JOURNAL OF MATERIALS SCIENCE 27 (1992) 2739–2742

Application of a molecular precursor to the preparation of tungsten and beta-tungsten nitride coatings and powders

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The use of the tungsten imido/amido complex (N–H-*t*-Bu)$_2$W(N-*t*-Bu)$_2$ (Complex **1**) (CAS number 72207-45-5) as a precursor to tungsten and tungsten nitride films, coatings and powders is reported. The alkane-soluble Complex **1** exhibits high solubility in solvents such as hexane and toluene, making it amenable to application to substrates via dip-coating or spot-spraying. This avoids the necessity of vapour deposition methods and the, presently common, use of tungsten fluorides. Thermolysis in an ammonia/nitrogen, ammonia/argon or exclusively nitrogen atmosphere at temperatures between 600 and 1200 °C provided a coating or powder comprised of elemental tungsten (75–95 mol %) and tungsten nitride (25–5 mol %). Oxygen content of these materials is less than 0.5%. Thermolysis in an argon atmosphere produced a coating on AlN substrates which were found to contain no β-W_2N (as detectable by X-ray diffraction), only tungsten metal. The coating was successfully applied to sintered aluminium nitride electronic and structural substrates. A coated aluminium nitride substrate exhibited improvement in erosion resistance when compared to an uncoated specimen.

1. Introduction

Refractory metal coatings have been proposed for, and used in, a number of applications including aerospace, defense, and cutting tools [1]. Tungsten and tungsten nitride, films of which are used in electronic applications as well as in refractory coatings, are generally prepared in one of three manners. These films are prepared by either (a) thermal spray techniques, (b) chemical vapour deposition (CVD) using volatile tungsten species such as WF_6 [2] or (c) via a variety of plasma deposition methods [3] (e.g. sputtering) utilizing either tungsten oxide [4] or tungsten metal as the tungsten source. Conversely, tungsten is applied to most electronic substrates through inking processes in which tungsten particles are suspended in a solvent. CVD techniques are often undesirable due to the formation of corrosive hydrohalic acid vapours as a by-product. Physical vapour deposition (PVD) methods are equipment-intensive processes. The present paper describes the use of the complex (N–H-*t*-Bu)$_2$W(N-*t*-Bu)$_2$ [5] as a molecular precursor to tungsten or composite tungsten/β-tungsten nitride (β-W_2N) coatings and powders.

2. Experimental procedure

Complex 1, (N–H-*t*-Bu)$_2$W(N-*t*-Bu)$_2$, was prepared as given in the literature [4] and used without recrystallization. All manipulations were carried out under an inert atmosphere either on a Schlenk line (high-purity nitrogen atmosphere) or in a vacuum atmosphere glove box (ultra-high-purity (99.9998%) argon atmosphere). Dissolution of Compound **1**, as well as subsequent application to the desired substrate, was carried out in an inert atmosphere glove box using *n*-hexane solvent which had been distilled from sodium under argon. Once the solvent had evaporated, the treated substrates were transferred, under an inert atmosphere, to a closed-atmosphere furnace for heat treatment.

A stock solution for dip-coating applications was prepared by dissolving 1.0 g W(N–H-*t*-Bu)$_2$(N-*t*-Bu)$_2$ in 1.0 ml hexane. The precursor, after solvent evaporation, is present as a microcrystalline coating on the specimens. The material is then heat treated under a slow stream of NH_3/N_2 (approximately 70:30 ratio), nitrogen or argon. Heat treatment involved an initial rise from ambient to 600 °C at a rate of 2 °C min^{-1}; the specimens were then held at 600 °C for 2 h, to complete thermolysis of the precursor. This was then followed by an increase in temperature to 1200 °C at a rate of 2 °C min^{-1} with a hold at 1200 °C for 5 h. Slow cooling to room temperature at 3 °C min^{-1} completed the heat-treatment cycle.

X-ray diffraction was carried out on a Phillips XRG-3100 vertical diffractometer. Oxygen and nitrogen analyses were performed using a calibrated LECO^{TM} TC-136 oxygen and nitrogen analyser.

Erosion testing (following ASTM G65) was performed at Dow. The conditions for the testing (both

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for the 90° and 30° testing) were 29 min test duration, a powder flow of 4.5 g min^{-1}, and a particle velocity of 227 ft s^{-1} (~ 69 m s^{-1}). Erosion numbers reflect the volume loss of material ($mm^3\,g^{-1}$).

3. Results and discussion

3.1. Powder preparation and characterization

A 1 g sample of the precursor Complex **1** dissolved in hexane was placed into an alumina combustion boat and the solvent allowed to evaporate. The resulting microcrystalline material was then heated at 1200 °C under an NH_3/N_2 atmosphere for 5 h. The resulting silver-grey powder was found to be a mixture of tungsten metal (85%) and beta-tungsten nitride (β-W_2N) (15%), by X-ray diffraction (Fig. 1, Table I) as well as by inference from the measured nitrogen content of 0.53%. The X-ray diffraction data (Table I) agreed with the JCPDS data for tungsten (4-806) and β-W_2N (25-1256). Oxygen analysis of the powder indicated an oxygen content of 0.25%.

3.2. Application of tungsten coating to aluminium nitride electronic substrate

A presintered experimental electronic substrate, was coated with the tungsten precursor **1** and then thermolysed at 1100 °C in an argon atmosphere. X-ray diffraction analysis indicated the presence of tungsten metal. No β-W_2N was observed in the X-ray pattern. Fig. 2 compares the X-ray patterns for the untreated substrate as well as the substrate after being coated and heat treated. The peaks at 40.6° and 58.5° (2θ) are the two highest intensity peaks characteristic of tungsten metal.

3.3. Application of tungsten coating to aluminium nitride and subsequent evaluation of erosion resistance

Two specimens of sintered aluminium nitride were prepared by cutting in half a single sintered block. One of the two specimens was coated three times with a hexane solution of the W/W_2N precursor – (N–H-*t*-Bu)$_2$W(N-*t*-Bu)$_2$, allowing the solution to dry prior to the subsequent application. The heat-treatment schedule was 4 °C min^{-1} from ambient to 600 °C, a 1.5 h hold at 600 °C; 4 °C min^{-1} from 600–1200 °C, a 2.5 h hold; then cool down at 5 °C min^{-1} to ambient in an Ar/NH_3 atmosphere. This provided a composite W/W_2N coating. Results of erosion tests conducted on the coated and uncoated specimens are given in Table II. Although no difference was observed in the 90° erosion test, some improvement in erosion resistance was observed in the 30° test. In addition, these experiments were not optimized for coating thickness nor adhesion, but rather were used to demonstrate the potential application of this coating process to the formation of wear resistant coatings.

TABLE I X-ray diffraction results of powder derived from the thermolysis of Complex **1** (1200 °C, NH_3/N_2 atmosphere, 5 h hold)

2θ (deg)	*d*-spacing (nm)	Assignment (composition)	JCPDS *d*-spacing (nm)
38.10	0.236	β-W_2N	0.238
40.60	0.222	W metal	0.224
44.20	0.207	β-W_2N	0.206
58.54	0.158	W metal	0.158
63.79	0.146	β-W_2N	0.146

JCPDS card numbers: W (4-806); β-W_2N (25-1257).

4. Conclusions

The current study examined the utility of the tungsten imido/amido complex (N–H-*t*-Bu)$_2$W(N-*t*-Bu)$_2$ (Complex **1**) (CAS number 72207-45-5) as a precursor to tungsten and tungsten nitride films, coatings, and powders where application of the material was performed via solution techniques (e.g. dip-coating or spraying). The alkane-soluble Complex **1** exhibits high solubility in solvents such as hexane and toluene,

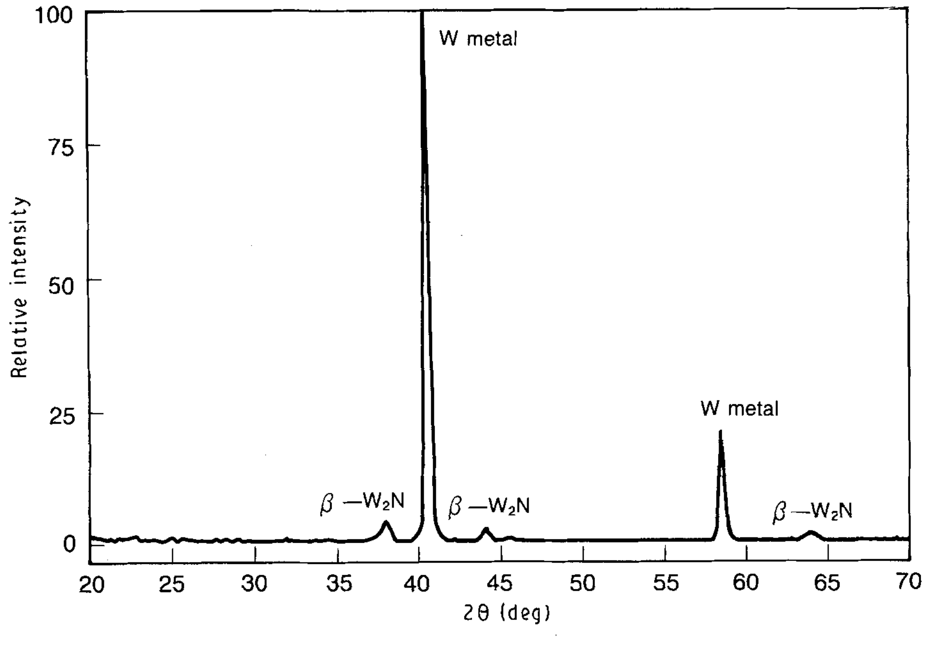

Figure 1 X-ray powder diffraction pattern for powder obtained from the thermolysis of (N–H-*t*-Bu)$_2$W(N-*t*-Bu)$_2$ at 1200 °C under NH_3/N_2.

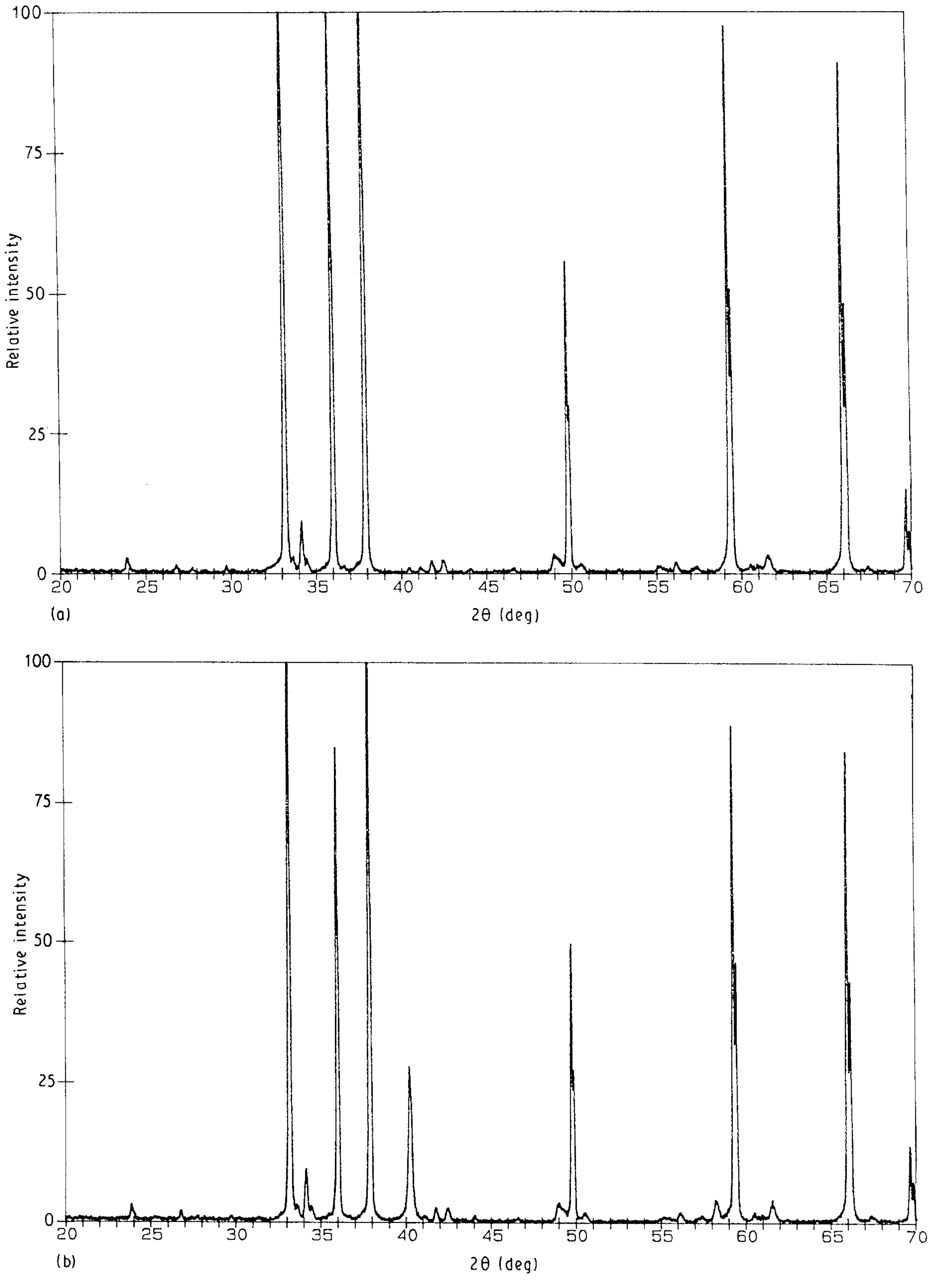

Figure 2 (a) X-ray powder pattern of uncoated, sintered AlN electronic substrate. (b) X-ray powder pattern of the same AlN substrate after application of complex **1** and heat-treatment at 1100 °C in argon.

TABLE II 30° and 90° erosion data for uncoated and W/W_2N-coated AlN specimens

Specimen	30° erosion ($mm^3 g^{-1}$)	90° erosion ($mm^3 g^{-1}$)
AlN sintered	20.34 (1.4)	7.53 (1.2)
AlN/W coated	19.46 (0.7)	7.69 (1.0)

Standard deviations (1σ) are given in parentheses. Each value is the average of three measurements.

making it amenable to application to substrates via dip-coating or spot-spraying. This avoids the necessity of vapour deposition methods and the, presently common, use of tungsten fluorides. Thermolysis in an ammonia/nitrogen, ammonia/argon or exclusively nitrogen atmosphere at temperatures between 600 and 1200 °C provided a coating or powder comprised of elemental tungsten (75–95 mol %) and tungsten nitride (25–5 mol %). The oxygen content of these materials is less than 0.5%. Thermolysis in an argon atmosphere produced a coating on AlN substrates which were found to contain no β-W_2N (as detectable by X-ray diffraction), only tungsten metal. The coating was successfully applied to sintered aluminium nitride electronic and structural substrates. A coated aluminium nitride substrate exhibited improvement in erosion resistance when compared to an uncoated specimen.

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Received 24 January
and accepted 7 June 1991