A Thermal Reduction–Nitridation Route to Nanocrystalline Chromium Nitride (CrN)

Jianhua Ma* and Yihong Du
Wenzhou University, Wenzhou, Zhejiang, 325035, P. R. China

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Nanocrystalline CrN was synthesized via thermal reduction–nitridation route by the reaction of $CrCl_3$ with NH_4Cl and Na in an autoclave at 400 °C. X-ray powder diffraction pattern indicated that the product was cubic CrN. An atomic ratio of Cr to N of 1.08:1 was determined from X-ray photoelectron spectra. Transmission electron microscopy image showed that the sample consisted of particles with the diameters of 20–40 nm.

Nitrides exhibit an interesting mixture of physical and chemical properties that makes them promising candidates for many technical applications. As one of the most important nitrides, chromium nitride (CrN) with the cubic rock-salt structure has been known as a technologically important material because of its hardness and excellent corrosion, oxidation, and wear resistance.[1,2] In addition, it shows a paramagnetic to antiferromagnetic transition, with a Néel temperature T_N of 273–290 K.[3] So it can find applications in many fields. Especially, CrN has been successfully used as a protective coating material for many applications, such as wear- and corrosion-resistant coatings for various materials, tools, machines parts, and so on.[4] In other fields, the CrN films may also be used for diffusion barriers[5] and solar selective absorbers.[6]

Traditionally, chromium nitride could be prepared through various methods, such as ion plating,[7] reactive sputtering,[8] and reactive evaporation.[9] Recently, benzene-thermal route to nanocrystalline chromium nitride was presented by Qian.[10] But from the results of the experiment, there exists a small amount (less than 20%) of amorphous carbon due to the carbonization of benzene at high temperature. Zhang[11] synthesized nanocrystalline chromium nitride in a reactor consisting of a quartz tube by the reaction of $CrCl_3$ with NH_3 flow. Another reference[12] reported that CrN powder was also successfully synthesized by the direct nitridation of nanosized Cr_2O_3 powder in a flow of NH_3.

In this paper, we have developed a convenient low-temperature method to prepare nanocrystalline CrN, which need not continuously providing the NH_3 flows. Nanocrystalline CrN has been synthesized via a thermal reduction–nitridation route by the reaction of $CrCl_3$ with NH_4Cl and Na in an autoclave at 400 °C. The reaction can be formulated as follows,

$$CrCl_3 + NH_4Cl + 4Na \rightarrow CrN + 4NaCl + 2H_2$$

All the reagents were analytically pure. All the manipulations were carried out in a dry glove box with flowing nitrogen gas. In a typical procedure, 0.01 mol of anhydrous $CrCl_3$, 0.01 mol of NH_4Cl and 0.04 mol of metallic sodium were placed into a stainless steel autoclave of 50-mL capacity. The autoclave was sealed under argon atmosphere and maintained at 400 °C for 10 h, followed by cooling to room temperature in the furnace. After that, the product was washed several times with absolute alcohol, 0.5 mol/L HCl and distilled water in turn to remove impurities. The final product was vacuum-dried at 60 °C for 12 h. A black product was obtained.

The powder product was analyzed by powder X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku γA) using Cu Kα radiation (wavelength $\lambda = 1.54178$ Å), and transmission electron microscopy (TEM) on a Hitachi 800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Mg Kα X-rays as the excitation source. The thermal analysis was performed on a thermal analyzer (Model: TA-50) below 1000 °C in air at a rate of 10 °C/min.

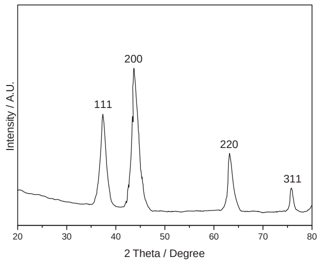

Figure 1. XRD pattern of the as-prepared sample.

A typical XRD pattern of the product is shown in Figure 1. There are four diffraction peaks on this pattern. And all these diffraction peaks at different *d* spacing can be indexed as (111), (200), (220), and (311) reflections of NaCl-type CrN (JCPDS No. 76-2494). The lattice parameter is calculated to be $a = 4.112$ Å, which is close to the reported value of $a = 4.140$ Å. No impurity XRD peaks, such as Cr, Cr_2O_3, CrO_2, CrO_3, and other chromium oxides, are detected in the experimental range. The crystallite size is estimated to be 30 nm, according to (200) reflection by the Debye–Scherrer equation with a shape factor of 0.9.

Figure 2 gives the XPS spectra of the as-prepared CrN sample. The N1s and Cr2p core-level regions are examined. The binding energies of N1s and Cr2p3/2 are found at 396.7 and 575.6 eV. These correspond well with the reported binding energies for CrN,[13] confirming the formation of CrN. On the basis of the calculation of the peak areas, the mole ratio of Cr/N is obtained to be 1.08 and close to the chemical stoichometry of CrN.

Figure 3 shows the TEM image and the selected area transition electron diffraction pattern. On the TEM, the product exhibits slightly agglomerated particle morphology owing to the fine size of the particles. The primary particle size is estimated in the range of 20 to 40 nm in diameter, and the average diameter is about 30 nm, which is close to the calculated value from the XRD pattern. While the diffraction pattern is composed of three obvious concentric diffuse diffraction rings on the TED pattern. All these rings are indexed as (111), (200), and (220). And the TED pattern can also confirm the nanocrystallinity of CrN, in

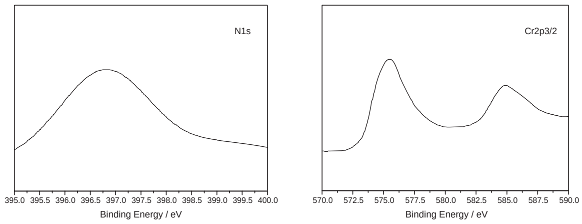

Figure 2. XPS spectra of the as-prepared CrN sample.

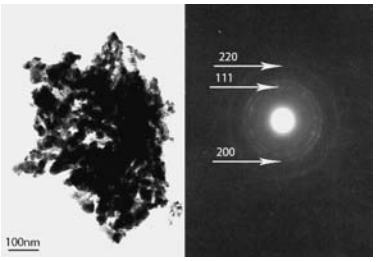

Figure 3. TEM and TED images of the as-prepared sample.

which the diffraction ring diameters and intensities again correspond well to those of CrN phase.

In our experiments, as the temperature rose, NH_4Cl could decompose generating NH_3 and HCl gases above 338 °C. So the pressure in the autoclave increased up to 2.5 MPa, as estimated by the ideal gas law from the decomposed NH_3 and HCl gases. At the reaction temperature, $CrCl_3$, NH_3 and metallic sodium could react with each other to produce CrN. The high pressure in the autoclave would be helpful for reducing the reaction temperature and enhancing the reaction speed. The produced HCl gas was strongly absorbed by the metallic sodium to form NaCl and H_2. Therefore, the possible thermal reduction–nitridation reaction might be expressed as follows;

$$NH_4Cl \rightarrow NH_3 + HCl$$

$$2CrCl_3 + 2NH_3 + 6Na \rightarrow 2CrN + 6NaCl + 3H_2$$

$$2Na + 2HCl \rightarrow 2NaCl + H_2$$

The influences of the reaction temperature and time on the formation of nanocrystalline chromium nitride were also investigated. When the temperature was below 300 °C, crystalline CrN could not form. An increase of the reaction temperature over 500 °C resulted in an increase of crystalline size more than 80 nm. An optimum reaction conditions for the formation of nanocrystalline CrN was 400 °C. The reaction was usually incomplete and the crystallinity was very poor in too short time, such as <3 h. Varying the reaction time in the range of 6–12 h at 400 °C did not significantly affect the crystallinity. Thus, the optimal reaction parameters were at the temperature of 400 °C and for 10 h.

Oxidation test was performed from room temperature to 1000 °C. Figure 4 shows the TGA/DTA curves of the sample heating at temperatures below 1000 °C under flowing air. From room temperature to 600 °C, the weight of the sample has not changed significantly, indicating its good thermal stability below 600 °C. When the temperature is above 600 °C, the weight of the sample increases gradually, meaning the beginning of the oxidation due to the diffusion of the oxygen[14] through the protective layer. Upon further heating at 950 °C, the weight basically has not changed. This is because the sample has been oxidized to Cr_2O_3 and the CrN is no longer present.[14]

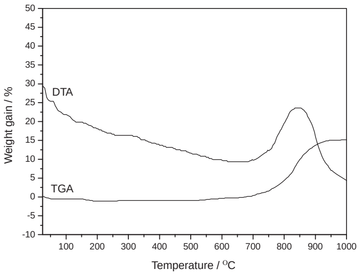

Figure 4. TGA and DTA curves of the as-prepared sample.

In summary, nanocrystalline CrN has been prepared via a thermal reduction–nitridation route in an autoclave at 400 °C. The product has the cubic CrN structure, and smaller size and high quality. This method is very convenient (without NH_3 flow), and needs lower temperature and shorter time. The prepared product has good thermal stability below 600 °C.

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