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Composition-dependent variation of magnetic properties and interstitial ordering in homogeneous expanded austenite

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ABSTRACT

The crystal structure and magnetic properties of austenitic stainless steel with a colossal interstitial content, so-called expanded austenite, are currently not completely understood. In the present work, the magnetic properties of *homogeneous* samples of expanded austenite, as prepared by low-temperature nitriding of thin foils, were investigated with magnetometry and Mössbauer spectroscopy. At room temperature, expanded austenite is paramagnetic for relatively low and for relatively high nitrogen contents (y_N = 0.13 and 0.55, respectively, where y_N is the interstitial nitrogen occupancy), while ferromagnetism is observed for intermediate nitrogen loads. Spontaneous volume magnetostriction was observed in the ferromagnetic state and the Curie temperature was found to depend strongly on the nitrogen content. For the first time, X-ray diffraction evidence for the occurrence of long-range interstitial order of nitrogen atoms in expanded austenite was observed for high nitrogen contents.

1. Introduction

Expanded austenite, also commonly referred to as S-phase, is a solid solution of a large (colossal) quantity of nitrogen (and/or carbon) in an f.c.c. Fe-based lattice with substitutional elements with a higher affinity for interstitials than iron. Such a solution is formed by the dissolution of nitrogen (and/or carbon) into austenitic stainless steel, while preventing the formation of nitrides (and/or carbides) by choosing a treatment temperature where the substitutionally dissolved atoms can be effectively considered immobile as compared to interstitially dissolved atoms. On dissolving nitrogen into austenitic stainless steel by nitriding below approximately 720 K, a solid solution is obtained with up to 38 at.% N, corresponding to an occupancy of the f.c.c. sublattice of octahedral interstices of y_N = 0.61 [1]. Obviously, the dissolution of interstitials at relatively low temperatures is limited to case depths of several tens of microns as a consequence of the competition between interstitial diffusion and the formation of nitrides or carbides. Treated austenitic stainless steels exhibit enhanced surface hardness of up to 1.4 GPa leading to improved wear resistance [2,3], while the corrosion performance is retained or even improved, in particular concerning localized corrosion [4,5].

A complete description of the crystal structure of expanded austenite is currently not available. Ten possible candidate structures were recently evaluated but all failed in correctly describing the experimental observations from X-ray diffraction (XRD) investigations [6]. Generally, inhomogeneous samples consisting of an expanded austenite surface zone on bulk stainless steel were used for crystal structure determination, implying that a functionally graded material with steep composition and (substantial) residual stress gradients were attempted to be reconciled with a crystal structure. The resulting depth variation in composition causes asymmetric broadening of diffraction peaks, and the induced macro-stress gradient over the expanded austenite zone causes *hkl*-dependent shifts of peak positions as a consequence of nitrogen-concentration dependent elastic anisotropy [7–11]. Furthermore, as a consequence of lattice rotations induced by plastic accommodation of the lattice expansion, texture and microstrain gradients occur over the expanded austenite case [12,13]. Currently, the best structural description for homogeneous samples

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[14] is an f.c.c. lattice with stacking faults contributing to systematic deviations of XRD peaks as described in Ref. [15].

The f.c.c. structure of iron (austenite, γ-Fe) has been predicted to exhibit either nonmagnetic (paramagnetic), antiferromagnetic or ferromagnetic behavior, depending on the separation of the iron atoms [16,17]. The ferromagnetic state is stabilized by larger interatomic distances and has been observed experimentally for epitaxial γ-Fe films grown on Cu and Cu_3Au [18,19]. Room temperature ferromagnetism has been reported for nitrogen expanded austenite (γ_N) [7,20,21] and is mainly attributed to the lattice expansion caused by incorporation of large amounts of nitrogen atoms, possible areas enriched in Fe and Ni and the similarity to the structure of γ′-Fe_4N, which is ferromagnetic at room temperature [22]. Ferromagnetic carbon expanded austenite (γ_C) has so far not been observed, which is in agreement with a limited carbon solubility and associated modest lattice expansion compared to nitrogen expanded austenite [23].

Similarly for published results on the crystal structure, available literature on Mössbauer studies and magnetic properties of expanded austenite is focused on specimens with gradients in composition and residual stresses [7,20,21,24–27], which is likely to influence the obtained results. In the current investigation the relation between interstitial content and magnetic properties is, for the first time, explored for *homogeneous* samples of nitrogen expanded austenite.

2. Experimental

2.1. Sample preparation

Thin foils of AISI 316 stainless steel of nominal composition (by mass) 18% Cr, 10% Ni and 3% Mo (Goodfellow Cambridge Ltd.) with thickness 12.5 μm were used for nitriding. Prior to nitriding, recrystallization and austenitization was achieved by heating to 1323 K in pure H_2 followed by immediate cooling to room temperature. A pretreatment was applied, which involves chemical stripping of the passive oxide film, followed by electrochemical deposition of Ni in a Wood's nickel bath, containing $NiCl_2$, $NiSO_4$ and H_2SO_4. The deposited nickel contributes to less than 0.5% of the total mass of the foils, cf. Ref. [1]. The thin electrodeposited nickel layer prevents repassivation of the stainless steel and catalyzes the dissociation of ammonia at the surface. Gaseous nitriding of the foil pieces was performed in a Netzsch STA 449 F3 Jupiter thermal analyzer with samples in ceramic crucibles using ammonia, hydrogen and nitrogen gasses of 99.999% purity. Total flow rates of 155–255 mL/min were used with a constant N_2 flow of 5 mL/min for protection of electronics in the measurement compartment.

A fully nitrided sample was synthesized in an atmosphere of 97 vol.% NH_3 and 3 vol.% N_2 (infinite nitriding potential, $K_N = p(NH_3)/p(H_2)^{3/2}$, where p is the partial pressure) at 693 K for 13 h. Three additional samples were synthesized by lowering the nitriding potentials to 2.40, 0.07 and 0 ($atm^{-1/2}$) after full saturation was achieved. Lowering the nitriding potential after saturation leads to denitriding of the foils until equilibrium (or a stationary state) is achieved between the nitrogen content in the foil and the adjusted nitriding potential in the gas phase. The nitrogen content in the foils is expressed as the fraction of occupied octahedral interstices in the f.c.c. host lattice, i.e. the occupancy y_N. The thus nitrided foils were powdered with ultra-sound while submerged in ethanol and, subsequently, dried in air. As reference, a sample of γ′-Fe_4N was prepared by nitriding iron powder with a mean particle size of 6–8 μm (99.0+% purity, Goodfellow Cambridge Ltd.) at 718 K in a gas mixture with a nitriding potential of $K_N = 1.45$ $atm^{-1/2}$, conforming to an equilibrium nitrogen content of $y_N = 0.249$ [28]. For determination of the lattice parameter, X-ray diffraction patterns were recorded with an Agilent SuperNova diffractometer with an Atlas S2 CCD detector using Mo K_α radiation and calibrated with a LaB_6 standard, with samples mounted on adhesive tape.

2.2. Magnetometry and Mössbauer spectroscopy

Characterization of the magnetic properties was performed with a Lake Shore Cryotronics 7400 Series Vibrating Sample Magnetometer (VSM) equipped with either a single-stage variable temperature option (model 74035) or a low-temperature variable temperature cryostat (model 74018). The ^{57}Fe Mössbauer spectra were recorded using conventional constant acceleration spectrometers with sources of ^{57}Co in Rh on samples mixed with boron nitride powder. Spectra obtained at low temperatures were recorded in a closed cycle helium refrigerator (APD Cryogenics) and isomer shifts are given with respect to that of α-Fe at room temperature. Mössbauer spectra were fitted with Lorentzian doublets constrained to equal width and intensity of the two lines and sextets were fitted with Voigt line profiles constrained to an intensity ratio of 3:2:1:1:2:3, with the Gaussian component describing a distribution in hyperfine fields. Isomer shifts were fitted separately for each component and quadrupole shifts were fixed to zero.

2.3. In situ X-ray diffraction

For investigation of possible magneto volume effects on the thermal expansion of expanded austenite, an additional sample with a composition in-between those of the ferromagnetic samples (see below) was prepared similarly to the description in Section 2.1 using a gas mixture corresponding to a nitriding potential of $K_N = 0.28$ $atm^{-1/2}$. Synchrotron X-ray diffractograms were collected up to a temperature of 890 K at a wavelength, $\lambda = 0.99471(2)$ Å from samples in sealed quartz capillaries with a Huber G670 Guinier camera at MAX-lab beamline I711 [29]. W powder (99.95% purity, Goodfellow Cambridge Ltd.) was used as internal standard for temperature calibration. For all Rietveld refinements, residual values of $R_p \leq 1.11\%$ and goodness-of-fit values $\chi^2 \leq 2.37$ were obtained. Additional details for *in situ* synchrotron X-ray diffraction and Rietveld refinements are provided elsewhere [30,31].

3. Results and interpretation

3.1. X-ray diffraction

X-ray diffractograms used for determination of lattice parameters and stacking fault probabilities are shown in Fig. 1. The interstitial nitrogen content can be estimated from the lattice parameter, a, using the reported relation between a and the interstitial nitrogen occupancy, y_N [1]. The obtained lattice parameter for denitriding at zero nitrogen potential is larger than for the untreated austenitic stainless steel, but below the minimum value in the reported relation. Consequently, the relation applying for low interstitial contents, as reported for carbon-expanded austenite [23], was used for this sample, improving the agreement with thermogravimetric results. The nitrogen occupancies thus determined from the lattice parameter as well as the obtained stacking fault probabilities are given in Table 1.

3.2. Magnetometry

Magnetic hysteresis curves measured at room temperature are presented in Fig. 2(*a*). Analogous to γ′-Fe_4N, expanded austenite with an intermediate nitrogen content ($y_N = 0.29$ and 0.38) displays only limited hysteresis and can thus be classified as a soft