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Novel "redox reaction" route for synthesis of faceted, microcrystalline coatings of tungsten, molybdenum and their composites

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Faceted, microcrystalline coatings of tungsten, molybdenum and their composites are fabricated for the first time using a novel redox reaction route. The method uses a hot filament to initiate pyrolytic reactions in desired gas mixtures. The method offers many technologically useful features—e.g. high growth rates, and hence fabrication of very thick coatings; no hazardous precursors are needed; control of the morphology/composition of the composites—which are not offered by other conventional methods of thin film fabrication.

Keywords: CVD coatings; Pyrolysis; Ceramics and refractories

Coatings of refractory metals, such as tungsten (W), molybdenum (Mo) and their compounds such as carbides, nitrides, etc., are of great technological importance [1–7] owing to their exotic properties [8–11]. These materials have applications in variety of areas such as armour and plasma facing materials [1], Schottky contacts [2], diffusion barriers [3], wear control [4–6], field emission devices [7], etc. However, problems arise in utilization of coatings of these materials primarily because of the lack of a suitable method for their production. Conventional methods [2–5,14,15] based on physical and/or chemical vapor deposition (PVD/CVD) have many limitations, due to the refractory nature of these materials. The problems are related to issues such as (i) limited growth rates, (ii) non-compatibility of methods for fabrication of coatings on larger areas, (iii) control of unwanted reactions and toxic materials used in CVD processes. There is therefore a need to develop a concept/method which can overcome these problems. In this paper, we report for the first time, a very simple but efficient approach that uses "redox reactions" to obtain high-quality coatings of W, Mo, their carbides and also their composites. This method offers a number of important advantages: (i) simple system set up; (ii) easy control of process parameters which ultimately control the morphologies and internal architecture of coatings; (iii) no hazardous precursors required; (iv) high growth rates and hence the possibility of obtaining thicker coatings (more than a few microns); (v) compatibility of the method with large area depositions; and finally (vi) the possibility of being able to synthesize composite coatings with control of the relative concentration of component materials. All these features are very useful in the context of commercial production of such coatings. The method could also be useful for exploring the synthesis of new materials such as multilayered and composite coatings.

The present method is based on the use of a hot filament of so-called "parent material" (such as W or Mo) which initiates controlled pyrolytic "redox reactions" in a suitable gas mixture. We have used this simple but novel concept for the first time, and in this communication we present some of our results on coatings of W, Mo, their carbides and composites to demonstrate its effectiveness.

In a typical experiment, the <100> Si and pure alumina (α-Al_2O_3) substrates (size $\sim 15 \times 10$ mm) are cleaned using standard procedures (for Si substrates, initial hydrofluoric acid treatment to remove surface oxide, followed by ultrasonication in soap solution, acetone and methanol) and are mounted in a reaction chamber

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in the proximity (0.5–1.5 cm) of a filament of parent material. High-purity (99%) methane (CH_4) and oxygen (O_2) gases are diluted with an excess of hydrogen (H_2), and then the gas mixture is flowed over the hot filament ($T_F > 1200$ °C). The gas compositions are controlled by using mass flow controllers (MFCs). It should be noted that no hazardous gas precursors are required in this method. The chamber pressure (10–200 Torr) is controlled by a microprocessor-based auto-throttle valve. The experiments are also carried out in steps by changing, in situ, the gas compositions and other process parameters depending upon the requirement of coating type. The specimens are characterized by using conventional (bulk) and glancing-angle X-ray diffraction (Bruker AXS D8 diffractometer, Germany), resistivity measurements (four-probe method, Keithley Instruments), scanning electron microscopy (SEM) and energy dispersive X-rays (EDX) (JEOL JSM-6360-A, Japan) and X-ray photoelectron spectroscopy (XPS) (VG Microtech ESCA 3000, UK).

Figure 1a and b show typical scanning electron micrographs, at different magnifications, corresponding to coating obtained on Si substrates using a hot ($T_F \sim 1700$ °C) W filament, a gas composition of H_2:O_2 = 100:2 sccm, a chamber pressure of ~30 Torr, a substrate temperature (T_S) of ~500 °C and a deposition time of ~20 min. The coating thus formed is found to be reasonably uniform and continuous, having cauliflower-type surface morphology. The XRD results indicated broad peaks corresponding to W and tungsten oxide (WO_3) phases. This proves that even a small quantity of oxygen in the reaction gas causes W to project from the hot filament onto the substrate. In fact, this forms a key factor of the present investigations. The transfer of “tungsten” from filament to the substrate can be understood in terms of “redox reactions”. Oxygen is prone to react with W and the nature of W–O reactions varies depending upon the temperature [9]. At lower temperatures ($T < 600$ °C) the non-stoichiometric tungsten trioxide (WO_{3-x}) is formed, while at higher temperatures, the growth of stoichiometric tungsten trioxide (WO_3) sets in. At $T \sim 750$ °C, the sublimation [9] of oxide also starts, but at a lower rate. At still higher temperatures ($T \sim 1500$ °C), the rates of oxidation and sublimation become almost equal. Thus, in the present experiment, WO_3 is continuously formed at the filament surface, and is then sublimated to reach to the substrate surface. The subsequent reaction of this oxide with atomic hydrogen (H) leads to the precipitation of pure W (due to the reduction process). The production of pure W powder (bulk) by reducing tungsten oxide powder using a stream of molecular hydrogen (H_2) and water vapor is known, although such processing has been found to be very slow and time consuming [9]. In the present case, the reduction process is characteristically different in nature. Firstly, there is no water vapor involved in the processing we describe here. Secondly, atomic hydrogen (H) is involved, which is much more efficient rather than molecular hydrogen (H_2). Finally, and most importantly, the present process leads to the formation of adhesive coating on given substrate rather than formation of powder (bulk). The role of atomic hydrogen as an efficient reducing agent has been studied in detail via extensive research on CVD diamond [11]. It is well established that the dissociation of molecular hydrogen (H_2) into atomic hydrogen (H) occurs for $T_F > \sim 1500$ °C, and this rate increases rapidly with filament temperature [12]. Atomic hydrogen plays key roles in the formation polycrystalline diamond [13]. In the present experiment also it plays a key role in the reduction of WO_3 and the formation of pure W. Thus, the result shown in Figure 1 confirms the occurrence of “redox reactions”. Indeed, one can expect competition between the rate of formation/sublimation of tungsten oxide at the filament surface vis-à-vis the rate of subsequent reduction due to atomic hydrogen, at the substrate surface. The dominance of a particular process depends upon different process parameters. In order to obtain pure W coatings, optimization of the oxygen concentration in the reaction gas vis-à-vis the filament temperatures is most important. This methodology leads to very exciting results, wherein we can obtain precipitation of very high-quality, faceted, microcrystalline W. It is necessary to keep the reduction process dominant so that conversion of oxide to pure W (or Mo) occurs continuously without accumulation of any oxide phase on the substrate.

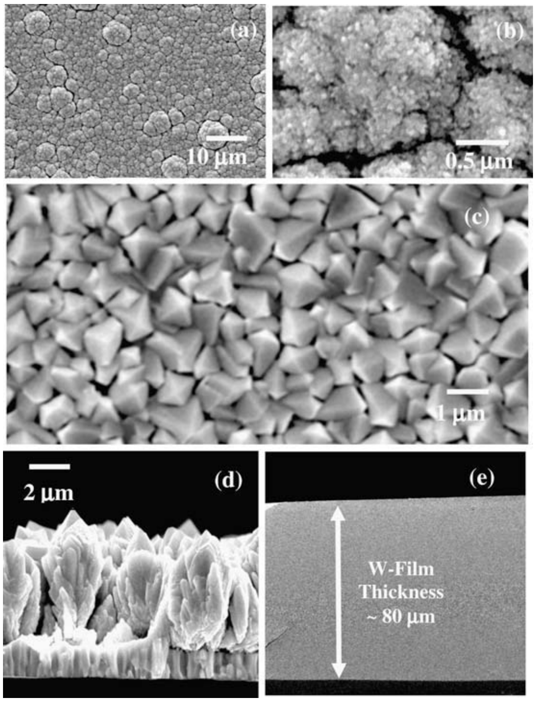

Figure 1. Scanning electron micrographs of tungsten coating obtained on silicon substrate: (a and b) at different magnifications, at nominally adjusted conditions; (c) at optimized conditions; (d and e) cross-sectional views of thin (showing columnar growth) and thick coatings, respectively.

Figure 1c shows a scanning electron micrograph of high-quality W coatings on silicon substrate processed at optimized conditions, i.e. $T_F \sim 1800$ °C, $T_S \sim 800$ °C, gas composition H_2:O_2 = 100:1. There is a precipitation of well-faceted W microcrystallites exhibiting pyramidal geometries with typical size ~1 µm. The coating is very uniform, dense and continuous throughout the sample area. As observed in Figure 1d, the cross-sectional view