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Research articles

Delta ferrite is ubiquitous in type 304 stainless steel: Consequences for magnetic characterization

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ABSTRACT

Using a vibrating-sample magnetometer with a maximum field of 20.5 kOe, we have measured over 50 samples of annealed 304 stainless steel, which is usually considered to be non-magnetic. In almost every case, we observe the presence of a small, usually less than 0.01, fraction of a ferromagnetic phase, which we believe to be equilibrium bcc delta ferrite. The consequences of this observation for the measurement and specification of the magnetic properties of annealed 304 stainless are discussed. Our measurements also establish the most likely value for the magnetic permeability of the fcc austenitic phase in 304 stainless steel austenite as 1.0033 ± 0.0003.

1. Introduction

According to standard reference sources, type 304 stainless steel in the annealed state is non-magnetic [1,2]. This actually means that it is paramagnetic, with magnetization M proportional to field H. The magnetic permeability $\mu = B/H$ is variously given, usually either as 1.02[1] or in the range 1.002–1.004 [3]. We will return to this discrepancy later. Type 304 is considered to be paramagnetic because it is a single phase face-centered cubic (fcc) structure, known to metallurgists as austenite.

The literature on welding of 304 stainless steel, however, is very much concerned with the presence of delta ferrite (δ-ferrite) in the weld [4,5,6]. The use of the label "delta" ferrite implies this is an equilibrium body-centered cubic (bcc) phase that forms during solidification, analogous to the delta phase of pure iron that exists from the melting point of 1532 °C down to 1493 °C. Delta ferrite is to be distinguished from the bcc (or slightly tetragonal) phase that forms by a shear transformation when 304 stainless is plastically deformed below 80 °C [7]. This phase is known as martensite, and is usually labelled α'. The martensite in 304 stainless steel is often described as stress- or strain- or deformation-induced martensite. Deformation-induced martensite must have the same chemical composition as the austenite from which it forms, since it is produced by a diffusionless shear transformation. Delta ferrite, by contrast, is a thermodynamically stable phase that exists in equilibrium with austenite, and so has a different composition from the austenite. How much different is uncertain. Both martensite and delta ferrite are ferromagnetic, with saturation magnetization on the order of 100 emu/g or 10,000 gauss (1 T). We will return also to this subject later.

Some delta-ferrite in a 304 stainless weld is regarded as desirable, to reduce the likelihood of crack formation during cooling. Therefore welding rod for 304 stainless is alloyed to contain a substantial content of delta ferrite. The presence of delta-ferrite apparently does not significantly affect the mechanical or corrosion-resistant properties of the alloy.

We have found some suggestions in the literature that commercial 304 stainless steel may contain some delta ferrite in the annealed state. A publication from the British Stainless Steel Association [8] notes that Grades 304, 321, and 316 have 'balanced' compositions to enable them to be readily weldable. This is achieved by ensuring that in their normal annealed (softened) condition they contain a few percent of delta ferrite. The web site of Atlas Specialty Metals (Australia) [9] says It is common for wrought austenitic stainless steels to contain a very small amount of ferrite, but this is not sufficient to significantly affect magnetic performance except in very critical applications. The Metals Handbook volume on Metallography [10] includes a micrograph of annealed 302 stainless steel (the composition limits of 302 and 304 stainless overlap) with scattered circular patches of a second phase identified as "ferrite." This is clearly an equilibrium phase, and not martensite. The ferrite appears to be present to about 1%, in the form of roughly spherical regions about 10 μm in diameter. A very recent paper from Iran [11] states as an accepted fact

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that austenitic stainless steels contain delta ferrite and that it is regarded as undesirable; the paper investigates possible treatments to reduce or remove delta ferrite.

2. Experiment

Over the course of several years, while investigating the formation of deformation-induced martensite and its reversion to austenite, we have measured about 50 samples of annealed and as-received (presumably annealed) 304 stainless steel, using a vibrating-sample magnetometer (VSM) [12] with a maximum applied field of 20.5 kOe. The samples were either disks about 6 mm in diameter and about 1 mm thick, magnetized along a diameter, or wires 6 mm long with a range of diameters up to 2 mm, magnetized along the length. The VSM was calibrated for disk samples with a disk of polycrystalline high-purity nickel, 0.25 inch (6.35 mm) in diameter and 0.050 inch (1.27 mm) thick. The wire sample calibration was a 6 mm long by 0.65 mm diameter high-purity polycrystalline iron wire.

The samples came from a variety of sources. All were either as-received and presumably annealed, or had been annealed at a temperature of at least 800 °C. Prior to annealing most of the samples had been deformed by varying amounts, by various methods, and at various temperatures. Some measurements were made on the same sample after different treatments. A few samples were type 304L or 304LN, indicating lower carbon, or lower carbon and higher nitrogen, than standard grade 304. One wire sample was type 302. In most cases the exact chemical composition is not known, and it may be important to note that the composition limits on 304 (and other) stainless steel are unusually wide. We make no claim that our samples are representative of anything; they are however, commercially-produced 304 stainless from several different sources, given a variety of deformation and annealing treatments. We report magnetization in emu/g (σ) rather than emu/cm^3 (M), since for small samples mass can be determined more accurately than volume.

In almost every one of our 50 cases, the VSM result is like that in Fig. 1. We interpret this figure as showing the presence of a ferromagnetic phase (bcc delta ferrite), whose contribution to the magnetization of the sample is given by the intercept of the linear high-field data on the + or − vertical axis, and a paramagnetic phase, fcc austenite, whose magnetic mass susceptibility is given by the slope of the linear high-field data. See Fig. 2. For the sample in Figs. 1 and 2, the magnetization resulting from the ferromagnetic phase gives a sample magnetization of 0.77 emu/g, and the mass susceptibility of the austenite is 33×10^{-6} emu/g-Oe. To convert this value to magnetic permeability (B/H), multiply by the density (8.0 g/cm^3) and by 4π, which is very nearly a factor of 100, and add 1, to give permeability $\mu = 1.0033$.

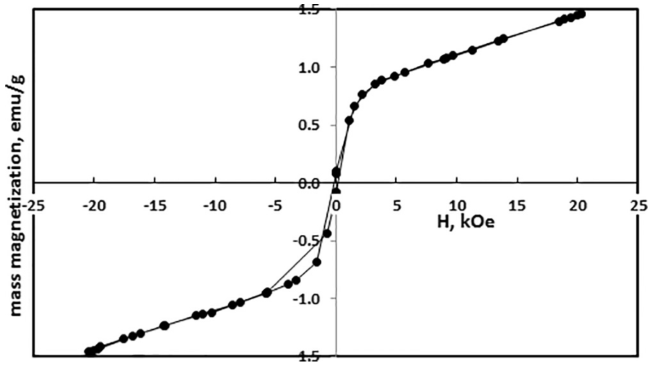

Fig. 1. Typical VSM hysteresis loop of annealed 304 stainless steel.

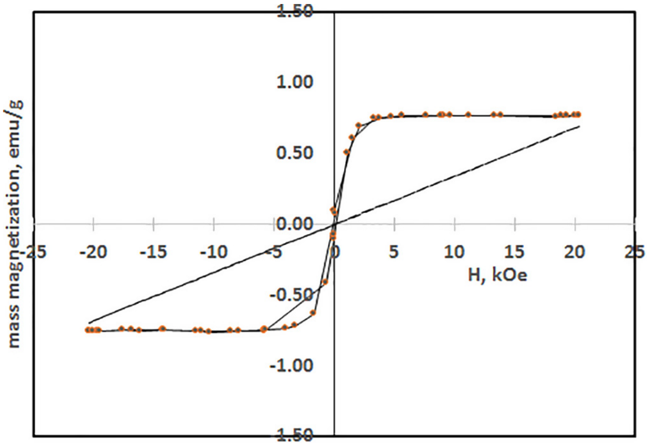

Fig. 2. Data of Fig. 1 replotted to show paramagnetic component (solid line) and ferromagnetic component (data points). Solid line is a linear fit to the high-field data. The slope of this line gives the mass susceptibility of austenite. The points are the data points of Fig. 1 with the paramagnetic component subtracted. Note that in this sample, the paramagnetic and ferromagnetic magnetizations are nearly equal at a field of 20 kOe.

The values of ferromagnetic magnetization σ in our samples ranged from 0 to 2 emu/g, in an apparently random way. See Fig. 3. The average value for 50 samples was 0.6 emu/g with a standard deviation of 0.65. A few values above 2 emu/g were eliminated from the data set on the grounds that the samples may have contained deformation-induced ferromagnetic martensite. It is not possible to distinguish martensite from delta ferrite simply on the basis of magnetic measurements.

The value of the saturation magnetization of pure delta ferrite is unknown. Presumably it is similar to that of deformation-induced martensite, although (as noted above) the chemical compositions of the two phases are not expected to be identical. We are aware of just one value for the saturation magnetization of martensite in 304 stainless steel: 160 emu/g by Angel, dating to 1954 [7] There is also an interesting result from 1988 [13] in which a thin film was sputtered from a commercial 304 target to produce a fully bcc structure with a magnetization of 136 emu/g. The magnetization value is likely to be somewhat composition dependent, and, as noted above, the composition limits on type 304 stainless are unusually broad. It seems reasonable to take a value of 150 ± 25 emu/g for the saturation magnetization of delta ferrite. On that basis, a measured sample magnetization of 1 emu/g would imply about 0.7% delta ferrite content.

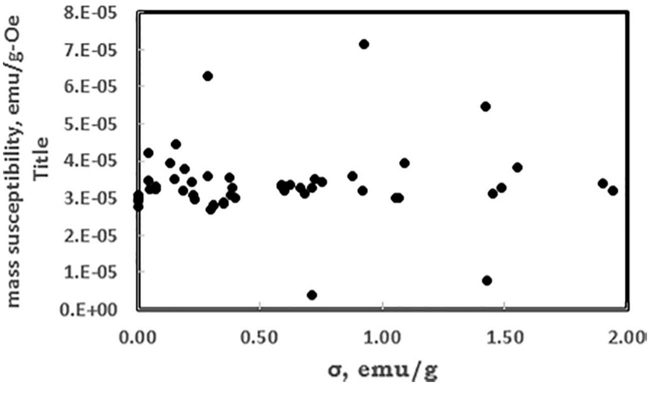

Fig. 3. Mass susceptibility vs. ferromagnetic magnetization σ for 50 samples of Type 304 stainless steel. Susceptibility is generally near 30×10^{-6} emu/g-Oe and is uncorrelated with the magnetization.