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PHASE RELATIONSHIPS OF THE HIGH CARBON PORTION OF THE
LANTHANIDE DICARBIDES

by

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ABSTRACT

A study of the rare earth dicarbides as well as YC_2 and LaC_2 to determine the MC_2 -C eutectic temperatures, and the tetragonal to cubic transformation temperatures by thermal analysis techniques is reported. Microhardness measurements of the dicarbides are also reported. Lattice parameters of the tetragonal dicarbides were measured as well as the parameters of the high temperature cubic form of some of the dicarbides.

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INTRODUCTION

The existence of the rare earth dicarbides, yttrium dicarbide, and lanthanum dicarbide has been observed by a number of investigators.⁽¹⁻¹⁰⁾ The crystal structures have been studied as well as some of the chemical properties. The tetragonal to cubic transformation of only lanthanum dicarbide however has been reported. This transformation was first reported by Bredig,⁽¹¹⁾ who prepared the dicarbide by heating a mixture of lanthanum oxide and carbon at 1750°C in a high temperature x-ray diffraction assembly. At this temperature he observed a cubic phase ($a_0 = 6.0 \pm 0.1\text{\AA}$) but did not report the specific transformation temperature. With the investigation of the lanthanum-carbon system,⁽¹²⁾ an attempt was made to observe the tetragonal to cubic transformation by the method of electrical resistance measurement. A change in electrical resistivity, which was attributed to this transformation was observed at about 1800°C.

The purpose of this work was to systematically investigate the eutectic temperatures of the lanthanide dicarbides with carbon, their microhardnesses and tetragonal to cubic transformation temperatures.

EXPERIMENTAL

Materials: The starting materials were buttons or arc-cast ingots of the rare earth metals and Carbon Products Company spectrographic grade graphite. The purity of the starting metals ranged from 99% to 99.9%. The major impurity in the metals was oxygen which was as high as 0.19% in erbium. The neodymium contained 0.20% Cu and the ytterbium contained 0.37% Ta.

The other reported impurities were in quantities of less than 500 ppm.

The spectrochemical analysis of the graphite indicated that B, Mg and Na were the major impurities, each being less than 50 ppm.

Sample Preparation: Two methods were used in the preparation of the dicarbides, depending on the volatility of the rare earth metal. Where possible, the compounds were prepared in a zirconium "gettered", helium atmosphere by arc melting the components on a water-cooled, copper hearth with a graphite electrode. In the preparation of YbC_2 , SmC_2 , EuC_2 , and TmC_2 , due to the extreme volatility of the metals, the compounds were prepared in a sealed tantalum crucible. The lid was welded on the crucible by the "heliarc" process in a helium filled drybox. Machined into the lid was a tantalum thermal probe which projected into the dicarbide-carbon mixture. LaC_2 was prepared by both techniques to check the validity of the thermal analysis measurements made in the tantalum containers. Samples were stored and handled in an airtight, helium-atmosphere drybox. Dies for hot pressing and cold pressing the dicarbide specimens and x-ray capillaries for room temperature patterns were loaded in the drybox. A 25 kw high frequency induction heater with an eddy current concentrator⁽¹³⁾ was used to heat the pressed cylindrical specimens. The samples were heated in a vacuum system capable of maintaining pressures of 10^{-5} or 10^{-6} torr at temperature, or in a purified partial atmosphere of helium -- again dependent on the volatility of the dicarbide. Annealing was also done with the same system.

Thermal Analysis: Except for the EuC_2 and YbC_2 specimens (which were sealed in Ta containers), and the SmC_2 and LaC_2 used as internal checks of the method,

both the tetragonal to cubic transformation and the MC_2 -C eutectics were determined using pressed plugs which consisted of mixtures of the rare-earth dicarbide and an excess of high purity spectroscopic grade graphite powder. These cylinders were prepared by cold pressing 5-10 g. of the mixture in a steel die 0.95 cm diameter at 100,000 psi. The cylinders were approximately 2.5 cm long and 0.95 cm diameter. A sight hole 1.5 mm and 9.5 mm long was drilled in the top of each cylinder to give black-body conditions for optical pyrometer and thermal analysis measurements. The cylinders were supported in the field of the eddy current concentrator by means of a tantalum wire tripod.

The MC_2 -C eutectic curves were determined by observing temperature vs. time cooling curves on the samples. Light from the sight hole in the cylinder was divided by a beam splitter so that one beam of the light from the sample was focused on a sensing diode which was connected to the y-axis of a time sweep oscilloscope.⁽¹⁴⁾ Upon heating or cooling through the eutectic temperature a flat in the trace was observed. The tetragonal to cubic transformation was also manifested in the same manner, except at a lower temperature. A Polaroid camera was used to record both the cooling and heating trace and subsequent constant temperature traces (the temperature was determined from the other beam while the trace was being photographed). By bracketing the flats with the constant temperature traces, the eutectic temperature and the transformation temperature could be determined with a high degree of precision. The thermal analysis apparatus can display not only the heating and cooling curves, but also the derivatives of these curves.

In the case of EuC_2 and YbC_2 , in the temperature domain below 1100°C , a sealed thin-walled tantalum reaction chamber containing a well for insertion of the ~~platinum-platinum-10% rhodium~~ thermocouple was used. Heating and cooling curves were taken using standard Brown-Honeywell recorders for the thermal analysis and differential thermal analysis curves. A standard wire-wound, well-insulated tubular resistance furnace was used for heating in this phase of the experiments.

The Pyro Micro-Optical pyrometer and optical system were calibrated against a standard lamp that had been certified by the United States National Bureau of Standards.

Chemical and X-ray Analysis: The starting arc melted dicarbides were chemically analyzed for rare earth metal, total carbon and free carbon. After measurements had been made, the samples were analyzed for only rare earth metal and total carbon.⁽¹⁵⁾ For room temperature x-ray analyses, the dicarbide was crushed in a "diamond" mortar. A representative sample was ground into powder (-325 mesh) for lattice parameter measurements. The x-ray samples were sealed in Lindemann glass capillaries, and the diffraction studies were carried out on a Norelco unit using nickel-filtered copper radiation and a 114.59 mm Debye-Scherrer camera. Where fluorescence of the sample by x-rays was a problem, the unfiltered x-ray beam was used with a thin (0.015 mm) strip of nickel foil in front of the film, thus prohibiting the fluorescence from increasing the background of the film.

The high temperature x-ray diffractometer traces obtained for LaC_2 , LuC_2 and TbC_2 were made on cylinders hot pressed in graphite dies. These cylinders were 1.90 cm long and 0.95 cm dia. They contained a temperature measuring

sight hole 1 mm dia and 9.5 mm deep. The measurements were made in a vacuum at 10^{-5} torr or better with equipment similar to that described by Lang and Franklin⁽¹⁶⁾ using an offset eddy current concentrator. The x-ray wave-length used in calculating the lattice parameters were:

$K_{\alpha_1} = 1.54050\text{\AA}$, $K_{\alpha_2} = 1.54433\text{\AA}$ and a weighted value (for unresolved doublets of $K_{\alpha} = 1.54178\text{\AA}$). For the powder patterns, lattice parameters were obtained from the back reflection lines by applying the modified least squares extrapolation of Hess⁽¹⁷⁾ using an IBM 7090 computer. Standard deviations were calculated for each lattice parameter. For high temperature x-ray diffraction, lines up to $2\theta = 65^\circ$ were used. Higher angle lines were too diffuse to be used with success for lattice parameter measurements.

Neutron Diffraction: Fifteen and thirty gram samples of powdered YC_2 and LaC_2 were placed in a thin walled graphite holder for exposure to the neutron beam for both room temperature and high temperature neutron diffraction.⁽¹⁸⁾

Microhardness Measurements: Microhardness measurements were made on annealed carbides. The samples were mounted in a phenolic resin and polished using kerosene at all stages of grinding and polishing to prevent oxidation during handling. The samples were etched with 1.5% Nitol solution. In order to get reproducible results it was necessary to measure the microhardness of the surface under kerosene. After one-half to two hours, the surface became oxidized and was consequently much softer. The Knoop microhardness measurements were made using a Kentron Microhardness Tester.

RESULTS AND DISCUSSION

In Table I are listed the MC_2 -C eutectic temperatures as measured by the thermal analysis technique for all the rare earth dicarbides except promethium and europium. The high vapor pressure of Eu over EuC_2 precludes such a measurement except possibly with an extremely high over-pressure of inert gas. The measured eutectic values fall within a 110°C range. In general the values increase from CeC_2 to a maximum at GdC_2 and then diminish toward LuC_2 .

Attempts to measure the YbC_2 -C eutectic in an atmosphere of helium using a pressed cylinder met with little success due to the extreme volatility of Yb, which necessitated the use of a sealed tantalum crucible as previously described. SmC_2 and TmC_2 showed a similar tendency, but not to the same extent as YbC_2 . We were able to determine the SmC_2 -C eutectic using a pressed cylinder ($2240 \pm 30^\circ\text{C}$) as well as in a sealed tantalum crucible with the thermal probe ($2190 \pm 25^\circ\text{C}$). The LaC_2 -C eutectic was also determined using both techniques, in order to make the correction for the effect of the container. The tantalum container also lowered the LaC_2 -C eutectic by 50°C ; however, the solid state transformation was essentially in agreement.

On the basis of chemical analysis for rare earth metal and total carbon, the various cylinders of MC_2 -graphite mixtures used for eutectic and solid state transformation measurements contained from two to six molar equivalents of free carbon if we assume that MC_2 was stoichiometric. The summation of metal and carbon ranged from 98.6 to 100%, in some cases with considerable spread in carbon values.

Only two eutectic values appear in the literature with which to compare our observations. For $\text{LaC}_2\text{-C}$, the value of 2230°C is approximately 40°C lower than that reported (2271°C) by Spedding, Gschneidner and Daane.⁽¹⁾ For $\text{CeC}_2\text{-C}$ our value is approximately 100°C higher than that shown by Stecher, Neckel, Benesovsky and Nowotny.⁽¹⁰⁾ Our values are the arithmetic average obtained from the heating and cooling curves. Figure 1 is a photograph showing the oscilloscope trace of the heating curve (A) and cooling curve (B) for the eutectic determination of $\text{LaC}_2\text{-C}$. The derivative curves (C) can also be seen in Fig. 1.

The solid state, tetragonal to cubic transformation temperatures are also listed in Table I. No transformation was observed for YbC_2 by thermal analysis. However, some change of structure was observed between $700\text{-}1000^\circ\text{C}$ during the slow heating of a YbC_2 cylinder in the high temperature x-ray diffraction apparatus. Even in high vacuum (10^{-8} torr) a Yb_2O_3 surface gradually formed and masked the results so that a definitive result for either the high temperature lattice parameter or the solid state transformation temperature cannot be given.

The transformation temperature of 355°C observed for the Eu-C mixture in the sealed tantalum bomb cannot be specifically attributed to EuC_2 since the room temperature x-ray patterns showed predominant lines for Eu rather than EuC_2 ; thus the break observed in the cooling and heating curves can be attributed to Eu metal or EuC_2 , or even an unknown phase.

With the exception of the questionable values for EuC_2 and YbC_2 , the transformation temperatures increase from LaC_2 through LuC_2 . The distinction between the lanthanum type metals and yttrium type metals may be noted from the YC_2 transformation temperature which may be placed between ErC_2 and HoC_2 in the series listed in Table I.

Our value of 1060°C for the LaC_2 transformation is some 740° lower than the 1800°C reported by Spedding, Gschneidner and Daane.⁽¹²⁾ Their plot of the high temperature electrical resistivity measurements (beginning at 1600°C) shows a definite change in slope between 1750 and 1800 on both the heating and cooling curves. Our thermal analysis curves showed no change in slope in this temperature domain. Spedding, et al.⁽¹²⁾ inferred a transformation from tetragonal to cubic, but a resistivity change could be manifested by a change in carbon content (implying a change in the phase boundary) at that temperature. This could readily happen if the rate of heating or cooling was relatively slow in their measurements compared to the faster rate of heating and cooling in the thermal analysis method used by us. Indeed they may have seen a phase change which is slow, but it cannot be the one described in their paper.⁽¹²⁾ The heating and cooling curves for the PrC_2 tetragonal to cubic transformation are shown in Fig. 2. It is an example showing some hysteresis between cooling and heating. Except for the observations on LaC_2 ,^(1,11,12) no other references exist pertaining to these transformations.

The lattice parameter measurements of earlier work^(1,8,10) are compared with the values obtained by us in Table II. The agreement is very good except for the LuC_2 and EuC_2 , which we could not definitely identify.

The LuC_2 was prepared by different techniques using metal from two different sources. Regardless of the method of preparation, or time-temperature treatment of the LuC_2 , all the room temperature powder patterns were identical and contained many more lines than reported in earlier work.^(1,6) Although we have not yet successfully indexed the pattern, the new structure appears to be of very low symmetry. Our observed interplanar spacings for LuC_2 are listed in Table III.

It appeared that a tetragonal LuC_2 phase might be stabilized by the addition of a rare earth metal having a similar atomic radius. Consideration of the volatility of the additive rare earth metal led to the choice of Er rather than the more volatile metals Tm and Yb. The experimental details of this work will be reported elsewhere.⁽¹⁹⁾ By the incremental addition of Er at the approximate compositions of 40, 55, 71 and 85 m/o ErC_2 to LuC_2 , a tetragonal phase was stabilized. From the cell parameters of the above solid solutions and ErC_2 (assuming the validity of a linear Vegard relationship), one finds an extrapolated value of $a_0 = 3.564\text{\AA}$ and $c_0 = 5.962\text{\AA}$ for tetragonal LuC_2 . These values compare favorably with the values reported by Spedding, Gschneidner and Daane⁽¹⁾ and Atoji.⁽⁶⁾ This series of experiments implies either the stabilization of tetragonal LuC_2 by rare earth metal contaminants or the stabilization of our more complex phase by an unknown impurity.

Due to the apparent complexity of the observed LuC_2 pattern, it was deemed necessary to examine the transformation of LuC_2 by high temperature x-ray diffraction. As can be seen in Table IV, the high temperature transformation of LuC_2 is to the cubic form with $a_0 = 5.505 \pm 0.005\text{\AA}$ measured at 1500°C . LaC_2 was investigated in the same manner to confirm the data from thermal analysis. At 1060°C , the cell parameter of $6.001 \pm 0.005\text{\AA}$ was observed confirming Bredig's⁽¹¹⁾ approximate value of $6.0 \pm 0.1\text{\AA}$. TbC_2 with $a_0 = 5.691 \pm 0.006\text{\AA}$ at 1285°C confirmed the thermal analysis change

observed at 1280°C. Thus, transformations to the cubic form have been observed directly with a high degree of consistency. The expected diminishing of cell parameters due to the lanthanide contraction is also manifested in the three values listed. High temperature neutron diffraction measurements⁽¹⁸⁾ on cubic LaC₂ and YC₂ will be reported elsewhere. However, the transformation temperatures for the crystallographic changes were within 20°C of those found by our thermal analysis technique.

Table V shows the Knoop microhardness values obtained using a 400 g. load with a thin layer of kerosene over the polished specimen. The dicarbides were annealed for 4 hours at 1500°C prior to mounting and making the measurements. Again the values obtained lend support to the general grouping of lanthanum and yttrium type dicarbides.

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Table I

SOLID STATE TRANSITIONS AND MC₂-C EUTECTICS FOR THE
RARE EARTH DICARBIDES

<u>Dicarbide</u>	<u>Tetragonal → Cubic Transformation ± 20°C</u>	<u>MC₂-C Eutectic, °C</u>
YC ₂	1320	2275 ± 25
LaC ₂	1060	2230 ± 20
CeC ₂	1090	2245 ± 20
PrC ₂	1135	2255 ± 20
NdC ₂	1150	2275 ± 20
SmC ₂	1170	2240 ± 30
EuC ₂	?	-
GdC ₂	1270	2315 ± 25
TbC ₂	1285	2275 ± 20
DyC ₂	1295	2290 ± 25
HoC ₂	1305	2270 ± 20
ErC ₂	1325	2255 ± 25
TmC ₂	1355	2245 ± 35
YbC ₂	?	2215 ± 40
LuC ₂	1500	2230 ± 20

Table II

LATTICE PARAMETERS OF THE RARE EARTH DICARBIDES

Dicarbide	This Work		Reference 1	
	a_o	c_o	a_o	c_o
YC ₂	3.665 ± 0.001	6.169 ± 0.003	3.665 ± 0.001	6.169 ± 0.004
LaC ₂	3.935 ± 0.001	6.577 ± 0.001	3.934 ± 0.002	6.572 ± 0.001
CeC ₂	3.877 ± 0.001	6.478 ± 0.001	3.878 ± 0.001	6.488 ± 0.002
PrC ₂	3.847 ± 0.001	6.428 ± 0.002	3.855 ± 0.002	6.434 ± 0.004
NdC ₂	3.822 ± 0.001	6.401 ± 0.001	3.823 ± 0.001	6.405 ± 0.003
PmC ₂	-	-	-	-
SmC ₂	3.775 ± 0.005	6.324 ± 0.003	3.770 ± 0.001	6.331 ± 0.003
EuC ₂	-	-	4.045	6.645*
GdC ₂	3.717 ± 0.001	6.264 ± 0.002	3.718 ± 0.001	6.275 ± 0.003
TbC ₂	3.692 ± 0.001	6.210 ± 0.001	3.690 ± 0.002	6.217 ± 0.005
DyC ₂	3.666 ± 0.001	6.162 ± 0.001	3.669 ± 0.001	6.176 ± 0.003
HoC ₂	3.644 ± 0.001	6.136 ± 0.004	3.643 ± 0.001	6.139 ± 0.002
ErC ₂	3.617 ± 0.001	6.099 ± 0.002	3.620 ± 0.001	6.094 ± 0.003
TmC ₂	3.604 ± 0.001	6.012 ± 0.011	3.600 ± 0.002	6.047 ± 0.007
YbC ₂	3.649 ± 0.005	6.133 ± 0.015	3.637 ± 0.004	6.109 ± 0.010
LuC ₂	3.564	5.962 **	3.563 ± 0.001	5.964 ± 0.006

*Reference 8

**From extrapolated data using Er

Table III

INTERPLANAR SPACING OF LuC_2

<u>d</u>	<u>Int</u>	<u>d</u>	<u>Int</u>	<u>d</u>	<u>Int</u>
6.691	W	2.593	S	1.848	M
5.514	F	2.528	S	1.816	M
4.498	VF	2.465	M	1.783	S
3.601	M	2.420	M	1.738	W
3.363	M	2.279	W	1.711	W
3.089	M	2.248	F	1.683	M
3.037	S	2.131	VF	1.627	S
2.947	VS	2.106	MS	1.599	MW
2.759	W	2.017	W	1.573	W
2.718	M	1.956	MW	1.559	W
2.676	W	1.937	MW	1.544	W
2.645	F	1.889	S	1.530	F
		1.860	VF	1.514	M

Table IV

LATTICE PARAMETERS OF CUBIC DICARBIDES BY
HIGH TEMPERATURE X-RAY DIFFRACTION

<u>Dicarbide</u>	<u>a_0</u>
LaC ₂	6.001 ± 0.005
TbC ₂	5.691 ± 0.006
LuC ₂	5.505 ± 0.005

Table V

KNOOP MICROHARDNESS (KN) 400 g. LOAD

<u>Dicarbide</u>	<u>Microhardness, kg/mm²</u>
YC ₂	400 ± 25
LaC ₂	215 ± 20
CeC ₂	219 ± 7
PrC ₂	166 ± 12
NdC ₂	213 ± 13
SmC ₂	224 ± 23
EuC ₂	-
GdC ₂	281 ± 31
TbC ₂	370 ± 9
DyC ₂	392 ± 16
HoC ₂	611 ± 40
ErC ₂	660 ± 65
TmC ₂	648 ± 72
YbC ₂	168 ± 3
LuC ₂	721 ± 29

Figure 1

$\text{LaC}_2\text{-C}$ EUTECTIC
HEATING & COOLING CURVES

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Figure 2

PrC_2 TRANSITION (TETRAGONAL $\rightarrow$ CUBIC)
A-COOLING CURVE
B-HEATING CURVE

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