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Formation of metastable monoclinic rare earth sesquioxides from the melt

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A number of rare earth sesquioxides prepared by rapid cooling of the melt consist entirely of the metastable monoclinic (B) form or a mixture of B and the cubic (C) form which is stable at room temperature. This may be explained by suppression of the B to C transformation for Sm_2O_3, Eu_2O_3, Tb_2O_3 but the B-form is metastable at all temperatures for Y_2O_3, Er_2O_3 and Yb_2O_3 and its appearance in these oxides is thus related to the nucleation kinetics of B and C from the melt.

1. Introduction

A feature of the rare earth sesquioxides is polymorphism which depends upon cationic radius [1, 2]. Thus the largest ions (lanthanum, cerium and praseodymium) exhibit the hexagonal (A) structure whereas the elements samarium to dysprosium form the monoclinic (B) and cubic (C) structures at high and low temperatures, respectively. The oxides of the remaining smaller cations, including yttrium, exist only as the C type although it has been suggested that Y_2O_3 may transform to the B structure at temperatures near the melting point [3], however two other hexagonal phases (X) and (H) have been reported at temperatures approaching the melting points of all the rare earth oxides [4]. The solid phase relationships are shown in Fig. 1 together with melting points determined by Coutures *et al.* [5]; the ionic radii used are those published by Zachariasen [6].

The B form of the sesquioxides is approximately 8% denser than the C form and, as expected, the B–C stability field boundary is moved towards smaller cationic radius at high pressures [3, 7] as shown in Fig. 1. Thus cubic Y_2O_3 transforms to the B form at approximately 1000° C under a pressure of 20 kbar, and is retained as a metastable phase at ambient pressure and temperature. Transformation to the stable C form occurs on reheating to 900° C for a few hours.

Rapid quenching of materials can often result in the retention of high temperature phases at ambient temperatures but Eu_2O_3 and Sm_2O_3 which exist as the B form above 1100 and 900° C, respectively, were reported to exist as the C form when prepared by various splat quenching techniques [8]. Other work, however, demonstrated that the B form was formed by rapid quenching of the melt in both of these oxides and that a mixture of B and C resulted from rapid quenching of molten Tb_2O_3 and Dy_2O_3 whereas slower cooling produced C (with a small quantity of B in the cased of Tb_2O_3) [4]. Quenching of the molten oxides Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Sc_2O_3 produced the C form only. The B form of Ho_2O_3, observed at 2200° C by high temperature X-ray diffraction, could not be retained by the most rapid quenching available [4]. All the sesquioxides between Sm_2O_3 and Yb_2O_3 can be prepared in the B form as a submicron powder by condensation of the vapour onto a cold substrate [9].

The present paper reports the formation of the monoclinic phase from the melt, by plasma treatment of the sesquioxides of the smaller rare earth cations, and interprets the results in terms of nucleation and transformation kinetics.

2. Experiments and results

The oxides used (Table 1) were supplied as −325 mesh powders of 99.9% purity by Cerac Inc., Milwaukee, USA. Terbium oxide was supplied as

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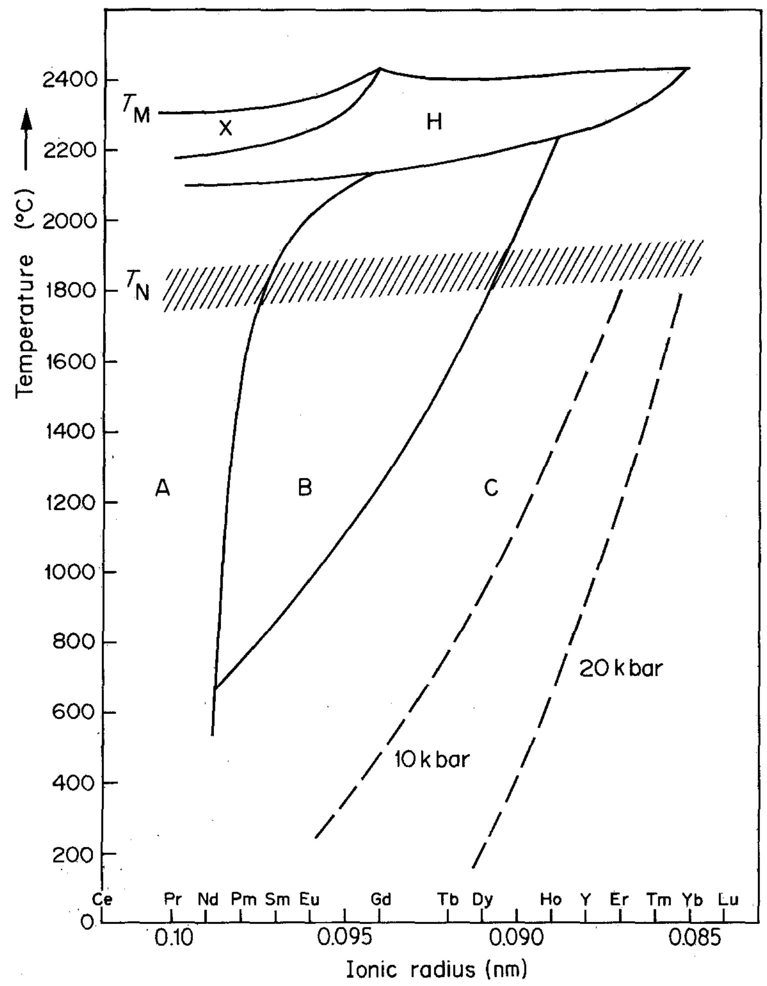

Figure 1 Range of stability of polymorphs of rare earth sesquioxides as a function of cationic radius [1, 2, 4]. Melting point, T_m [5]; estimated homogeneous nucleation temperature, T_N 0.8 T_m. The lines marked 10 and 20 kbar refer to the B–C equilibria at these pressures [7].

Tb_4O_7 and converted to Tb_2O_3 by heating to 1400° C in argon which had been passed over heated titanium chips.

Powders were plasma sprayed as a thin deposit onto cool aluminium plates using the following plasma torch operating conditions.

Nitrogen flow rate	$50\,l\,min^{-1}$
Hydrogen flow rate	$10\,l\,min^{-1}$
Voltage	100
Current	250 amp

Y_2O_3 and Er_2O_3 powders were also spheroidized using the same d.c. plasma torch operating within a closed reactor system, as described previously [10]. The treated Y_2O_3 powders were separated into a number of narrow particle size fractions, ranging from 5 to 50 μm, by means of a "Cyclosizer" elutriation apparatus, for X-ray diffraction analysis to determine if there was a particle size effect on the crystal structure.

The phases present in coatings and spheroidized powders were determined by X-ray diffraction using Cu$K\alpha$ radiation in a Philips diffractometer with the results shown in Table I. Typical patterns are illustrated in Fig. 2.

Nd_2O_3 was the only oxide to completely retain the initial (equilibrium) structure after plasma treatment. The oxides Sm_2O_3, Eu_2O_3 and Dy_2O_3 consisted entirely of the metastable monoclinic form and Tb_2O_3 consisted predominantly of this phase with a trace of the cubic form. The Y_2O_3, Er_2O_3 and Yb_2O_3 coatings consisted of a mixture of the B and C forms, however the Er_2O_3 coating contained a much higher proportion of B than the others (Fig. 2).

Spheroidized Y_2O_3 and Er_2O_3 powders, suspended in a liquid of high refractive index (bromoform), were also examined by transmission optical

TABLE I Crystal structure of as-received powders, sprayed deposits and spheroidized powders

Sample	As-received	Deposit	Spheroidized
Nd_2O_3	hexagonal	hexagonal	–
Sm_2O_3	cubic	monoclinic	–
Eu_2O_3	cubic	monoclinic	–
Tb_2O_3	cubic	monoclinic (trace of cubic)	–
Dy_2O_3	cubic	monoclinic	–
Y_2O_3	cubic	cubic/monoclinic	cubic/monoclinic
Er_2O_3	cubic	monoclinic/cubic	monoclinic/cubic
Yb_2O_3	cubic	cubic/monoclinic	–

microscopy under crossed polars. With these conditions the isotropic cubic phase may be distinguished from the birefringent monoclinic phase as illustrated in Fig. 3 which shows spheroidized Y_2O_3 (10 to 15 μm faction) under partially crossed polars; the monoclinic phase appears bright, the cubic phase grey and internal voids black.

The proportion of B in spheroidized Y_2O_3 was similar to that in the coating and did not appear to depend significantly on the initial powder particle size. Particle counting indicated that the spheroidized Y_2O_3 contained less than 10% monoclinic phase. The proportion of the B form in spheroidized Er_2O_3 was estimated using X-ray diffraction by comparing the integrated intensities of the (4 0 0) cubic and (1 1 2) monoclinic lines in the spheroidized product and mixtures of this with a range of additions of the initial cubic powder; this showed that spheroidized Er_2O_3 contained approximately 70% of the monoclinic form. Optical microscopy confirmed that most of the spheroidized Er_2O_3 particles consisted of the monoclinic phase and that the cubic phase occurred predominantly in unmelted feed particles.

3. Discussion

The observations that Sm_2O_3 and Eu_2O_3 consisted entirely of the monoclinic B form after plasma spraying is in agreement with the results of rapid cooling of these melts in a solar furnace [4] and may simply be explained by the suppression of the B to C transformation, which occurs at temperatures less than 1100° C. The formation of B type Tb_2O_3 and Dy_2O_3 can be explained in the same way, the higher cooling rates obtained by plasma spraying ($\cong 10^{6\circ}$ C $\sec^{-1}$ [11]) resulting in complete retention of the high temperature form whereas the lower cooling rates available in the previous work allowed partial transformation to the C form.

The oxides Y_2O_3, Er_2O_3 and Yb_2O_3 do not exist as the B form at any temperature (Fig. 1) so that the observation of a mixture of B and C forms after plasma spraying or spheroidization must mean that metastable B is nucleated directly from the melt rather than the stable C form (or H form near the melting point) and retained at room temperature because of the rapid cooling rate. Formation of metastable phases in this manner has been treated in detail for the case of Al_2O_3 in which γ-Al_2O_3 and δ-Al_2O_3 are observed to form from the melt under certain circumstances [12]. Thus, a stream of isolated molten particles will crystallize to the δ-Al_2O_3 form, rather than α-Al_2O_3 the only stable crystalline phase, if the particle size is less than $\cong 10\,\mu$m, and molten Al_2O_3 droplets sprayed onto a cold substrate crystallize to the γ-Al_2O_3 form. The evidence suggests that γ-Al_2O_3 is nucleated from the melt at the large undercooling required for crystallization of isolated droplets because of a lower barrier to nucleation from the melt than α-Al_2O_3. Similar large undercoolings also occur during solidification of plasma sprayed coatings [11]. γ-Al_2O_3 is retained to ambient temperature in sprayed deposits because the high cooling rate suppresses the γ-Al_2O_3 to α-Al_2O_3 transformation. In the case of a stream of isolated droplets, the balance between the rate of heat transfer from the surface and the rate of release of the heat of diffusion results in a thermal spike, the magnitude of which depends upon particle radius; above a critical radius the initial γ-Al_2O_3 nucleus transforms to α-Al_2O_3. The lower cooling rates obtained during spheroidization treatments are not sufficient to prevent ordering of γ-Al_2O_3 to the related δ-Al_2O_3 form.

Similar conditions apparently apply to the rare earth sesquioxides. Thus sprayed deposits of Y_2O_3, Er_2O_3 and Yb_2O_3 consist of mixtures of B and C forms, either because the energy barriers

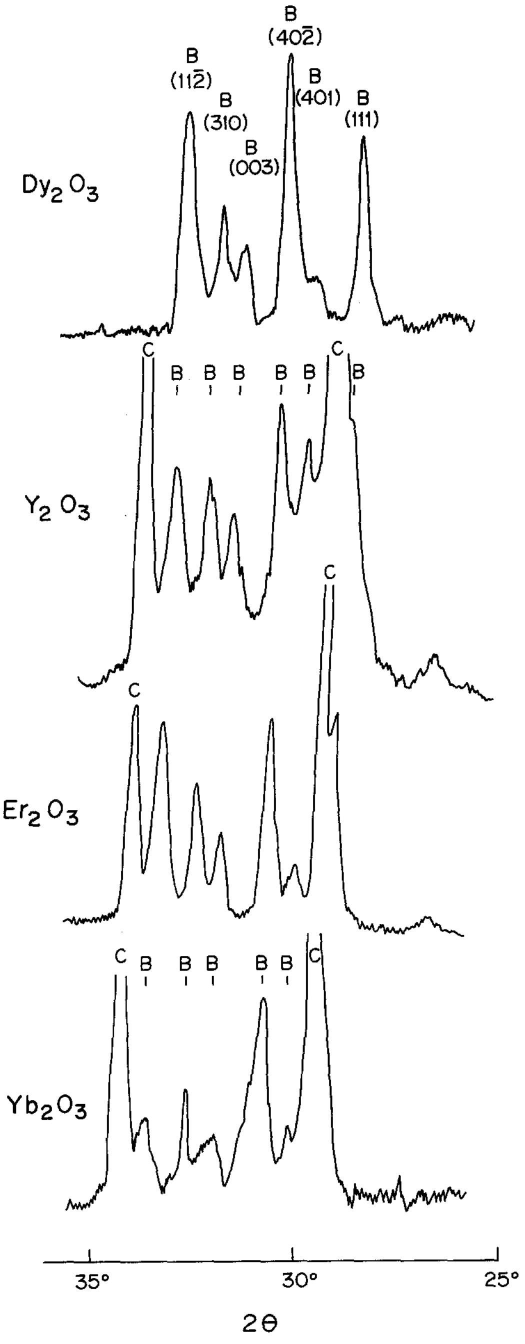

Figure 2 X-ray diffraction patterns (25 to 35° 2θ) for plasma sprayed films of Dy_2O_3, Y_2O_3, Er_2O_3 and Yb_2O_3 showing lines for B and C forms.

to nucleation of the forms are similar and differences in undercooling result in crystallization of one phase or the other in individual droplets, or the B form is nucleated and partly transforms to C on cooling. The very fast cooling rate experienced by spray coatings (10^{6} °C sec^{-1}) and the observation that the proportion of the two forms of Y_2O_3 and Er_2O_3 are similar for coatings and spheroidized particles, which have cooled much more slowly, suggest that nucleation kinetics are more important than transformation rates in determining the extent to which the metastable phase is formed.

Spheroidization results in the formation of a stream of isolated molten particles and, under these circumstances, crystallization in initiated by homogeneous nucleation at considerable under cooling, usually estimated to be approximately 20% of the absolute melting temperature although recent work suggests that it may be greater than this [13]. The estimated nucleation temperature (T_N) for the rare earth oxides are indicated in Fig. 1 which shows that the equilibrium phase at T_N would be B-type for Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3 and Dy_2O_3 and C-type for Y_2O_3, Er_2O_3, Yb_2O_3.

A further possibility is that, since the original nucleus is extremely small, the effective pressure due to surface tension will be quite high resulting in a shift of the B–C equilibrium towards smaller cationic radii. The effective pressure experienced by a small particle is $2\gamma/r$ where γ is the surface tension and r the particle radius. The surface tension between the liquid and crystalline phase of a substance is relatively low and for oxides is probably a few tenths Nm^{-1} [12]. This gives a pressure of the order of 1 kbar in the initial nucleus, insufficient to significantly shift the equilibrium, and the presure would of course drop to a negligible value as the nucleus grew in size. It therefore appears that the interfacial energy difference between the crystal nucleus and liquid is lower for the B form than the C form thus to some extent compensating for the difference in free energy per unit volume of the two crystalline forms relative to the liquid. This results in similar nucleation rates for the B and C forms of Y_2O_3, Er_2O_3 and Yb_2O_3 in the vicinity of T_N. The proportion of the two crystalline forms observed in the final product would thus be expected to be a sensitive function of the interfacial energy and this is probably the reason for the much larger proportion of monoclinic phase observed in spheroidized Er_2O_3 compared with Y_2O_3.

The formation of B form oxides from Sm_2O_3 to Lu_2O_3 (Yb_2O_3 was a mixture of B and C) by condensation from the vapour [9] can also be explained in a similar manner, that is the crystal–vapour surface energy is lower for the B than

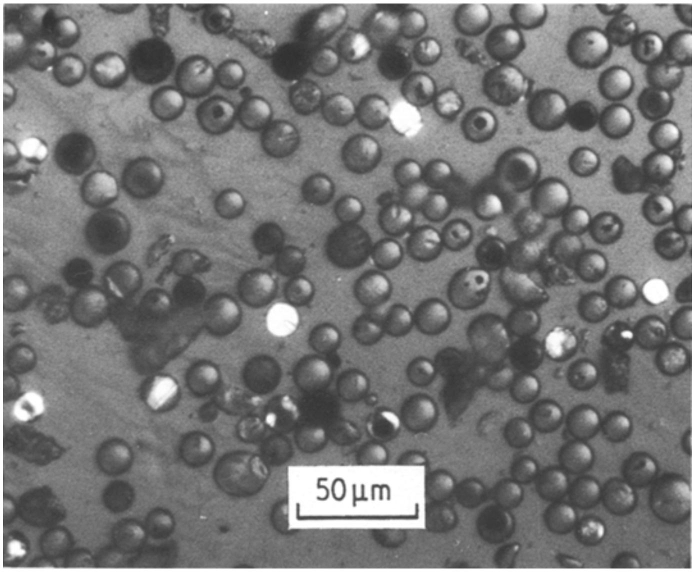

Figure 3 Transmission optical micrograph of plasma spheroidised Y_2O_3 dispersed in bromoform; 10 to 15 μm size fraction. Partially crossed polars.

the C form, compensating for the free energy difference. In this case, where condensation occurred on a cold substrate, B would always be metastable with respect to C. The very small size of the condensed particles (3.0 to 4.0 nm diameter), and large surface tension ($\cong 1\ \text{Nm}^{-1}$) would mean an effective pressure of the order of 10 kbar, however this would still not be sufficient to result in the B form becoming the stable phase at room temperature (Fig. 1) but it would mean a significant reduction in the free energy difference between the B and C forms.

4. Conclusion

Formation of the monoclinic (B) form of Sm_2O_3, Eu_2O_3, Tb_2O_3 and Dy_2O_3 by plasma spraying onto a cold substrate is a result of suppression of the B to C transformation by rapid cooling. The formation of the B form of Y_2O_3, Er_2O_3 and Yb_2O_3 in this way, and by plasma spheroidization of Y_2O_3 and Er_2O_3 in which B is metastable at all temperatures at atmospheric pressure, is a result of the influence of crystal–melt interfacial energy on the nucleation kinetics of the B and C forms.

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