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The influence of nitrogen on the oxidation resistance of low alloy steels*

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Experiments in simulated boiler flue gas have shown that the oxidation resistance of mild steel is increased by up to two orders of magnitude by a surface nitriding treatment. Oxidation resistance was determined under isothermal conditions and during cyclic changes of temperature and oxygen potential. The oxide scale has a fine grain size, is extremely adherent and is therefore protective.

A nitrided surface layer is produced by gas–metal equilibration with $NH_3:H_2$ gas mixtures under conditions to form austenite (γ) at nitriding temperature. On cooling to room temperature, martensite (α') is formed with retained austenite, the relative proportions of which depend on cooling rate. During oxidation at 420 °C, martensite and austenite in the immediate surface layer temper within a few minutes to form ferrite (α) containing a fine dispersion of γ'-Fe_4N platelets *ca.* 50 nm in diameter. X-ray analysis at increasing depth from the surface of nitrided mild steel shows that tempering of the $\alpha' + \gamma$ structure to $\alpha + \gamma'$-Fe_4N is accelerated at the free surface of the alloy relative to the remainder of the nitrided layer, and results in formation of incoherent nitride precipitates on the surface. The nitride particles act as nucleation sites for oxide formation, and electron microscopy shows that the oxide nuclei are of the same order of size as the nitride particles.

If a stable nitride forming element is present in the steel, nitriding may be carried out at lower temperature and/or nitrogen potential, and alloy nitride particles or substitutional–interstitial g.p. zones are formed in preference to γ'-Fe_4–N. A nitrided iron alloy containing 0.16% Ti (by mass), oxidized in air at 420 °C, shows enhanced oxidation resistance relative to the un-nitrided alloy and an adherent, protective oxide is formed. Electron microscopy shows that TiN particles act as oxide nucleation sites in the same manner as γ'-Fe_4N in mild steel.

The nitride interparticle spacing in these alloys is small and so an extremely fine grain size oxide is formed. The mechanical strength of an oxide layer increases with decreasing grain size and the present results demonstrate that the fracture strain of the oxide on the nitrided alloys is not exceeded under the experimental conditions investigated. The oxide is therefore coherent and protective. Improved oxidation resistance of nitrided low alloy steels is therefore attributed to the effect on oxide fracture strain of oxide grain size resulting from a fine distribution of nucleation sites on nitride particles.

* Extended abstract; the full paper appears in *Metal Sci.* **13**, 315 (1979).