

network of hydrogen bonds, in which bonds of the type O-H...N, N-H...O and O-H...Cl⁺ are involved.

In view of the fact that virtually all other copper complexes of the type CuL₂X₂ (L = a heterocyclic amine, X = Cl or Br) have tetragonal planar, polymeric halide bridged, or distorted tetrahedral coordination geometries, it is significant that the dimeric unit found in the adenine inner complex persists in the compound Cu(Ade)₂Cl₂·3H₂O. From the available e.p.r. and magnetic evidence^{5,6} this is now almost certainly true for several other Cu(Ade)₂X₂·nH₂O compounds, though in some of them water molecules and not anions will occupy the terminal coordinate positions. The key bridging arrangement of donor atoms in adenine is found in several other molecules of biological significance, so systems containing closely held and electronically interacting pairs of metal ions may be more widespread than has been realized hitherto.

Finally, we note that although the extent of spin-coupling in the compound under discussion is comparable with that in copper acetate ($\mu_{\text{eff}} = 1.45$ BM at 295 K) the relatively long Cu-Cu distance of 3.066 Å reinforces the conclusion drawn previously⁵ that the spin coupling in copper dimers of this type proceeds predominantly via a superexchange mechanism involving the bridging groups, and not by any significant direct metal-metal bonding.

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Vonsenite in Oxide Scales on Iron

INTEREST in the use of inorganic oxide powder coatings to suppress or minimize the oxidation of steel surfaces during high-temperature processes has been growing in recent years¹⁻³. The nature of the powders used and the operative protective mechanisms, however, are complex.

In the course of studying the oxidation process for a simplified system (ortho-boric acid coatings on high purity iron) at temperatures between 700° and 1,100° C in pure oxygen, a complex reaction product in the oxide scale was identified as iron boro-ferrite (4 FeO·Fe₂O₃·B₂O₃), which we believe to be identical to the mineral "vonsenite"⁴. We have not been able to trace any previous published reference to this complex oxide in the oxidation of metals literature. This communication summarizes our preliminary work.

Vonsenite is described⁴ as an opaque mineral, a high-temperature ferrous ferric borate of the ludwigite-vonsenite series, which occurs in skarn in the pyrometasomatic magnetite deposit near New York. The chemical analysis given by Leonard and Vlisidis was: FeO ~ 54 wt.%; Fe₂O₃ ~ 30 wt.%;

B₂O₃ ~ 13 wt.%. The oxide ratios are thus 4.01 : 1.07 : 1.00, which are close to the ideal 4 FeO·Fe₂O₃·B₂O₃ or approximately Fe₂" Fe'" BO₅.

The experimental work involved coating a clean, polished iron surface with ortho-boric acid at room temperature, after which the sample was oxidized in pure oxygen in the temperature range 700°-1,100° C. At 480° C, ortho-boric acid had fully transformed to a melt of boric oxide, which dissolved the initial oxide film. In the continuing oxidation process, reactions between the melt and iron oxides produced a solid, multilayered scale structure.

Metallographic evidence indicated that the innermost scale layer (~40-100 μm thick) comprised a granular structure associated with extensive void formation. The layer became increasingly disrupted as the temperature of oxidation was increased. The remainder of the scale structure was mainly wüstite with a thin, outermost layer of magnetite. At 1,100° C, a thin, outer layer of haematite was observed above the magnetite. The microhardness of the inner granular layer was of the same order as that for magnetite. No evidence of a "glassy" phase or residual boric oxide was observed.

Electron probe microanalyses of the inner layer revealed a composition of 65.2 wt.% iron, 30.3 wt.% oxygen and, by difference, the remaining 4.5 wt.% was assumed to be boron. This analysis corresponded closely to the theoretical composition of iron boro-ferrite (vonsenite) containing 64.8 wt.% iron, 30.9 wt.% oxygen, 4.3 wt.% boron. X-ray evidence from powdered, detached scales indicated lattice parameters which were in close agreement with published data⁵ for ortho-rhombic iron boro-ferrite.

The ortho-boric acid coating was found to decrease the oxidation rate of high purity iron. The determination of oxidation kinetics from thermogravimetric data supported the hypothesis that the porous vonsenite layer at the scale/metal interface forms a "blocking layer" which restricts diffusion. The effective surface area for diffusion of iron ions in wüstite is therefore, decreased. The "blocking" effect seems to be enhanced by the extensive voids associated with the vonsenite layer. Work is in progress to clarify the constitutional and reaction kinetic aspects of the observed protective effects.

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Silicon Nitride Ceramic Composites with High Toughness

THE brittleness of ceramic materials, compared with metals, limits their use in engineering, in spite of such attractive properties as high temperature strength and oxidation resistance. Possible solutions to the brittleness problem therefore continue to be of interest. One approach advocated¹ for silicon nitride has been that of fibre reinforcement, practical feasibility of which has been demonstrated². In the carbon/silica system Crivelli-Visconti³ and Cooper have shown that high