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To cite this article: C Guillaume et al 2008 J. Phys.: Conf. Ser. 121 092005

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Synthesis of metal-nitrides using high pressures and temperatures

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Abstract. Technologically, high density nitrides are showing promise for both ceramic and electronic applications. In a laser-heated diamond cell we prepare high density metal-nitrides by reaction of the nitrogen pressure medium with an elemental substrate. Two of our objectives are to develop criteria governing whether denser than ambient nitride phases will form, and to in particular establish the parameters required for synthesis in a multianvil press using elemental starting materials. We have already synthesized transition metal nitrides in a multianvil press using elemental starting materials, including hexagonal nickel nitride and alkali rhenium nitrides. Unlike previous metals, we also report that Cu does not form a nitride after heating with NaN₃ at 2000 K and 20 GPa. Notably, Cu₃N is a semiconductor exhibiting weak directional bonds, whereas the immediately adjacent lower atomic number systems are metallic interstitial nitrides. We also briefly mention our work on processing high pressure and temperature recovered reaction products with focused ion beam methods for tailored characterization using electron microscopy.

1. Introduction

Novel dense nitrides in a laser-heated diamond cell, have been optimally prepared by heating elements in the presence of a nitrogen pressure medium[1,2]. In piston-cylinder or multianvil presses, confining a nitrogen medium is difficult. Thus synthesis of dense nitrides there, is typically achieved by using carefully prepared nitrogen containing precursors that can then be compressed and heated without the need for a nitrogen pressure medium. This approach is not always (or at all) feasible as such precursors are not always available. We are thus exploring the parameters of synthesis in a multianvil apparatus where elements can still be used as starting materials together with azides, as nitrogen providers. Broadly, this requires addressing a number of issues including whether starting materials react with the capsule material, and/or with the metal azide provider and at what temperature, whether such reactions and their associated temperature depend on pressure, and what these additional structures formed are, and at what pressure, and what the minimum temperature required for reaction is and how this constrains the maximum pressure we can achieve.

In this study we investigate the effect of high pressure and temperature on the synthesis of nickel, iron and copper nitride using nickel, iron and copper together with sodium azide starting materials, with the latter serving as a nitrogen provider for nitride synthesis in a piston cylinder or a multianvil apparatus. The only bulk ambient pressure modification of nickel nitride has Ni₃N stoichiometry with hexagonal symmetry and P6₃22 space group [3][4]. In this arrangement one third of the octahedral voids present in the hexagonal close packing of nickel atoms are occupied by nitrogen. The NNN₉ octahedra share common vertices only, and the nitrogen atoms in most of these syntheses have shown essentially complete occupational order. Ni₃N belongs to the class of interstitial nitrides and is metallic. We further present some preliminary lower pressure work on iron nitride synthesis which is also an interstitial nitride whose Fe₃N modification is isostructural to Ni₃N[5]. The principal ambient pressure copper nitride has Cu₃N stoichiometry with cubic Pm₃m symmetry[6,7]. The structure is made of nitrogen centered octahedra which are corner connected to each other. Cu₃N is a semiconductor with a small indirect band-gap. In the broader context of our work employing multianvil methods for materials synthesis, we also present some of our work employing focused ion
beam methods, a typical mainstay of the microelectronics industry, for nanometre level sectioning of reaction products. We employ scanning electron microscopy as well as transmission electron microscopy for chemical, morphological and structural characterization of the reaction products.

2. Experimental techniques

The starting materials for the syntheses were nickel powder (99.7%) (Aldrich), iron powder (99.5%) (Alpha), copper powder (99.999%) (Alpha) and sodium azide powder (99.99+ %) (Aldrich). For the piston cylinder runs approximate mixtures of 30 at% iron (Fe) and 70 at% sodium azide were placed in a welded 50:50 Silver-Palladium capsule or in a graphite crucible that slip fits into an iron crucible. The sample was pressurized to 3.5 GPa and heated there for about 1300 K for 2 hours and then recovered for further analysis. For the multianvil runs approximate mixtures of 30 at% nickel (Ni) and 70 at% sodium azide (NaN$_3$), 50 at% Cu and 50 at% sodium azide respectively were loaded in capsules made of double wrapped rhenium foil. The nickel and copper containing samples were pressurized to 20 GPa, heated at 2000 K for 1 minute and cooled to room temperature in about 20 minutes. All samples were recovered for further analysis. Recovery involved cutting the capsules, polishing and coating for scanning electron microscopy [Philips XL30CP, with an energy dispersive X-ray analyser Oxford instruments EDX detector – SiLi crystal with PGT spirit analysis software for chemical analysis] and transmission electron microscopy [Philips CM30, Transmission Electron Microscope (TEM), equipped with a Gatan SS CCD camera and with Digital Micrograph software for acquisition of electron diffraction patterns and bright-field imaging]. Voltages of between 10 – 20 kV were employed for scanning electron microscopy measurements and a 300 kV acceleration voltage for transmission electron microscopy measurements.

3. Results and discussion

The nickel based sample recovered from 20 GPa and 2000 K reveals the presence of Ni$_3$N and a new Na-Re-N nitrogen phase whereas the copper based sample recovered from the same conditions only exhibits pure copper and the same Na-Re-N phase (Figures 1, 2).

Figure 1. Backscattered scanning electron microscopy (BSE) images of (a) Cu and Na-Re-N and (b) Ni$_3$N and Na-Re-N, recovered after heating Cu and Ni respectively, with sodium azide at 20 GPa and 2000 K followed by slow cooling to ambient pressure.

The nickel nitride phase was found to match ordered hexagonal Ni$_3$N structure with space group P6$_3$22 and lattice parameters $a = 4.62$ Å , $c = 4.30$ Å, $Z = 2$ (Figure 3). The Na-Re-N phase arose through reaction of the azide with the rhenium foil. Only one sodium rhenium nitride phase was known till now, prepared at ambient pressure[8]. It is monoclinic. In addition to our measured electron diffraction patterns on the new dense phase we also noted a basic physical property of our dense ternary nitride phase that differs from that of the known one. In particular, while the ambient pressure prepared phase is very water and air sensitive, the dense modification is stable in both of these environments as well as in ethanol. We are now focusing on a detailed evaluation of the structure. Preliminary high resolution electron microscopy images reveal a degree of structural disorder.
Figure 2. Energy dispersive X-ray analysis (EDX) spectra from spot 1 (a) and from spot 2 (b) in figure 1. The dark contrast region contains pure Cu and the bright contrast region contains Re, Na and N.

Figure 3. Microdiffraction zone-axis diffraction spot patterns of zone [-1013] of the hexagonal (space group \( P6_322 \) \( a = 4.62 \, \text{Å}, \, c = 4.30 \, \text{Å}, \, Z = 2 \) ) nickel nitride (Ni\(_3\)N) structure.

Figure 4. (a) Backscattered scanning electron microscopy (BSE) images of an iron nitride sample recovered after heating Fe with sodium azide at 3.5 GPa and 1300 K. (b) Energy dispersive X-ray analysis (EDX) spectra from the dark region documenting the presence of an iron nitride phase.

Analysis of the recovered products from the piston cylinder reveal an iron nitride phase (Figure 4) but its structure has not yet been established, while semi-quantitative EDX measurements on two samples reveal Fe:N stoichiometries of between 1:2 and 1:3. We have however, already previously identified short repulsive N – N distances as a principal reason that the ambient pressure modification of nickel nitride is retained after synthesis at high pressure[9]. Unlike the interstitial metallic nitrides, we find that no nitride is formed after heating copper with NaN\(_3\) under the same conditions of 2000 K at 20 GPa. One important factor for this can be traced back to ambient Cu\(_3\)N which has an extremely low heat of formation, low dissociation temperature, limited thermal stability and is a semiconductor exhibiting weak directional bonds. These results are consistent with previous work where Fe\(_3\)N, Ni\(_3\)N and pure Cu were recovered from 10 GPa after heating transition metals in nitrogen at 1800 K. Nitride
stability was interpreted in terms of the electron arrangement of the 3-d transition metals, with for example, copper’s inability to form a nitride being attributed to its 3d\(^{10}\) 4s\(^{1}\) electronic arrangement which does not allow formation of sp\(^{3}\)d\(^{2}\) hybridized orbitals[10].

We briefly also present here in the context of our multianvil syntheses, images of samples sectioned with one of the methods we have been using for processing high pressure reaction products, namely the focussed ion beam method. This method has traditionally been a mainstay of microelectronics. We are finding this method to also be extremely powerful in high pressure materials synthesis because of the capability of nano-sectioning targeted regions for further analysis, particularly using high resolution electron microscopy methods (Figure 5).

**Figure 5.** Overview of FIB sections of (a) a partially thinned sample with Ga+ ions after recovery from a multianvil press and (b) after the thinning process is complete.

4. Conclusions

This work demonstrates the feasibility of using elemental starting materials together with azides at high pressure to synthesize nitrides without the need to resort to tailored precursors. Thus, apart from the crystal chemical and potential technological importance of this work, it also has practical importance for synthesis in a multianvil apparatus. First Cu\(_3\)N itself can be used as an, albeit poor, yet relatively inert (metal-wise) nitrogen source. Second, when sodium azide is employed, the current work will allow us to quickly differentiate between crystals resulting from reaction of the azide with rhenium and other synthetic products under investigation in the same vessel. Our brief account of materials processing using FIB methods illustrates the promise of integrating this method in extreme conditions research.

Acknowledgments

High-pressure experiments were performed at the Bayerisches Geoinstitut under the EU “Research Infrastructures: Transnational Access” Programme (Contract No. 505320 (RITA) – High Pressure). We also acknowledge the use of the EPSRC Chemical Database Service at Daresbury and the particular generous assistance of R. A. Meeking. We further thank, N. Odling for many discussions, J. Craven for assistance with scanning microscopy and M. Hall for demanding solids processing.

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