

Tds Measurement Of Hydrogen Released From Cr₂O₃ Scale Formed In N₂-O₂-H₂O Atmospheres

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It is well known that an oxide scale (Cr₂O₃ or Fe-Cr spinel oxide) is formed in the early stage of oxidation of Fe-Cr alloys and stainless steels in atmospheres containing water vapor. After the initial stage, nodule-like oxides are formed locally, and then the alloy shows accelerated oxidation behavior, resulting in a large mass gain. Some mechanisms supporting the change from the initially formed Cr₂O₃ scale to a nodule-like oxide have been suggested. They can be grouped into two main groups. One group concerns the reaction of a Cr₂O₃ scale with H₂O(g) to probably form CrO₂(OH)₂(g), resulted in the conversion of a Cr-rich oxide scale into a non-protective iron-rich oxide scale. Another group of possible mechanism relates the degradation of the mechanical property of a Cr₂O₃ scale. Dissolved hydrogen into a Cr₂O₃ scale might affect the ability of the scales to deform plastically. However, mechanism that an initially formed Cr₂O₃ scale changes into a nodule like oxide is not clear.

In the present study, release behavior of hydrogen from Cr₂O₃ scales formed on SUS 430 stainless steel was investigated by thermal desorption spectroscopy (TDS). Based on the results, the property change of Cr₂O₃ scale formed in H₂O-containing atmospheres is discussed.

The specimen used in this study was SUS 430. The stainless steel specimens (15 × 5 × 3 (10⁻³ m)) blocks and then the surfaces were polished up to a micrometer diamond finish. Prior to the oxidation tests, the specimens were ultrasonically cleaned in an ethanol bath, and the mass and precise size were measured. Oxidation was carried out for up to 43.2 ks (12 hr) at 1173 K in N₂-O₂, (N₂-O₂)-H₂O, and N₂-H₂O atmospheres. N₂-3%O₂ mixed gas was used as a carrier gas to obtain N₂-O₂ and (N₂-O₂)-H₂O atmospheres, and N₂ gas (purity: 99.999%) was used as a carrier gas to obtain N₂-H₂O atmospheres. The water vapor concentrations in the carrier gases were 6.9, 12.2, 19.7, and 45.4 vol. %. The H₂O concentrations were obtained by bubbling the N₂-O₂ mixed gas or the N₂ gas through distilled water maintained at 313, 323, 333, and 353 K. For the oxidation test, the specimen was quickly inserted into the hot zone of a reaction tube (internal diameter: 2.5 × 10⁻² m) in an electric furnace maintained at a desired temperature and atmosphere. The specimen was heated and then quickly removed from the hot zone and cooled in air. After the oxidation tests, the specimen was moved to the TDS apparatus for measurement of the trapped amount of hydrogen. Typical pressure before the TDS measurement was about 1 × 10⁻⁷ Pa. In the TDS analysis, the specimen was located on a heater made by tantalum. The specimen was linearly heated from RT to 1023 K in 1500 s and kept at 1023 K for 300 s. The heating rate was 0.5 Ks⁻¹. During the heating, the amount of desorbed hydrogen was measured by a quadrupole

mass spectrometer (QMS). In addition, depth profile analysis of hydrogen in a Cr₂O₃ scale was carried out by glow discharge optical emission spectroscopy (GD-OES).

Desorption rate of hydrogen reached to the maximum point around 800-900 K and increased with increasing H₂O concentration. Further, the peak of the desorption rate was prone to shift to high temperature side with increasing H₂O concentration.

The amount of released hydrogen per surface area was calculated from the integration of the hydrogen desorption rate, and the mol amount of Cr₂O₃ formed on the surface by using the mass gain of SUS 430 oxidized in N₂-O₂-H₂O. The amount of hydrogen in Cr₂O₃ scale was estimated by using above values. In this case, it is assumed that SUS 430 forms only Cr₂O₃ scale and hydrogen dissolved into the Cr₂O₃ scale is released by heating. The amount of dissolved hydrogen increased with increasing H₂O concentration in oxidized atmosphere, but it became almost constant in H₂O concentrations of 20% or more. It was estimated that the maximum amount of dissolved hydrogen in Cr₂O₃ scale formed in N₂-O₂-H₂O atmospheres was about 0.4 mol %. In addition, the GD-OES results demonstrated that the most amount of the dissolved hydrogen existed near the scale/substrate interface.

As an additional experiment, Vickers hardness tests were carried out. The results showed that the Cr₂O₃ scale formed in N₂-O₂ is harder than that formed in N₂-O₂-H₂O. In addition, occurrence of cracks and exfoliation was observed only in the Cr₂O₃ scale formed in N₂-O₂. These results demonstrate that the brittleness of Cr₂O₃ scale formed in N₂-O₂-H₂O is improved, though hydrogen is dissolved into the Cr₂O₃ scale.

These results supports that the degradation of Cr₂O₃ scale in H₂O-containing atmospheres is caused by the reaction of Cr₂O₃ scale with H₂O (A. Yamauchi, K. Kurokawa, and H. Takahashi: *Oxid. Met.*, 59, 517-527) rather than embrittlement of Cr₂O₃ due to dissolution of hydrogen.