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The structure of Al_2O_3–Cr_2O_3 powders condensed from a plasma

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The structure of Al_2O_3-Cr_2O_3 powders prepared by plasma oxidation of the mixed halides has been examined by X-ray diffraction, electron microscopy and electron spin resonance. The powders consisted predominantly of faceted spherical particles of a well crystallized solid solution of Cr_2O_3 in θ-Al_2O_3, with diameters of the order of 0.1 µm. Some larger particles of α-Cr_2O_3 were present in powders containing 17.8 and 24 wt % Cr_2O_3. The maximum solid solubility of Cr_2O_3 in θ-Al_2O_3 observed was 18 wt%. It is suggested that nucleation of crystallization of liquid Al_2O_3-Cr_2O_3 droplets occurs as a structure based on cubic close packing of oxygen ions and that the presence of chromium results in ordering to the θ-Al_2O_3 form rather than the δ-Al_2O_3 form usually observed in alumina powders prepared by plasma methods.

1. Introduction

Barry *et al* [1, 2] prepared Al_2O_3-Cr_2O_3 and TiO_2-Cr_2O_3 powders by the oxidation of $AlCl_3$-CrO_2Cl_2 and $TiCl_4$-CrO_2Cl_2 mixtures in an argon-oxygen high-frequency plasma torch. Although a high degree of solid solution was achieved in TiO_2-Cr_2O_3 powders, negligible solution of Cr_2O_3 in Al_2O_3 was observed. This was attributed to the large difference in vapour pressures of Al_2O_3 and Cr_2O_3 at high temperatures resulting in condensation and solidification of liquid Al_2O_3 droplets well in advance of condensation of Cr_2O_3.

A prerequisite for the preparation of Al_2O_3-Cr_2O_3 solid solution powders by condensation from a plasma will be the formation of liquid solution droplets. This will only be possible if the effective partial pressure of Cr_2O_3 in the flame is significantly greater than the partial pressure of Cr_2O_3 in equilibrium with a solution of Cr_2O_3 in Al_2O_3 at temperatures greater than the freezing point of the solution. Solidification of isolated droplets will be initiated by homogeneous nucleation and the undercooling will be approximately one-fifth the equilibrium melting-point [3], giving a solidification temperature for Al_2O_3 droplets of approximately 1850 K. From the data of Grimley *et al* [4] the vapour pressure of Cr species in equilibrium with solid Cr_2O_3 under oxidizing conditions is of the order of 10^{-6} atm at 2000 K. The effective Cr_2O_3 partial pressure in equilibrium with a dilute liquid solution of Cr_2O_3 in Al_2O_3 would probably be in the range 10^{-6} to 10^{-5} atm. In the work of Barry *et al* [1] the effective partial pressure of Cr_2O_3 was approximately 10^{-5} atm, so that condensation of Cr_2O_3 into alumina droplets could only be expected at temperatures close to the freezing point of the droplets. This paper describes the structure of Al_2O_3-Cr_2O_3 powders condensed from a plasma flame in which considerably higher oxide pressures were attained.

2. Experimental and results

Three powders prepared by the injection of mixtures of Al_2Br_6 and CrO_2Cl_2 vapour into the tail flame of an oxygen h.f. plasma were examined. Under the conditions of preparation, vere much higher reactant concentrations may by achieved than by feeding through the plasma torch [5]; in this case the effective partial pressure of Cr_2O_3 in the flame was of the order of 10^{-2} atm.

The structure of the powders was examined by X-ray diffraction using a Philips diffractometer and by electron microscopy using a JEM-120 electron microscope. The powders consisted predominantly of θ-Al_2O_3 with traces of δ-Al_2O_3 or α-Al_2O_3 and two of the powders also contained α-Cr_2O_3. The α-Cr_2O_3 content was determined

TABLE I Structure of co-condensed Al_2O_3-Cr_2O_3 powders

Number	Colour	Wt % Cr_2O_3 by chemical analysis	Wt % α-Cr_2O_3	Other phases	Wt % Cr_2O_3 in solution in θ-Al_2O_3
1	Grey	4.6	0	Trace δ-Al_2O_3	4.5
2	Green	17.8	4	Trace α-Al_2O_3	14
3	Green	24	7	Trace α-Al_2O_3	18

by comparing the integrated intensities of the (100) Cr_2O_3 and (200) θ-Al_2O_3 lines using known mixtures of Cr_2O_3 and θ-Al_2O_3 (sample 1) for calibration. The results are summarized in Table I. No appreciable solution of Al_2O_3 in α-Cr_2O_3 could be detected by change in lattice spacings. Increase of the interplanar spacing of θ-Al_2O_3 with Cr_2O_3 content was observed, as shown in Fig. 1 for the (313), (512), and (71$\bar{2}$) lines.

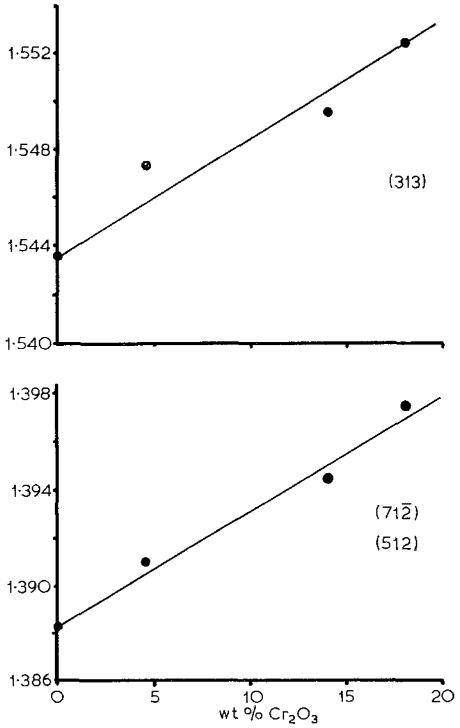

Figure 1 Interplanar spacings of θ-Al_3O_2 as a function of estimated wt % Cr_2O_3 in solution.

Powders 2 and 3 were found to consist of two widely different particle size ranges. A green sediment and grey suspension were formed when an ultrasonically dispersed sample of powder 2 in water was allowed to stand for 16 h. X-ray diffraction showed that the suspension consisted entirely of θ-Al_2O_3 and the sediment a mixture of θ-Al_2O_3, α-Al_2O_3 and Cr_2O_3. The electron micrograph in Fig. 2 is typical of the suspension and the major proportion of the other samples; selected area diffraction confirmed that the particles were θ-Al_2O_3. The sediment consisted of a mixture of large plates of Cr_2O_3 as shown in Fig. 3 together with some large spherical particles and agglomerates of partially sintered θ-Al_2O_3.

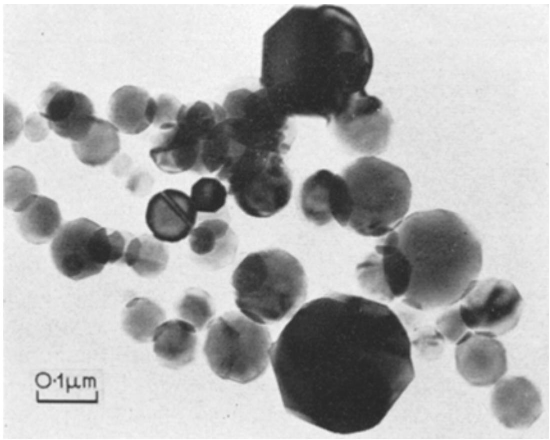

Figure 2 Electron micrograph typical of fine fraction of powder 2.

Electron spin resonance observations were made on powders 1 and 3 at 77 and 300 K using a Decca spectrometer at 9270 MHz with the results shown in Fig. 4. The 77 K spectrum for powder 1 (4.5 wt % Cr_2O_3) shows well-defined resonances typical of isolated Cr^{3+} in octahedral sites in θ-Al_2O_3 [6]. The resonance at 3400 G with peak-to-peak line width (ΔH) of 700 G was also detected. The spectra for powder 3 (18 wt % Cr_2O_3 in solution) are dominated by the large resonance ($\Delta H = 350$ G) at 3400 G although there is some trace at 77 K of the peaks due to isolated Cr^{3+} in θ-Al_2O_3.

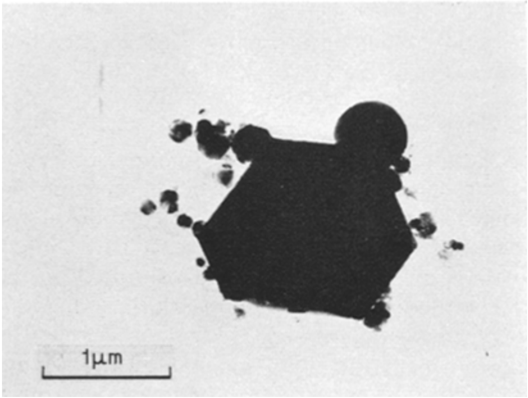

Figure 3 Electron micrograph typical of coarse fraction of powder 2.

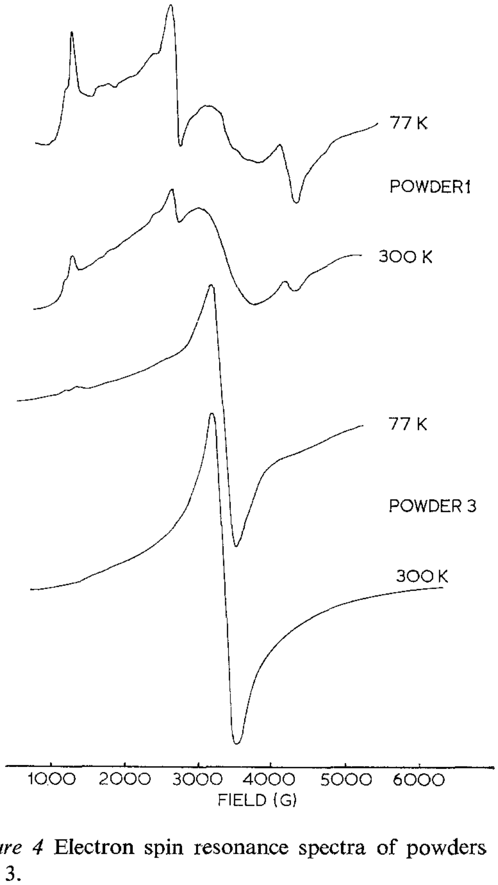

Figure 4 Electron spin resonance spectra of powders 1 and 3.

3. Discussion

The results are consistent with the condensation of liquid alumina-chromia solution droplets which have crystallized as a solid solution of Cr_2O_3 in θ-Al_2O_3. The Cr_2O_3 remaining in the vapour phase after soldification of the Al_2O_3-Cr_2O_3 droplets has then condensed directly to large crystals of α-Cr_2O_3. The faceting of the θ-Al_2O_3 particles could have arisen by some growth of the particles after soldification by absorption of Cr_2O_3 from the vapour. The small amount of α-Al_2O_3 present has probably been formed by the melting of sintered agglomerates of θ-Al_2O_3 recirculated in the flame.

The X-ray diffraction patterns of the metastable aluminas prepared by dehydration of hydroxides tend to be poorly defined with broad lines. The diffraction pattern from the present powders showed the presence of more lines than given by the ASTM Index for θ-Al_2O_3 prepared from boehmite, and the lines were sharper than those reported for a well-crystallized θ-Al_2O_3 prepared by hydrothermal and thermal treatment of η-Al_2O_3 [7]. For example the (400) and $(40\bar{1})$ lines were resolved for the Al_2O_3-Cr_2O_3 powder whereas they completely overlapped in the latter work. All lines could be indexed using the interplanar spacings calculated for θ-Al_2O_3 on the basis of the β-Ga_2O_3 structure [7]. The Al^{3+} ions in θ-Al_2O_3 are equally distributed between tetrahedral and octahedral sites in a distorted cubic close packed oxygen structure [8] and in a solution of chromium in θ-Al_2O_3 the Cr^{3+} ions would be expected to occupy the octahedral sites because of their high octahedral stabilization energy [9].

The e.s.r. spectrum of powder 1 at 77 K agrees closely with the published spectra for chromium-doped β-Ga_2O_3 and θ-Al_2O_3 prepared by dehydration of boehimite [6], and clearly indicate the replacement of Al^{3+} by Cr^{3+} in octahedral sites. The small peaks at 1700 and 8150 G do not unambiguously correspond to any lines reported for alumina polymorphs containing chromium [6]. These peaks were also observed by Barry *et al* [2] in their plasma-prepared Al_2O_3-Cr_2O_3 powders and ascribed by them to Cr^{3+} in octahedral sites with only slight orthorhombic distortion; however, more data are required before a definite conclusion may be drawn.

The resonance at 3400 G observed in powder 1 is more intense and narrower in powder 3 and overshadows the peaks due to isolated Cr^{3+}. Powder 3 contains free α-Cr_2O_3; however, the paramagnetic resonance of α-Cr_2O_3 disappears below the Néel temperature of approximately 300 K [10] and the observed resonance could not therefore have arisen from this source. The resonance appears to be similar to the β_N resonance in α-Al_2O_3-Cr_2O_3 [11] and the ϕ resonance in chromium-doped spinel [12], and probably has a similar origin, that is from exchange-coupled Cr^{3+} in octahedral sites. θ-alumina may be regarded as a distorted spinel structure in which octahedron edges are shared, and therefore might be expected to correspond more closely in behaviour to spinel than to α-Al_2O_3 in which there are face-shared octahedra. If Cr^{3+} only occupy octahedral sites, the fraction occupied will be 0.06 for powder 1 and 0.39 for powder 3. The line-width for powder 3 at 300K (350 G) lies between the values observed for spinel (420 G) [12] and α-Al_2O_3 (220 G) [11] at a similar fraction of octahedral sites occupied by Cr^{3+}, but is closer to that observed for α-Al_2O_3 at the low chromium fraction. The temperature-dependence of the line-width of θ-Al_2O_3 also appears to be similar to that observed for α-Al_2O_3-Cr_2O_3 solutions, suggesting that although short-range interactions are probably weaker than in α-Al_2O_3, long-range ordering occurs. This is in contrast to spinel in which only short-range Cr^{3+} interactions appear to be involved [12].

Pure alumina particles less than approximately 10 μm diameter prepared by flame or plasma methods are usually the metastable δ-Al_2O_3 or γ-Al_2O_3 forms rather than the stable α-Al_2O_3 structure. This may be explained on the basis of the relative nucleation rates of the various forms of alumina from liquid, and the rates of transformation of one polymorph to another [13]. The formation of θ-Al_2O_3 in the presence of Cr_2O_3 may then be a result of either a change in the relative energy barriers to nucleation of the various forms of alumina resulting in nucleation and growth as the θ-Al_2O_3 form or, alternatively, since the γ, δ and θ forms are basically different arrangements of the cations within the tetrahedral and octahedral sites of a distorted cubic close packed oxygen structure, nucleation of a structure based on cubic close packing of oxygen ions may be followed by ordering of the cations into a lower energy arrangement. This point of view is supported by the observation that the incorporation of a small quantity of Na_2O within spinel type aluminas prepared from hydroxides results in complete inhibition of δ-Al_2O_3 formation and the stabilization of θ-Al_2O_3, apparently because the occupation of octahedral site by Na ions prevents the ordering of the γ-Al_2O_3 structure into the δ-Al_2O_3 form [14]. On the other hand, the presence of Mg, Ni or Li ions which occupy tetrahedral sites tends to favour the formation of δ-Al_2O_3 [15].

4. Conclusions

1. Sub-micron particle-size alumina-chromia solid solution powders may be prepared by plasma flame oxidation of mixed halides if the effective Cr_2O_3 partial pressure is sufficiently high to allow condensation as liquid solution droplets.
2. The presence of chromium in solution stabilizes the metastable θ-Al_2O_3 form rather than the δ-Al_2O_3 structure observed in pure aluminium oxide powders prepared by condensation from a plasma under similar conditions.
3. Electron-spin resonance spectra are consistent with the replacement of Al^{3+} in octahedral sites by Cr^{3+} in θ-Al_2O_3.

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References

1. T. I. BARRY, R. K. BAYLISS, and L. A. LAY, *J. Mater. Sci.* **3** (1968) 229.
2. *Idem, ibid* **3** (1968) 239.
3. D. TURNBULL, *J. Appl. Phys.* **21** (1954) 1022.
4. R. T. GRIMLEY, R. P. BURNS, and M. G. INGHRAM, *J. Chem. Phys.* **34** (1961) 664.
5. A. AUDSLEY and R. K. BAYLISS, *J. Appl. Chem.* **19** (1969) 33.
6. L. L. VAN REIJEN, Thesis, Technological University, Eindhoven (1964).
7. G. YAMAGUCHI, I. YASUI, and W. C. CHIU, *Bull. Chem. Soc. Jap.* **43** (1970) 2487.
8. S. GELLER, *J. Chem. Phys.* **33** (1960) 676.
9. D. DUNITZ and L. E. ORGEL, *J. Phys. Chem. Solids* **3** (1957) 318.
10. E. S. DAYHOFF, *Phys. Rev.* **107** (1957) 84.
11. F. S. STONE and J. C. VICKERMAN, *Trans. Faraday Soc.* **67** (1971) 316.
12. J. C. VICKERMAN, *ibid* **67** (1971) 665.
13. R. MCPHERSON, *J. Mater. Sci.* **8** (1973) 851.
14. B. C. LIPPENS and J. H. DEBOER, *Acta Cryst.* **17** (1964) 1312.
15. ANNE MARIE LEJUS and R. C. COLLONGUES, Proc. 5th Internat. Conf. Reactivity of Solids, ed. G. M. SCHWANK (Elsevier, Amsterdam, 1964) p. 373.

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