

Research Article

Effect of Nitrogen Pressure on the Structure of Cr-N, Ta-N, Mo-N, and W-N Nanocrystals Synthesized by Arc Discharge

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Received 28 March 2011; Revised 10 June 2011; Accepted 5 July 2011

Academic Editor: Theodorian Borca-Tasciuc

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The effect of nitrogen pressure on the structure of Ta-N, Cr-N, Mo-N, and W-N nanocrystals formed in arc discharge process was investigated. At the nitrogen pressure of 5 ~ 20 kPa, the pure cubic-phase TaN and CrN nanocrystals were formed, whereas pure cubic phase of Mo₂N and W₂N cannot be obtained. A little of metal Mo and a mass of metal W were mixed with the products of Mo₂N and W₂N, respectively. At the nitrogen pressure of 30 ~ 50 kPa, subnitride Ta₂N and Cr₂N and metal Cr were gradually formed in the product; furthermore, the proportion of metal Mo and W increased in the product of Mo₂N and W₂N, respectively. It indicated that the low nitrogen pressure makes cubic mononitride formation favorable. We explain this experimental observation in terms of the evaporation rate of anode metal and the ionization of nitrogen.

1. Introduction

Transition metal nitrides are well known for having a number of technologically interesting properties: abrasive resistance, reflectance, hardness, electrical conductivity, inertness and diffusion resistance [1, 2]. These outstanding properties make them as bulk or thin film materials applicable to various fields such as high-temperature structural ceramics, catalysts, solar control coatings, hard phases in steels, drill bit, tool coating, interconnects, and diffusion barriers in microelectronics as well as decorative coatings and jewellery [3]. Recently, the nitrides of tantalum and chromium and its homologues molybdenum and tungsten have attracted great research attention due to their special properties of extreme hardness, high metallic conductivity, good thermal conductivity, corrosion resistance, and high melting points, so they were extensively applied in mechanical, tribological and catalyst fields [4–13]. It is known that ultrafine particles possess unique characteristics that cannot be obtained for conventional bulk materials. With the aim of developing advance materials, a number of studies on the synthesis of ultrafine particles or nanosized materials have been carried out actively in metal, alloys, and ceramics [14].

There has been an increasing interest in the synthesis of TaN, CrN, Mo₂N, and W₂N nanocrystals recently [15–21]. Of course, these nitrides are the most difficult to form by direct reaction through transition metal with nitrogen. This is because they exhibit the lowest reactivity towards nitrogen, the lowest stability, and the narrowest regions of existence in the phase diagrams. In addition, N₂ is very stable and inert due to having strong covalent bonds. Consequently, in order to enhance the diffusion of nitrogen atoms into the metal, the use of synthesis techniques (solid-state precursors, molecular precursors, etc.) has been explored to achieve faster reaction rates and to circumvent diffusion problems [15–21]. Usually, the kinetic limitations imposed by slow diffusion rates can be overcome by using higher reaction temperatures. The DC (direct-current) arc discharge is an important method to synthesize ultrafine nitride powder, because the plasma produced by discharging can provide the condition of a high temperature, which is responsible for very short reactive time, high chemical activity, and enhanced reaction kinetics. Furthermore, the large temperature grads during plasma irradiation open up the possibility of synthesizing high temperature metastable phases. TiN ultrafine particles have been prepared by DC arc discharge in nitrogen gas [10].

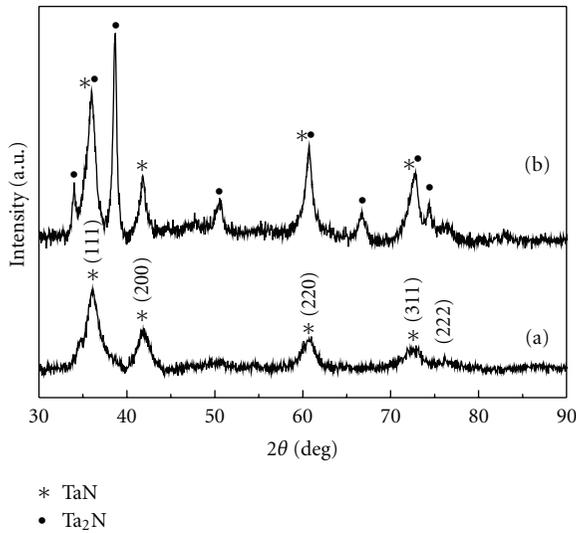


FIGURE 1: XRD patterns of the tantalum nitride powders synthesized at nitrogen pressures of (a) 10 kPa, (b) 40 kPa. The diffraction peaks marked as “*” and “•” correspond to the cubic TaN and hexagonal Ta₂N, respectively.

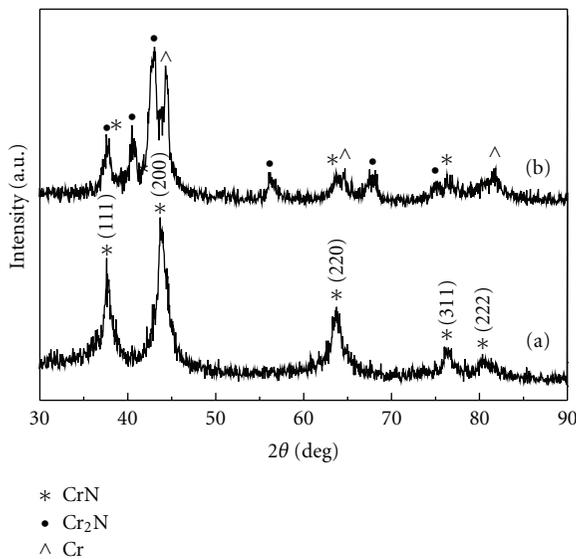


FIGURE 2: XRD patterns of the chromium nitride powders synthesized at nitrogen pressures of (a) 10 kPa, (b) 40 kPa. The diffraction peaks marked as “*”, “•” and “^” correspond to the cubic CrN, hexagonal Cr₂N, and metal Cr, respectively.

However, there are few reports that nitrides of tantalum and chromium and its homologues molybdenum and tungsten were synthesized by direct nitridation method. In this paper, we are interested to investigate the effect of nitrogen on the structure of transition metal nitride by considering the evaporation rate of anode metal and the ionization of nitrogen.

2. Experiments

The transition metal nitrides nanocrystals were synthesized by direct-current arc discharge apparatus. In brief, the pure

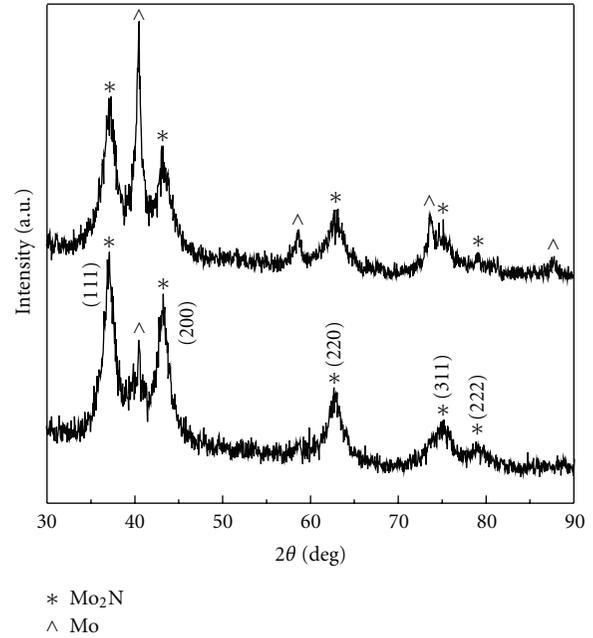


FIGURE 3: XRD patterns of the molybdenum nitride powders synthesized at nitrogen pressures of (a) 10 kPa, (b) 40 kPa. The diffraction peaks marked as “*” and “•” correspond to the cubic Mo₂N and metal Mo, respectively.

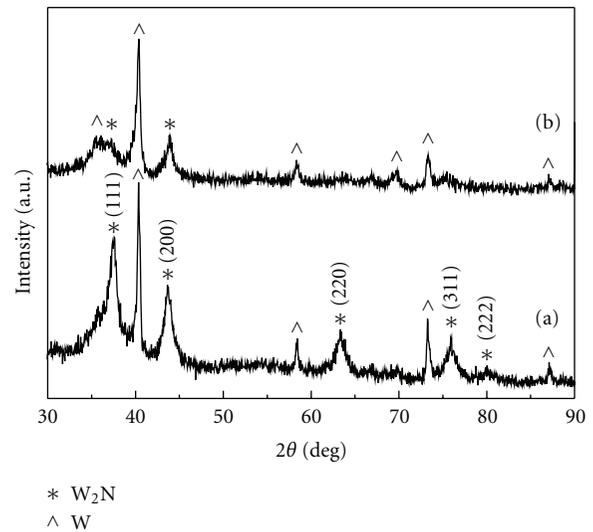


FIGURE 4: XRD patterns of the tungsten nitride powders synthesized at nitrogen pressures of (a) 5 kPa, (b) 40 kPa. The diffraction peaks marked as “*” and “•” correspond to the cubic W₂N and metal W, respectively.

metal W rod (3 mm in diameter, purity 99.99%) was used as the cathode. The anode metal (Ta, Cr, Mo, W) rod as raw material was fixed on a graphite column (30 mm in diameter) which was drilled 10 mm in diameter. The anode metal rod stretched out 20 mm above the graphite column which was located in a water-cooled anode copper crucible. The graphite column can prevent the melting metal from destroying the copper crucible. After the reaction chamber

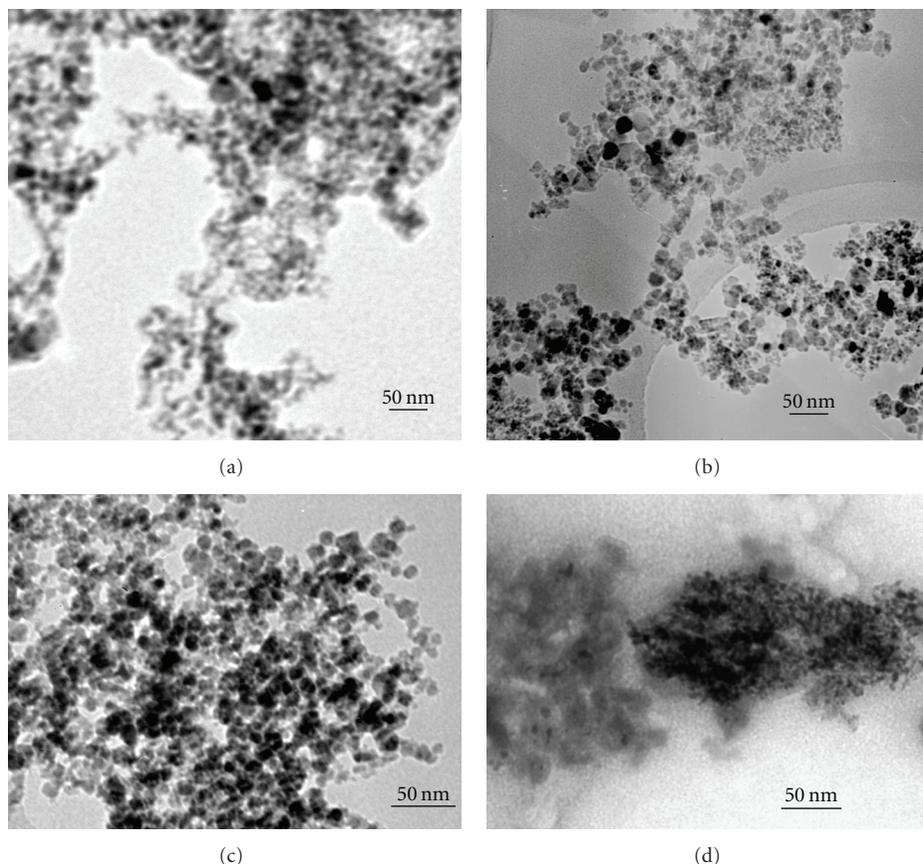


FIGURE 5: TEM images of as-synthesized (a) TaN, (b) CrN, and (c) Mo₂N nanopowders at the nitrogen pressure of 10 kPa and (d) W₂N at 5 kPa.

was first evacuated to less than 1 Pa (about 10^{-2} Torr), pure nitrogen gas was used as a reactant gas and a source of nitrogen plasma. In our DC arc-discharge system, before the arc was ignited, the gas pressure and current was set at 5–50 kPa and 100 A, respectively. At arc discharging, the DC voltage was controlled in the ranges of 30–50 V. In order to reach a high condensation rate of the particles, the collector used was cooled by water. The discharging process was maintained for 20 minutes. Finally, the products were passivated in 80 kPa argon gas about twelve hours.

The prepared powder was characterized by powder X-ray diffraction (XRD) using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) with a Rigaku Rotaflex diffractometer. The morphology and sizes of the powders were observed using transmission electron microscopy (TEM, Hitachi-8100, 100 kV). The surface composition of the products was analyzed by X-ray photoelectron spectra (XPS) recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K α X-ray as the excitation source.

3. Results and Discussion

Figures 1–4 show the XRD patterns of as-synthesized products of tantalum, chromium, molybdenum, and tungsten nitride at different nitrogen pressure. At relatively low nitrogen pressure range (5–20 kPa), cubic-structure TaN,

CrN, Mo₂N and W₂N were formed. These nitrides have similar XRD patterns. The broad diffraction peaks for every nitride can be indexed to the (111), (200), (220), (311), and (222) planes of NaCl-type (space group: Fm3m) structure. The lattice parameters $a = 4.317 \text{ \AA}$ for TaN, 4.121 \AA for CrN, 4.174 \AA for Mo₂N, and 4.140 \AA for W₂N calculated from the XRD patterns are slightly smaller than those of corresponding bulk materials (JCPDS card). This might be attributed to the effect of surface stress of the nanoparticles with small size. The broadening of the peaks implies that the average crystallite size of the powders is very small, and this was confirmed by subsequent TEM analysis. The single-phase TaN and CrN nanocrystals can be obtained at a range of 5–20 kPa, whereas pure phase of Mo₂N and W₂N cannot be obtained. There is a little Mo in the product of Mo₂N and a mass of W in the product of W₂N, respectively. This indicates that the metal Ta and Cr exhibit higher reactivity towards nitrogen in comparison with the Mo and W. When the nitrogen pressure increases to 30–50 kPa, the following occur. (1) The mixed phase of cubic TaN and hexagonal subnitride Ta₂N is clearly observed and the subnitride Ta₂N becomes the dominant phase, as shown in Figure 1(b). (2) The mixed phases of cubic CrN, hexagonal Cr₂N, and metal Cr were clearly observed. The Cr₂N becomes the dominant phase, as shown in Figure 2(b). (3) The diffraction peaks

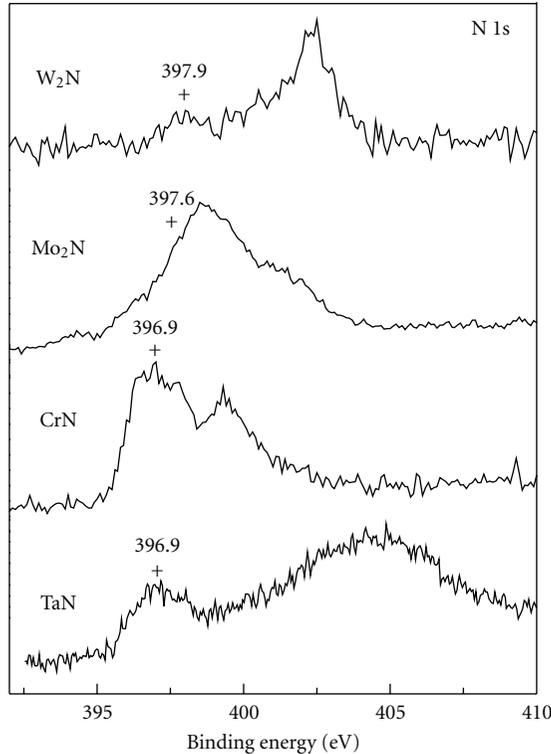


FIGURE 6: XPS spectra of the N 1s in TaN, CrN, MoN, WN nanocrystals.

of Mo become clearly strong, which indicates that the proportion of Mo increases in the mixed phase, as shown in Figure 3(b). (4) The diffraction peaks of W dominate in the XRD patterns of product, which indicates that there is a little W_2N in the product, as shown in Figure 4(b).

Figure 5 shows the TEM images of the powders prepared at low nitrogen pressure of 10 kPa. As can be seen in Figure 5, these TEM images indicate that as-synthesized nanoparticles with the sizes less than 10 nm mostly cluster together and have irregular shape.

The survey XPS spectra (not shown here) of all the samples indicate the presence of Ta, Cr, Mo and W and the surface contamination of C and O. The higher-resolution XPS spectra of the Ta, Cr, Mo, and W nitrides in the N 1s region are shown in Figure 6 with the main C 1s set to 284.8 eV as reference. The binding energy of N 1s in TaN (396.9 eV), CrN (396.9 eV), MoN (397.6 eV), and WN (397.9 eV) is consistent with the reported values of transition metal nitrides [7, 19, 22], suggesting formation of Metal-N bond. The other peaks around 400 eV in transition metal nitrides are caused by the adsorption of N-related groups (such as N^+ and NO) on the surface of nanocrystal. Furthermore, surface oxidation had occurred, so N/Metal stoichiometries at the surface region is only qualitative in nature. The peak areas and values of N 1s in nitrides reflect that the N/Metal stoichiometries are maximal in TaN and CrN, middle in MoN and minimal in WN.

In what follows, we explain the counterintuitive phenomena that low nitrogen pressure enhances the nitridation of metal in our experiment and that we analyze the effect of

nitrogen pressure on the structure of metal nitrides. The formation of these nitrides can be understood in terms of the homogeneous gas phase “nucleation and growth” under a highly nonequilibrium arc-plasma process. The ionic and/or atomic species of metal generated from the anode surface react with a substantial population of nitrogen ions in high-density plasma. At low nitrogen pressure, the evaporation rate of anode metal is low [23], leading to formation of small metal particles due to the reduction of collision’s probability. These small metal particles having high chemical activity can react completely with the nitrogen ions or nitrogen gas. Moreover, nitrogen can be ionized easily due to the increased of N radicals’ mean free path at low nitrogen pressure, which results in enough active nitrogen radicals for the reaction with metal particles. These factors result in complete nitridation of Ta and Cr particles, forming cubic TaN and CrN nucleus. In addition, these factors also enhance the conversion of Mo to Mo_2N and W to W_2N , respectively. These nucleated crystals collide and grow up, finally, the nanoparticles are retained upon quenching on the water-cooled collector. It was worthy of note that most nanoparticles cannot also grow beyond a certain size due to the reduction of collision’s probability in low nitrogen pressure. This can be confirmed by TEM images in Figure 5. At the relatively high nitrogen pressure, the evaporation rate of anode metal is gradually accelerated and a mass of metal particles is formed in nucleation region. The metal particles with a large size are also formed due to the increase of collision’s probability. The large metal grain might suppress reactive ability with the N radicals. Furthermore, the active nitrogen ions/radicals are correspondingly less in comparison with increased metal particles, because the frequent collision of nitrogen ions enhanced the combination of nitrogen. Consequently, the subnitride and metal nanocrystallines form gradually and their amount increases gradually, at the same time the amount of cubic nitrides reduces. Single-phase cubic TaN and CrN can be effectively obtained at low nitrogen pressure. However, there are a little Mo in the product of cubic Mo_2N and a mass W in the product of W_2N , respectively. It is most likely that TaN and CrN are more thermodynamically stable than the Mo_2N and W_2N in high temperature plasma and that the W_2N is most thermodynamically unstable in these nitrides [24].

4. Conclusions

In conclusion, the relatively low nitrogen can promote the formation of cubic-structure TaN, CrN, Mo_2N , and W_2N nanocrystals. The size of most nitrides particles is less than 10 nm. The diffusion of nitrogen atoms into the metal was lowered with the increase of nitrogen pressure. The evaporation rate of anode metal and the ionization of nitrogen at different nitrogen pressure can be responsible for the formation of different structure nitride and the proportion of every phase in the mixed phases. The low-pressure synthesis of cubic transition metal nitrides in temperature plasma should be beneficial to the formation of refractory metal nitride with nitrogen-rich.

Acknowledgments

This paper was financially supported by the National Natural Science Foundation of China (no. 11004138) and the Scientific Research Foundation of the Technological Bureau of Liaoning Province (no. 20090908).

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