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Note

The enthalpy of formation of aluminium titanate

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The enthalpy of formation of Al_2TiO_5 from the component oxides near the transition temperature has been reported to be 272 kJ/mole[1]. However, during a DTA investigation of phase transformations which occur during the heat treatment of Al_2O_3–TiO_2 powders condensed from a plasma, the enthalpy of formation from the oxides has been found to be an order of magnitude lower than the previously reported value.

The Al_2O_3–TiO_2 powder used was prepared by the oxidation of mixed aluminium and titanium halides in an oxygen high frequency plasma torch and consisted of spherical particles approximately 0.1 μm diameter. In the composition range 14–79 weight % TiO_2, each particle consisted of a finely dispersed two phase mixture of δ-Al_2O_3 and rutile[2].

Differential thermal analysis of the powders was carried out using a Rigaku model M8076 micro-DTA TGA apparatus at a heating rate of 20°C min^{-1} to a maximum temperature of 1500°C with α-Al_2O_3 as reference material. An exothermic peak, the temperature of which varied between 1000 and 1240°C depending upon the TiO_2 content, and an endothermic peak which began at 1340 and was complete at 1375°C, independent of TiO_2 content, were observed. X-ray diffraction of heat treated powders showed that the exotherm was due to the transformation of δ-Al_2O_3 to α-Al_2O_3, and the endotherm to the formation of Al_2TiO_5 from α-Al_2O_3 and rutile. The enthalpies of the transformations were determined from the areas under the DTA peaks using the known enthalpy of transition of 5.94 kJ mole^{-1} at 1200°C for the tetragonal to monoclinic phase change in zirconia[3] for calibration. Zirconia was chosen because of the similarity of the temperature and enthalpy of the transformation to those for the transformations of γ-Al_2O_3 and δ-Al_2O_3 to α-Al_2O_3; "Ugine Kuhlmann" 99.9% zirconia powder was used. The enthalpies of transformation of pure δ-Al_2O_3 powder prepared by the plasma method and "Linde B" γ-Al_2O_3 powder to α-Al_2O_3 were also determined. The mean value of seven measurements for δ-Al_2O_3 was -11.7 kJ mole^{-1} with a range of -9.6 to -13.8 and the mean value of four measurements for γ-Al_2O_3 was -24.3 kJ mole^{-1} with a range of -18.8 to -31.4. Several values for the enthalpy of transition from γ-Al_2O_3 to α-Al_2O_3 have been reported with ΔH° ($t = 25$°C) ranging from -18.4 to -63.2 kJ mole^{-1} [4,5]; the present results for both γ-Al_2O_3 and δ-Al_2O_3 however agree reasonably well with the values derived from enthalpies of solution of −22.2 and −11.3 kJ mole^{-1} at 750°C[6].

A mean value of 25.1 kJ mole^{-1} from seven measurements, with a range of 22.6–26.8 was obtained for the heat of reaction of α-Al_2O_3 and TiO_2 to form Al_2TiO_5 at 1340°C. Although similar methods for the estimation of heats of reaction from DTA measurements have been reported[5,7,8] it is recognized that the method may be subject to relatively large experimental errors, due mainly to changes in thermal conductivity of the sample while the reaction is taking place, particle size effects, and variation in sample packing[9]. Kostomaroff and Rey[5] have shown that the thermal conductivity of fine powders is low, and changes during reaction have a negligible effect. The other effects were minimised in the present work by the small sample size (20–30 mg) and uniform packing of the powders using a hand press, leading to an estimated error of ±8 kJ mole^{-1} in the enthalpy of reaction.

There is evidence that the reaction $Al_2O_3 + TiO_2 \rightarrow Al_2TiO_5$ is reversible, and equilibrium occurs at approximately 1300°C. Lang et al.[10] have found that Al_2TiO_5 is unstable at temperatures in the range 750–1300°C and stable from 1300°C to fusion. Hamelin[11] reported no reaction between the oxides at 1250°C and complete reaction at 1450°C and DTA measurements have given 1380°C as the reaction temperature[12]. At equilibrium the change in free energy is zero and the enthalpy of reaction may be estimated from the standard entropies of Al_2TiO_5[13], α-Al_2O_3 and rutile[4]. Assuming equilibrium at 1300°C, the calculated value is $\Delta H = 17.6$ kJ mole^{-1}, which is reasonably consistent with the DTA results.

The temperature correction for the heat of reaction from 1340 to 25°C, based on heat capacity data[3,4] is 1.7 kJ mole^{-1} and may be neglected. The standard enthalpy of formation of aluminium titanate from its constituent elements is then

$$\Delta H^{\circ}_{Al_2TiO_5} = H^{\circ}_{Rutile} + H^{\circ}_{\alpha\text{-}Al_2O_3} + H^{\circ}_{React} = -2.600 \text{ kJ mole}^{-1}$$

using the reported enthalpies of formation of α-Al_2O_3 and rutile[4]

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1 R. A. Slepetys and P. A. Vaughan, *J. Phys. Chem.*, 73 (1969) 2157.
2 M. S. J. Gani and R. McPherson, *J. Aust. Ceram. Soc.*, 8 (1972) 65.
3 E. G. King and J. P. Coughlin, *J. Amer. Chem. Soc.*, 72 (1950) 2262.
4 *JANAF Thermochemical Tables*, Dow Chemical Co., Mich., 1967.
5 V. Kostomaroff and M. Rey, *Silicates Ind.*, 28 (1963) 9.
6 T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.*, 68 (1964) 3246.
7 C. N. R. Rao and K. J. Rao, *J. Mat. Sci.*, 1 (1966) 238.
8 B. R. Currell, in R. F. Schwenker Jr. and P. D. Garn (Eds.), *Thermal Analysis*, Academic Press, New York, 1969, p. 1185.
9 R. C. MacKenzie and B. D. Mitchell, in R. C. MacKenzie (Ed.), *Differential Thermal Analysis*, Vol. 1, Academic Press, New York, 1970, p. 108.
10 S. M. Lang, C. L. Fillmore and L. H. Maxwell, *J. Res. Nat. Bur. Stand*, 48 (1952) 298.
11 M. Hamelin, *Bull. Soc. Chim. Fr.*, (1957) 1421.
12 B. N. Battacharyya and Sudhir Sen, *Glass Ceram. Bull. (India)*, 12 (1965) 92.
13 K. R. Bonnickson, *J. Amer. Chem. Soc.*, 77 (1955) 2152.