PHASE EQUILIBRIA IN THE SYSTEM Cr_2O_3-Al_2O_3

By E. N. Bunting

ABSTRACT

A study of the phase equilibria in the Cr_2O_3-Al_2O_3 system has shown these oxides to be completely miscible in the liquid and solid states, with no compound formation. The melting point of Cr_2O_3 has been redetermined to be 2,275° ± 25° C.

CONTENTS

I. INTRODUCTION

A dilute solution of Cr_2O_3 in Al_2O_3 has long been known as the ruby. More concentrated solutions do not possess the desirable color of the ruby, but are of interest because of their refractory properties.

Duboin[1] reported that on heating mixtures of Cr_2O_3 and Al_2O_3 to a "red white" heat, from 15 to 16 per cent Cr_2O_3 united with the Al_2O_3. Passerini[2] made an examination by X rays of mixtures which had been heated to 600° C. and found that limited solution in the solid state occurred at this temperature.

II. MATERIALS AND GENERAL PROCEDURE

A homogeneous solution of "C. P." $Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ and $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ in warm water was treated with an excess of ammonium hydroxide. Since both hydroxides are very insoluble a thoroughly mixed precipitate is obtained in this way and mixtures of known composition could be made from weighed amounts of the salts. The washed and filtered hydroxides were ignited to oxides in a platinum crucible over a Méker burner.

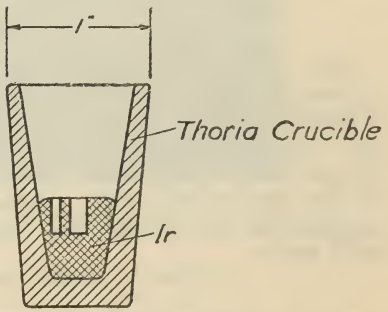

FIGURE 1.—*Crucible with iridium vessel used to obtain temperatures up to 2,300° C. in an oxidizing atmosphere*

The melting temperatures of these mixtures were determined by means of an iridium button (fig. 1) heated by high frequency induction. A small piece of the material, about one-half millimeter in size, was placed in the central hole and covered with a larger piece of the same mixture to promote uniformity of temperature within the space occupied by the small piece. The

[1] Duboin, Compt. rend., 134, p. 840; 1902.

[2] Passerini, Gazz. chim. ital., 60, p. 544; 1930.

button was heated to a series of temperatures in steps of 10° C., as measured by an optical pyrometer sighted into the smaller of the two holes in the bu n. After each temperature step the larger piece of material was removed from the cold button and the smaller piece examined with a magnifying glass. An error of 10° or more is possible in judging the condition of partial melting. The calibration of the optical pyrometer was checked before and after these observations were made, and the results are probably accurate within ±25° C.

The temperature of complete fusion was obtained by observing two or three very small pieces of a mixture in the hole as the temperature was raised. Mixtures containing up to 30 mole per cent Cr_2O_3 readily "wet" the iridium on melting, while those with high Cr_2O_3 content did not, so that the temperature of complete melting of the high Cr_2O_3 mixtures could not be determined accurately.

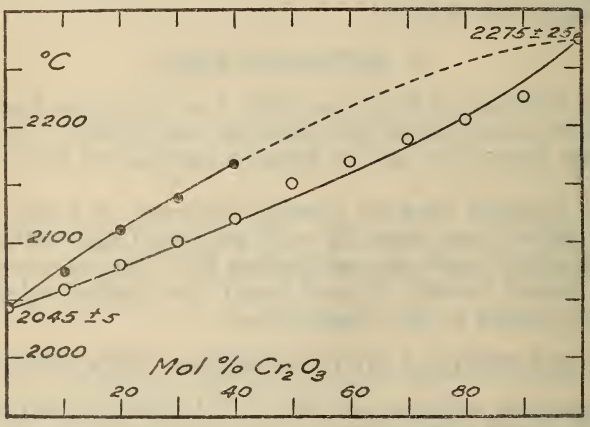

FIGURE 2.—*Phase diagram for the system Cr_2O_3-Al_2O_3*

III. RESULTS

The data obtained are shown in Table 1 and Figure 2. They indicate a continuous series of solid solutions. X-ray spectrograms[3] of mixtures containing 20, 40, and 70 mole per cent Cr_2O_3 and which had been fused are shown in Figure 3. The absence of additional lines in the spectrograms of the mixtures and the progressive shifting of the lines as the Al_2O_3 content is increased demonstrate that no compounds are formed, but that complete miscibility occurs in the solid state.

TABLE 1.—*Melting points of Cr_2O_3-Al_2O_3 mixtures*

Mole per cent Cr_2O_3	Solidus temperature	Liquidus temperature	Mole per cent Cr_2O_3	Solidus temperature	Liquidus temperature
	°C.	°C.		°C.	°C.
0	2,045	2,045	60	2,170	----------
10	2,060	2,075	70	2,190	----------
20	2,080	2,110	80	2,205	----------
30	2,100	2,140	90	2,225	----------
40	2,120	2,170	100	2,275	2,275±25
50	2,150	----------			

[3] The X-ray spectrograms were made by the metallurgical division of this bureau.

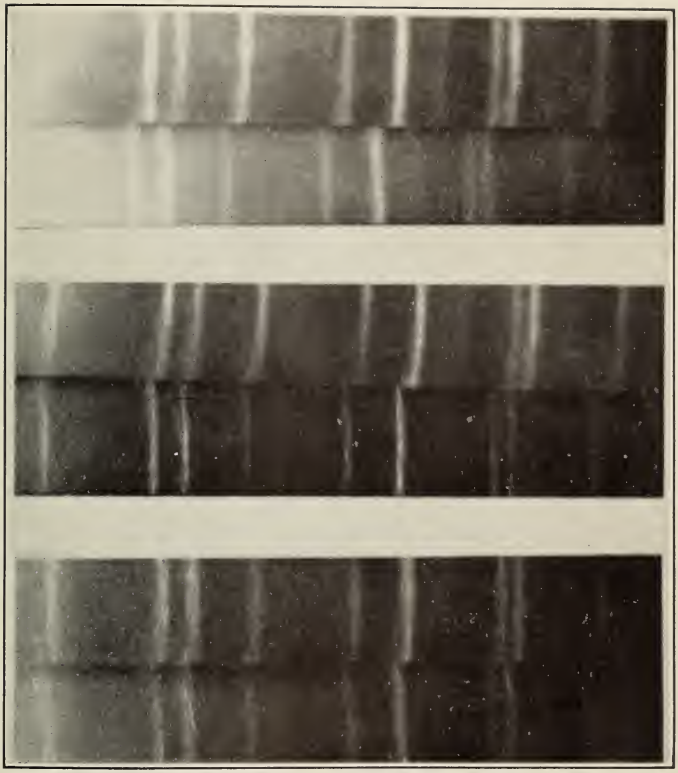

FIGURE 3.—*X-ray spectograms of* Cr_2O_3-Al_2O_3 *mixtures*

IV. THE MELTING POINT OF Cr_2O_3

In a previous paper [4] the melting point of Cr_2O_3, which had been prefused in an oxyhydrogen flame, was reported to be 2,140° ± 25° C. As there is a possibility of reducing some of the Cr_2O_3 by prefusion in this manner,[5] a sample of unfused Cr_2O_3 was prepared from $Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$. The melting point of this unfused Cr_2O_3 was found to be 2,275° ± 25° C., as determined in the iridium button. The vapor pressure of Cr_2O_3 at this temperature must be considerably under atmospheric pressure, as small pieces kept at this temperature for several minutes did not evaporate from the hole in the button. Wartenberg and Werth could not obtain the melting point of Cr_2O_3 in a zirconia furnace, fired with oxygen and atomized oil, because of excessive vaporization above 2,200° C., and concluded that Cr_2O_3 sublimed before reaching its melting point. In the presence of reducing gases, which would diffuse through a zirconia tube at this temperature, the Cr_2O_3 may have been reduced and vaporized as the metal or a lower oxide, since Cr_2O_3 is very susceptible to reduction at high temperatures.

Washington, March 19, 1931.

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[4] Bunting, B. S. Jour. Research, 5, p. 325; 1930.
[5] Wartenberg and Werth, Zeit. anorg. allgem. Chem., 190, p. 183; 1930.

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