A REVIEW ON ALUMINA - CHROME (AL2O3 - CR2O3) AND CHROME -SILICA (CR2O3 - SIO2) REFRACTORIES ALONG WITH THEIR BINARY PHASE DIAGRAMS

Although refractories belonging to the Alumina - Chrome (Al₂O₃ - Cr₂O-3) refractory oxides system has found many applications in the industry yet not much research work on these two refractory oxides system have been done and therefore, data on the pure Alumina - Chrome $(Al_2O_3 - Cr_2O_3)$ or Al-Chrome refractories are also either sparse or have scarcely been reported. Rather because of their improved properties, Alumina - Chrome or Al-Chrome refractories with some Silica (SiO₂) content and other minor impurities have always been proposed by the refractory technologists for applications in numerous industries (areas).Nevertheless, this article is not to discuss the properties and applications of Mullite - Chrome refractories or those belonging to Alumina - Chrome - Silica $(Al_2O_3 - Cr_2O_3 - SiO_2)$ system which have been discussed in a separate article. Here we have tried to put together or review the past work done on the two (binary) refractory oxide systems.

Alumina - Chrome (Al₂O₃ - Cr₂O₃) Refractory System

A dilute solution of Cr_2O_3 in Al₂O₃ has been called as '**Ruby**'since long. More concentrated solutions do not possess the desirable colour of the Ruby, but are of considerable interest because of their refractory properties. Dubion [Dubion, Compt. rend. 134, 1902, p. 840] reported that on heating mixtures of alumina (Al_2O_3) and chromia (Cr_2O_3) to red white state, 15 - 16% Cr_2O_3 united with alumina. Passerini [L. Passerini, Gazz. chim. Ital. 60, 1930, p.544] made an X-ray examination of mixtures and found that limited solution in the solid state occurred at 600^oC. Bonthron and Durrer [K.J.A. Bonthron and E. Durrer, Z. anorg. u. allgem. chem. 198(1), 1931, p.141] reported a eutectic at 30% Cr₂O₃. Barks et al. [R.E. Barks, D.M. Roy, and W.B. White, Am. Ceram. Soc. Bull. 44(4), 1965, p.317] showed that below 925°C, there exists a miscibility gap in the solid solution series between the two oxides. Bunting [E.N. Bunting, J. Res. Natl. Bur. Std. 6(6), 1931, p.947], whose work was accepted Wilde and Rees [W.T. Wilde and W.J. Rees, Trans. Br. Ceram. Soc. 42, 1943, p.123] and Roeder et al. [R.L. Roeder, F.P. Glasser, and E.F. Osboron, J. Am. Ceram. Soc. 51(10), 1968, p.585], made the attainment of equilibrium easier by precipitating chromium and aluminium hydroxides with ammonium hydroxide from the aqueous solution of $Cr_2(SO_4)_3$.(NH₄)₂SO₄.2H₂O and Al₂(SO₄)₃.(NH₄)₂SO₄.24H₂O. Their study of the Phase equilibria in the Alumina - Chrome system showed a complete solid solution series with no compound formation. The phase diagram for the Alumina - Chrome refractory oxides system sketched from the data of Bunting is shown in the adjacent phase diagram.

A patent [T.G. McDongal, A.H. Fessler, and K. Schwartzwalder, U.S. Pat. 2218584, Oct. 22, 1940; Ceram. Abstr. 20(1), 1941, p.21] assigned to the AC Park Company also confirmed the formation of complete solid solution between alumina and chromia. On the basis of microscopic examination Preston found the crystals of the Alumina - Chromia solid solutions, like hexagonal plates having the appearance of **Corundum**. He referred to these crystals as *Chrome*

Corundum [F.W. Preston, J. Am. Ceram. Soc. 17, 1934, p.356].

An investigation into the sintering behaviour of this binary refractory oxide system without using any additive was made by Rai and Roy [H.L. Rai and P.B. Roy in "Proceedings of the symposium on the Sintering and Sintered Products", Oct.29-31, 1979, BARC, Bombay, India, p.655]. Their results showed that Alumina-Chrome or Al-Chrome refractory can be made having higher cold and hot strength at relatively low temperature of 1650° C. While the Chromia (Cr₂O₃) content ranging 5-11%, is suitable for end use requirement of certain industries, it has also been found 15% Chromia (Cr₂O₃) addition and above with Alumina (Al₂O₃) can be even better in getting a better refractory material. However, the latter will need higher firing temperature.

In another paper Bogum and Faizullah [Proceedings of the International Symposium on Refractories, Nov. 1988, Hangzhou, China] have stressed on the important properties like high corrosion and thermal shock resistance properties of Alumina-Chrome or Al-Chrome bonded refractories. The vulnerable areas of glass melting furnace (e.g. overcoating refractory blocks at the metal line, throat assemblies, electrode blocks, doghouse corner refractory blocks and arches) can be upgraded with bonded Alumina - Chrome - Silica refractories for the remaining lining of the furnace. Chrome corundum phase containing refractories have been prime candidate for the working lining of slagging coal gasifier. Alumina - Chrome (Al-Chrome) refractories formed spinel reaction products at the slag-refractory interface which is one of the reasons for which they can be suitably applied in some areas of Slide Gate refractory assemblies. Fraser and many other workers reported exceptional resistance to corrosion by highly siliceous slag along with better results for Alumina - Chrome (Al-Chrome) refractories from service in coal gasifier, fiber glass tank and carbon reactors.



Chrome - Silica (Cr₂O₃ - SiO₂) Refractory System

Phase relations in the Silica - Chrome ($Cr_2O_3 - SiO_2$) refractory oxides system as was determined by Bunting [E.N. Bunting, J. Res. Natl. Bur. Std. 5(2), 1930, p.325] are illustrated in the adjacent phase diagram. The liquid miscibility shown by him extend virtually across the phase diagram may actually be less extensive as suggested by the studies of Glasser et. al. [F.P. Glasser, I. Warshaw, and R. Roy, Phys. Chem. Glasses, 1(12), 1960, p.39] Due to the absence of sufficient additional data Bunting's work was, however, accepted by many authors subsequently. The phase diagram of Chrome - Silica ($Cr_2O_3 - SiO_2$) refractory oxides system shows no intermediate compounds; over most of the range of composition between chrome and silica there are two immiscible liquids at high temperatures and the primary crystalline phase is chromic oxide.

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