

SYNTHESIS OF NITRIDES BY MECHANICAL ALLOYING

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ABSTRACT

A simple synthesis method for producing bulk metal and metalloid nitrides is reported. The process involves room temperature ball milling of elemental metal or metalloid powder in a molecular nitrogen atmosphere. The nitrides obtained in this work are: TiN, ZrN, VN, BN, Mo₂N, Si₃N₄, AlN, Cu₃N, Mg₃N₂, W₂N and WN. The influence of milling conditions on the end milling product has been studied. Structure evolution has been monitored by X-ray diffractometry.

1. INTRODUCTION

Metal and metalloid nitrides have considerable interest because of desirable properties such as extreme hardness, high temperature stability, high thermal conductivity and high corrosion resistance. They are usually synthesized on a commercial scale by direct reaction of the metal with nitrogen at high temperature and pressures. This process is carried out under almost isothermal conditions and the end product is often unhomogeneous and can contain unreacted material. There are a number of conventional nitriding processes, such as gas and salt bath nitriding, ion nitriding or deposition methods that can be applied to create nitrides in thin surface layers. Metal nitrides can also be synthesized using chemical reactions or through solid-gas combustion reactions. All of these processes give nitride coatings rather than bulk nitrides.

In this paper, a new and simple synthesis method for producing metal and metalloid nitrides is reported. It has been found that direct reaction of metals or metalloids with nitrogen can be achieved at room temperature during ball milling of elemental powders if a sufficient amount of molecular nitrogen (N₂) is introduced constantly into the ball mill. The milling process is carried out in a ball mill specifically designed for enhancing solid state reactions between different species [1,2].

2. EXPERIMENTAL

In this experiment, powders of Co, Fe, Mo, Ni, Ti, V, Zr, Cr, Al, Ta, W, Cu, Mg, B and Si with particle sizes of 50-200 μ m and a minimum purity of 98% were used.

The alloying process was performed using a planar-type ball mill that consists of a few hardened steel balls confined in a stainless-steel, horizontal type cell [1,2]. The ball movement during the milling process is confined to the vertical plane by the cell walls and it is controlled by an external magnetic field. The intensity and direction of the field can be externally adjusted allowing the ball trajectories, impact energy and the shearing energy to be varied in a controlled manner (Fig.1) [1,2].

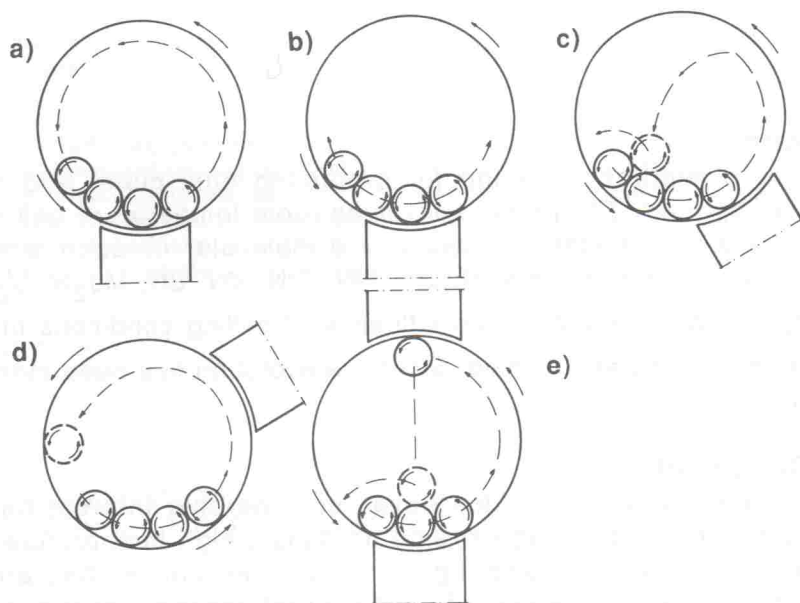


Fig 1. Schematic diagram of the ball milling device with controlled ball movement.

Modes of operation of the ball mill:

- a) high-energy mode, high rotation frequency,
- b) low-energy mode, low rotation frequency,
- c) high-energy mode, two points of equilibrium,
- d,e) high-energy mode, intermediate rotation frequency.

During milling a constant pressure of high purity (99.99%) nitrogen (N_2) was maintained. The progress of milling was monitored by X-ray diffractometry (XRD) using $CoK\alpha$ radiation. X-ray diffractograms were taken in the range of 2θ from 10-110 deg. The as-milled powders were pressed into pelles and annealed in vacuum at 800°C for 1 hour and analysed by X-ray diffractometry.

3. RESULTS

The transformation of elemental Ti powder into TiN compound is shown in Fig.2. After 12 hours of milling; broadened Ti peaks are seen (Fig.2a). The first visible changes in the XRD pattern, indicating presence of the TiN phase, were noticed after 36 hours of milling (Fig.2b). After 60 hours of milling, the fully developed structure of TiN is seen (Fig.2c). The broadening of the characteristic XRD peaks is due to the very fine grain size. Using the Scherrer formula, the calculated grain size is 90Å. This result indicates the nanostructural character of the ball milled compound.

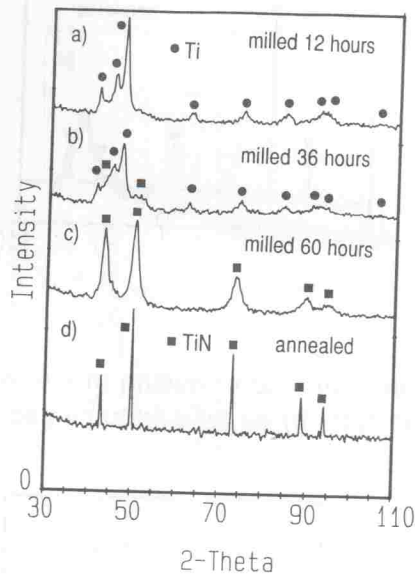


Fig. 2. XRD patterns of Ti milled in nitrogen atmosphere, a) for 12 hours, b) for 36 hours, c) for 60 hours, d) as (c) and annealed at 800 °C for 1 hour.

In order to determine the single phase structure of the as-milled powder pressed pellets were annealed under vacuum at 800°C for 1 hour. The resulting XRD pattern is seen in Fig.2d. Only a full set of XRD peaks resulting from a TiN phase is seen.

Similar nitride formation behaviour has been found for V and Zr. Typical XRD patterns of the end milling product are seen in Figs.3 and 4. The grain size of as-milled VN and ZrN samples were found to be 110Å and 140Å respectively. The colour of the as-milled TiN and ZrN powders was black presumably as a result of very small grain size. However, annealed pellets show characteristic golden-yellow colour.

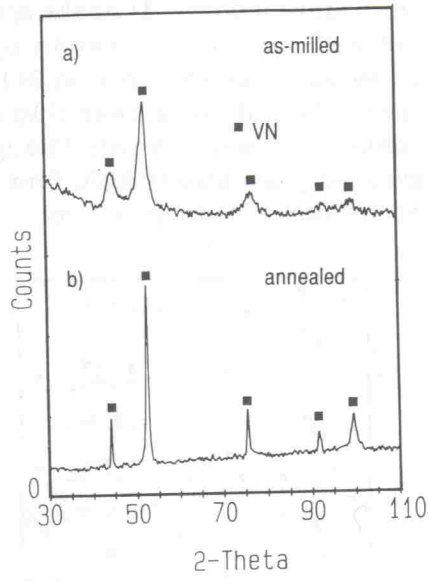


Fig. 3. XRD patterns of V after milling in nitrogen atmosphere, a) as-milled sample, b) as (a) and annealed at 800°C for 1 hour.

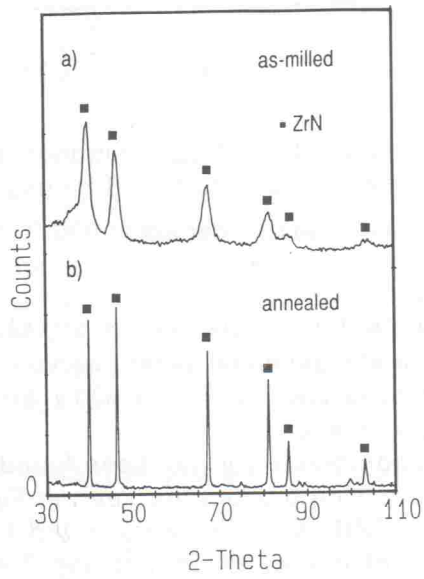


Fig. 4. XRD patterns of Zr after milling in nitrogen atmosphere, a) as-milled sample, b) as (a) and annealed at 800°C for 1 hour.

A different transformation process was observed during milling of polycrystalline boron. After 140 hours of milling, structure was developed with an XRD pattern which does not show any peaks due to presence of crystalline phase (Fig.5a). Presumably it indicates amorphous like structure. However, the XRD pattern of the annealed sample can be matched only with BN structure. Although the XRD peak intensities are slightly different from those reported in the XRD powder diffraction file [3], the peak positions indicate clearly the presence of a BN compound.

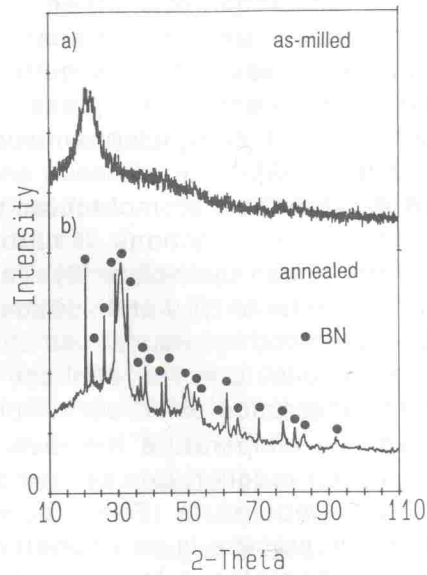


Fig. 5. XRD patterns of B milled in nitrogen atmosphere, a) as-milled sample, b) as (a) and annealed at 800°C for 1 hour.

In contrast to the above results, only partial transformation to a nitride phase was achieved after prolonged milling of Mo, W and Si for 300 hours. After 300 hours of milling of Mo in N_2 , the XRD pattern show broadened Mo peaks only. The grain size (150\AA) and characteristic asymmetry of the XRD peaks indicates the nanostructural character of the sample. More or less similar XRD patterns were obtained for Cr, W and Si. The result of annealing is to produce the following phases: Mo+ Mo_2N , Si+ Si_3N_4 , W+ W_2N +WN and Cr+ Cr_2N +CrN. Under the same milling conditions no reaction between Fe, Co, Ni and N_2 was found. In these cases, after 300 hours of milling, the XRD patterns show only slight broadening of Fe, Co, and Ni peaks. The annealed samples did not show any traces of nitrides [4]: To

suppress excessive cold welding, a very low energy milling condition was selected for Al, Cu and Mg (shearing action predominant, Fig.1b). In this work the following nitrides have been synthesized: AlN, Cu₃N and Mg₃N₂.

Further detailed results of these materials will be published elsewhere.

4. DISCUSSION

In spite of over 30 years of very active research in the field of surface chemistry and catalysis the precise role of the surface condition and imperfections, near surface defects and stress/strain relations in the kinetics of gas adsorption and reaction is still not clearly understood [5,6]. However, it is known that adsorption of nitrogen onto rough metal surfaces is many times higher than on perfect surfaces [7]. Also, the effect of crystal surface structure on adsorption is quite dramatic. The rate of adsorption of nitrogen on different crystal planes is very different. It has been found, for example, that nitrogen chemisorbs slower by selected planes eg. W(110) [6], Pd(111) [8].

Surface induced dissociation of molecular nitrogen must play an important role in surface-related reactions. If nitrogen comes into contact with a clean metal surface it can dissociate [9]. The rate of dissociation is strongly dependent on the material type and surface condition. Nitrogen that has been dissociated is absorbed by metals (and subsequently reacts) much more rapidly than in molecular form. All of these processes are strongly temperature dependent. Adsorption of nitrogen increases with temperature up to 400°C but above this temperature the reverse process, desorption, may occur [10,11]. Also, the reaction rate of nitrogen with metals (to form nitrides) increases with temperature. The precise role of near-surface defects and stresses in this process is only superficially known.

The milling process generates a large number of new, rough, and, presumably highly reactive surfaces which are freshly exposed to molecular nitrogen. The continual creation of such surfaces may substantially enhance the adsorption and reaction of nitrogen. However, the precise mechanism by which nitrogen adsorbs (and reacts) on metal surface during milling is not yet clear. One can not, that, the locally increased temperature during milling must enhance the rate of adsorption and reaction. Indeed, during impact a locally increased temperature of up to 300°C [12] might be expected. This temperature rise not only aids adsorption and reaction but can also promote diffusion to supply a source of nitrogen below the surface of individual particles. The role of surface stress, plastic deformation during the milling process and defect creation and migration on nitrogen diffusion and reaction is not understood. However, there must be strong driving forces operative during the milling process to account for the high degree of intermixing and reaction that is observed to take place at such low temperature. Indeed, deep penetration of nitrogen into stainless steel during wear testing of nitrided surfaces has previously been observed, suggesting that stress, deformation and defects can dramatically enhance

nitrogen diffusion [13].

During mechanical alloying of pure metal powders a large negative heat of mixing can provide the driving force for solid state reactions[14]. In the case of alloying elemental powders with nitrogen we are clearly dealing with a more complicated process in which absorption plays a significant role. However, in any event the environment occurring during milling must be favourable for promoting the nitriding reaction and heats of adsorption and mixing would seem to be most relevant parameters.

The results obtained in this work are in good agreement with the variation of the heat of adsorption (H_{ads}) of N_2 by different transition metals [15]. A decrease of the binding energy along a transition-metal series, due to the progressive filling of the metal d, band has been reported [16]. The heat of adsorption is a decreasing function, going from left to right, across a transition metal series. Moreover, dissociative chemisorption occurs on metals on the left of the transition series, whereas on the right, one observes a tendency for molecular adsorption [9]. These properties of transition metals may explain why, Fe,Co and Ni nitrides are difficult to obtain.

Another of our experimental findings is also consistent with the above properties. The formation of Ti and Zr nitrides is only slightly sensitive to the variation in milling conditions as compared with the formation of V,Mo and W nitrides. It was found that the end product for milling of Ti and Zr is not sensitive to the ball movement pattern (Fig.1) and is affected mainly by the amount of N_2 which is delivered to the milling cell. If the amount of gas is insufficient enough $M(\text{metal})+MN$ structures can be created. This behaviour is consistent with heat of adsorption for Ti and Zr. Different behaviour was observed during milling of V, Mo, and W. In this case, the end product is dependent not just on the amount of gas but also by the milling condition. Using different milling parameters, rotation rate, pulling force, ball movement pattern, nitrides of different type M_xN_y may be created. Moderate milling conditions (modes c and d in Fig.1) were the most effective in the formation of V,Mo, and W nitrides.

5. CONCLUSIONS

To the authors knowledge, this is the first time that metal and metalloid nitrides have been synthesized by the simple ball milling of elemental powders under an atmosphere of molecular nitrogen. This method is particularly attractive for two reasons: 1) it has potential as a practical technique for the large scale manufacture of various nitride powders in a very simple way, 2) it is attractive for basic research as a means of studying interactions and reactions between solids and gases.

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