PHASE EQUILIBRIA IN THE SYSTEM $\text{Cr}_2\text{O}_3\text{-SiO}_2$

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ABSTRACT

A study of the phase equilibria in the system $\text{Cr}_2\text{O}_3\text{-SiO}_2$ has shown that no compounds exist and that the two oxides are practically immiscible in the solid and liquid states. The melting point of Cr_2O_3 was found to be $2,140^\circ \pm 25^\circ \text{C}$.

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I. INTRODUCTION

Although chrome ores have long been used in the metallurgical and ceramic industries, nothing has been reported on the phase equilibria existing at high temperatures between Cr_2O_3 and the other oxides usually associated with it. Chrome refractories¹ seldom contain more than 60 per cent of Cr_2O_3 , since they are made from chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) ores, which contain, in addition to the FeO present, several per cent of silica, alumina, etc., as impurities. As chrome refractories are often used in contact with silica in furnace construction, the simple binary system of Cr_2O_3 and SiO_2 seemed most appropriate for an initial investigation.

II. GENERAL METHOD

Mixtures of powdered Cr_2O_3 (99.2 per cent) and SiO_2 (99.7 per cent) were prepared in stick form and fused in the oxyhydrogen flame. Repeated grindings and fusions were made to obtain homogeneous mixtures. Small pieces (10 to 20 mg) of the mixtures were placed in the central hole of an Ir-Pt alloy button and heated for an hour or more in an Ajax induction furnace.²

Temperatures were measured with a disappearing filament optical pyrometer³ sighted on the outer hole in the button. The coil of the induction furnace was mounted on a rotatable platform so that it could be inverted to allow the button to drop out into a quenching bath of water. Granular thoria was placed under the button to keep it from sticking in the crucible in which the button was heated. In this quench instantaneous cooling to room temperature was not

¹ McDowell and Robertson, J. Am. Ceram. Soc., 5, p. 865; 1922.

² This iridium-button furnace has been described in a previous paper. This Journal, 4, p. 131; 1930.

³ The pyrometer was calibrated before use by the pyrometry section of this bureau.

obtained, since the button weighed about 50 gm, but a drop in temperature of several hundred degrees took place rapidly enough to prevent any appreciable shift in the equilibrium attained at the high temperature.

The melts were removed from the hole in the button by breaking them up with a pointed hardened steel punch. Mixtures containing not more than a few per cent of Cr_2O_3 were sufficiently transparent to be examined under the microscope. The opaque mixtures were examined by the powder method in the X-ray spectrograph.⁴

In order to obtain a uniform distribution of the Cr_2O_3 in mixtures containing less than 1 per cent of it, a hot-water solution of ammonium silicofluoride and chromium nitrate was treated with excess ammonium hydroxide, giving a precipitate of chromium hydroxide intimately mixed with silicic acid. This precipitate was washed, dried, and fused in stick form in the oxyhydrogen flame.

III. RESULTS

Under the microscope mixtures containing 0.1 per cent or more of Cr_2O_3 and which had been heated to $2,100^\circ \text{C}$. for an hour showed the presence of undissolved Cr_2O_3 in substantially the same amount as before the heat treatment. The mixture containing 0.1 per cent Cr_2O_3 was colored a light bluish green, the color becoming dark green with higher Cr_2O_3 content. There is probably a slight solubility of Cr_2O_3 in SiO_2 , but not enough to determine or to distinguish the eutectic temperature from the melting point of silica. A very slight but undetected solubility of SiO_2 in Cr_2O_3 above $2,140^\circ$ must also be assumed.

X-ray spectrograms of mixtures containing 92, 86, 71, 57, 43, 29, and 14 per cent by weight of Cr_2O_3 , which had been heated for two hours at $1,750^\circ$ and then quenched, indicated that no compounds were formed and that the only crystals present were of Cr_2O_3 .

All mixtures containing more than about 35 weight per cent of Cr_2O_3 had to be heated to over $2,100^\circ \text{C}$. before becoming noticeably fluid. Quenched mixtures which had been heated in the oxyhydrogen flame above the melting point of Cr_2O_3 showed the presence of two immiscible liquid phases.

IV. THE MELTING POINT OF Cr_2O_3

The melting point of Cr_2O_3 was determined by direct observation on a small piece of prefused Cr_2O_3 ⁵ placed in the Ir-Pt button. The field of view in the pyrometer covered both holes in the button, and when a temperature of $2,140^\circ \text{C}$. was reached the Cr_2O_3 was seen to melt. Duplicate determinations agreed within 5°C ., but the measurements are considered to be accurate only to $\pm 25^\circ \text{C}$. The pyrometer was used soon after calibration, but, as an additional check, a similar determination was made of the melting point of pure Al_2O_3 , which was found to be $2,040^\circ \text{C}$. This is in good agreement with the value ($2,050^\circ$) given in the International Critical Tables.

⁴ X-ray spectrograms were made by the metallurgical division of this bureau.

⁵ This Cr_2O_3 was prepared from $\text{C. P. Cr}(\text{NO}_3)_3$ by precipitating a hot 1 per cent water solution with pure NH_3 gas. The precipitated $\text{Cr}(\text{OH})_3$ was washed, dried, and fused in the oxyhydrogen flame. Analysis by conversion to chromate and titration with KI and thiosulphate gave 99.9 per cent Cr_2O_3 . The 99.2 per cent Cr_2O_3 melted at $2,125^\circ \text{C}$.

All previous observations⁶ on the melting point of Cr_2O_3 have been made in carbon resistor electric furnaces in which partial reduction of the Cr_2O_3 may have occurred. Thus, Ruff obtained values ranging from $1,830^\circ$ to $2,080^\circ \text{C.}$, depending upon the rate of heating and the nature of the gas present in the furnace, and concluded that the true melting point could not be determined in a carbon furnace.

V. ACKNOWLEDGMENTS.

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⁶ ($2,059^\circ$) Goecke, *Metallurgie*, 8, p. 667; 1911. ($2,059^\circ$) Ruff and Goecke *Z. für angew. Chem.*, 24, p. 1459; 1911. ($2,080^\circ$) Ruff, *Z. für anorg. Chem.*, 82, p. 373; 1913. ($1,990^\circ$) Kanolt, *Bur. Std. Bul.*, 10, p. 295; 1914.