MAGNETIC AND TRANSPORT PROPERTIES OF STAINLESS STEELS AT LOW TEMPERATURE

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Received: 04.07.2017
Accepted: 18.09.2017

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Abstract

Magnetic and transport properties of cold rolled SUS304 stainless steels were investigated via measurements of X-ray diffraction, magnetization, thermoelectric power (TEP), thermal conductivity and electrical resistivity from 300 K down to low temperatures. Saturation magnetizations at 300 K were 1.6, 37.5, 72.6 and 105.6 emu/g for rolled thickness reduction ratios of 0, 33, 50 and 75%, respectively. The thermoelectric power (TEP) values at 300 K were found to be -1.3, -0.4, 1.6 and 2.9 μV/K for the reduction ratios of 0, 33, 50 and 75%, respectively. Least-squares fits of the experimental data predicted a saturation magnetization of 141 emu/g and a thermoelectric power of 4.3 μV/K for SUS304 in the martensite phase at 300 K.

Keywords: stainless steels, thermoelectric power, magnetization, thermal conductivity

1 Introduction

Austenite stainless steels are widely used due to their high corrosion resistance and excellent ductility. It is well know that mechanical deformation and stress cause a crystal structure transformation from the γ austenite phase of the fcc crystal structure to the α' martensite phase of the bcc crystal structure (strain induced martensitic transformation) [1-3]. As a consequence, nonmagnetic steel in the austenite phase becomes magnetic in the martensite phase. This change of magnetic property enables a nondestructive testing method to inspect defects, fatigue, cracks, etc. during fabrication of the stainless steel. Magnetization depends on a volume fraction of magnetic phases of a tested sample and the measurement is relatively easy. As a result there are a large number of studies of the martensitic transformation in stainless steels using magnetization [4-6].

The thermoelectric power (TEP) has been also known to be sensitive to crystallographic phase transitions since the TEP primarily depends on the differential of the state density at the Fermi level and the electron concentration if it is dominated by the diffusion process [7, 8]. TEP measurements have advantages: 1) experimental setup is simple and, 2) the TEP value is independent of sample dimensions and thus reproducibility of data is high. TEP properties of steels at high temperature have been described in the literature [9]. A comprehensive study of thermal aging effect on TEP with a duplex steel was carried out by Kawaguchi and Yamanaka

DOI 10.12776/ams.v23i3.981 p-ISSN 1335-1532
e-ISSN 1338-1156

[10], who compared observed TEP with the density of states at the Fermi level utilizing the XPS method. Recently, the TEP technique has been applied to a duplex stainless steel by Lara et al. [11] in which a linear relationship between TEP and ferrite content was observed. It is, therefore, meaningful to apply both techniques to the same samples to investigate the relationship between the magnetization and TEP, with a view to improve reliability of nondestructive testing with the two methods. In this paper we report experimental results of X-ray diffraction, magnetization, TEP, thermal conductivity and electrical resistivity of cold-rolled SUS304 samples. Additional measurements of magnetization, TEP, thermal conductivity and electrical resistivity of SUS316L in the austenite phase and SUS630 in the martensite phase were carried out for comparison.

2 Experimental

Original samples of SUS304 and SUS316Lwere purchased from Nilaco Corporation. The sample of SUS630 was provided from Pacific Steel Mfg. Co. Ltd. Four kinds of SUS304 samples were prepared by cold rolling with thickness reduction of 0 (as received), 33, 50 and 75 %. No heat treatment was applied to the sample, only mechanical polishing with an emery paper, gradeNo. 2000, was applied to the surface, and thus there was residual strain on the surface. X-ray diffraction measurements were carried out with the SUS304 samples using Cu K_α radiation using a RINT2200PC at room temperature. Small sample pieces of approximately dimension $1\times1\times1$ mm^3 were cut out from the samples for the magnetization measurements. These were carried out using a superconducting quantum interference device (SQUID, MPMS-7, Quantum Design) in the temperature range from 4 K to 300 K. A physical property measurement system (PPMS-9, Quantum Design) was employed to measure TEP (30 K - 300 K), thermal conductivity (2 K - 300 K) and electrical resistivity (2 K - 300 K), for which the sample was cut to a rectangular shape of about 1 × 0.2~0.5 × 15 mm^3.

3 Results and Discussion

X-ray diffraction patterns with the SUS304 samples indicated that the predominant austenite phase with the 0 % reduction but the samples gradually changed to the martensite phase with increased reduction ratio as shown in **Fig. 1**. The observed peak intensities were different from those expected from purely random orientation of either the austenite phase or martensite phase most likely due to the crystal texture on the surfaces. An attempt was made to evaluate volume fractions of the martensite phase to the austenite phase using the peak intensities of (211) α' and (220)γsince these two peaks showed significant changes by the rolling. The α' to γ phase ratios were found to be 4, 33, 50 and 77 % for the reduction ratios of 0, 33, 50 and 75%, respectively, in which the relative intensities of (211) α' and (220)γ peaks in each phase are taken into account, but preferred orientation was ignored.

Externally applied magnetic field dependence of the magnetization was measured at 300 K. Magnetization of the samples was near saturation with the applied field above 1 T as seen in **Fig. 2**. The observed magnetization values with the SUS304 samples in **Fig. 2(a)** in3 T were 1.6, 37.5, 72.6 and 105.6 emu/g for the reduction ratios of 0, 33, 50 and 75%, respectively. The results for the SUS316L (austenite phase) and SUS630 (martensite phase) samples from **Fig. 2(b)** were 0.9 and 128.1 emu/g in 3T, respectively. The temperature dependence of the magnetization from 300 K down to 4.2 K for the SUS304 samples is shown in **Fig. 3**. It can be seen that the plots are almost constant, suggesting that there are no noticeable phase transitions with the samples.

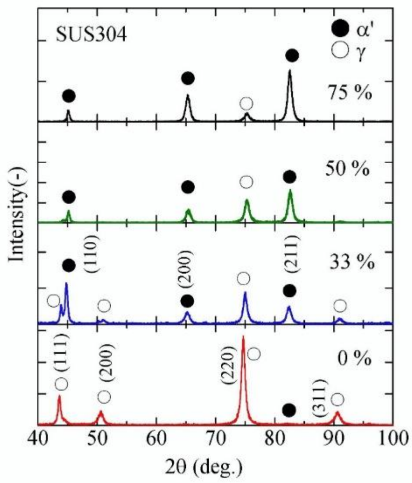

Fig. 1 X-ray diffraction patterns of SUS304 with reduction of 0 % (as-received), 33 %, 50 % and 75 % by cold rolling

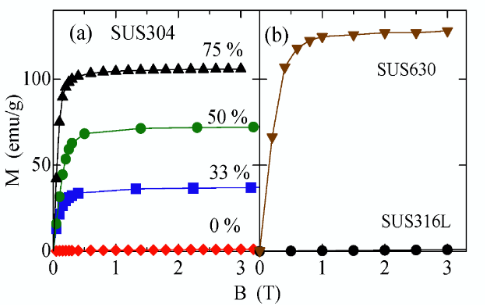

Fig. 2 External magnetic field dependence of magnetizationfor(a) SUS304 samples, and (b) SUS316L and SUS630 at 300 K (see text)

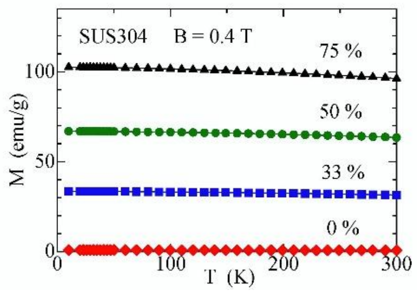

Fig. 3 Temperature dependence of magnetization with the SUS304 samples at an external magnetic field of 0.4 T

TEP of transition metals, such Cr, Fe and Ni, are an order of magnitude larger than those of simple metals, like Cu, Ag and Au, because of the larger state densities of d-bands, $N_{\mathrm{d}}(\varepsilon)$, of the transition metals at the Fermi energy level. This characteristic in the electronic structure of transition metals brings about interesting aspects in the TEP: 1) the $N_d(\varepsilon)$ at the Fermi level can vary greatly in transition metal alloys depending on the chemical compositions, which in turn has a large influence on TEP values as observed with Fe-Ni alloys [12]. 2) The energy derivative of the density of states at the Fermi level, $(dN_d(\varepsilon)/d\varepsilon)\varepsilon_{EF}$, can change sign, which results in a change of sign of the TEP values; e.g. typical TEP values of Cr, Fe and Ni at 273 K are +18.8, +15.0 and -18.0 μV/K, respectively [7]. According to a recent work by Lara et al.[11] for a duplex steel, the TEP value of the austenite phase at room temperature is about -1.7 μV/K, and that of the ferrite phase, which has the similar crystal structure to the martensite phase, is about +1.0μV/K. These values can be compared with those of the present study.

Temperature dependence of the TEP was observed in the temperature range from 30 K to 300 K. The observed TEP in **Fig. 4** varied almost linearly with temperature, implying that the TEP of the samples are dominated principally by diffusion processes as predicted by Mott-Jones theory: $S \sim T$ [13]. The temperature coefficient of the TEP, however, is rather different among the samples. The TEP values obtained for SUS304 in **Fig. 4(a)** at 300 K are -1.3, -0.4, 1.6 and 2.9 μV/K for the reduction ratios of 0, 33, 50 and 75%, respectively. It is clear that the sign and magnitude of the TEP of SUS304 in the austenite phase (0% sample) is similar to thatof SUS316L (-1.60 μV/K at 300 K); likewise the TEP of SUS304in martensite phase (75% case) is close to that of SUS630 (4.47 μV/K at 300 K) in the martensite phase of **Fig. 4(b)**. This result indicates that the crystal structure mainly dominates the TEP properties as well as the magnetism. A least-squares fit of the TEP values versus the reduction ratios (R) of SUS304 gives the equation:

$$S\,[\mu\text{V/K}] = 5.84 \times 10^{-2}\, R\,[\%] - 1.61 \qquad (1.)$$

which in turn implies an extrapolated TEP value of 4.2 μV/K for$R$ = 100 %.

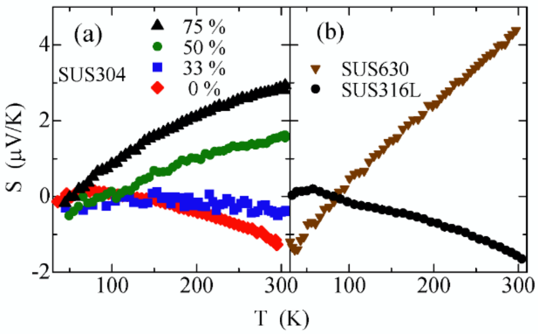

Fig. 4 Temperature dependence of thermoelectric power with (a) SUS304 samples, and (b) SUS316L and SUS630

The transport properties of thermal conductivity in **Fig. 5** and electrical resistivity in **Fig. 6** are found to be less sensitive to the crystal structures of the samples. The thermal conductivity of metals or alloys at low temperature is generally thought to have two contributions: the electrical conductivity, $\kappa_e = (aT^2 + bT)^{-1}$ and the phonon conductivity, $\kappa_{ph} = (cT^2 + dT)$; the coefficients, a, b, c and d for SUS304 are available in the literature [14]. The broken line in the **Fig. 5(a)** is a result of the calculation, which roughly follows the observed κ vs T tendency. The electrical resistivity ρ of the samples in **Fig. 6** appears rather constant. A literature value of electrical resistivity of austenite SUS304 at room temperature is about ρ = 0.72 μΩm [15], which is quite similar to the present value of 0.79 μΩm for the 0% sample. According to Wiedemann-Franz law, a product of thermal conductivity and resistivity over temperature is a constant value of $L = \kappa\rho/T = 2.44\times10^{-8}$ WΩ/K^2, as known as the Lorenz number. The literature value of L for austenite SUS304 is 3.5×10^{-8} WΩ/K^2 at room temperature. The estimated values with the as-received SUS304, SUS316L and SUS630 samples at 300 K are about 4.7×10^{-8}, 5.2×10^{-8}, and 5.4×10^{-8} WΩ/K^2, respectively. The order-of-magnitude agreement among these L values indicates a reliability of the present results of κ and ρ.

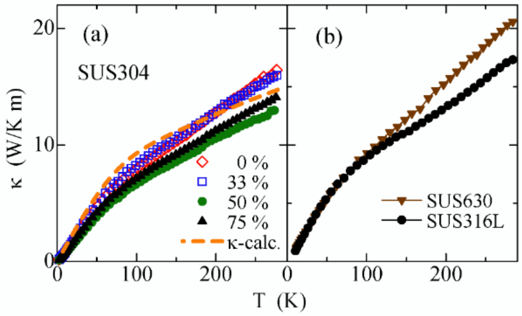

Fig. 5 Temperature dependence of thermal conductivity with (a) SUS304 samples, and (b) SUS316L and SUS630. The broken line in (a) illustrates a result of calculation (see text)

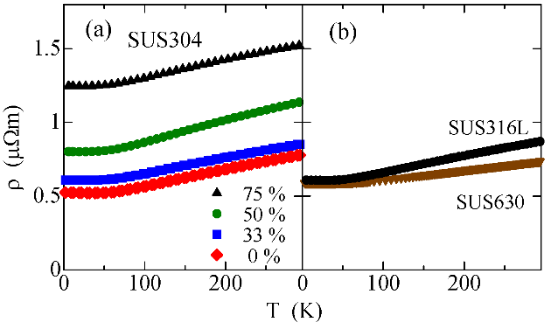

Fig. 6 Temperature dependence of electrical resistivity with (a) SUS304 samples, and (b) SUS316L and SUS630

There are many studies that investigate the relationship between TEP and volume fraction of the martensite phase (V), or alternatively the magnetization and V, but little work has been done to examine the correlation between TEP and magnetization. This latter relationship is expected to be quite meaningful since both TEP and magnetization reflect bulk properties of a sample. A plot of TEP vs magnetization together with a plot of V (estimated from **Fig. 1**) vs magnetization for the SUS304 samples is shown in **Fig. 7**. Both sets of data appear to show are asonably linear variation with magnetization. Linear least squares fit of the TEP vs magnetization data yields the equation:

$$S\,[\mu\text{V/K}] = -1.56 + 4.29\times10^{-2} \times M\,[\text{emu/g}] \tag{2.}$$

While the fit of the volume fraction vs magnetization data produces a relation:

$$V\,[\%] = 4.06 + 0.689 \times M\,[\text{emu/g}] \tag{3.}$$

which predicts a saturation magnetization of a fully martensite phase to be *M*s = 141 emu/g for SUS304. Further these two relations enable us to estimate the TEP value of a martensite phase to be 4.3 μV/K. This value agrees with that extrapolated usingthe *S* vs. *R* relation.

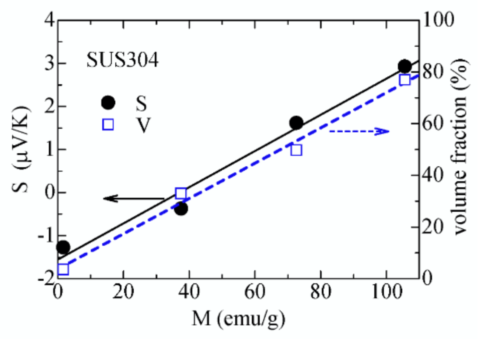

Fig. 7 Plots of thermoelectric power or volume fraction of the martensite phase (estimated from **Fig.1**) against magnetization for theSUS304 samples. The solid and broken lines indicate the results of the fits for S and V, respectively.

Conclusions

In this work the observed results for cold rolled SUS304forthe volume fractions of the martensite phase, measured by x-ray diffraction, are compared to saturation magnetization and thermoelectric powers. We show that there are linear relationships among these properties near room temperature. The least-squares fits of experimental data predict a saturation magnetization of 141 emu/g and a thermoelectric power of 4.3 μV/K for SUS304 in the purely martensite phase at room temperature. These values of the saturation magnetization and thermoelectric power enable us to evaluate volume fractions of martensite relative to austenite via magnetization and TEP measurements.

References

[1] P. L. Mangonon, G. Thomas: Metallurgical Transactions, Vol. 1, 1970, p.1587-1594, DOI: 10.1007/BF02642004

[2] T. Shintani, Y. Murata: Acta Materialia Vol. 59, 2011, p. 4314-4322, DOI: 10.1016/j.actamat.2011.03.055

[3] A. K. De, D.C. Murdock, M.C. Mataya, J.G. Speer, D.K. Matlock: Scripta Materialia Vol. 50, 2004, p. 1445-1449, DOI: 10.1016/j.scriptamat.2004.03.011

[4] K. Mumtaz, S. Takahashi, J. Echigoya, Y. Kamada, L. F. Zhang, H. Kikuchi, K. Ara, M. Sato: Journal of Materials Science, Vol. 39, 2004, p.85-97, DOI: 10.1023/B:JMSC.0000017761.64839.fc

[5] I. Mészáros, J. Prohászka: Journal of Materials Processing Technology, Vol. 161, 2005, p.162-168, DOI: 10.1016/j.jmatprotec.2004.07.020

[6] S. S. M. Tavares, J. M. Neto, M. R. da Silva, I. F. Vasconcelos, H. F. G. de Abreu: Materials Characterization, Vol. 59, 2008, p.901-904, DOI: 10.1016/j.matchar.2007.07.007
[7] F. J. Blatt, P. A. Schroeder, C. L. Foiles, D. Greig: Thermoelectric power of metals, Plenum Press, New York and London, 1976, Chap. 5
[8] R. D. Barnard: Thermoelectricity in metals and alloys, Taylor & Francis Ltd, London, 1972, Chap.6.
[9] F. G. Caballero, C. Capdevila, L. F. Alvarez, C. G. de Andrés: Scripta Materialia, Vol. 50, 2004, p.1061-1066, DOI: 10.1016/j.scriptamat.2003.12.017
[10] Y. Kawaguchi, S. Yamanaka: Journal of Alloys and Compounds, Vol.336, 2002, p.301-314, DOI: 10.1016/S0925-8388(01)01897-7
[11] N. O. Lara, A. Ruiz, C. Rubio, R. R. Ambriz, A. Medina: NDT&E International, Vol. 44, 2011, p.463-468, DOI: 10.1016/j.ndteint.2011.04.007
[12] Y. Tanji, H. Moriya, Y. Nakagawa: Journal of The Physical Society of Japan, Vol. 45, 1978, p.1244-1248, DOI: 10.1143/JPSJ.45.1244
[13] N. F. Mott, H. Jones: The theory of the properties of metals and alloys, Dover Publications, New York, 1958, Chap. 15
[14] R. Xu, L. Xu: Cryogenics, Vol. 45, 2005, p. 694-704, DOI: 10.1016/j.cryogenics.2005.09.002
[15] M. Oka, T. Yakushiji, Y. Tsuchida, M. Enokizono: E-Journal Advanced Maintenance, Vol. 1, 2009, p.77-82