NEW NITRIDE MINERALS IN CARBONADO DIAMOND

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SUMMARY

Very few nitride minerals are known, but some occur widely in certain classes of meteorites; they are simple compounds. We have found delicate crystals of several new nitride minerals inside a single broken sample of carbonado diamond, not previously reported from Earth or meteorites, but comparable to synthetic compound mixtures between Ti-Cu-N. In addition to chemical stoichiometries from electron microprobe data, we have obtained *in-situ* non-destructive X-ray diffraction data, of the actual cluster of crystals imaged by the SEM, using a high brightness microbeam. Three new nitride phases have been identified; Ti_3CuN (tetragonal), $CuTiN_2$ (orthorhombic) and a Cu-N compound. However, we are less confident of the exact stoichiometry of the Cu-N phase and although there are several candidates ranging from Cu_3N to CuN_2 (azide), the X-ray diffraction pattern is most consistent with Cu_3N (tetragonal). The three new Ti-Cu nitride minerals coexist in a sub-mm scale cavity with minor copper nitrate, silver chloride and faceted polycrystalline host diamond.

The delicate nitride crystals (<20 microns) contain between ~6 and ~20 wt % N and occur in three growth forms: (a) slender hollow needles (b) platy crystals with round holes and (c) euhedral spinel-shaped equant grains. In addition to major Ti and Cu, which vary sympathetically, the crystals also contain variable amounts of silver (up to ~4 wt %). The unusual metal association (Ti-Cu-Ag) of the nitride, and delicate growth forms within unconnected cavities suggest an unusual origin. Occasional probe detection of oxygen probably reflects surface alteration to oxynitride, similar to synthetic behaviour.

Our working hypothesis for origin of the nitrides, is growth from a high temperature vapour; nitrides such as osbornite (TiN) can form at temperatures of ~2500. Such a high temperature is found in the mid-lower mantle at a depth in excess of 2000 km. This is consistent with recent synthesis of polycrystalline diamond in a few minutes at 2,300-2,500^{o}C at mantle pressures (Irifune et al, 2003). If the new nitride minerals are stable within the Earth's mantle, they may represent a significant reservoir for nitrogen, and could explain the large isotopic imbalance between nitrogen in mantle diamond and atmospheric nitrogen, as predicted by Javoy (1998).

Occurrence

The new nitride mineral occurs in a cavity within a broken carbonado diamond, which is partly lined by positive polycrystalline diamond faces. The carbonado itself is from Brazil, and was broken in half mechanically. The new nitride minerals were discovered on the broken surfaces, during subsequent routine electron microprobe examination. The nitrides are associated with small botryoidal patches of secondary silver chloride (few microns), thorn-shaped silver sulphide (acanthite, Ag_2S), and accessory copper nitrate. The new Ti-Cu nitrides occur in a cavity lined by well-formed faces of diamond. Diverse origins and old ages (3.8 Ga) for carbonado have been recently reviewed by Kletetschka et al (2000) Sano et al (2002) and Nadolinny et al (2003).

Electron Probe Analysis

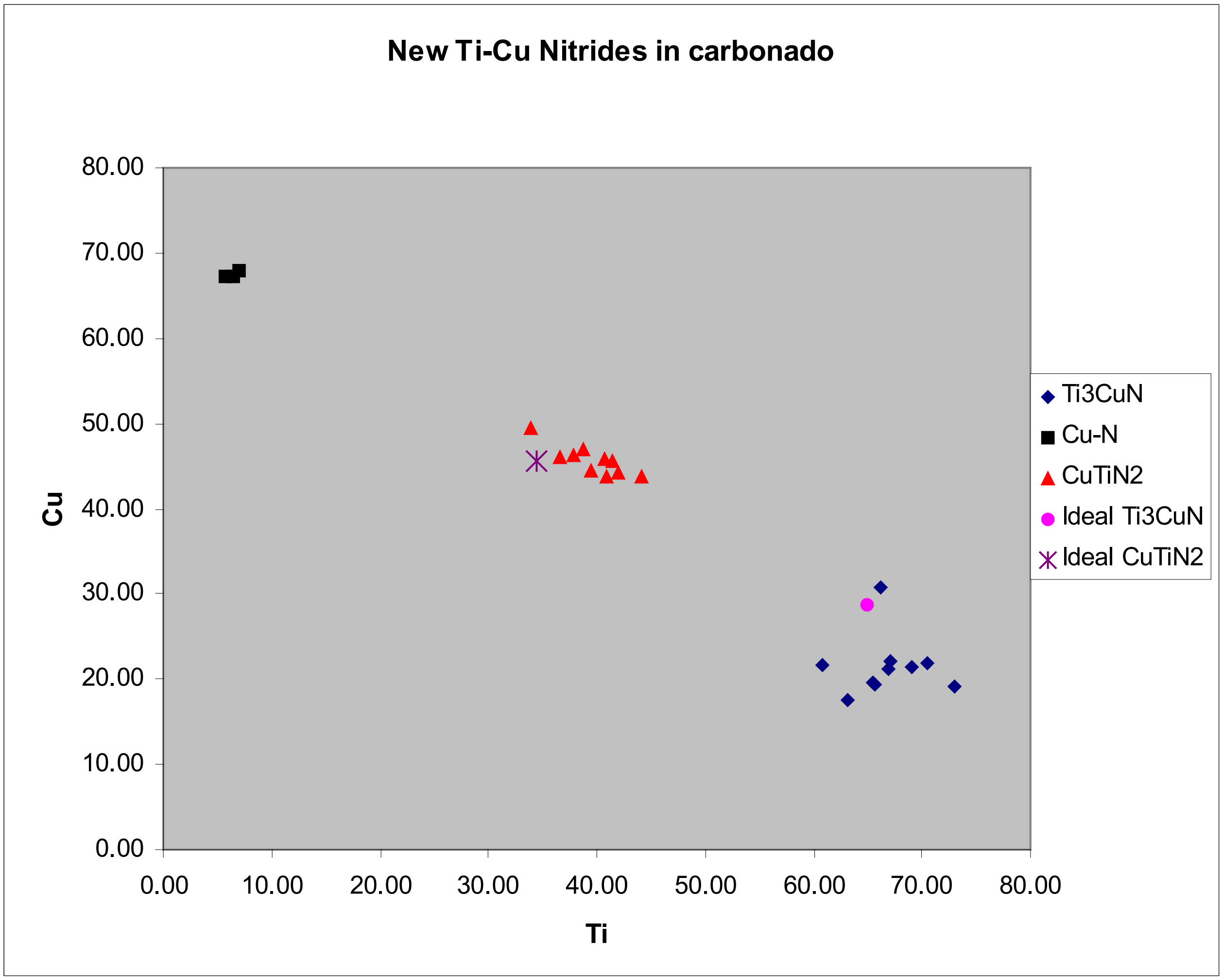
The minerals were analysed by both EDS and WDS on two separate instruments, using well-documented methods for peak deconvolution of severe overlaps between titanium and nitrogen. Further details are available upon request. All reported data here was obtained by WDS using the Cameca probe at the Natural History Museum, London. Combined with the variable surface geomtery presented by unpolished crystals in non-horizontal orientations, this yielded surprisingly reproducible standards and metal concentrations, but, as expected, nitrogen analysis was restricted to much poorer precision. We verified the technique for nitrogen using several different polished nitride standards (natural and synthetic osbornite (TiN), and synthetic cubic boron nitride). The natural minerals contain minor silver in solid solution (up to a few percent), which differs from synthesised nitride. The probe analyses reported here have been corrected for removal of minor variable oxygen, which occasionally reached several percent, and is attributed to secondary surface oxidation of nitride to oxy-nitride. It is worth emphasising that the likely main source of errors is attributable to nitrogen determinations (see Probe Analysis above).

X-ray Diffraction

X-ray Micro-diffraction experiments were carried out at The Natural History Museum, London, using a high brightness Bede Microsource and an INEL 120° curved Position Sensitive Detector (PSD), with a beamsize of 0.04 x 1 mm. With the sample surface spinning in its own plane, the beam irradiated a spot of 1mm in diameter. Phases were identified from this composite XRD pattern using the diamond peaks as an internal standard. After identification of known phases from the JCPDS database, the remaining peaks were indexed on an orthorhombic unit cell.

New minerals

Three new nitride minerals have been identified, and their average compositions are listed in Tables 1-3. X-ray structures, electron probe data and morphologies for two of these phases appear to represent the first documented occurrence of compounds known from synthesis work (Durlu et al). These are **(1)** Ti_3CuN with average composition based on 10 analyses from different crystals, of Ti(0.73)Cu(0.27)Ag(0.03)N compared with ideal Ti(0.69)Cu(0.31)N; **(2)** Ti(1.05)Cu(0.92)Ag(0.03)N2 compared with ideal $TiCuN_2$. X-ray data for the third nitride matches simple Cu_3N, although the probe data allows for a substantially different stoichiometry. Figure 1 (below) shows electron microprobe analyses of nitrides in carbonado diamond coinsistent with three minerals.



Known Nitride Minerals

Pure nitride minerals are rare, but occur widely in some classes of meteorites (Khodakovsky and Petaev, 1981). These are osbornite (TiN; cubic; Casanova, 1992; Weber et al, 1994), carlsbergite (CrN; cubic), and nierite (Si_3N_4; trigonal; Russell et al, 1995). In addition, the only natural oxynitride, sinoite is also known from meteorites (Si_2N_2O; Hoppe et al, 1989; Muenow et al, 1992;Rubin, 1997), and has tentatively been identified as the first terrestrial oxy-nitride based on a qualitative probe analysis of a single inclusion in kimberlitic moissanite, SiC, from Yakutia (Mathez et al, 1995). Two iron nitrides are also known; Siderazot Fe_5N_2 (hexagonal), as surface coatings on lava from Vesuvius and Etna, and Roaldite, Fe_4N (cubic) from iron meteorites.

Table 1: New Ti-Cu Nitride: Ti_3CuN

	1 observed n = 10	(σ)	2 ideal
Ti	67.1	(3.5)	65.0
Cu	21.8	(3.6)	28.7
Ag	1.9	(0.5)	0.0
N*	10.5	(5.0)	6.3
Total	100.73		100.00

Structure: Tetragonal, a: 11.968Å, c: 3.0217Å;
See JCPDS file [50-1475]

Table 2: New Ti-Cu Nitride mineral: CuTiN2

	3 observed n = 10	(σ)	4 ideal
Ti	39.9	(2.9)	34.4
Cu	45.8	(1.8)	45.6
Ag	2.8	(0.7)	0.0
N*	12.3	(2.0)	20.1
Total	99.99		100.1

Structure: Orthorhombic; new.
Preliminary cell parameters:
a=6.977Å; b=5.951Å; c=4.542Å

Table 3: New Ti-Cu Nitride mineral: Cu3N

	5 observed n = 3	(σ)	6 ideal
Ti	6.4	(0.3)	0.0
Cu	67.5	(0.4)	93.2
Ag	1.8	(0.4)	0.0
N*	24.3	(2.0)	6.9
Total	100.00		100.1

Structure: Cubic; a: 3.817Å
See JCPDS file: [47-1088]

Synthetic nitrides

Titanium nitride, and several other nitrides are commonly synthesised due to their commercial applications, and are stable over a wide range of temperatures, with very high condensation/ vapourisation temperatures (typically 2,500-3,000 degrees C). Most synthesised nitrides are extremely fine grained, nanocrystalline, and are identified on the basis of X-ray (eg cubic silicon nitride; Zerr et al, 1999).
However, when larger crystals are occasionally produced, these notably can include slender elongated crystals, rather similar to our new phase(s) such as the hexagonal "whiskers"of Si_3N_4 (Chen et al, 1997). Fortuitously, a number of Ti-Cu nitrides have been synthesised in an exploratory phase equilibria study of light metal alloys in the system Ti-Cu-Al-N (Durlu et al, 1997). These include Ti-Cu-N alloys, titanium nitride (TiN_{1-x}), εTi_2N, Ti_3CuN and $Ti_3Cu_2AlN_{0.8}$. They were all formed by arc melting under pure argon (no temperature given), subsequently annealed in vacuum-sealed quartz tubes at lower temperature (850, then 600 degrees C). At high concentrations of nitrogen, there is high solubility of N in the metal alloys of Ti-Cu-Al, and the non-stoichiometric cubic phase TiN_{1-x} (37 to 50 at % N) is very stable. The phase Ti_3CuN synthesized by Durlu et al (1997) is directly comparable to one of our new nitrides (Schuster, pers comm, 2003).

Formation conditions

The spectacular delicate growth forms, and wide range of thermal stabilities of the combined mineral assemblage, leads us to suspect deposition form deposition from an initially very high temperature vapour. By comparison with osbornite (TiN), this implies temperatures possibly in excess of 2500 degrees C. Since the space occupied by the nitrides is partly evacuated, some additional (unknown) component has subsequently been lost. This is s feature of carbonado diamond in general, and accounts for its lower density compared to cubic diamond. The faceted nature of enveloping diamond is consistent with pressures sufficient to stabilise diamond during growth of the nitrides. Such a temperature would be found in the mid-lower mantle at a depth in excess of 2000 km. This represents a very different growth environment to the widespread association of carbonado with other minor inclusions whose elemental signatures, including REE, hydrous alteration, and growth features suggest involvement of terrestrial crustal rocks. The origin of carbonado itself is not understood, with theories including impact formation, polycrystalline growth in high-P melts and even meteoritic. It is difficult to reconcile the very high temperatures required for nitride stability, with an ultra-deep origin, due to the apparent contemporaneous existence of voids in carbonado. Therefore, as an alternative to an entirely Earth-bound origin, and since an impact origin is unlikely to produce diamond of sufficient size directly (DeCarli et al 2002), we cannot rule out the possibility of a non-terrestrial stage of growth (cf Haggerty, 1998). Carbonado diamond itself has very low nitrogen contents, which leads us to conjecture that if the nitride equilibrated with the host carbonado diamond, the new TiCu nitride may have acted as a nitrogen getter, similar to Ti metal in commercial diamond synthesis (Sumiya et al, 2002).

Metal association Ti-Cu-Ag

There is no obvious geological analogy to explain the provenance of the associated metals in the new nitride mineral. The three elements Ti, Cu and Ag might perhaps be expected to coexist with sulphur as sulphides, and even Ti can exist as a complex sulphide, as also known from meteorites (heideite: $(FeCr)_1+x(Ti,Fe)_2S_4$. Cu and Ag both exist as sulphides and solid solutions thereof. Decomposition of exotic meteoritic sulphides during impact volatilization is one possible scenario, which might explain the origin of the new phase. Small amounts of oxygen suggest the presence of limited surface reaction to oxynitride $((Ti,Cu,Ag)N_xO_y)$ which is commonly seen in synthetic nitrides, and together with accessory nitrate, is interpreted as secondary.

Discussion

The new mineral requires quite different formation conditions to the “normal” suite of REE-rich minerals like florencite, often associated with the cavities in carbonado diamond. The likely stability of the nitride(s) together with their morphologies suggests deposition from a very high temperature vapour, in the absence of oxygen. Apart from the diamond itself, there is no independent information about pressure, but similar nitrides are well known from meteorites, where high pressure is not required. The shape of the cavities in the carbonado are also similar to negative crystal lined cavities and irregular cavities commonly displayed in some meteorites. The nitrides crystallised after formation of the carbonado diamond, and in the absence of isotopic information, it is unclear how they are related. It is likely that isotopic analysis could be extremely valuable in understanding the genesis of the nitride and its relationship to the host carbonado. In addition, the potential role of the nitride as a nitrogen-getter is interesting. We have found other Ti-minerals with similar elongated morphology in different broken carbonado samples, namely rutile (TiO_2), and off-composition rutile (TiO_3?), some of which also appear to contain minor nitrogen.

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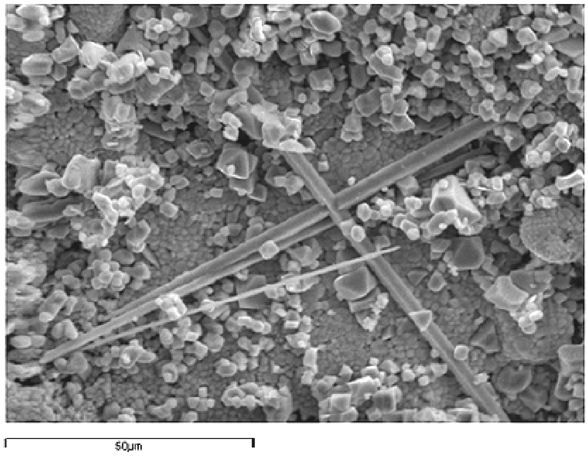

New nitride minerals on a broken surface of a carbonado diamond.