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Ferromagnetism in metastable 304 stainless steel with bcc structure

J. Childress
The Johns Hopkins University, Baltimore, Maryland

Sy_Hwang Liou
University of Nebraska-Lincoln, sliou@unl.edu

C.L. Chien
The Johns Hopkins University, Baltimore, Maryland

Ferromagnetism in metastable 304 stainless steel with bcc structure

J. Childress, S. H. Liou,[a] and C. L. Chien
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

We have studied the consequence of structure on the magnetic properties of 304 stainless steel in two distinct crystalline states. Ordinary 304 stainless steel has an fcc structure and is nonmagnetic at room temperature. By using a vapor quenching method, we have fabricated single-phase metastable bcc 304 stainless steel which is strongly ferromagnetic. Films a few μm thick have been made by high-rate sputter deposition onto substrates at room temperature or liquid-nitrogen temperature. Vibrating sample magnetometry and ^{57}Fe Mössbauer spectroscopy reveal that the bcc phase has a magnetization of 130 emu/g, due largely to the Fe moment. The Curie temperature is found to be excess of 550 °C. Upon subsequent annealing above 550 °C, the metastable bcc state transforms back into the usual nonmagnetic fcc phase. The changes in the magnetic properties and the structure of these films during the transformation are examined.

I. INTRODUCTION

The diversified magnetic properties of pure Fe and Fe-based alloys is one of the most interesting aspects of magnetism. Ordinary bcc (body-centered-cubic) α-Fe is strongly ferromagnetic, whereas the fcc (face-centered-cubic) γ-Fe is not. This structural dependence of the magnetic properties is often observed as well in many Fe-based alloys.[1] The magnetic properties of Fe-based amorphous alloys with high Fe concentration, although different but not unrelated, also exhibit interesting systematics.[2] For example, amorphous Fe-metalloid alloys (e.g., Fe-B, Fe-Si, etc.) are strongly ferromagnetic with high Curie temperatures, whereas amorphous Fe-metal alloys (e.g., Fe-Zr, Fe-Nb, etc.) are not.[3]

An interesting case in point is 304 stainless steel (SS). Ordinary 304 SS, with a nominal composition of 72-wt. % Fe, 18-wt. % Cr, 8-wt. % Ni, and 2-wt. % Mn, normally appears in the fcc phase, which is nonmagnetic despite its high Fe content. The metastable bcc phase of 304 SS cannot be obtained by equilibrium methods, but cold-working or low-temperature deformation are known to partially retain this bcc state.[4] By far the most effective way of producing single-phase bcc 304 SS is through rapid quenching methods, in particular vapor quenching.[5,6] Hence, once the bcc phase is obtained, it is possible to examine the properties of 304 SS in two distinct crystalline states, a stable fcc state and a metastable bcc state, as well as the transformation from bcc to fcc. A major difference between the bcc and fcc 304 SS is their magnetic properties; unlike the fcc phase, the bcc phase is strongly ferromagnetic. In this work, we have examined the magnetic properties of the metastable bcc phase, and its transformation to the fcc state.

II. EXPERIMENTAL METHOD

Thin films of 304 SS were obtained using a high-rate dc magnetron sputtering system with a base pressure of 10^{-7} Torr, and 4 mTorr of argon as the sputtering gas. The sputtering targets were machined disks of commercial 304 SS. Films of a few μm in thickness were deposited on mica and Al_2O_3 substrates kept at liquid-nitrogen temperature or room temperature. No difference was found between samples deposited at these two substrate temperatures. After deposition, the samples could easily be lifted from the substrates and left free standing. The structure of the films was investigated using a Phillips APD3720 diffractometer in the θ-2θ geometry, by mounting the substrate-free films on glass. The magnetic properties of the films were determined up to 700 °C with a vibrating sample magnetometer (VSM) manufactured by Digital Measurements Systems. For structural and magnetic studies as a function of annealing conditions, samples were heated in a high-temperature furnace, up to 800 °C in an atmosphere of flowing argon. The magnetic transformation was also studied by the Mössbauer effect, in which case, the samples were encased in boron nitride and heated in an evacuated oven. A conventional Mössbauer spectrometer with a ^{57}Co source in a rhodium matrix was used.

III. RESULTS

X-ray diffraction patterns of the 304 SS target and sputtered 304 SS are shown in Figs. 1(a) and 1(b). The 304 SS target is essentially fcc, as expected. However, the as-sputtered 304 SS is single-phase bcc (lattice parameter $a = 2.87$ Å) with no evidence of either the fcc phase or the amorphous phase. Thus, by employing a vapor-quench method, such as high-rate sputtering, the metastable bcc phase can be very conveniently fabricated.

The transformation from the metastable bcc state to fcc state was investigated by annealing the as-sputtered samples at elevated temperatures; each at a specific temperature for 20 min. The x-ray diffraction pattern was then recorded at room temperature. Two such examples, annealed at 600 and 800 °C, are shown in Figs. 1(c) and 1(d), respectively. The sample annealed at 600 °C exhibits both bcc and fcc phases, indicating that a portion of the metastable bcc phase has transformed into the fcc phase. At 800 °C for 20 min, the transformation has been completed and only the fcc phase (lattice parameter $a = 3.59$ Å) is found. To more quantita-

[a] Present address: AT&T Bell Labs, Murray Hill, NJ 07974.

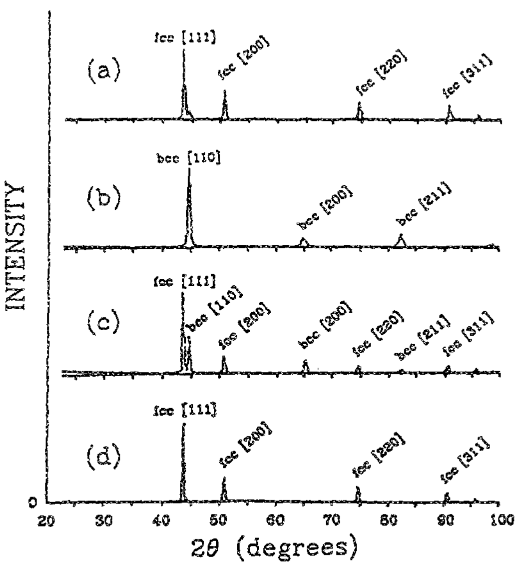

FIG. 1. X-ray diffraction patterns at room temperature of 304 stainless steel: (a) original target material of fcc 304 SS, (b) as-sputtered bcc 304 SS, (c) sputtered 304 SS film annealed 20 min at 600 °C, and (d) sputtered 304 SS annealed 20 min at 800 °C.

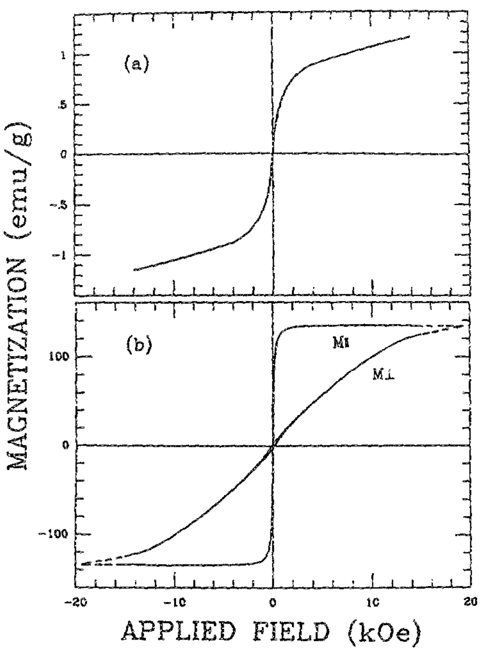

FIG. 3. Magnetic hysteresis loop at room temperature of 304 stainless steel: (a) original target material of fcc 304 SS and (b) as-sputtered bcc 304 SS.

tively characterize the transformation kinetics, the normalized sum of the bcc [110] and bcc [200] peaks and the sum of the fcc [111] and fcc [200] peaks are plotted as a function of the annealing temperature, as shown in Fig. 2. It is found that the transformation begins slowly near 500 °C, with a 5% yield, and quickly reaches 50% near 550 °C. The transformation is completed near 800 °C.

The fcc phase is essentially nonmagnetic. Indeed, the magnetization of the 304 SS target material is about 1 emu/g under an external field of 14 kOe [Fig. 3(a)]. The bcc phase of the as-sputtered 304 SS, however, is strongly ferromagnetic with a spontaneous magnetization of 130 emu/g [Fig. 3(b)]. Thus, the strong structural dependence of magnetic properties is vividly demonstrated in bcc and fcc 304 SS. Differences between measurements made with the applied field parallel ($M_{\parallel}$) and perpendicular ($M_{\perp}$) to the sample plane are mainly the result of the different geometrical demagnetization effects. It is also found that the bcc 304 SS is magnetically soft with a coercivity of about 50 Oe.

Since the magnetic properties of 304 SS depend critically on the structure being bcc or fcc, the structural transformation can be directly related to the resulting magnetic properties. The spontaneous magnetization of the sputtered 304 SS sample was measured at progressively higher annealing temperatures (T_A) with the sample in a flowing Ar atmosphere. Each measurement of about 10 min at T_A was always followed by a measurement at 30 °C, before heating the sample to the next higher T_A. The results of the measurements at T_A and 30 °C are shown in Fig. 4 as a function of

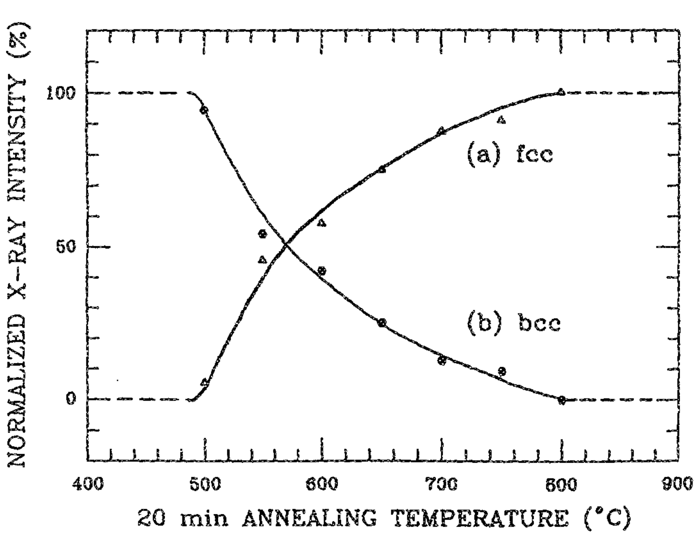

FIG. 2. Normalized sum of the x-ray intensities of (a) fc [111] and [200] peaks and (b) bcc [110] and [200] peaks in the x-ray diffraction pattern of sputtered 304 stainless steel, as a function of annealing temperature.

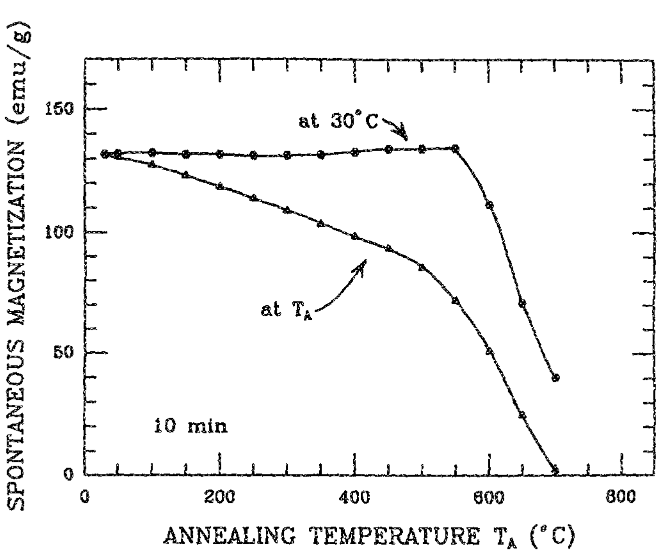

FIG. 4. Spontaneous magnetization of sputtered 304 stainless steel as a function of annealing temperature T_A, measured at 30 °C and at T_A.

T_A. It is seen that the spontaneous magnetization at 30 °C of 130 emu/g is maintained up to $T_A = 550$ °C. After 550 °C the magnetization at 30 °C decreases rapidly, signaling the structural transformation. The sample annealed at 800 °C is fcc and essentially nonmagnetic at 30 °C with a magnetization of about 1 emu/g under a field of 14 kOe, and demagnetization effects can no longer be observed.

Because of the structural transformation commencing at about 550 °C, it is not possible to directly determine the Curie temperature (T_c) of the metastable bcc phase. However, from the temperature dependence of the magnetization, as shown in Fig. 4, T_c is estimated to be at least 600 °C.

The distinct magnetic properties of the fcc and bcc states of 304 SS, and the associated structural transformation, have also been fruitfully investigated by Mössbauer spectroscopy. In the nonmagnetic state of the starting fcc 304 SS, the Mössbauer spectrum exhibits a single peak as expected. In the as-sputtered sample of bcc 304 SS, one instead observes a six-line spectrum with a mean hyperfine field of about 255 kOe. Pure Fe (bcc α-Fe) has a moment of 2.2 μ_B, a magnetization of 220 emu/g, and a magnetic hyperfine of 330 kOe. If we use the magnetic hyperfine field to gauge the Fe moment, the moment in bcc 304 SS is about 1.7 μ_B. Since 304 SS has 72% of Fe, this accounts very well for the observed magnetization of 130 emu/g. Hence, it can be concluded that in the bcc 304 SS, only the Fe atoms contribute significantly to the magnetization. After the bcc 304 SS has transformed completely to the fcc state, the resulting spectrum is once again a single line.

IV. CONCLUSIONS

We have obtained single-phase bcc thin films of 304 stainless steel by dc magnetron sputtering. The samples are strongly ferromagnetic and only the Fe atoms contribute to the magnetization. The bcc phase begins to transform to the fcc state at 550 °C, and the transformation is completed after 20 min at 800 °C. During the transformation the magnetization is directly proportional to the amount of bcc phase present. The magnetic properties of the transformed films are very similar to those of the original 304 SS material, i.e., essentially nonmagnetic.

ACKNOWLEDGMENT

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