

RAPID PUBLICATION

Role of Melt Basicity on the Composition of Electrodeposits in Tungsten-Carbon System

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The role of basicity of the melt during electrodeposition of tungsten carbide from the $\text{Na}_2\text{WO}_4\text{-Na}_2\text{O-B}_2\text{O}_3\text{-NaCl}$ system using the graphite electrode has been studied by UV-vis reflectance spectroscopy of tungsten species formed. It has been shown that tungsten in the melt is predominantly found as W^{6+} at low basicity, as ditungstate in an intermediate basicity range and as monomeric $(\text{WO}_4)^{2-}$ species in highly basic melts leading to deposition of W, W_2C and WC during electrolysis depending upon the $\text{Na}_2\text{O:B}_2\text{O}_3$ ratio of the melt. Addition of NaCl was found to play no direct role in changing the tungsten species in the melt; its role probably is to increase the electrical conductivity or to decrease the viscosity/surface tension of the melt.

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I. Introduction

Monotungsten carbide (WC) is the world's most important hard metal compound and is the most important constituent of cemented, hard metal tools. The extreme hardness of WC at temperatures exceeding 1000°C makes it an ideal material for making cutting tools and dies. Tungsten carbide is also used in hard-facing earth moving equipment and rock crushing machines.

Ceramic-coated WC cutting tools are finding more and more use in machining precision components. The conventional metallurgical process for making high-purity tungsten is through hydrometallurgical processes followed by high-temperature hydrogen reduction. Fine powder of tungsten is made to react with carbon at high temperature to produce monotungsten carbide-base for eventual production of WC cutting tools. Datta⁽¹⁾ has investigated the electrodeposition of tungsten from Na_2WO_4 dissolved in molten salts consisting of mixtures of $\text{Na}_2\text{B}_4\text{O}_7$, $\text{Na}_4\text{P}_2\text{O}_7$ and NaCl. He found that with a bath containing NaBO_2 instead of $\text{Na}_2\text{B}_4\text{O}_7$ and without $\text{Na}_4\text{P}_2\text{O}_7$ carbide of tungsten deposited instead of tungsten metal. This was supposed that the basicity of melt has something to do with the carburization of tungsten. This has led to the formulation of the present investigation. This change of deposited material from pure tungsten to tungsten carbide with changing basicity is

probably due to formation of oxy-tungsten/oxy-chloride-tungsten species in the bath⁽²⁾. Figure 1 shows some typical SEM micrographs of deposited W, W_2C and WC.

Sodium tungstate (Na_2WO_4) contains monomeric tungsten species⁽³⁾⁽⁴⁾ with tetrahedral crystal structure like other metals in group VI of the periodic table (*e.g.* Cr and Mo). Tungsten is also known to form polymeric acidic groups with homopoly as well as heteropoly acids⁽⁵⁾⁽⁶⁾; in addition there is possibility of ligand substitution in these poly acids by chlorides for oxygen. Besides the degree of polymerisation depends on the basicity of the solvent⁽⁷⁾.

In the present studies, the effect of the ultra violet spectra of sodium tungstate (W^{6+}) dissolved in $\text{Na}_2\text{O-B}_2\text{O}_3\text{-NaCl}$ melts on the type of tungsten species formed was investigated as a function of the basicity, *i.e.* the $\text{Na}_2\text{O:B}_2\text{O}_3$ ratio.

II. Experimental

Accurately weighed amounts of Na_2CO_3 and orthoboric acid were thoroughly mixed and melted in a platinum crucible by heating to 1000°C to obtain a clear bubble free melt. The melt was cast, cooled in air and crushed to fine powder. Appropriate amounts of this powder were then mixed with anhydrous NaCl and anhydrous Na_2WO_4 and melted in a platinum crucible at 1000°C for 1 h. The melt was cast over a thick aluminium sheet and allowed to cool in air. The cooled sample was crushed to fine powder and reflection spectra of this powder was recorded on a Beckman 5207 spectrophotometer using MgO as the reference.

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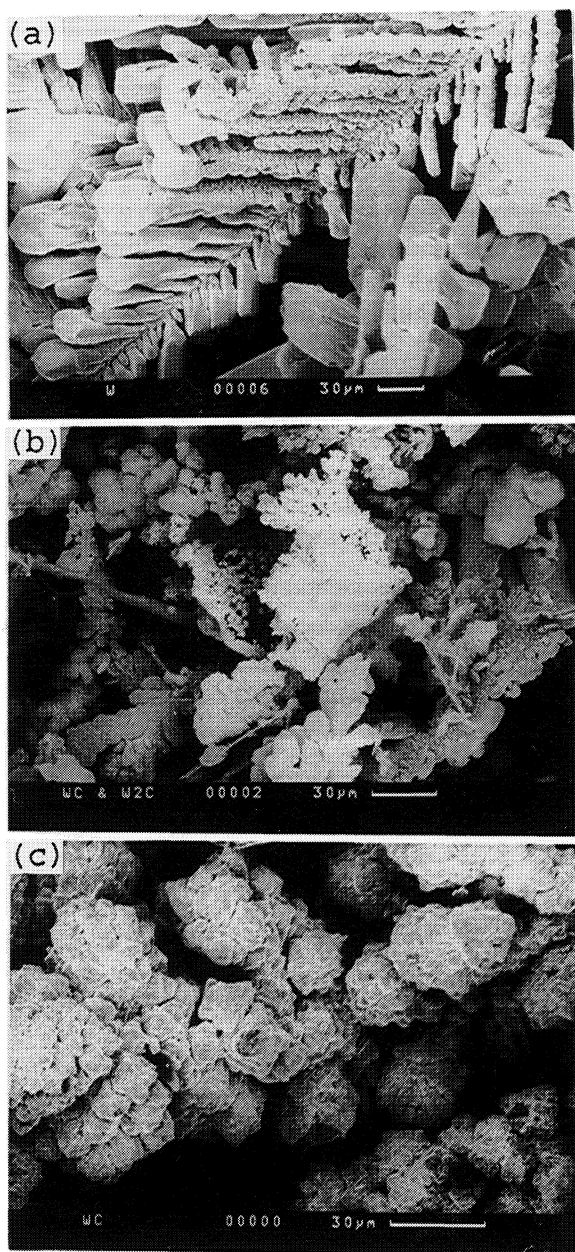


Fig. 1 SEM micrographs of W, W_2C and WC.

III. Results and Discussion

The reflection spectra of crystalline powdered Na_2WO_4 and that dissolved in a sodium borate melt having $Na_2O:B_2O_3$ in the 1:4 molar ratio are shown in Fig. 2. Both the spectra show a strong absorption band at $46511.63 \times 10^2 m^{-1}$ (215 nm); in addition to it, sodium tungstate in sodium borate shows even a stronger absorption band centered around $37735.85 \times 10^2 m^{-1}$ (265 nm) whereas pure Na_2WO_4 shows only signs of a weak shoulder around $40816.33 \times 10^2 m^{-1}$ (245 nm). In the Na_2WO_4 crystal, W^{6+} is known to be present in tetrahedral symmetry surrounded by four oxygen atoms⁽⁸⁾. This monomeric tetrahedral tungsten ion remains stable in alkaline aqueous and alkaline non aqueous solutions. However, when the basicity of the solution is decreased, polymeriza-

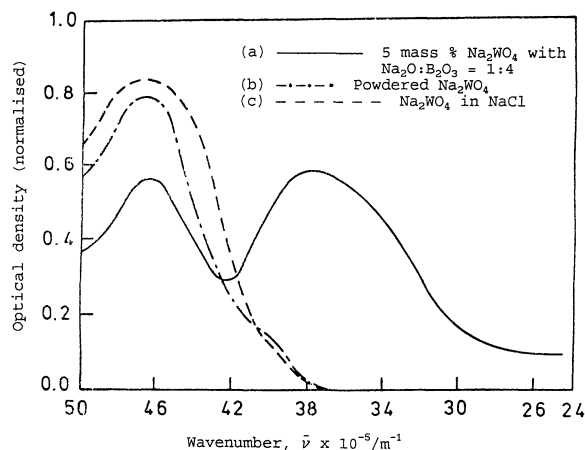


Fig. 2 Reflectance spectrum of (a) Sodium tungstate in sodium borate glass, (b) Powdered sodium tungstate and (c) Sodium tungstate in sodium chloride.

tion occurs with the formation of homo-poly or hetero-poly acids, in aqueous solution depending upon the solvent composition. When an acid sodium tungstate solution is heated under a mildly reducing condition, "tungsten bronze", an oxygen deficient sodium tungstate is formed. Tungsten bronzes thus formed are extremely inert and have semimetallic properties, specially metallic lustre, good electrical conductivity in which the charge carriers are only electrons. It is believed this high electrical conductivity originates from "small polaron" hopping in this type of materials⁽⁹⁾⁽¹⁰⁾.

According to molecular orbital calculation done by Ballhausen and Grey⁽¹¹⁾ a tetrahedral tungstate group $(WO_4)^{2-}$ should produce, two charge transfer bands which are evident in Fig. 2(a).

The building units in both isolated tungstate tetrahedral group and poly-tungstate group is $(WO_4)^{2-}$, it is known that in similar systems, such as acid chromate, like $HCrO_4^-$ or $Cr_2O_7^{2-}$ get converted to basic monomeric $(CrO_4)^{2-}$ with increasing basicity of the melt and as a consequence the low energy charge transfer band makes a red shift and gains in intensity⁽⁷⁾. Figure 3 shows the reflection spectra of Na_2WO_4 dissolved in a sodium borate glass having different $Na_2O:B_2O_3$ ratios. It is clear from Fig. 3 that as the Na_2O content of the melt has increased, the intensity of the band around $37735.85 \times 10^2 m^{-1}$ (265 nm) has increased and shifted to slightly longer wavelengths; with increasing basicity of the melt, the degree of polymerization of tungsten anions decreased and eventually reached the orthotungsten group. Figure 2(c) shows the ultra violet reflection spectrum of Na_2WO_4 dissolved in the pure anhydrous NaCl melt. The spectrum of Fig. 2(c) and that of pure crystalline Na_2WO_4 , Fig. 2(a), are almost identical indicating that even in pure molten NaCl no ligand substitution around $(WO_4)^{2-}$ tetrahedra took place with the chlorides.

In acidic melts (low $Na_2O:B_2O_3$ ratio) tungsten is present as poly-tungstate species; but due to the strong acidic nature of the melt the bonding of W^{6+} with the ligands of the melt is weak and as a consequence tungsten

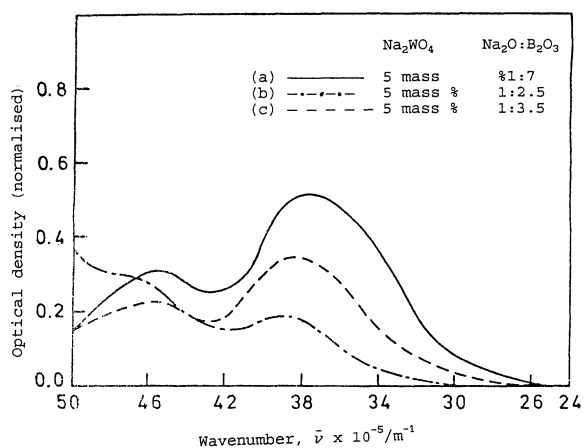


Fig. 3 The effect of $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratio on the reflectance spectrum of sodium tungstate in $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ melts.

has low reduction potentials and thus "pure tungsten" can be deposited. In the intermediate region, di-tungsten group ($\text{W}_2\text{O}_7^{2-}$) is probably present, which with the ambient carbon potential of the melt, get reduced at the cathode as ditungsten carbide. In the basic melt, monomeric tungsten species is present which deposits at the cathode as monotungsten carbide.

Under the moisture-free conditions of the melt the NaCl content apparently does not affect the deposit quality. Its role is limited as a charge carrier to increase the conductivity of the melt. Various electrodeposits obtained from melts of different $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratios show that basic melts deposit monotungsten carbide, melts with intermediate basicity deposit ditungsten carbide,

and highly acidic melts produce almost pure tungsten. These results agree with the precursor species as identified with spectroscopic studies.

IV. Conclusion

Hexavalent tungsten form monomeric $(\text{WO}_4)^{2-}$ group in highly basic sodium borate melt and ditungstate group (probably $(\text{W}_2\text{O}_7)^{2-}$) in sodium borate melts of intermediate basicity. In highly acidic sodium borate melts (less than 20 mol% Na_2O), the bonding between W^{6+} and surrounding ligands is weak, and thus almost pure tungsten can be electrodeposited from these melts; where as highly basic sodium borate melts produce WC and sodium borate melts with intermediate basicity produce W_2C during electrodeposition due to the occurrence of similar precursor species in the melt with oxide coordination.

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