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Transformation temperatures and hydrolysis rates of three series of dicarbide solid solutions: YC_2–HoC_2, YC_2–LuC_2 and GdC_2–ErC_2

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Abstract

Three series of tetragonal substitutional solid solutions have been prepared for the systems $Ho_{1-x}Y_xC_2$, $Lu_{1-x}Y_xC_2$ and $Er_{l-x}Gd_xC_2$ and the kinetics of their reaction with water have been studied. A linear reaction rate constant was observed for all samples. The reaction rate for YC_2 at 1.93 cm cm^{-2} min^{-1} is anomalously fast from ionic size considerations; YC_2 is shown to be closer to GdC_2 in its hydrolysis and hardness behaviour than to HoC_2 with which it is closely related in size. The results are discussed in terms of C–C bond length distances and f character of the bonding electrons in the covalent component of the M–C_2 bond.

1. Introduction

YC_2, with a 4f electron band level too far above the Fermi level to give rise to any 4f band electrons in the sense defined by Gschneidner [1], has properties that place it in the heavy group of lanthanide carbides. The Vickers hardness value measured for YC_2 [2] also places it in this group with a value closest to that found for GdC_2, which according to Gschneidner [1] also has no f band electrons. In terms of volume per metal atom in the b.c.t. unit cell it can be seen in Table 1 that YC_2 is closer to HoC_2, which is in accord with the Ahrens radii (Y^{3+}, 0.092 nm; Ho^{3+}, 0.091 nm), than to GdC_2 to which it is often related. Furthermore, in a neutron diffraction study of YC_2, HoC_2 and some of their solid solutions [3] no change in the C–C bond distance was found, but negligible B_{33} values for carbides containing 50% or more of yttrium were noted. This might be associated with stronger C–C bonds consistent with the presence of strong Y–Y interactions and consequent weakening of the M–C_2 bonds. Such a situation might be examined by comparing the hydrolysis reaction rates of these dicarbides and some of their solid solutions in water at 20 °C as described for other dicarbides in two recent publications [4, 5]. The earlier work in refs. 4 and 5 did not report hydrolysis rate data for ErC_2 or LuC_2, which is now rectified in this paper where reaction rate data for some tetragonal solid solution phases are also reported and discussed. Transformation temperatures for YC_2, HoC_2, LuC_2 and some binary phases on transforming from the cubic, high temperature phase to the tetragonal phase are also reported for the first time.

TABLE 1. The volume per metal atom (*V*/M) in the unit cell of some dicarbides

Dicarbide	*V*/M (nm^3)
HoC_2	0.04083
YC_2	0.04138
DyC_2	0.04141
GdC_2	0.04328
LuC_2	0.03780

2. Experimental details

The dicarbides YC_2, HoC_2, YC_2 and ErC_2 were made from sheared pieces of re-sublimed metal of 99.99% purity supplied by Rare Earth Products Ltd. and pieces of specpure graphite rod melted in a flow of purified argon gas at a pressure in excess of 1 atm in the small arc furnace described before [6, 7]. Solid solutions were prepared by melting and mixing appropriate weights of the dicarbides. X-ray and metallographic methods used for sample characterization have all been previously described [6]. Small, nearly hemispherical samples about 20 mg in weight were made for the hydrolysis investigation in equipment previously described [4, 5] using identical procedures.

The transition temperature determinations were made on a Stanton Redcroft Thermal Analyser 674 using iron powder as a reference material at a heating

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rate of 10 °C min^{-1}. Samples and standard were enclosed in evacuated silica ampoules 0.8 cm high and 0.4 cm in diameter.

3. Results

For the HoC_2–YC_2 system, formation of solid solutions depresses the transformation from the cubic to the tetragonal polymorph by 75 °C, which from earlier work [6] indicates a unit cell volume difference of the order of 2%. The transformation temperatures found for YC_2 and HoC_2 are identical, whilst that for LuC_2 is some 70 °C higher as a result of the decrease in cell volume. The 9.4% difference between YC_2 and LuC_2 gives rise to a maximum 170 °C depression in T_t compared to LuC_2 as the larger volume YC_2 phase is alloyed with LuC_2. These transformation temperature values are shown in Table 2.

Linear kinetics were observed for the hydrolysis reactions studied at 20 °C for times in excess of 40 min, after which time the surface area of the small beads was significantly reduced. The linear reaction rate constant K_L found for ErC_2, 0.79 cm cm^{-2} min^{-1}, and that for LuC_2, 0.46 cm cm^{-2} min^{-1}, follow the trend of the results for other dicarbides as listed in Table 2 of ref. 4.

YC_2 appears to be more reactive in water than HoC_2 and in terms of its K_L value it behaves more like GdC_2. The implication is a weaker $M-C_2$ bond than that encountered in $Ho–C_2$ given that the cations are close in size and the $(C-C)^{n-}$ bond length is only slightly longer, 0.1288 nm compared to 0.1285 nm [3]. The unusual feature of the results from the hydrolysis rate constant experiments is the greatly enhanced reaction rate for the $Ho_{0.75}Y_{0.25}C_2$ sample. No obvious reason for this enhanced reactivity can be discerned, with the volume per metal atom *vs.* composition plot (Fig. 1) appearing quite linear and the C–C bond length only being slightly smaller than the HoC_2 precursor at 0.1281 nm [3].

Insufficient samples from the $Lu_{1-x}Y_xC_2$ system were available to check if the enhancement in reaction rate on substitution of the smaller by the larger metal atom was a general trend. Consequently, a series of tetragonal solid solutions from two other heavy group lanthanide dicarbides, ErC_2–GdC_2, were made and examined.

The volume per metal atom *vs.* composition plot for this series of solid solutions (Fig. 2) indicates a Vegard relationship from ErC_2 up to approximately $Er_{0.3}Gd_{0.7}C_2$ and less ideal behaviour up to GdC_2. Examination of the *a*, *b* and *c* parameters *vs.* composition (Fig. 3) shows a sharper increase in the *c* axis length between $Gd_{0.7}$ and $Gd_{1.0}$, which may be responsible for this effect since it indicates a lengthening of the C–C distance at this composition.

When the $Er_{1-x}Gd_xC_2$ samples were hydrolysed in water at 20 °C, the reaction rates showed an enhanced rate of reaction for the more dilute solid solutions before returning to values around the line connecting the two precursor phases (Fig. 4). Thus the enhanced reactivity of the $H_{0.75}Y_{0.25}C_2$ sample may be indicative of a general effect for binary dicarbide solid solutions when both metals come from the heavy lanthanides.

4. Discussion

The rates of hydrolysis in water of ErC_2 and LuC_2 fit the pattern of a gradually increasing $M-C_2$ bond strength for the heavy lanthanide dicarbides that essentially arises from the increased ionic bond strength as the metal cation size decreases. Destabilizing features in the $M-C_2$ covalent bonding from f-type band electrons become negligible for the heavy lanthanides. Thus the expectation of a hydrolysis reaction rate constant

TABLE 2. Transformation temperatures and hydrolysis reaction rate constants for some tetragonal dicarbides

Material	T_t (°C)	K_L at 20 °C (cm cm^{-2} min^{-1})	a_0 (nm)	c_0 (nm)	V/M (nm^3)
HoC_2	1320	0.97	0.3646	0.6142	0.0408_3
$Ho_{0.75}Y_{0.25}C_2$	1250	2.72	0.3651	0.6149	0.0409_8
$Ho_{0.5}Y_{0.5}C_2$	1245	0.80	0.3657	0.6158	0.0411_8
$Ho_{0.25}Y_{0.75}C_2$	1260	1.69	0.3660	0.6166	0.0413
YC_2	1320	1.93	0.3663	0.6171	0.0414
LuC_2	1390	0.46			
$Lu_{0.9}Y_{0.1}C_2$	1260	–			
$Lu_{0.7}Y_{0.3}C_2$	1230	–			
$Lu_{0.5}Y_{0.5}C_2$	1220	–			
$Lu_{0.3}Y_{0.7}C_2$	1235	0.92			
$Lu_{0.1}Y_{0.9}C_2$	1275	–			
ErC_2		0.79			

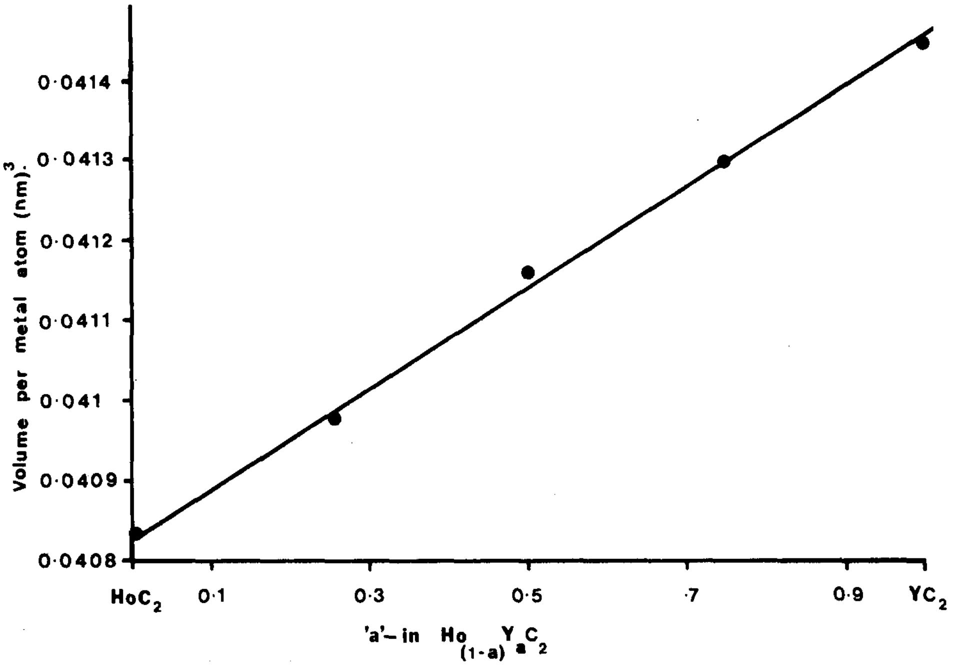

Fig. 1. Volume per metal atom in the unit cell of the tetragonal $Ho_{1-x}Y_xC_2$ solid solutions.

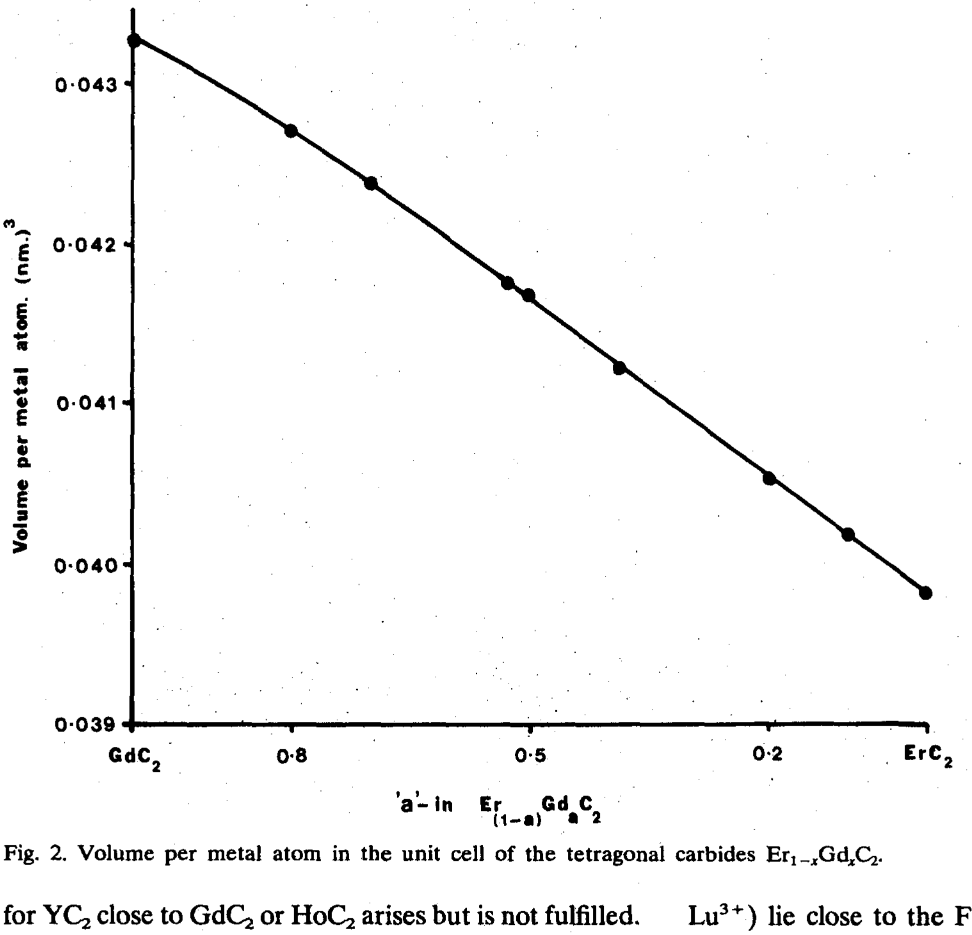

Fig. 2. Volume per metal atom in the unit cell of the tetragonal carbides $Er_{1-x}Gd_xC_2$.

for YC_2 close to GdC_2 or HoC_2 arises but is not fulfilled. In Gschneidner's model of bonding in lanthanide compounds [1], 4f band electrons exist and occur because the empty 4f energy levels (14 for La^{3+} to zero for Lu^{3+}) lie close to the Fermi level and are thus partly occupied by the conduction electrons. The implication of this is that electrons involved in the Ln^{3+}–C_2 $2p_\pi^*$ band have some f character. From a series of physical

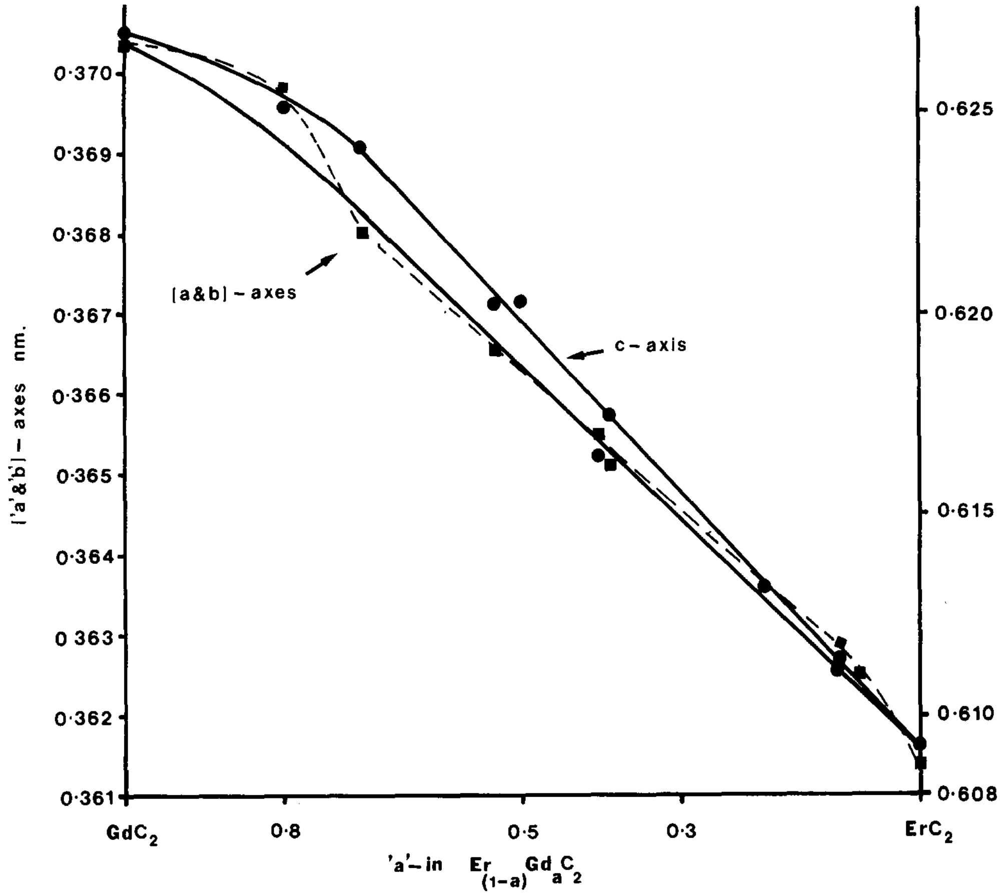

Fig. 3. X-ray lattice parameters for tetragonal phases $Er_{1-x}Gd_xC_2$.

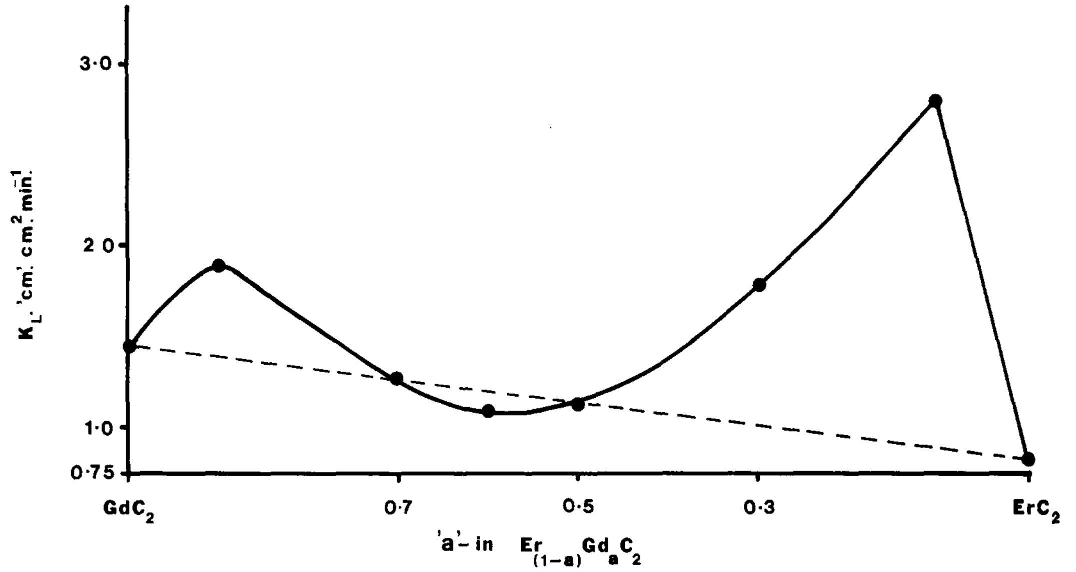

Fig. 4. Linear reaction rate constants at 20 °C for the reaction of $Er_{1-x}Gd_xC_2$ phases with water.

property variations of the metals and some compounds the f character was found to be 0.7e$^-$ for the light lanthanides, dropping sharply to 0.1e$^-$ for the heavy lanthanides at samarium, and was zero for lutetium and yttrium. This f electron character in the bonding is believed to weaken the $Ln^{3+}-C_2$ bond, a factor which can be seen in the way hardness values of the LnC_2 phases change [2] and recently too in the hydrolysis reaction rates of dicarbides [5]. On this argument YC_2 should be more resistant to hydrolysis and be harder than HoC_2, as LuC_2 certainty is. Hence the K_L value for YC_2 at 1.93 cm cm^{-2} min^{-1} is anomalously fast compared to HoC_2 at 0.97 cm cm^{-2} min^{-1} and is in fact closer to the value found for GdC_2 at 1.43 cm cm^{-2} min^{-1}. As far as the Vickers microhardness goes [2], YC_2 with a hardness of 5.01 GN m^{-2} is closer to GdC_2 at 4.63 GN m^{-2} than to HoC_2 at 5.61 GN m^{-2}. Thus, despite the closeness in ionic size between Ho^{3+} and Y^{3+}, it seems that YC_2 more closely resembles GdC_2. The reason for this could be the anomalously low B_{11} parameter found in the neutron diffraction study of YC_2 [3], which was interpreted as arising from stronger C–C bonds in the YC_2, $Y_{0.25}Ho_{0.25}C_2$ and $Y_{0.5}Ho_{0.5}C_2$ phases and stronger Y–Y bonds, with both effects leading to weaker $Y-C_2$ bonding, hence the easier, faster hydrolysis and decreased hardness than expected from the analogy with HoC_2. Formation of the tetragonal solid solutions $Ho_{1-x}Y_xC_2$ and $Gd_{1-x}Er_2C_2$ produces similar enhanced chemical reactivity and decreases hardness on initial substitution, quite markedly so where the larger cation is substituted for the smaller cation. It is not obvious why this should be so, since the cell volume changes indicate nearly Vegard behaviour. Other systems need to be examined to see if this is quite general for the heavy lanthanide pairs, since there is a decrease in the hydrolysis reaction rate constant for all solid solutions found in the series between the light lanthanide dicarbides LaC_2–NdC_2 [7].

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