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Template Mediated Growth of Rare Earth Carbides

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Highly oriented pyrolytic graphite (HOPG) consists of an array of grains that share a common *c* axis, but which are randomly oriented in the *a*−*b* plane. Here we demonstrate that HOPG wafers can be fully reacted with thulium to produce carbides with similar texture and morphology. In this process the graphite is totally consumed as the individual carbon atoms are dispersed into the interstitial sites in the thulium lattice. We call this process *template-mediated growth* since the graphite provides a template for the growth of the carbide sample, yet it is totally consumed during the reaction. Similar growth processes have been observed in textured oxide films on titanium substrates,[1] textured silicide films on silicon substrates,[2] and in the recent fabrication of novel carbide nanorods from carbon nanotubes;[3] however, to our knowledge, the present case is the first observation of a complete reaction on a macroscopic scale. While the particular material produced here is a rare earth hypocarbide (Tm_2C_{1-x}), we hope to achieve similar results with a variety of species.

Rare earth (RE) hypocarbides are solid solutions which exist over a wide compositional range by virtue of their defect structure. After the first identification of the cubic hypocarbide[4] (nominally RE_3C) in which carbon atoms randomly occupy the octahedral sites of a cubic close packed metal sublattice, Atoji *et al*.[5] observed a closely related trigonal counterpart (nominally RE_2C) which exhibits an ordering of the interstitial carbon atoms such that alternating layers are preferentially filled (Figure 1). To date, trigonal RE_2C phases have been found with yttrium and all the heavy lanthanides from gadolinium to ytterbium, with the exception of thulium.[6] Here we show that thulium also forms the trigonal hypocarbide phase.

Our thulium hypocarbide samples were prepared by exposing pristine HOPG[7] to low-pressure (∼10^{-6} bar) metal vapor for a period of about 30 days. The reactions took place within a vacuum sealed quartz vessel loaded with several HOPG wafers at one end and several chunks of bulk thulium (∼10 g total) placed in a tantalum boat at the opposite end. The initial mass m_i (typically 50 mg), thickness t_i, and surface area A_i of each HOPG wafer were recorded. After reaction, the HOPG is transformed into a carbide wafer of roughly the same area but with increased thickness and mass.

The synthesis of oriented carbides was performed using a two-zone furnace with the HOPG held at 745 °C and the thulium at 730 °C for a duration of about 30 days. This two-zone technique was utilized to inhibit the formation of carbide powder or metallic thulium on the samples. We selected thin ($t_i \sim 0.03$ mm) HOPG wafers in order to obtain fully reacted (no detectable HOPG remaining) samples with considerably increased thickness ($t_f \sim 7t_i$) and mass ($m_f \sim 29m_i$). The pristine carbide samples had a silver metallic appearance, which rapidly changed to a green/blue hue when exposed to air. Since the carbide samples decompose into a white powder after several hours in air, they were sealed in helium-filled aluminum or vanadium cans for subsequent analysis.

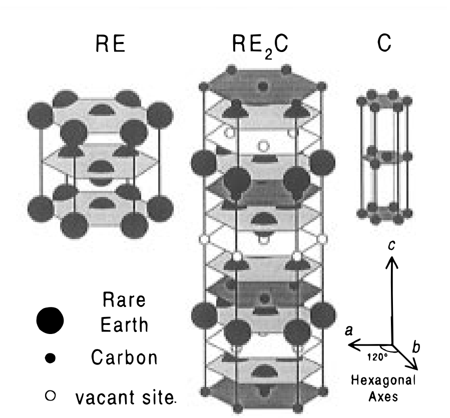

Figure 1. A comparison, drawn to scale, of the typical rare earth metal (RE), trigonal hypocarbide (RE_2C), and graphite (C) crystal structures. Note the hypocarbide's similarity to the pure metal and its dissimilarity (particularly in lattice spacing) to graphite.

Table 1. Observed (I_{OBS}) and Calculated (I_{CALC}) Bragg Intensities

sample A[a]			sample B		
Miller index	I_{OBS}	I_{CALC}	Miller index	I_{OBS}	I_{CALC}
(0 0 3)	8	8	(1 1 0)[b]	100	100
(0 0 6)	20	19			
(0 0 9)	0	0	(1 1 0)[c]	106	100
(0 0 12)[b]	100	100	(1 1 3)	6	6
(0 0 15)	18	19	(1 1 6)	16	14
(0 0 18)	7	8			
(0 0 21)	2	1	(1 0 1)	3	3
(0 0 24)	37	39	(0 1 2)	9	17
(0 0 27)	15	15	(1 0 4)	90	108
(0 0 30)	2	1			
(0 0 33)	2	2	(0 0 3)	7	8
(0 0 36)	16	8	(0 0 6)	13	17
			(0 0 9)	0	0
			(0 0 12)	56	86
			(0 0 15)	16	16

[a] Samples A and B are assumed to have identical structure. [b] Scaled to 100 arbitrary units for normalization. [c] Transverse (1 1 0) data, i.e. from (1 1 *l*) scan, do not exactly agree with the normalized (longitudinal) peak because of experimental error.

Neutron diffraction data were obtained on triple axis spectrometers at the National Institute of Standards and Technology.[8] Table 1 shows the observed (corrected for spectrometer resolution, sample mosaic, and powder ring effects)[9] and the calculated Bragg intensities. The observed intensities are independent of sample rotations about the *c* axis, but reveal a *c*-axis mosaic spread of about 3°, somewhat larger (e.g. 30%) than the HOPG reactant. The space group was identified as $R\bar{3}m$, the same as all other RE_2C compounds, with unit cell parameters $c = 17.45 \pm 0.02$ Å and $a = 3.56 \pm 0.01$ Å, comparable to the RE_2C phases of neighboring rare earths. Each independent lattice site is specified by the parameter *z* which gives the following hexagonal coordinates: $\{(0,0,0);(^2/_3,^1/_3,^1/_3);(^1/_3,^2/_3,^2/_3)\} \pm (0,0,z)$. While a perfectly ordered RE_2C compounds has one fully

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(1) Wiesler, D. G.; Toney, M. F.; Melroy, O. R.; McMillan, C. S.; Smryl, W. H. *Surf. Sci.* **1994**, *302*, 341−349.

(2) Hutchins, G. A.; Shepela, A. *Thin Solid Films* **1973**, *18*, 343−363.

(3) Dai, H.; Wong, E. W.; Lu, Y. Z.; Fan, S.; Lieber, C. M. *Nature* **1995**, *375*, 769−772.

(4) Spedding, F. H.; Gschneidner, K. A., Jr.; Daane, A. H. *J. Am. Chem. Soc.* **1958**, *80*, 4499−4503.

(5) Atoji, M.; Kikuchi, M. *J. Chem. Phys.* **1969**, *51*, 3863−3872.

(6) Gschneidner, K. A., Jr.; Calderwood, F. W. *Bull. Alloy Phase Diagrams* **1986**, *7*, 421−437.

(7) HOPG was obtained from Advanced Ceramics Corporation (this product identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the product is necessarily the best available).

(8) (a) Prask, H. *Neutron News* **1994**, *5*, 10−14. (b) http://rrdjazz.nist.gov

(9) (a) Yessik, M.; Werner, S. A.; Sato, H. *Acta Crystallogr.* **1973**, *A29*, 372−382. (b) Expanding the above treatment, we find the approximate powder ring correction (L_{PR}) in terms of the mosaic single crystal correction (L_{MS}) such that $L_{PR} = mL_{MS}\,(2\pi M'_{33}Q^2_{hk})^{-1/2}$, where *m* is the multiplicity, Q_{hk} is the "in-plane" component of the scattering vector, and the terms M'_{33} and L_{MS} are defined in ref 9a.

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occupied carbon site at $z_C = 0$, we found two partially occupied carbon positions given by $z_{C1} = 0$ and $z_{C2} = {}^1/_2$, with occupation probabilities $P_1 = 0.76 \pm 0.05$ and $P_2 = 0.16 \pm 0.04$, respectively. The two fully occupied thulium sites are specified by $z_{Tm1} = -z_{Tm2} = {}^1/_4 + \delta$, where the δ parameter represents a slight shift of a thulium layer toward the higher density interstitial carbon layer ($\delta = [3.9 \pm 0.5] \times 10^{-3}$). Finally, we characterize the combined static and thermal lattice distortions by the root mean square atomic displacement ($u = 0.20 \pm 0.04$ Å).

Our most important result is not the crystal structure, but rather that the carbide sample adopts the same orientational texture and morphology as the parent HOPG material. We propose that this occurs via the following sequence: adsorption of thulium atoms at the HOPG surface, slow removal of carbon atoms from the graphite lattice, rapid diffusion of the carbon atoms throughout the interstices of the metal sublattice, and the continued adsorption of thulium atoms on the newly formed carbide surface. This mechanism is consistent with several observations. Diffraction measurements on partially reacted samples reveal a homogeneous surface region of oriented carbide and a pristine HOPG region below the surface. Since the diffraction peaks originating from the carbide region are sharp, the carbon concentration gradient must be small. Therefore, while the thickness of a fully reacted HOPG wafer increases 7-fold and the shortest carbon−carbon distance increases from 1.42 to 3.56 Å, requiring a tremendous amount of interdiffusion, the rate-limiting step in this reaction is probably the removal of carbon atoms from the graphite lattice. This is consistent with the reported diffusion coefficients D of carbon in heavy rare earth metals[10] which are large enough to allow carbon atoms to diffuse across a thulium layer of 0.1 mm in just 1 h at 750 °C. Even though the diffusion rate will likely slow as the carbon concentration increases (no data are currently available) one expects that D will remain relatively large given the small change in the thulium sublattice.

These same diffraction measurements show no evidence of pure thulium metal on the surface. Thus, the surface thulium layer must remain very thin, probably no more than several atomic layers. We believe that the diffusion of carbon atoms into this surface thulium layer prevents Tm atoms from re-vaporizing due to the Tm−C interaction (note that the Tm atoms are displaced toward the C atoms).

It is unclear exactly how the texture and morphology are preserved throughout this reaction. Many materials tend to adopt an oriented texture when grown on any flat surface (e.g. Pd_2Si).[2] However, interfacial and intrinsic stresses often cause such a film to crack at a critical thickness, typically a few microns. The present system may avoid such a fate, in part, because of its interfacial properties. Thulium metal and Tm_2C_{1-x} should form a low-stress interface because their {001} planes are commensurate.[11] The HOPG−Tm_2C_{1-x} interface has no apparent commensuration, but it may be stable because of a low corrugation potential felt by the thulium atoms on the graphite (001) surface. In other words, the graphite (001) surface looks very flat to the large thulium atoms, and therefore the interfacial stress is small. Additionally, both interfacial and intrinsic stresses may be relieved to some extent by grain boundaries.

The above mechanism is consistent with the observed data, but we have no direct observation of such a mechanism, and there remain other possibilities to explore. For instance, graphite allows several species (including rare earth atoms) to intercalate into its interlayer galleries, forming graphite intercalation compounds.[12] The present case clearly differs from intercalation in that the graphitic layers decompose, but intercalation as an intermediate step in this process remains a possibility. One may also be tempted to identify this reaction simply as the epitaxial growth of a carbide on an HOPG substrate. Note, however, that the HOPG "substrate" may be fully consumed.

In summary, we have demonstrated that HOPG can be completely decomposed but still serve as a template for synthesizing highly oriented carbides, in particular, Tm_2C_{1-x}. A growth mechanism has been proposed where the carbide forms between two distinct interfaces, one with the thulium vapor and the other with the graphite which provides a low-energy templating surface. In this model, the growth phase must exhibit a low corrugation potential with respect to graphite, a tendency to orient with respect to the interface, and a relatively high diffusion coefficient for carbon. Perhaps a defect structure is necessary for such diffusion rates. With these criteria in mind, we are attempting to react a variety of metal species with HOPG, with the goal of synthesizing and studying new highly textured materials.

Supporting Information Available: Listing of crystallographic data for Tm_2C_{1-x} (2 pages). See any current masthead page for ordering and Internet access instructions.

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[10] Deshkevich, YE. V.; Dubovtsev, R. M.; Zotov, V. S. *Phys. Met. Metallogr.* **1985**, *60*, 154−159.

[11] Thulium metal forms a hexagonal close-packed lattice ($a = 3.54$ Å $c = 5.56$ Å). Similarly, thulium carbide (Tm_2C) forms layers of close-packed thulium atoms ($a = 3.55$ Å), but with a different c-axis stacking sequence (i.e. ABC) and larger interlayer spacing.

[12] (a) El Makrini, M.; Guérard, D.; Lagrange, P.; Hérold, A. *Physica* **1980**, *99B*, 481−485. (b) Lagrange, P.; Setton, R. In *Graphite Intercalation Compounds I: Structure and Dynamics*; Zabel, H., Solin, S. A., Eds.; Springer-Verlag: Berlin, 1990; pp 283−285.