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The C-Ho (Carbon-Holmium) System

12.011 169.9304

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No phase diagram is available for the Ho-C system, although some structural and compound data have been reported.

[58Spe] established the existence of tri-holmium carbide, Ho_3C, a high-temperature form that can exist metastably at ambient temperature (see "The Carbon-Rare Earth Systems," in this issue). This compound has a cubic structure of the Fe_4N-type. The lattice parameter for a C-rich Ho_3C composition are listed in Table 1. No parameters for a Ho-rich composition were reported.

The stable form at ambient temperature has the approximate composition Ho_2C and has a rhombohedral structure of the $CdCl_2$-type. [66Bac] prepared Ho_2C with this structure by sintering a mixture of C and holmium hydride at 800 °C (no further details are available). [81Ato] prepared this compound by arc melting 99.9% (at.%?) Ho and spectrographic grade C (graphite) powder. Analysis of the arc-melted boule gave the molar ratio Ho-to-C = 2.00 ± 5. Lattice parameter measurements by these investigators are in good agreement, and the averaged values are listed in Table 1.

[58Spe] found that Ho_2C_3 is dimorphic and occurs in both a cubic structure of the Pu_2C_3 type and in a lower-symmetry form that had not been indexed at that time. Lattice parameters for cubic Ho_2C_3 are presented in Table 1 for Ho-rich and C-rich compositions. [58Spe] observed that the lower-symmetry sesquicarbide of Ho, as well as that of Er, Tm, and Lu, appeared to be isostructural with Y_2C_3. [68Car] investigated the Y-C system and observed this phase, but were not successful in indexing the pattern and determining the structure. [71Ato] reported "δHo_2C_3" as an impurity in their "αHo_2C_3" and stated that the interplanar spacings of "δHo_2C_3" were found to be nearly identical to the X-ray spacings reported by Carlson and Paulson for "δY_2C_3." However, [71Bau], who investigated the ternary Y-B-C system, derived the crystal structure of the "δ phase" for the Y-C system. They reported the composition to be $Y_{15}C_{19}$ with the tetragonal $Sc_{15}C_{19}$-type structure. No reports were found wherein the lower-symmetry form of the holmium sesquicarbide was indexed on the basis of a $Sc_{15}C_{19}$-type tetragonal cell, but it is quite likely that the low-symmetry pattern observed by [58Spe] was from the $Ho_{15}C_{19}$ phase. This needs to be verified experimentally.

In the region between 55 and 60 at.% C, the phase relationships in the Ho-C phase diagram may be quite similar to those observed in the Y-C system (see "The C-Y (Carbon-Yttrium) System," to be published). HoC_2 was observed by [58Spe] to crystallize in the bct CaC_2-type structure (Table 1). The temperature for the $\alpha \rightleftarrows \beta$ transformation in HoC_2 was reported by [73Mcc] as 1280 °C, by [76Loe] (same authors as [73Mcc]) as 1322 ± 8 °C, and by [67Kri] as 1305 ± 20 °C. The average value of 1300 ± 20 °C agrees well with the systematic variation of this property for REC_2 compounds (see "The Carbon-Rare Earth Systems," in this issue). No specific details on the structure of βHoC_2 were reported, but it has been stated

Table 1 Ho-C Crystal Structure and Lattice Parameter Data

Phase	Composition range, at.% C	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm a	b	c	Density, g/cm³	Reference
(Ho)	0	*hP*2	$P6_3/mmc$	*A*3	Mg	0.35778	···	0.56178	8.795	[86Gsc]
αHo_2C	~33	*hR*3	$R\bar{3}m$	*C*19	$CdCl_2$	0.6248(1)(a)	···	···	8.785	[66Bac, 81Ato]
βHo_3C	~25 to ~33	*cF*5	$Fm3m$	L'_1	Fe_4N	0.5061(2)	···	···	8.759	[58Spe]
Ho_2C_3	~54 to ~60	*cI*40	$I\bar{4}3d$	$D5_c$	Pu_2C_3	0.8172(b)	···	···	8.718(b)	[70Kru]
						0.8175(7)(c)	···	···	8.897(c)	[58Spe, 70Kru, 71Ato]
αHoC_2	~66.7	*tI*6	$I4/mmm$	$C11_a$	CaC_2	0.3648(4)	···	0.6144(4)	7.676	[58Spe, 67Kri, 81Sak, 84Jon]
βHoC_2(d)	~66.7	*cF*12	$Fm3m$	*C*1	CaF_2	···	···	···	···	[67Kri, 73Mcc 76Loe]
$\alpha' HoC_2$(e) ...	~66.7	*o*??	···	···	LuC_2	1.307	2.702	0.7530	···	[68Kru]
(C)	100	*hP*4	$P6_3/mmc$	*A*9	C(graphite)	0.24612	···	0.67090	2.266	[Pearson2]

(a) α = 33.07°. (b) Ho-rich. (c) C-rich. (d) Structure of this form has not been reported, but $\alpha \rightleftarrows \beta$ transition indicates that a high-temperature form exists. (e) Formed during long anneal (100 to 270 h) at 1155 ± 10 °C.

to be cubic and it is reasonable to assume that it has the CaF_2-type structure reported for the β rare-earth dicarbides.

[68Kru] reported that a third form of HoC_2 exists, forming during long anneals at 1155 ± 10 °C (100 to 270 h) from CaC_2-type αHoC_2. This form ($\alpha' HoC_2$) has the LuC_2-type orthorhombic structure (Table 1).

[67Kri] reported 2270 ± 20 °C as the HoC_2-C eutectic temperature, and this is in reasonable agreement with the systematic investigation of this function. No melting data for HoC_2 are available.

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The C-La (Carbon-Lanthanum) System

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Equilibrium Diagram

[59Spe] proposed a phase diagram for the La-C system based on thermal, metallographic, X-ray, dilatometric, and electrical resistance data. Earlier investigators [1895Pet, 31Sta, 52Bre] had prepared LaC_2 and reported some details of its structure.

[59Spe] used La metal that had been prepared by metallothermic reduction of the fluoride wih Ca metal. Chemical and spectrographic analysis showed 0.01 wt.% Y, Ca, Cu, Fe, and Si; 0.02% Ca and Mg; and 220 ppm C and 115 ppm N in their La metal. Two types of C were used: (1) "National Special Graphite Spectroscopic Electrodes," and (2) high-purity Acheson graphite, ATE, which on analysis showed less than 0.01 wt.% Ca, Mg, and Si. Alloys were prepared by arc melting weighed amounts of massive La (30 to 50 g) and C (1 to 10 g) under an atmosphere of purified helium or argon. Alloys containing less than 46 at.% (7 wt.%) C were inverted and remelted several times to attain complete homogeneity. Alloys containing more C were crushed into chunks 1 cm long between remeltings and the process repeated until no C was observed on freshly broken surfaces. Alloys were analyzed for combined and free C.

The wide range of melting points of the various La-C alloys necessitated the use of several techniques to obtain liquidus-solidus temperatures. When the C content did not exceed 46 at.% (7 wt.%), thermal analyses were conducted in *vacuo*, using a calibrated chromel-alumel thermocouple to measure temperature. Heating rates were 1.5 to 2 °C/min. For alloys containing more than 46 at.% C, the liquidus points were determined by a diffusion and