

INTERNAL STRESS IN ELECTRODEPOSITED CHROMIUM

V MUTHUMEENAL, MALATHY PUSHPAVANAM, RM KRISHNAN AND S R NATARAJAN

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

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Chromium electrodeposited from the conventional bath exhibits high internal stress depending upon factors such as current density, nature of underlying metal, etc. This paper deals with the effects of various underlying metals on the internal stress and microstructure of conventional chromium.

Key words: Internal stress, microcracking, electrodeposition of chromium

INTRODUCTION

Electrodeposited chromium is known to exhibit high tensile stress due to an increase in deposit volume usually attributed to transformation of the unstable hexagonal chromium interstitial phase to the cubic modification [1].

Considerable interest has been shown in recent years in the use of microcracked chromium as a means of increasing the corrosion resistance of composite nickel-chromium coatings. It has been observed that a variety of crack patterns are produced when chromium is deposited from a standard plating solution on to different substrates or undercoats [2]. Directionally oriented microcracks are reported [2] to occur at right angles to the polishing direction when conventional chromium is deposited on polished dull nickel. The crack pattern of chromium on bright nickel undercoat deposited on an abraded steel substrate is similar to that on mild steel. Directional cracking does not occur when abraded wrought nickel is annealed before chromium deposition.

In the course of development of a suitable protective coating on maraging steel for aeronautical applications, a similar influence of the substrate metal, undercoats, pretreatment procedure etc. on the internal stress crack pattern of subsequently plated chromium layers was observed and the results are reported in this paper.

EXPERIMENTAL

A set-up based on Hoar and Arrowsmith design [3] was used to determine the internal stress of chromium deposits. Due to the nonavailability of thin maraging steel specimens, experiments were carried out on spring steel strips. Specimens were heat treated at 473K for two hours before carrying out the experiments, since direct plating was not possible without the treatment. The composition of the chromium plating solution was the conventional one with 250 g.l⁻¹ chromic acid and 2.5 g.l⁻¹ sulphuric acid. Deposition was carried out at three different current densities, maintaining the bath temperature at 325±2K. Plating on different substrates was done for a duration of 40 minutes at 30 A.dm⁻². A fresh chromium electrolyte was used for each condition, to avoid the influence of any trivalent chromium build up. Specimens were heat treated at 473K for two hours before carrying out the experiments, since direct plating was not possible without the treatment. Chromium was deposited either on the spring steel or spring steel having an undercoat of copper, electrodeposited nickel and electroless nickel each of 15 µm thickness.

Copper was deposited from a cyanide bath, nickel from a Watts' bath and electroless nickel from a bright Watts' bath and electroless nickel from a hypophosphite based electroless solution. Chromium plating was carried out directly also on polished mild steel specimens. The bath compositions used

are summarised in Table I. Cathode current efficiencies were determined for chromium deposition on different substrates for comparison.

TABLE-I: Bath compositions and operating conditions used for producing different undercoats

Undercoat	Concentrations of the bath (g.l ⁻¹)	Conditions
<i>Copper</i>		
(1) Rochelle copper	Copper cyanide — 25	Temp. 328K pH 12.5 1.5 A.dm ⁻²
	Sodium cyanide — 35	
	Rochelle salt — 45	
	Sodium carbonate — 30	
(2) Acid copper	Copper sulphate — 200 H ₂ SO ₄ - 50	Temp. 303K 1.5 A.dm ⁻²
<i>Nickel</i>		
(1) Watts solution	Nickel sulphate — 250	Temp. 331K 3 A.dm ⁻² pH 4.0
	Nickel chloride — 30	
	Boric acid — 40	
(2) Sulphamate nickel	Nickel sulphamate — 290	Temp. 328K 2 A.dm ⁻² pH 3.5
	Nickel chloride — 10	
	Boric acid — 30	
(3) Bright nickel	Watts solution	Temp. 331K 3 A.dm ⁻² pH 4.0
	with butyne diol — 0.8	
	Saccharin — 1.0	
(4) Electroless nickel	Nickel sulphate — 40	Temp. 333K pH 7.2
	Sodium hypophosphite — 35	
	Trisodium citrate — 50	

Crack patterns were examined under a metallurgical microscope after anodic etching in a solution of 10% NaOH at 10 A.dm⁻² for one minute [4].

RESULTS AND DISCUSSION

Preliminary experiments on chromium plating on specimens without heat treatment were quite unsuccessful. In spite of depositing for 1 hour at 30-35 A.dm⁻², a thin coating of chromium with an efficiency range 5-6% only could be obtained. This can be attributed to the high tensile strength of the specimens with a low hydrogen overpotential. Heat treatment relieves the high stress and helps to improve the efficiency. Chromium deposited on untreated specimen has no crack pattern (Fig. 1(a)) probably due to the low thickness of the deposit, but undergoes random exfoliation.



Fig. 1(a): Structure of chromium deposited on Untreated spring steel ($\times 500$)

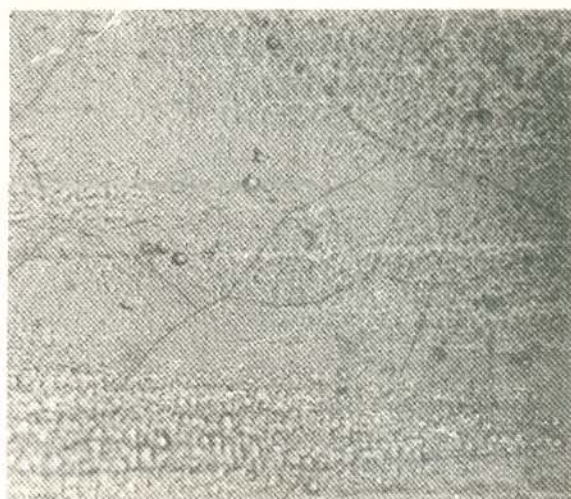


Fig. 1(d): Structure of chromium deposited on Sulphamate nickel ($\times 500$)



Fig. 1(b): Structure of chromium deposited on Heat treated spring steel ($\times 100$)

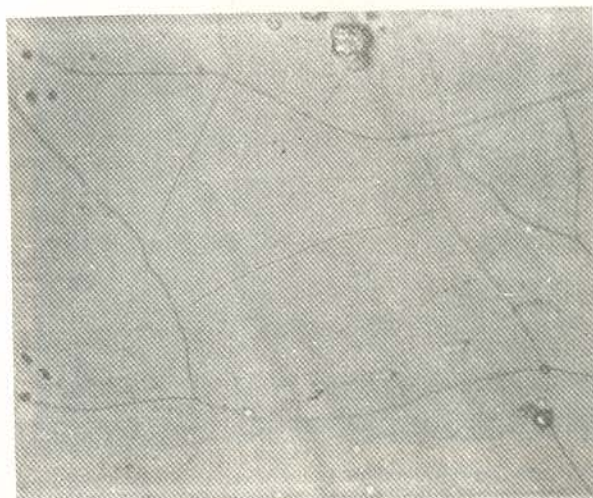


Fig. 1(e): Structure of chromium deposited on Watts nickel ($\times 400$)

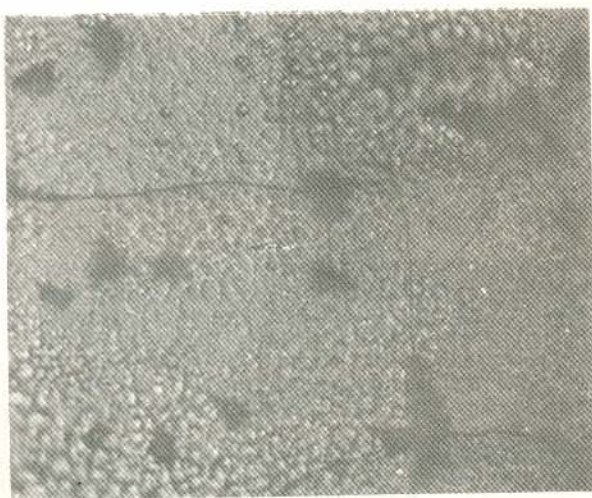


Fig. 1(c): Structure of chromium deposited on Copper ($\times 500$)



Fig. 1(f): Structure of chromium deposited on Bright nickel ($\times 400$)



Fig. 1(g): Structure of chromium deposited on Bright nickel ($\times 1000$)

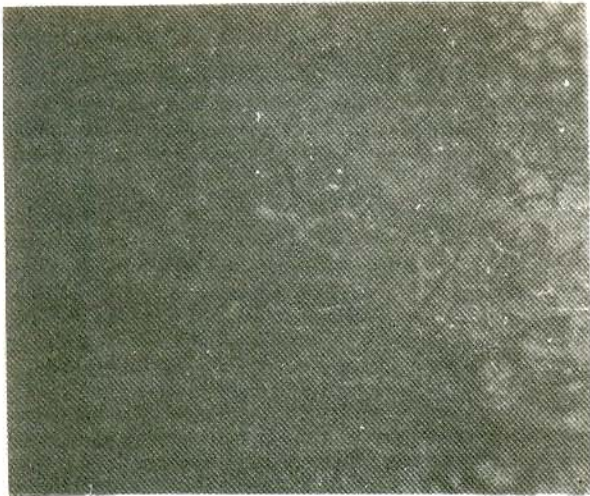


Fig. 1(h): Structure of chromium deposited on Electroless nickel ($\times 500$)

Internal stress versus thickness curves for deposition on heat treated spring steel at different current densities (Fig. 2) show an initial compressive region. Stress shoots up to a tensile value in the thickness range of $0.25 - 1.0 \mu\text{m}$ depending upon the current density of deposition, then decreases and attains a steady value at higher thicknesses. This change-over from compressive to tensile stress has been attributed to the onset of microcracking [5]. Thus deposits produced at 20.0 A.dm^{-2} and 25.0 A.dm^{-2} develop microcracks at fairly low thicknesses (Fig. 1(b)), but the extent of cracking is maximum for deposits produced at 20 A.dm^{-2} as indicated by the steep decrease from the peak to the steady value. Curve at 15 A.dm^{-2} shows negligible decrease indicating that cracking does not occur all of a sudden at this current density. Considering the quality of deposit, current efficiency and cracking nature, the current density of 20 A.dm^{-2} was chosen as the optimum one for further experiments.

When chromium deposition was carried out on polished cold rolled steel and on heat-treated spring steel with copper undercoat, the typical compressive portion was not observed (Fig. 3). The peak maximum was the highest in the case of copper undercoat under the studies made. These observations preclude the possibility that microcracking occurs on these above two substrates, namely, copper and mild steel, at a lower thickness, unlike on spring steel specimens. However, photomicrograph (Fig. 1(c)) confirms that the microcracking is not appreciable on copper plated steel. Therefore the sudden decrease from peak maximum should be due to macrocracking which is also evident from Fig. 1(c).

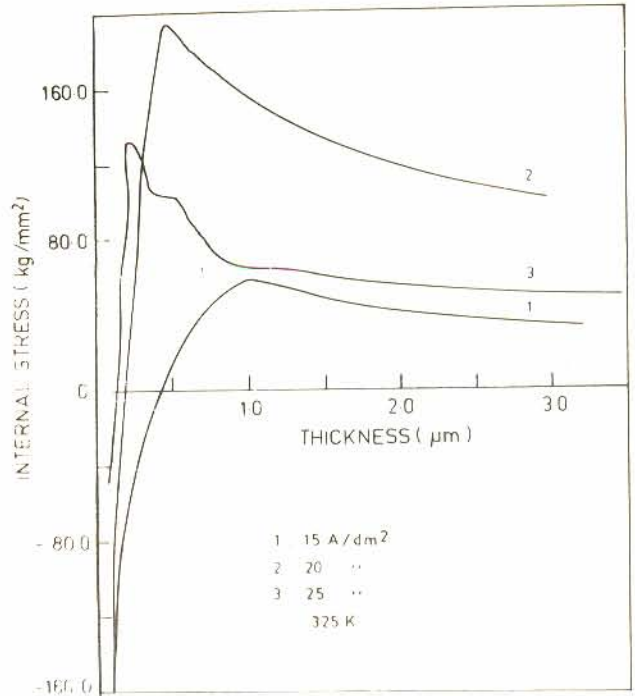


Fig. 2: Effect of current density on the internal stress of chromium deposits on pretreated spring steel

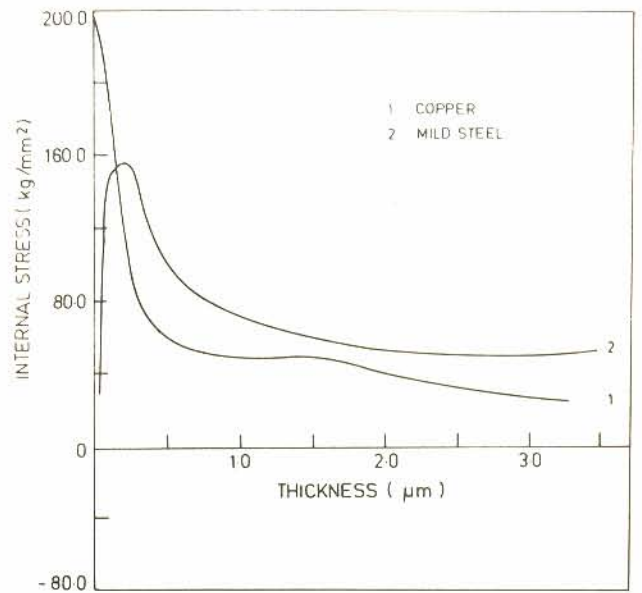


Fig. 3: Internal stress of electrodeposited chromium on (1) copper and (2) mild steel. C.d. 20 A.dm^{-2} , 325 K

The internal stress curves for chromium deposition on dull Watts, sulphamate nickel and bright nickel are shown in Fig. 4. A more rapid change from very low compressive values to tensile ones, as compared to heat-treated spring steel could be observed. The compressive region is most elongated for bright nickel, moderate for dull Watts' nickel and sulphamate nickel and least for heat treated spring steel. It is also understood that extensive cracking does not occur.

The variations in the stress for chromium deposition on different substrates/undercoats in the compressive region are compared in Fig. 5. Dennis [2, 5] reports that hydrogen adsorption results in high compressive stresses in the surface layers of bright nickel, but dull nickel and mild steel are much less sensitive to this effect and

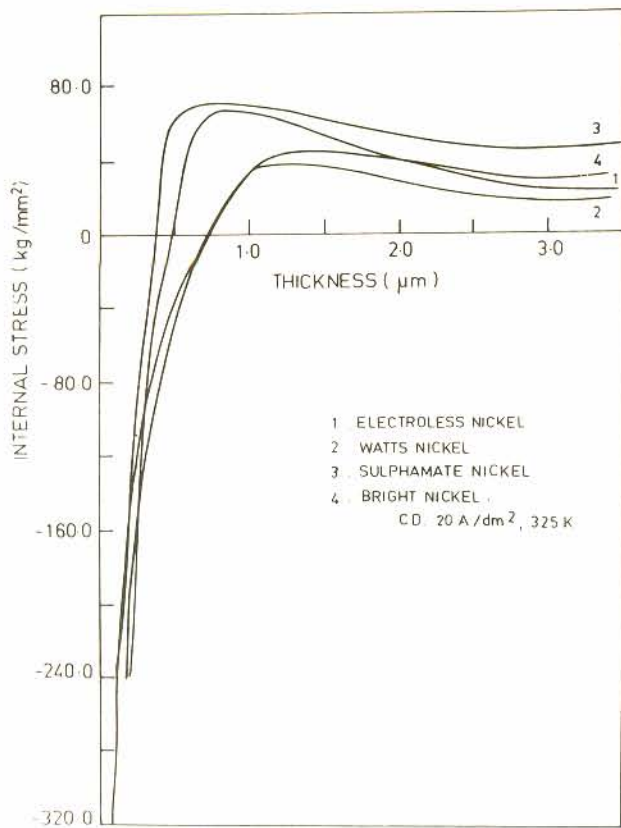


Fig. 4: Effect of undercoats of nickel on internal stress of electrodeposited chromium

cause only slight modification in the stress of chromium coatings. As the thickness of chromium becomes more significant, the rate of diffusion of hydrogen to the undercoat is reduced and results in the change from compressive to tensile type.

The stress curve for chromium deposition on electroless nickel (Fig. 6) shows the most elongated compressive region. The decrease in stress after the peak is not significant indicating that cracking occurs less readily. Table II compares the results of internal stress measurement results for chromium deposition on various substrates under study.

Photomicrographs of chromium deposits on matte nickel, bright nickel and electroless nickel are shown in Fig. 1(d) - 1(h). Deposits obtained in sulphamate nickel (Fig. 1(d)) show less cracking than with a Watts nickel undercoat (Fig. 1(e)). Examination at a higher magnification of chromium deposits obtained on bright nickel reveal that the crack patterns are superimposed (Fig. 1(g)) so that some cracks are more clearly defined than others. This effect referred to as 'Zoning' [5] is not observed with chromium deposits with steel as substrates or those produced on matte nickel or copper. Photomicrograph (Fig. 1(h)) of deposit produced on electroless nickel undercoat shows the globular structure of deposited chromium with very few cracks.

CONCLUSION

The nature and surface texture of the substrate/undercoat have great influence on the crack pattern of electrodeposited chromium.

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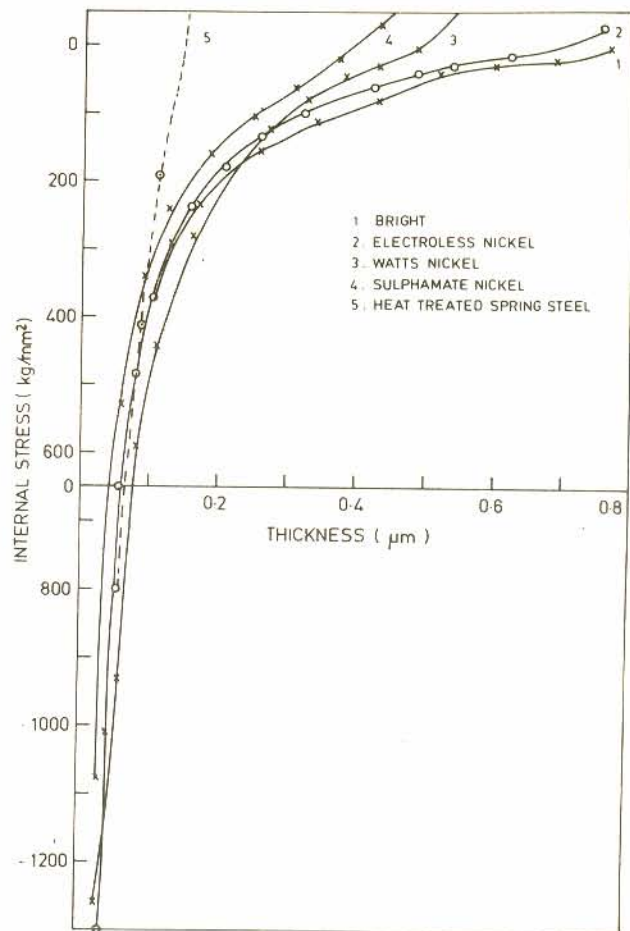


Fig. 5: Effect of undercoats on internal stress of electrodeposited chromium $20 A.dm^{-2}$, 335K

TABLE-II: Effect of substrate material on the bath efficiency and deposits stress in chromium deposition

Substrate	Current efficiency (%)	Maximum stress (σ_m) ($kg.mm^{-2}$)	Thickness for $3\mu m$ (μm)	Residual stress at $3\mu m$ ($kg.mm^{-2}$)
1. Spring steel untreated	6.0	895.0	0.10	—
Spring steel heat treated	10.5	198.0	0.5	108.0
Cold rolled steel	10.5	158.0	0.2	53.0
2. Heat treated spring steel with nickel undercoat				
(a) Watts	9.5	68.0	0.8	22.0
(b) Sulphamate	10.7	70.0	0.75	45.0
(c) Bright nickel	12.9	44.0	1.15	44.0
(d) Electroless nickel	10.3	32.0	1.4	16.0
3. Copper	9.5	300	0.1	50.0

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