# STUDIES ON THE FUSED PRODUCTS OF $Cr_2O_3$-$SiO_2$ SYSTEM.

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Glasses coloured by various metal oxides were known from ancient time, but there are, however, only few studies on the colouring of fused silica glass. Copper and cobalt oxides give red and blue silica glass respectively. Chromic oxide has a special property of producing many kinds of colours on silica glass. Experimental conditions affect on the colours of silica glass containing chromic oxide, since black, green and other colours are obtained by the different treatments. The following studies were carried out to make clear the special and complex properties of the obscure $Cr_2O_3$-$SiO_2$ system.

## Experimental.

The materials used are an ordinary chromic oxide for chemical use and natural quartz sands which were purified by hydrochloric acid. The mixture of a definite proportion of these materials was fused by an electric furnace of high voltage. The experimental results are as follows.

When the temperature of the mixture is nearly to the melting point of silica (1700°C.) or a little higher, there is no chemical reaction between two oxides. And it is observed that the chromic oxide powder, owing to its high melting point (ca. 2000°C.), was heterogeneously distributed in the fused silica. Subsequently a homogeneous fused product should be obtained by raising temperature far above 1700°C. The product thus obtained was striped on the whole by the consequence of high viscosity of fused silica and inhomogeneity of the temperature raised, and the initial granular form of the chromic oxide was not found in it as in the first case.

The colour of the fused product depends upon the concentration of chromic oxide, the temperature of the fusion and the cooling velocity of the heated mass. At a very high temperature and with a low concentration of chromic oxide (about 0.5%) it gives a transparent and homogeneous mass of blue, violet or reddish brown colour. High concentrations of the oxide (few percent) give non-transparent products, and their colours are too many to point out strictly. But it may be said that by the rapid cooling the product is black and glassy, and by the slow cooling dark blue, reddish brown or dark green and brittle. The relation between the experimental conditions and the colours of the fused product may be summarized as follows.

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|---|---|
| (A). Low concn. of $Cr_2O_3$ | Transparent, glassy and homogeneous mass with a colour of blue, violet or reddish brown. |
| (B). High concn. of $Cr_2O_3$ and rapid cooling | Glassy and apparently black mass, its thin plate is, however, transparent and reddish brown. |
| (C). High concn. of $Cr_2O_3$ and slow cooling | Non-transparent and not glassy mass of dark green, dark blue, reddish brown etc. |

A beautiful green glass can not be obtained by one heating operation, but it is occasionally obtained only by the second heating. This second heating operation upon the fused product will be mentioned by the term of "reheating" in this paper. No characteristic changes were observed on the reheated products of (A) and (B) to 1700°C., but a remarkable change was found on (C). By the reheating of (C) somewhat below the melting point of silica it becomes a very brittle and pure green mass. When the temperature of the reheating was elevated to 1700°C., it, however, becomes a very beautiful green and glassy fused mass which may be useful to ornaments.

**Microscopic Studies of the Fused Products.** A petrographic microscope was used to examine the products. (A) is completely transparent under the microscope. And considering that there is no compound between two oxides and are many varieties of the colour, it is perhaps the colloidal solution of chromic oxide in fused silica. (B) is also glassy and its thin plate is homogeneous and reddish brown, but it contains very little particles of chromic oxide which is a small fraction of its initial quantity.

The studies by the petrographic microscope were almost limited to (C), since the very beautiful green and glassy fused mass was obtained by its reheating. Fig. 1, 2, 3 and 4 are the examples of (C). Figs. 2 and 4 are those of under the crossed Nicols. In the figures only needle-like crystals are found, but the crystals are not really needle and are very thin plate of which section appears needle-like. The form of the crystal is shown by the following diagram. This crystal is a very thin tridymite. The main part of the chromic oxide mixed are distributed in the tridymite as little green crystals which can be observed by the microscope. The other small part of it exists homogeneously in the same tridymite with the different colours like (A) and (B). The occurrence of chromic oxide in two different kinds in the fused product as above may be the reason why so many varieties of (C) are obtained. By the ratio of the both kinds of the oxide and by the size of the particle, it can be conceived to be obtained so

Fig. 1. (×1000)

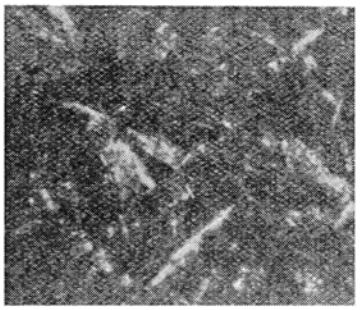


Fig. 2. (×1000).

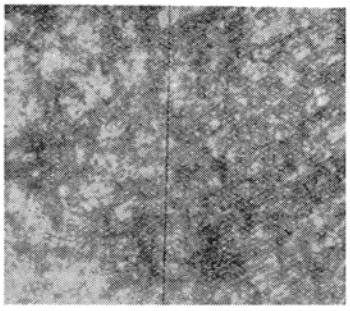


Fig. 3. (×1000)

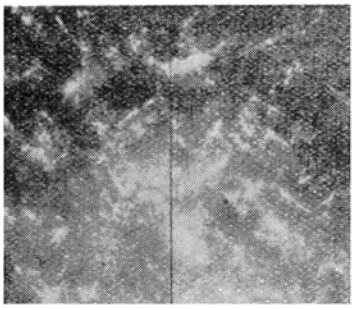
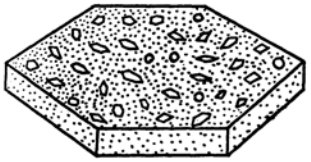


Fig. 4. (×1000)



Diagram

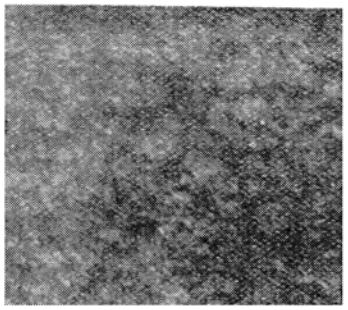


Fig. 5. (×1000)

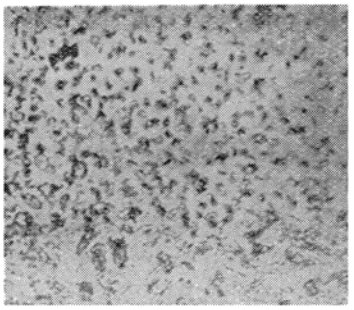


Fig. 6. (×1000)

many colours of the fused products as they can not be expressed by proper words.

The mechanism of the second reheating operation on the product is explained by the results of the microscopical studies. Fig. 5 shows a product of which the colour changed from reddish brown to green and the crystal of chromic oxide did not disappear. In this case it was known that the transformation of tridymite to cristobalite occurred and the main part of the chromic oxide which existed as green crystals remained in the cristobalite as before, and the other small part of the oxide disappeared which gave the different coloured products. Thus the change of colours of (C) to pure green by reheating can be well explained. When the temperature is raised over the melting point of cristobalite but not far over, the cristobalite becomes silica glass and the above pure green crystals of chromic oxide distribute in it, and the beautiful green and glassy fused product will be obtained by rapid cooling. Fig. 6 shows the portion of the reheated mass which contains the specially big, hexagonal, tabular and green crystals of chromic oxide.

## Discussion.

Considering that the crystal of chromic oxide is different from its initial form by the cooling velocity, it may be seen that at high temperature chromic oxide dissolves in silica of fused state and recrystallizes as the temperature falls. The nature of the particles produced by the recrystallization of chromic oxide depends upon the concentration of the oxide and especially upon the cooling velocity by the consequence of very high viscosity of fused silica. The formations of (A), (B) and (C) may be explained by this view.

Efforts to obtain cristobalite by the cooling of the fused $Cr_2O_3$-$SiO_2$ system was in vain, because it always accompanys the formation of silica glass or tridymite (by the proper cooling velocity crypto-crystalline tridymite) contrary to the Ostwald's principle. The colour change by the reheating process is an interesting phenomenon. It is perhaps related to the fact that the recrystallization of chromic oxide in tridymite is not fully developed but completely in cristobalite by the natures of its crystal structure.

The experiments on obtaining the fused products were carried out in the laboratory of the Institute of Physical and Chemical Research at Hongo, Tokyo, since it was very convenient to use a special apparatus to get easily the products of high melting point.

## Summary

(1) The mixtures of chromic oxide and silica were electrically fused and by the experimental conditions the products of different colours were obtained.

(2) The beautiful green and glassy fused product was obtained only by the second reheating process.

(3) The products of different colours were examined by the petrographic microscope.

(4) The experimental conditions to obtain the each product of different colours were discussed.



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