Electrodeposition of Tungsten Carbide Coatings from Molten Salts

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Dense, adherent coatings of tungsten carbide have been electrodeposited on nickel substrates from the ternary (Li, Na, K)F eutectic at 750–800°C. The source of tungsten was Na₃WO₄; the source of carbon was K₂CO₃. The concentration of both solutes was less than 10 wt%. By applying a voltage between a tungsten anode and the nickel cathode, the anions are reduced to the elements and react on the cathode to form the carbide. Current efficiencies of up to 50% have been achieved for the deposition of W₁C. The dependence of surface structure on melt composition is shown.

Introduction

Refractory carbide coatings provide good protection for metal substrates because of their great hardness and good oxidation resistance at moderately high temperatures. Tungsten carbide coatings have been prepared commercially by plasma processing in which the finely divided carbide impinges directly on the surface to be coated. However, this method requires very high temperatures and is line-of-sight.

Electrodeposition from molten salts offers the advantages of lower temperatures, the ability to coat complex shapes, and the fine control that can be applied to electrical variables.

We have recently shown (1) that adherent coatings of tantalum carbide can be electrodeposited from the ternary (Li, Na, K)F eutectic (FLINAK) containing K₂TaF₇ as the source of tantalum and K₂CO₃ as the source of carbon. The method depends on the simultaneous deposition of tantalum, first worked out by Senderoff, Mellors, and Reinhart (2), and carbon. The elements react on the cathode at 750–800°C; a temperature ~600° lower than that of the reaction of the elements in bulk.

Tungsten carbide was first prepared electrochemically by Weiss (3) from an alkaline borate-fluoride melt containing WO₃ as the source of tungsten and Na₂CO₃ or Li₂CO₃ as the source of carbon. Small crystals, whose composition depended on the carbonate/oxide ratio, were produced. More recently Gomes and Wong (4) reported the electrodeposition of WC from a NaCl melt containing Na₃WO₄ as the

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tungsten source and a graphite anode as the source of carbon. However, this method was not intended to produce a protective coating. Senderoff and Mellors (5) reported the deposition of dense, adherent tungsten metal coatings from FLINAK melts. However, their method is complicated by the requirement that the valence of tungsten be +4.5, which is achieved by the reaction of WF$_6$(g) with metallic tungsten dispersed in the melt. The authors concluded that an irreversible step is required for the deposition, but did not otherwise elucidate the mechanism.

Because the preparation of W$^{4.5+}$ is rather cumbersome, we investigated the possibility of plating tungsten using WO$_4^-$ as the solute; Gomes and Wong (4) had already shown the reduction occurred in NaCl. Senderoff and Mellors (2,5) had found that FLINAK was necessary to form adherent coatings, therefore we retained FLINAK as the solvent. Because F$^-$ is more electronegative than O$^{2-}$ and is present in large excess, the effective species for electrodeposition may be a tungsten fluoride complex; e.g.

$$WO_4^{2-} + nF^- = WF_{6-n}^n + 4O^{2-}$$

This procedure was successful and, combined with simultaneous carbonate reduction, has led to adherent tungsten carbide coatings.

**Experimental**

The procedure follows closely that employed for tantalum carbide deposition (1). Reagent Na$_2$WO$_4$·2H$_2$O was vacuum-dried at 150$°$C to remove water.

Quarter inch diameter tungsten rods were obtained from the Rembar Company.

**Results**

Current-voltage curves were determined for the addition of Na$_2$WO$_4$ in FLINAK using the cell C/FLINAK + Na$_2$WO$_4$/C. As described previously (1), the solvent was first pre-electrolyzed between carbon electrodes to remove impurities. As seen in Fig. 1, the current increases substantially, even at very low Na$_2$WO$_4$ concentrations relative to the pure solvent, showing that the solute is electro-active. Fig. 2 shows current-concentration curves at various constant voltages for the data in Fig. 1. At low voltages the current is low and nearly independent of concentration. As the voltage increases, the concentration dependence of the current becomes more pronounced and rises linearly after an initial rapid rise. Corresponding curves for carbonate reduction in FLINAK were published previously (1). We have not made any attempts to elucidate the electrode reactions. Although the mechanism is unknown, hexavalent tungsten is reduced on the cathode to the metal. The
Anodic reaction is believed to be the oxidation of $O^{2-}$ to elementary oxygen.

When tungsten is to be plated, the inert carbon anode is replaced by a tungsten anode and the anodic process changes from $O^{2-}$ oxidation to tungsten oxidation. Therefore, assuming the same electrode area, for a given voltage the current will be much larger. For example, at 1.5V the current increased by a factor of ~5 when the carbon anode is replaced by tungsten. Electroplating experiments were carried out at 1.5V to maintain the current below 2A, the limit of the coulometer.

Because tungsten coatings previously had not been obtained from tungstate-containing melts, a series of experiments was run in which tungsten was plated onto nickel coupons (5x0.8 cm) from FLINAK melts containing various concentrations of $Na_2WO_4$. The plated cathodes were cleaned ultrasonically to remove loose deposit and adherent frozen melt. The current efficiencies were determined by weighing the cleaned cathodes. Thus, they are less than electrochemical efficiencies, which apply to the total reduced material, but are more significant for a material of interest as a coating. Current efficiencies were based on $W^{6+} + 6e = W$ and $CO_3^{2-} + 4e = C + 3O^2-$ (when carbide is being plated) as the only cathodic processes. Therefore, the weight of material theoretically plateable depends on the nature of the deposit. For example, for 0.01 equivalents of charge passed, the weights of $W$, $W_2C$, and WC are 0.306, 0.207, and 0.186 grams, respectively.

Current efficiencies (C.E.) for plating adherent tungsten alone generally did not exceed 20%, but higher C.E. were achieved for some carbides. Table 1 summarizes the results of several experiments relating melt composition, stoichiometry of the deposit (identified by X-ray diffraction), and C.E. Although the results are somewhat contradictory, some tentative conclusions emerge: (a) Composition - The usual composition of the coating is $W_2C$. Whether WC is produced depends not only on the C/W ratio, higher values favoring WC, but also on the individual concentrations. For example, with 3wt% each of $Na_2WO_4$ and $K_2CO_3$, (C/W = 2.13) $W_2C$ is produced; but at 7% each, WC is formed; for C/W $\leq$ 2, only $W_2C$ forms. These results contrast with those of Weiss (3), who used borate melts and found that $W_3C$ formed for 4 $\leq$ C/W $\leq$ 7, WC formed for C/W between 12 and 14 and mixtures were obtained between 7 and 12. Evidently the reaction medium and/or other differences between the two processes also affect the composition of the deposit. Current efficiencies are generally in the range 30-50% for $W_3C$, but are less for WC. (b) Surface Features - Deposits were examined by scanning electron microscopy (SEM), both for the surface features and the cross-section. A typical example of the latter is shown in Fig. 3. In contrast to tantalum carbide, which shows a broad Ta-Ni interdif-
Fusion zone between the carbide coating and the nickel substrate, an interdiffusion zone between the tungsten carbide coating and the nickel substrate is not visible.

Although all the coatings examined exhibit the same gross cross-sectional features, this is not true of the surface features. Figures 4 to 9 show a series of W2C coatings at 2000X for various melt compositions between 2 and 7 wt% Na2WO4 and K2CO3. For the more dilute melts (Figs. 4 and 5) the crystals exhibit a substructure which is clearly evident at 5000X. For melts 6 and 7 wt% Na2WO4 (Figs. 6, 7, 8) substructure is absent, although the carbonate concentration varies from 3 to 5% (1.06 ≤ C/W ≤ 1.52). However, a small increase in the carbonate concentration, from 5 to 7% (C/W = 2.13), has a dramatic effect on both stoichiometry and structure (Fig. 9). The coating now is WC, and the coating consists of ball-like structures; angular crystals are not evident. The relation of these surface features to the wear characteristics of the coatings remains to be explored.

Oxidation Tests

The oxidation resistance of the coatings was tested in still, ambient air. Coated specimens were contained in small, open alumina crucibles in a Mettler TGA apparatus, capable of measuring weight changes to ± 0.1mg. The temperature was raised in 50° steps to determine the temperature at which weight changes became noticeable. A weight loss was taken to indicate the oxidation of carbon (without oxidation of tungsten), whereas a weight gain indicated the oxidation of tungsten as the predominant reaction.

Several representative samples were tested to see if the oxidation resistance is related to the melt composition and the deposition parameters. Six of the seven samples tested had been analyzed by X-ray diffraction to be W2C, one was WC. For all the W2C samples, weight changes began near 450°, and each gained weight rapidly above 600°. The final product was always an adherent coating of WO3. Some variations in stability occurred within this temperature range, but we cannot unambiguously attribute these reactions to differences in the electrodeposition procedure.

References

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Fig. 1 Current-voltage curves for the reduction of Na₂WO₄. Cell: C/FILNAK + Na₂WO₄/C.

Fig. 2 Current-voltage plots for reduction of Na₂WO₄. Data of Fig. 1.
Fig. 3
Cross-section of tungsten carbide coating on nickel substrate

a  Coating by SEM

b  W X-ray map

c  Ni X-ray map
Fig. 4
Surface of $W_2C$ coating. 2wt% $Na_2WO_4$, 1% $K_2CO_3$
Fig. 5
Surface of W$_2$C coating. 5% Na$_2$WO$_4$, 3% K$_2$CO$_3$

a 2000X

b 5000X
Fig. 6 Surface of W:C coating
6% Na₂WO₄, 3% K₂CO₃, 2000X

Fig. 7 Surface of W₂C coating
7% Na₂WO₄, 5% K₂CO₃, 2000X

Fig. 8 Surface of W₃C coating
7% Na₂WO₄, 4% K₂CO₃, 2000X
Fig. 9
Surface of WC coating. 7% Na$_2$WO$_4$, 7% K$_2$CO$_3$

a 2000X

b 5000X