

Electrodeposition of tantalum and tantalum–chromium alloys

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As part of a programme to develop erosion resistant coatings for advanced gun barrels, electrodeposition of tantalum and tantalum–chromium alloys from fused Flinak has been investigated. Tantalum–chromium alloys containing 2–6% chromium were obtained by co-depositing tantalum and chromium from an electrolyte containing 10 wt% TaF₅ and 0.5–1.5% Cr (as K₃CrF₆) at 800° C. The alloy coatings are smooth and columnar in structure. The microhardness of these coatings increases with the increase of chromium content. With chromium-rich alloys, an equiaxed alloy structure is observed, with a hardness greater than for pure tantalum or chromium.

1. Introduction

The present investigation is part of a programme to develop erosion resistant coatings for various metal substrates, such as gunsteels, through the electrodeposition of refractory metals from molten salts. In advanced gun barrels the increasingly high flame temperature and the severe firing schedules lead to serious erosion, particularly in the critical area of the origin of the rifling. One approach to protect the bore surface [1] is to use a liner or a coating of a material which has a melting point higher than gunsteel and good high-temperature strength. It should also be resistant to the reactive propellant combustion gases and thermomechanically compatible with the main gunsteel body. If a coating is used, it should also be well bonded to the substrate and the thickness should be optimized for protection of the gunsteel from the effects of heat, the main cause of degradation of its mechanical strength.

The nine transition elements of groups IVA, VA, and VIA of the periodic table, known as the refractory metals, are strong candidates for the present needs. With the exception of chromium, aqueous electrodeposition can be discounted. Currently chromium electroplates (from aqueous

solutions) are being used in large and small calibre guns, but these have serious limitations, i.e., microcracks, brittleness and bonding faults. After a certain number of firing rounds, such plates chip and flake off, adversely affecting the performance of the guns. Of the other possible metal cladding routes, such as chemical and physical vapour deposition, diffusion coating processes (such as metallizing), plasma spray deposition and electrodeposition from fused salts, the last one appears the most promising [2–7] for application in gun liners.

Fig. 1 shows a magnified view of a transverse section of a tantalum-coated rifling achieved by fused-salt electrodeposition. The uniform thickness of the tantalum coating on both the lands and the grooves illustrates the excellent throwing power that is possible using the fused-salt approach. Because exposure of the gunsteel to the plating temperatures (750–900° C) is undesirable, the approach here is to use a short liner insert which can be coated independently of the main gun tube. Such liners have been tested [8] with severe firing schedules in the M24A1 gun; the erosion resistance appeared quite superior but the coating was found to swage by the engraving stresses of the projectiles. The latter is undoub-

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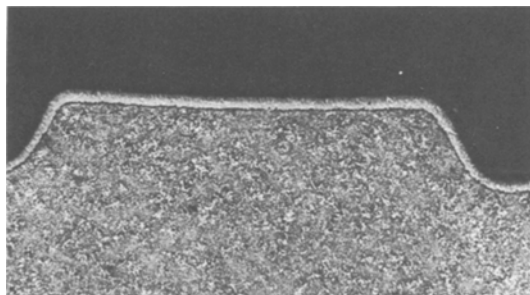


Fig. 1. Transverse section of a rifling land showing uniformity of the tantalum coating thickness achieved from fused-salt electrodeposition.

tedly due to the softness of high-purity tantalum (180–250 KHN). One interest of the present investigation was to explore the modifications of the hardness properties and structures of such coatings through the addition of chromium to such electrolytes. Results are reported for a series of tantalum-rich chromium alloys obtained with increasing amounts of chromium (as K_3CrF_6) added to the Flinak tantalum plating bath.

2. Experimental

2.1. Chemicals and materials

Anhydrous, powdered, reagent-grade LiF, NaF, KF, K_2TaF_7 , KHF, CrF_3 and Cr_2O_3 were vacuum dried at $180^\circ C$ for 100 hours and stored in vacuum desiccators until needed. K_3CrF_6 was synthesized [9] by fusing Cr_2O_3 with KHF_2 (1:6 ratio) in a platinum crucible (contained in a graphite crucible with a graphite cover) and maintaining in the molten state for ten minutes. The mixture was allowed to cool, then extracted three times with 5% aqueous HF. The resultant product was insoluble, and paris-green in colour. It was pulverized, vacuum dried at $180^\circ C$ for 72 hours and then stored in a desiccator. High-purity argon (99.999%) was used as an inert atmosphere throughout this study.

The LiF, NaF and KF were mixed by direct weighing in a molar ratio of 46.5:11.5:42.0 respectively, to obtain the ternary eutectic (m.p. $454^\circ C$). The mixture was ground and vacuum dried at $150^\circ C$ until the residual pressure was $\sim 1.5 \times 10^{-2}$ mmHg. It was premelted in a vitreous carbon crucible under argon and kept at

$600^\circ C$ for 20–30 minutes, cooled to just above the melting temperature and decanted into an etch-cleaned nickel crucible. The melt appearance was from water-clear to light yellowish in colour. After solidification the ternary eutectic and nickel crucible were transferred into the electroplating assembly without further pre-treatment, unless otherwise noted.

2.1.1. *Anodes.* Tantalum and chromium metals were used as soluble anodes. Tantalum anodes were machined from a 3 mm thick, unannealed, metallurgical-grade plate. Prior to use this was etch-cleaned for five minutes in a 2:5:1 solution of concentrated HAc:HCl:HF which produced a bright clean finish. The chromium was in the form of discs and these were cleaned with a 3:1:4 solution of H_2O_2 :HCl: H_2O .

2.1.2. *Cathodes.* Copper and type-304 stainless steel coupons (~ 3.2 mm \times 12 mm \times 50 mm) were used as cathodes. They were polished (to 400 and 600 grit finish) and etch-cleaned with 1:1 H_2O : HNO_3 and 3:27:70 KNO_3 : H_2SO_4 : H_2O solutions, respectively. All etched electrodes were cleaned with distilled water, dried at $110^\circ C$ and stored in a desiccator until used.

2.2. Electroplating assembly and procedures

The electrolytic cell assembly was designed after that of Mellors and Senderoff [7] and is illustrated in Fig. 2. The lower 16 cm of the plating cell was placed in a Lindberg crucible furnace. The hot-zone temperatures were controlled with a time-proportioning temperature controller ($\pm 10^\circ C$). The plating cell was loaded with the electrolyte contained in the nickel crucible and with the preweighed electrodes suspended above the crucible. The assembly was evacuated and back-filled with argon. Maintaining a steady flow of the inert gas, the electrolyte was heated to $450^\circ C$ for six hours and the temperature was then raised to the deposition temperature ($\sim 800^\circ C$). Preweighed amounts of the solutes (e.g., K_2TaF_7 , K_3CrF_6 , . . .) were next added under argon atmosphere to the melt and allowed to equilibrate for 48–72 hours. The anode was then positioned in the melt and a pre-electrolysis step (at 40–50 mA cm^{-2} for ~ 1 hour) was used to remove trace im-

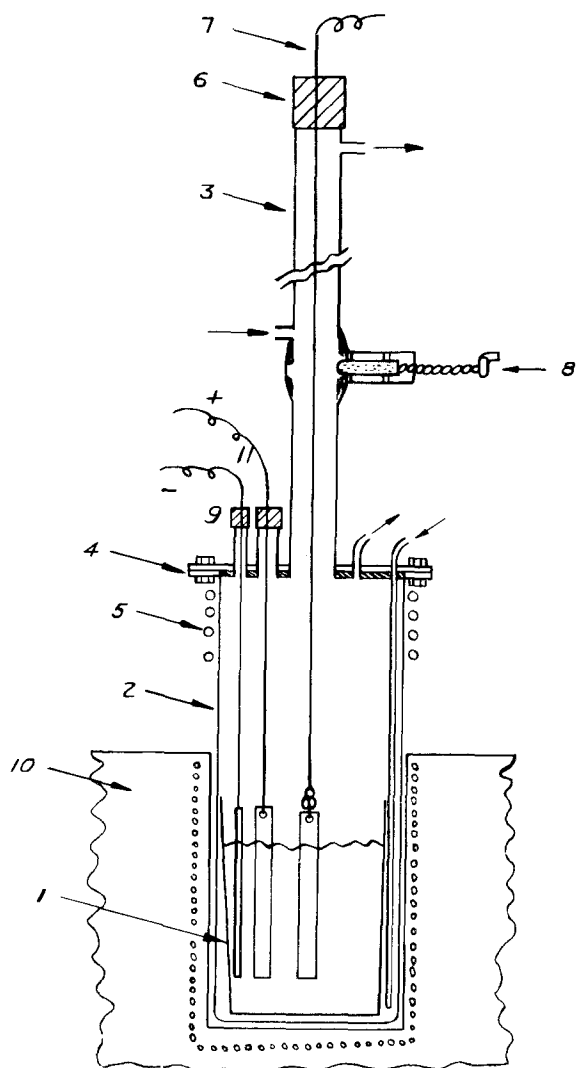


Fig. 2. Electroplating cell assembly: 1, crucible; 2, stainless steel cell; 3, head; 4, flange; 5, cooling coil; 6, entry ports; 7, suspension rod for the cathode; 8, gate valve; 9, entry port for reference electrode; 10, Lindberg crucible furnace; 11, entry port for anode.

purities. The cathode coupon was then removed and the plating was carried out at the predetermined current density. All current densities are apparent current densities, i.e., calculated from the apparent immersed electrode area. On the completion of the plating experiment, the coupon was withdrawn, ultrasonically washed in distilled water for $\sim 1-3$ hours to remove adherent salts, and weighed. The area of the deposit was measured and the plate thickness calculated. The coupon was then sectioned and polished for metallographic examination, electron microprobe analysis (EMPA) and microhardness measurements using standard techniques.

The compositions of the electrolytes investigated for deposition of tantalum, tantalum-rich chromium alloy, chromium, and chromium-rich tantalum alloys on copper and stainless steel substrates are summarized in Table 1, together with the associated parameters of temperature and current density.

3. Results and discussion

3.1. Tantalum

The rate of deposition versus current density for about 20 runs is plotted in Fig. 3. Runs with low current efficiency are shown as small crosses. Dense, columnar, high-purity (indicated by a microhardness similar to that of high purity bulk Ta) coatings were obtained, as illustrated in Fig. 4, at a current efficiency of almost 100%. The analysis of the electrolyte after numerous electroplating runs showed the oxidation state of tantalum in the melt to be +5 as reported by Senderoff *et al.* [9] who suggested that the reduction of $(\text{TaF}_7)^{2-}$

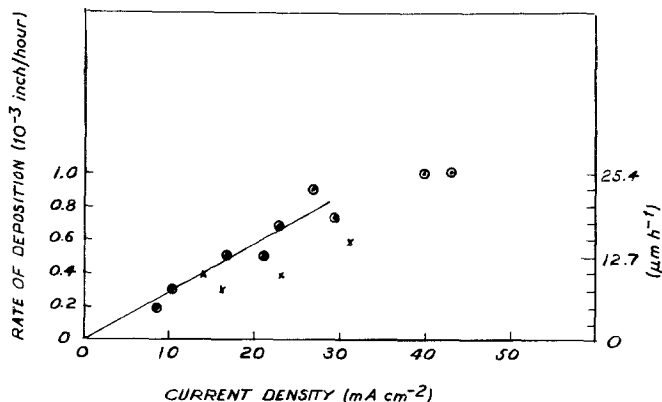


Fig. 3. Rate of deposition of tantalum versus current density. x, Runs with low current efficiency.

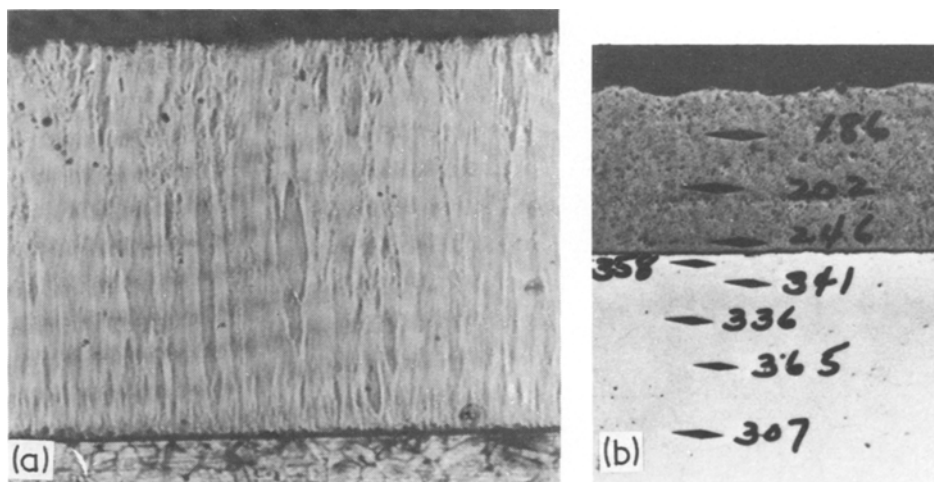
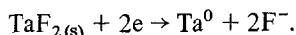
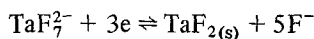


Fig. 4. (a) Transverse section of a typical tantalum coating (136 X). (b) Microhardness profile.

takes place in the following two steps:



The first step is reversible (controlled by the diffusion of Ta^{5+}); and the second step is not diffusion controlled and is irreversible. The rate of deposition is shown in Fig. 3; up to about 30 mA cm^{-2} it is an almost linear function of current density and can be represented approximately by: rate (in $\mu\text{m h}^{-1}$) = $0.762 \times$ current density (in mA cm^{-2}). At higher current densities, only a few runs were made and it is not certain if the apparent deviation from linearity is due to polarization effects.

3.2. Tantalum-rich chromium alloys

In three series of runs (SB, SC, SD) chromium to the extent of 0.5, 1.0 and 1.5% as K_3CrF_6 was added to the Flinak bath containing 10 wt% of TaF_5 as K_2TaF_7 . The coating rates as a function of current density for the three series are shown in Fig. 5. A transverse section of a typical alloy is shown in Fig. 6, which indicates dense columnar structure, rather similar to those of Ta coatings. Selected specimens from the three series were sectioned, polished and the variation of both microhardness and chromium in the coatings was determined (the latter by EPMA). EPMA analyses were made by scanning the coatings at $10 \mu\text{m}$ in-

Table 1. Plating baths and related parameters investigated, Flinak electrolyte

Solute 1	Solute 2	Temperature range ($^{\circ}\text{C}$)	Current density (mA cm^{-2})	Coating
TaF_5 (1–10 wt%) as K_2TaF_7	—	770–800	5–45	Ta
TaF_5 (10 wt%)	K_3CrF_6 (0.5–1.5 wt%)	750–800	5–40	Ta-rich tantalum–chromium alloys
CrF_3 (6 wt%)	—	800–835	0.8–50	Cr
CrF_3 (6 wt%)	TaF_5 (~ 0.05 wt%) as K_2TaF_7	800–835	0.8–50	Cr-rich chromium–tantalum alloys

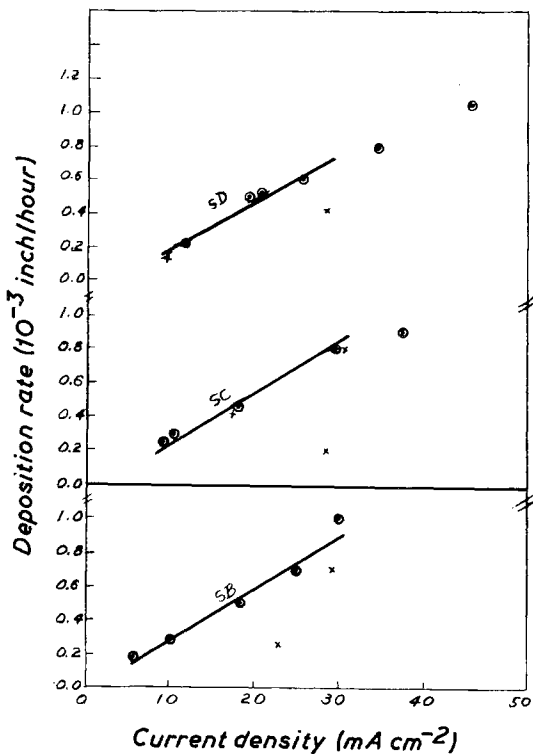


Fig. 5. Ta-Cr alloy coating rates as a function of current density for three series of runs. X, Low current efficiency runs. (10^{-3} inch = $25.4 \mu\text{m}$).

tervals from the substrates-plate interface to the plate edge. Results are summarized in Table 2.

Fig. 7 shows the hardness and composition of profiles of a Ta-Cr alloy specimen (SD-3). An EPMA profile of tantalum at $2 \mu\text{m}$ intervals across the interface in specimen DS-3 is shown in Fig. 8, indicating a diffusion zone of about $10 \mu\text{m}$. As seen from inspection of Fig. 9, the chromium distribution in the alloy is good. The sensitivity of the measurement of chromium by the EPMA technique was $\pm 0.5\%$.

From Fig. 5 it appears that alloying with chromium did not noticeably change the rate of deposition of tantalum. However, as seen from Table 2 the current efficiency decreased from 99% to 74% with an increase in the amount of chromium added to the electrolyte. Fig. 9 further shows that the concentration of Cr is the highest at the coating-substrate interface (i.e., at the start of electrodeposition) and then it gradually decreases. This is reflected in the decrease in the hardness at the corresponding positions in the coating.

The hardness of the coating, as expected, increased with chromium content. The data are summarized in Fig. 10. The bars indicate the vari-

Table 2. Electrodeposition of Ta and Ta-Cr alloy coatings from Flinak supporting electrolyte

Coupon (stainless steel)	Electrolyte		Conditions				Coating	
	TaF ₅ (wt%)	CrF ₃ (wt%)	Temperature (°C)	Current density (mA cm ⁻²)	Current efficiency (%)	Deposition rate ($\mu\text{m h}^{-1}$)	Cr (wt%)	Hardness (KHN)
SA 5	10	—	755	17.5	99.3	13	—	217
SA15	10	—	755	27.7	99.6	23	—	217
SB 6	10	0.5	800	18.7	92.2	14	2.2	475
SC 3	10	1.0	800	36.7	89.4	23	4.7	669
SC 5	10	1.0	800	29.1	88.2	20	4.7	634
SD 3	10	1.5	800	20.4	74.4	13	6.6	772

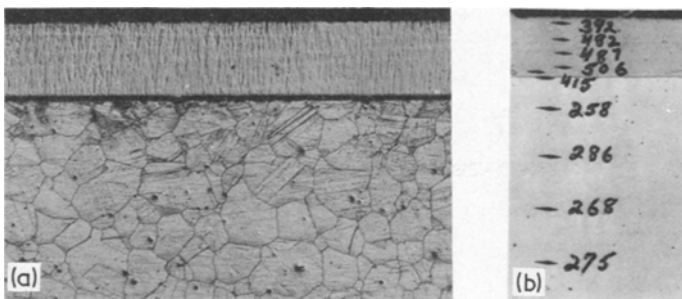


Fig. 6. Transverse section of a typical Ta-Cr alloy coating. (a) SB-6 specimen: 0.5% Cr (70 X); (b) hardness profile.

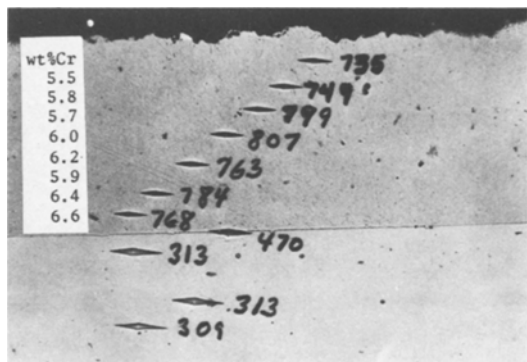


Fig. 7. Hardness and Cr composition profile of a selected coating SD-3 (interval between data points: 20 μm).

ation of hardness across the specimens. This figure shows that it is possible to increase predictably the hardness of tantalum by the addition of small amounts of chromium. No high-temperature hardness data were obtained at this time but is expected that like other Ta alloys, the Ta-Cr alloy will also maintain its hardness (or yield strength) at elevated temperatures.

3.3. Chromium and chromium-rich alloys

A limited number of runs were undertaken to explore the feasibility of plating Cr and Cr-Ta alloys. In the case of chromium, pieces contained in a nickel basket were used as an anode. Copper coupons were used as cathodes. The electrolyte was Flinak containing 6 wt% CrF_3 . For Cr-Ta alloys, in addition to CrF_3 , 0.05 wt% TaF_5 as

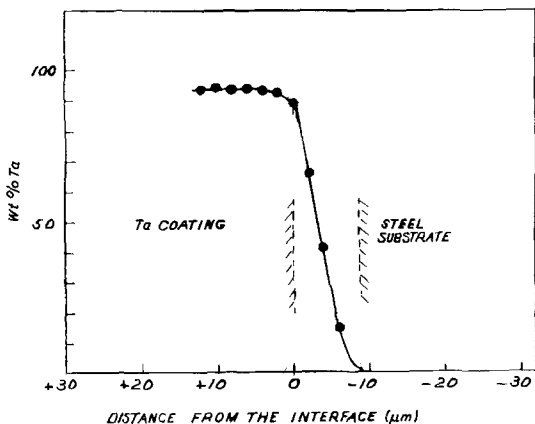


Fig. 8. EPMA profile of Ta-Cr/steel interface in SD-3 specimen.

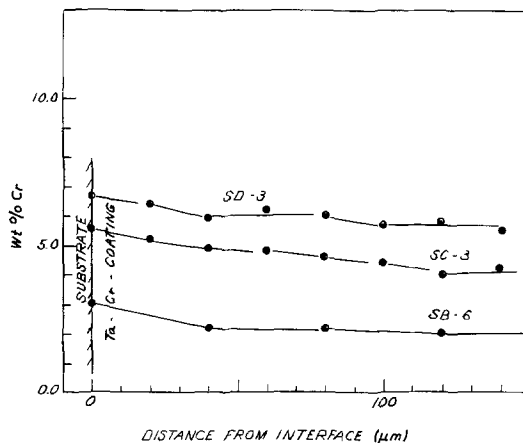


Fig. 9. Variation of chromium in SB-6, SC-3 and SD-3 coatings.

K_2TaF_7 was also added. For pure chromium deposition, current densities in the range 0.8–49.9 mA cm^{-2} and melt temperatures of 800–853° C were selected. In these runs some anodic dissolution of nickel (from the basket) was noted. The coatings obtained were mostly dendritic and porous and the current efficiency was, in general, low. However, the hardness values in the non-porous areas of these deposits were in the range of 137–205 KHN indicating high-purity chromium. The purity of Cr was confirmed by EPMA. Addition of 0.05 wt% TaF_5 gave coherent dense coating such as shown in Fig. 11, which was obtained at a current density of 25.8 mA cm^{-2} . In 11 hours

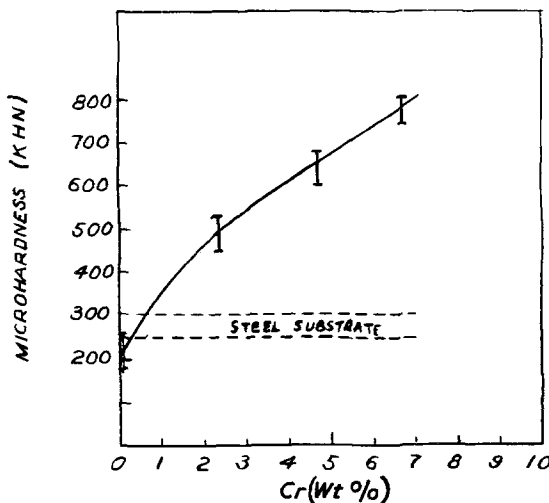


Fig. 10. Variation of hardness of tantalum alloy with chromium content.

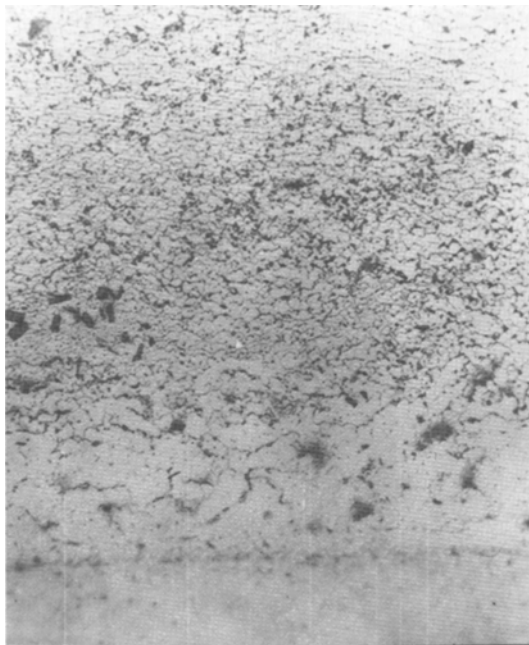


Fig. 11. Cr-rich Ta alloy, showing the equiaxed grain structure (1100 ×).

a thickness of 165 μm was obtained (current efficiency 65%). The average microhardness of the coatings was found to be 294 KHN, i.e., higher than pure chromium or tantalum. The presence of Ta in this coating could not be confirmed by the EPMA technique (detection limit $\sim 0.5\%$ Ta), and it is assumed that the alloy contained Ta only in trace amounts. A further noteworthy feature of this coating is the grain structure. Inspection of Fig. 11 shows that it is almost equiaxed instead of

the more general columnar structure. The very fine grain size of the equiaxed structure would be expected to confer superior mechanical properties. Such alloy structures appear a desirable feature for the erosion resistant coatings required for the present applications. Investigations of the electrodeposition of chromium and chromium-rich alloys are being extended.

Acknowledgements

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