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Plasma Nitridation of Metal Oxides

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The synthesis of ceramic materials is often plagued by extremely long reaction times caused by slow diffusion rates in solids. One area in which diffusion limitations are particularly severe is the synthesis of metal nitrides. Many transition metals readily form nitride coatings through which the diffusion of nitrogen atoms is notoriously slow.[1,2] Usually, the kinetic limitations imposed by slow diffusion rates can be overcome by using higher reaction temperatures. However, higher reaction temperatures can lead to product decomposition into the metal and nitrogen gas, as well as, to higher costs for manufacturing and processing equipment. Consequently, the use of alternative synthesis techniques (solid-state precursors, molecular precursors, fluxes, etc.) have been explored to achieve faster reaction rates and to circumvent diffusion problems.[3−7] In addition, some research groups have attempted to find synthetic approaches that utilize more active nitrogen species (metal amides, ammonia, nitrogen plasmas, etc.) in the hope of lowering the reaction temperature and/or reaction time.[3−12]

In the past, much of our work has centered on the use of nonequilibrium ammonolysis reactions of ternary transition-metal oxide precursors to form ternary transition-metal nitrides, which are unattainable by other routes. This approach has lead to the synthesis of a number of new ternary nitride materials, such as $(Fe_{0.8}W_{0.2})WN_2$,[4] $FeWN_2$,[13] $MnMoN_2$,[13] Fe_3Mo_3N,[14] α- and β-$MnWN_2$,[15] and $M_5N_{6-\delta}O_y$ (M = Ta, Nb).[6] However, many potentially interesting reactions have been precluded by a large positive free energy of reaction. For example, for the reaction

$$Al_2O_3 + 2NH_3 \rightarrow 2AlN + 3H_2O$$

ΔG_{rxn} has been calculated to be +223 kJ/mol at 1000 K.[16] In addition, kinetic barriers further limit the number of binary nitrides which can be synthesized through ammonolysis of the oxide. ΔG_{rxn} for the reaction

$$3TiO_2 + 4NH_3 \rightarrow 3TiN + 6H_2O + {}^1/_2N_2$$

has been calculated to be only +24.1 kJ/mol at 1000 K and becomes negative at higher temperatures.[16] However, despite the negative free energy of formation, kinetic limitations imposed by the formation of a nitride coating on the surface of the TiO_2 particles make this ammonolysis reaction too slow to be practical except for very high surface area precursors. As a result, only a small portion of the periodic table contains elements whose oxides are viable candidates for conversion into nitrides by ammonolysis reactions.

In an effort to explore more active nitrogen species that might lead to faster synthesis times or new nitride phases, we have been exploring the use of microwave-generated N_2/H_2 plasmas as synthetic tools. An extension of earlier work utilizing microwave heating to effect the synthesis of binary nitrides such as TiN,[12] Cr_2N,[12] and AlN[11] is the reaction of a metal oxide in a microwave-generated N_2/H_2 plasma. If the N_2/H_2 plasma is allowed to flow across the reactant, oxygen containing species which are evolved can be swept away by the plasma, and could provide additional driving force for the reaction. In addition, in a plasma there exists a high concentration of H^+ and N^+,[17] which are rapidly accelerated by the electric component of the microwave field. These cations would bombard the metal oxide surface, roughing the surface, and causing the release of oxygen from the precursor material. Together with the highly reactive nitrogen and hydrogen species and the high concentration of free electrons in the plasma, pseudo-ammonolysis reactions can be achieved which could effect reactions that would be difficult at best under ordinary ammonolysis conditions.

To test this hypothesis, TiO_2 (Alfa, 99.9%) was placed in an alumina boat under 5 Torr of flowing forming gas (5% H_2/95% N_2). The sample is heated under a N_2/H_2 plasma which is formed using a 1.2 kW microwave source (Cober Electronics) equipped with a plasma applicator. The titania is heated for 12 h, ground, and reheated for an additional 12 h. The product is a golden colored powder identified as TiN by powder X-ray diffraction (Figure 1). The calculated ΔG_{rxn} for the corresponding ammonolysis reaction at 1000 K is +24.1 kJ/mol K.[16] Although the free energy of formation can be forced less than zero through higher reaction temperatures and low partial pressures of water, kinetic barriers for the diffusion of nitrogen atoms through the TiN skin formed on the surface of the TiO_2 particles make conventional ammonolysis routes nearly impossible. However, by using a N_2/H_2 plasma, complete conversion of the oxide precursor into TiN can be

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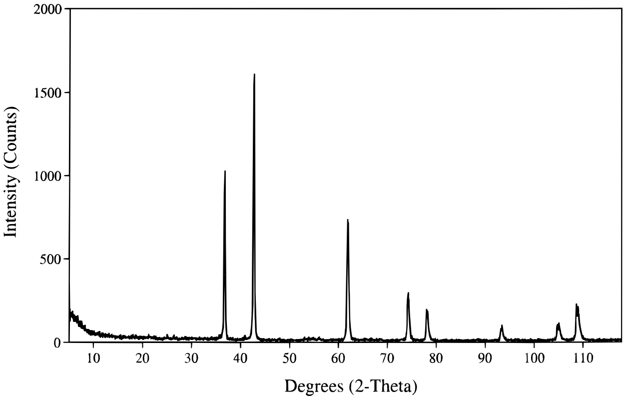

Figure 1. Powder X-ray diffraction pattern of TiN made by plasma nitridation of TiO_2.

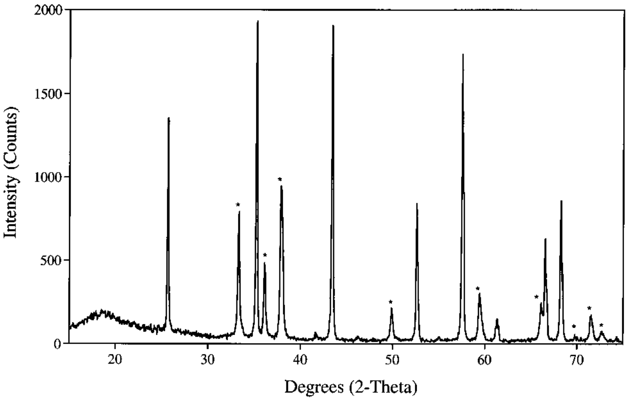

Figure 2. Powder X-ray diffraction pattern of AlN and Al_2O_3 made by plasma nitridation of Al_2O_3. * = AlN.

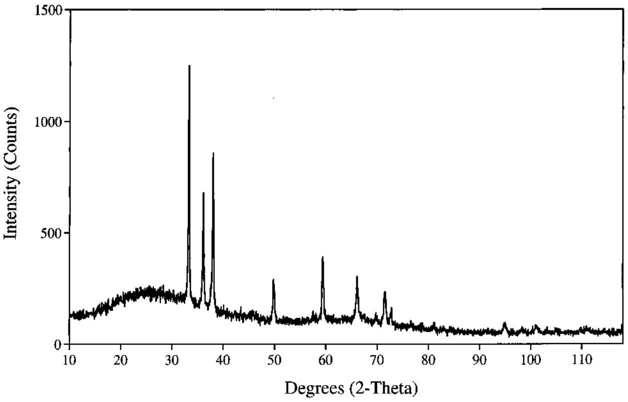

Figure 3. Powder X-ray diffraction pattern of AlN made by plasma nitridation of $Al(OH)_3$.

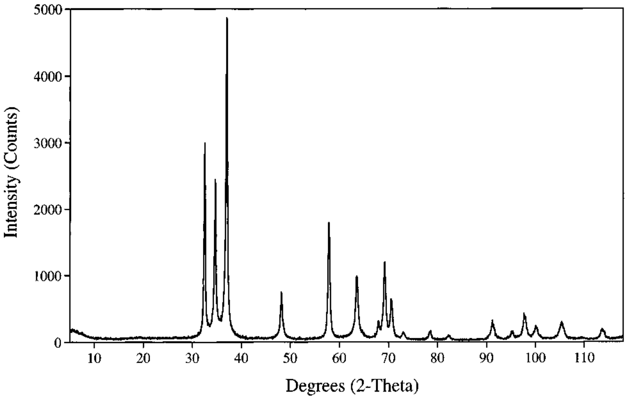

Figure 4. Powder X-ray diffraction pattern of GaN made by plasma nitridation of Ga_2O_3.

obtained, even using low surface area powders. Interestingly, the lattice parameters of TiN made by the reaction of TiO_2 with a N_2/H_2 plasma (a = 4.241(1) Å) are nearly identical with those reported for TiN (a = 4.241(1) Å[18]), indicating a low residual oxygen content.

Aluminum oxide (Aesar, alpha phase, 99.99%) can be reacted under similar conditions to yield a mixture of Al_2O_3 and AlN. Since Al_2O_3 is insulating, nitrogen plasmas are not readily ignited over the sample. However, once the plasma is ignited using a small amount of titanium metal powder located in an adjacent reaction vessel, it can be sustained in the plasma applicator and the alumina sample can be moved into the plasma. ΔG_{rxn} for the ammonolysis reaction of Al_2O_3 at 1000 K is substantially higher (223 kJ/mol K[16]) than for the conversion of TiO_2 to TiN. Even after 6 heatings of 24 h with intermediate grinding, Al_2O_3 is only partially converted into AlN by powder X-ray diffraction (Figure 2). However, if $Al(OH)_3$ is used as the starting material, complete conversion to AlN can be obtained in less than 24 h (Figure 3). The unusual background in Figure 3 arises from clay used in the mounting of the sample.

Gallium oxide (Johnson-Matthey, 99.999%) can be reacted under similar conditions to yield GaN (Figure 4). Powder X-ray diffraction analysis of the GaN product confirms the presence of the GaN structure type. However, the product is light yellow, suggesting the presence of small amounts of oxygen. Using the method of Elder and DiSalvo,[16] ΔG_{rxn} for the ammonolysis reaction of Ga_2O_3 at 1000 K (227.9 kJ/mol) is found to be comparable to that for the conversion of Al_2O_3 to AlN (223 kJ/mol).

Our estimates of the reaction temperatures are rather approximate, consisting primarily of estimates derived from experience with materials which heat sufficiently to melt in the microwave. The uncertainty in temperature determination leads to the question as to whether a microwave nitrogen plasma actually aids in nitride formation or if plasma heating merely allows access to temperatures at which nitride formation becomes thermodynamically favorable. On the basis of thermodynamic data reported by Elder et al., the ammonolysis reaction of Al_2O_3 to form AlN becomes thermodynamically favorable at 2686 K, an unlikely temperature for an insulating or semiconducting material to achieve through microwave heating. Therefore, the presence of the nitrogen/hydrogen plasma undoubtedly helps to overcome the large thermodynamic barrier for the formation of AlN. The enhanced nitridation in a nitrogen/hydrogen plasma is not unexpected. Although the conversion of the above-mentioned oxide materials into the corresponding nitrides through ammonolysis is thermodynamically unfavorable, by using a nitrogen/hydrogen plasma, the reaction pathway is changed. In a nitrogen/hydrogen plasma, the oxide reactant is exposed to energetic electrons and cationic species. The energy contained in these species appears to be enough to disrupt the Al−O bonds in the material and make nitridation possible.

Besides the obvious application of these techniques to the synthesis of bulk nitrides from inexpensive oxide

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starting materials, the results presented in this communication have important applications in the processing of nitride materials. One common contaminant in all nitride materials is oxygen, especially as oxide coatings on nitride films. Our results indicate that residual oxygen can be removed from refractory nitrides using a nitrogen/hydrogen plasma under flow through conditions. Even oxides for which conversion to the nitride using ammonia is difficult can be easily and quickly converted to a nitride product.

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