Sensitization processes in two high Ni-Cr-Fe alloys are studied with the Huey and accelerated Strauss tests, magnetic permeability measurements and scanning electron microscopy. There is good agreement between the corrosion tests for Incoloy* Alloy 800 but not for Inconel* Alloy 600. High Huey corrosion rates are associated with large magnetic permeabilities which result from chromium depletion near the grain boundaries. The relative contribution of the chromium depleted region and of electrochemical effects to the Huey corrosion rate could not be determined because the formation and disappearance of the chromium depleted zone and of the continuous grain boundary carbides occur concurrently.

SENSITIZATION in austenitic Fe-Ni-Cr alloys is associated with the precipitation of carbides in the grain boundaries in the temperature range of 500° to 800°C (932° to 1472°F). Interest in this phenomenon stems from reported significance in the intergranular corrosion cracking for some stainless steel-environment combinations.1-2 Two frequently employed methods for detecting sensitization in stainless steels are the Huey (performed in boiling nitric acid) and the accelerated Strauss (copper-copper sulfate-sulfuric acid solution). The Huey test has been used to index sensitization in high Ni-Cr-Fe alloys whereas no published data were found on the application of the accelerated Strauss test to these alloys.

Baumel3 et al. have reviewed the theories on sensitization (nitric or sulfuric acid media) and support the chromium-depletion theory.4-5 The chromium-depletion theory is also supported by recent publications of Strawstrom and Hillert6 and Tedmon7 et al. In this theory, the formation of the chromium-rich carbide develops a chromium impoverished region next to the grain boundary. These regions have a chromium content of 12 pct or less and corrode preferentially. The other main theory is electrochemical, in which the highest degree of sensitization is associated with connected grain boundary carbides. Intergranular attack is considered to result because of an electrochemical cell between the carbide and the matrix.8,9

Nondestructive magnetic methods have been evaluated for following sensitization of near 18-8 stainless steels and higher nickel alloys. The onset of ferromagnetism in the 18-8 stainless steels was associated with the formation of ferrite during sensitization.10-12 However, in higher nickel content alloys (18-12 stainless steel), no ferrite formed and sensitization occurred without an increase in magnetic induction.10 for still higher nickel content alloys, a magnetic method appears to have merit because the Curie temperature decreases rapidly with an increase in chromium content.13,14 In a study of a 37 pct Ni-10 pct Cr steel, Chevenard15 related intergranular attack to heterogeneities (variations in Curie temperature). Later Philibert16 showed that these heterogeneities consisted of regions low in chromium and augmented in nickel around the precipitated carbides.

The objectives of the present study were to determine the relationship between the boiling nitric acid and copper-copper sulfate-sulfuric acid tests, magnetic permeability, and microstructure for two high Ni-Cr-Fe alloys and thereby to obtain additional insight into the mechanism of sensitization.

EXPERIMENTAL PROCEDURES

Two commercial alloys of the compositions given in Table I were used. The principal elements in Alloy 800 are 31.85 pct Ni, 21.81 pct Cr, and 44.57 pct Fe and in Alloy 600 are 76.05 pct Ni, 15.4 pct Cr, and 7.92 pct Fe. They were obtained in the hot rolled, annealed, and pickled condition (~ in. thick). Specimens were cut ~ in. wide by 5 in. long from each alloy. These were solution heat treated in argon and water quenched. The time-temperature cycle for Alloy 600 was 2 h at 1121°C (2050°F) and for Alloy 800 was 1 h at 1093°C (2000°F). Subsequently, the specimens were aged in <50°C dew point hydrogen for combinations of the following annealing temperatures and times: Temperatures—871°, 760°, 649°, and 538°C (1600°, 1400°, 1200°, and 1000°F); Times—0, 1, 10, and 100 h. Rapid cooling rates from the aging
temperatures were employed as effected by pulling the specimens from the hot zone into a water cooled chamber. After aging, no mechanical working was employed and visible oxide films were removed by etching in aqua regia to minimize effects of these variables on the magnetic properties.

The boiling nitric acid and copper-copper sulfate-sulfuric acid tests were done per ASTM A262-68. Sensitization in boiling nitric acid is associated with a high weight loss and in the other environment with the formation of cracks in specimens which are bent after exposure. For the boiling nitric acid tests, the logarithm of the corrosion rates was plotted against time or temperature on a linear scale to obtain data for contouring the time-temperature sensitization diagrams.

DC magnetic permeability measurements were made in a magnetizing field of 200 oe by a modification of ASTM 342-64. The specimen was placed in the magnetic field and its intensity of magnetization measured with the aid of a ballistic galvanometer when the specimen was removed from the solenoid. The permeability ($\mu$) is represented by:

$$\mu = 1 + \frac{\pi IV}{H}$$  \hspace{1cm} (1)

Where $I$ is the intensity of magnetization of the ferromagnetic phase in gauss, $V$ is the volume fraction of ferromagnetic phase, and $H$ is the magnetic field in Oersteds. This permeability is likely to be influenced by the distribution of the ferromagnetic phase because of demagnetization effects in this low field. For a given volume fraction of ferromagnetic phase, connected particles would be expected to yield a higher permeability than isolated particles.

To facilitate interpretation of the results, the second phases were extracted from a mechanically cleaned specimen in a 10 pct HCl in methanol electrolyte using a platinum cathode and a current density of 0.06 A/cm$^2$. The residue was collected on a Millipore filter, air-dried, weighed, and examined by X-ray diffraction and dispersive X-ray analysis. Its saturation magnetic moment per gram was measured at room temperature by determining the force on a specimen in a high field. This is equal to the saturation intensity of magnetization divided by the density. The applied field was 11,500 oe and the field gradient was 975 oe/cm. The location of the ferromagnetic phase in the microstructure was identified with a colloidal solution of magnetite. The morphology of the particles was observed with the scanning electron microscope. Specimens were prepared for examination by mechanical grinding and polishing in a bath containing 700 ml Ethanol, 100 ml of ethylene glycol monobutyl ether, 120 ml of distilled water, and 78 ml of perchloric acid. The alloy 600 specimens were etched lightly with bromine prior to microscopic examination.

RESULTS

The corrosion rates in boiling nitric acid and the locations of sensitized specimens as revealed by the copper-copper sulfate-sulfuric acid test are given in the time-temperature sensitization diagrams in Figs. 1 and 2 for Alloy 800 and Alloy 600. The X's designate the specimens which failed the accelerated Strauss test. For Alloy 800, there is good agreement between the two tests; the high corrosion rate region in the Huey test corresponded with the location of

![Fig. 1--Time-temperature-sensitization diagram for Alloy 800. Contour lines are corrosion rates in milligrams/dm$^2$/day, mils per year in boiling 65 pct nitric acid. Specimens which failed the copper-copper sulfate-sulfuric acid test are designated by X's.](image1)

![Fig. 2--Time-temperature-sensitization diagram for Alloy 600, aged as designated, boiling nitric acid. No specimens which failed the copper-copper sulfate-sulfuric acid test are designated by X's.](image2)