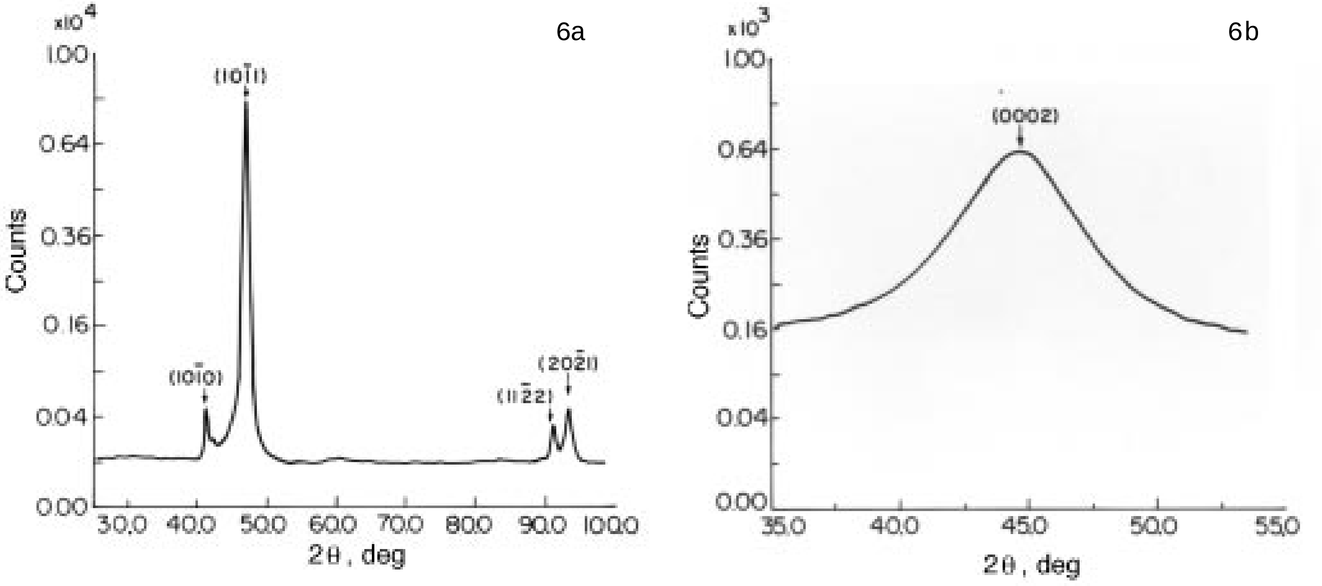

Fig. 6—X-ray spectrum of the Co-W coating deposited with the W-anode (a) and Pt-anode (b) at 90 °C and 50 °C, respectively.

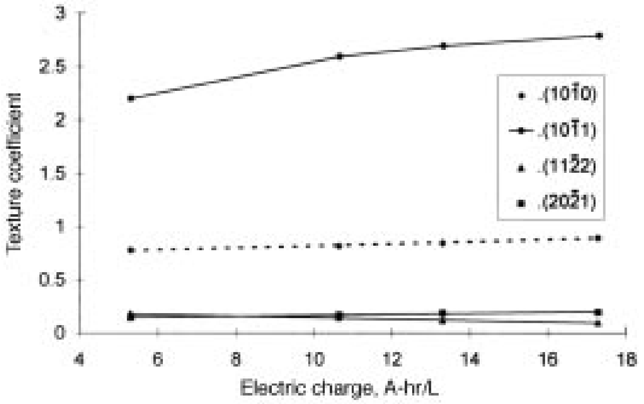

Fig. 7—Texture coefficients vs. electric charge through the bath. Deposition with the W-anode.

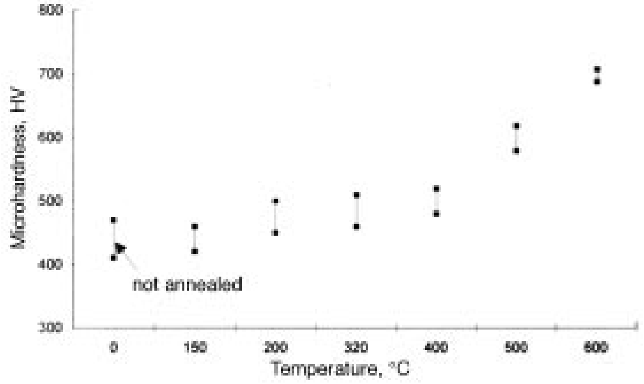

Fig. 8—Effect of annealing temperature on microhardness.

operating at high temperatures, but would be suitable for reliable protection against corrosion attack at moderate heating. It is noticeable also that deposition conditions of alloys are of little significance for wear and corrosion resistance, while heating conditions seem to be the decisive factor.

Conclusions

Some features in deposition of the Co-W alloy coatings with ≅30 percent tungsten from the Rochelle salt-ammonium chloride bath were examined, as well as a number of deposit properties. The advantage of the bath with the soluble W-anode and deposition temperature of 90 °C was shown to be in prolonged bath stability, up to 22-25 A-hr/L, high current efficiency of 92 to 96 percent and less stressed deposits, compared to electroplating at 50 °C with the Pt-anode.

The deposits produced with a tungsten anode at 90 °C were textured and fine-grained, with crystallite size of about 90-150 Å. At 50 °C and using the Pt-anode, a nanocrystalline alloy coating was deposited with crystallite size of 10-20 Å, estimated from line broadening of X-ray spectra.

Microhardness increased from about HV 450 to HV 650 for untreated deposits and those heated at 500 °C, respectively. The higher temperature might yield further enhancement in hardness, but caused peeling of the deposit from the steel substrate. Deposits heated at 400-500 °C in air were coated with the Co_3O_4 oxide layer, which successfully withstood corrosion attack in 0.5 M NaCl solution at pH 7.0. Corrosion resistance of alloys was found comparable or even better than that of conventional Cr, but the maximum wear resistance was about 1.7 times lower.

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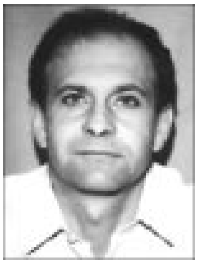

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