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MAGNETOSTRICTION IN ALUMINIUM-SUBSTITUTED TITANOMAGNETITES[1]

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Abstract. Using the strain gauge technique, the magnetostriction constants λ_s have been measured on sintered polycrystalline specimens of titanomagnetites with $Fe_{2.4-\delta}\ Ti_{0.6}\ A\ell_\delta\ O_4$ compositions ($0.05 \leq \delta \leq 0.20$) in the temperature range between 25°C and T_c. The cell-edge, saturation magnetization, and Curie temperature decrease with increasing aluminium concentration. The room-temperature λ_s values are 95.7, 70.6, 52.9 and 25.2×10^{-6} for δ=0.05, 0.10, 0.15 and 0.20 respectively. A linear relationship is found between the magnetostriction constant and the aluminium content at room temperature. The constant $\lambda_s(T)$ is proportional to approximately the third power of the saturation magnetization $M_s(T)$. The values of the index n in $\lambda_s(T) \sim M_s^n(T)$ are 2.72, 3.16, 3.35 and 3.60 for δ=0.05, 0.10, 0.15 and 0.2 respectively. This if the first reported measurement of $\lambda_s(T)$ at elevated temperatures for $A\ell$-substituted titanomagnetites. Such data are urgently needed in theoretical and experimental magnetic domain structure studies in rock magnetism.

Introduction

Magnetostriction is the fractional change in length of a sample upon magnetization and arises from the strain dependence of magnetocrystalline anisotropy. It is one of the most important factors determining the coercivity in titanomagnetites, $Fe_{3-x}Ti_xO_4$. In titanomagnetites, magnetostriction is the major contributor to the total anisotropy and the magnetostriction constant λ_s becomes very large for titanium concentration x>0.5 [Syono, 1965; Klerk et al., 1977]. Magnetic domain structure observations on Ti-rich titanomagnetites indicate high levels of residual stress, resulting in persistent and complex stress-controlled domain patterns [Appel and Soffel, 1985; Halgedahl, 1987; Moskowitz et al., 1988]. In addition, magnetoelastic interactions between the stress fields associated with crystalline defects and domain walls are thought to be partly responsible for the grain size and thermal dependence of coercivity and remanence in multidomain grains of magnetite and titanomagnetite [e.g., Hodych, 1986; Xu and Merrill, 1992]. A knowledge of λ_s and its temperature dependence at elevated temperatures is therefore important for theoretical modelling of domain structures, coercivity, and thermoremanence. Recently Moskowitz [1992] has measured λ_s as a function of temperature from 25°C to the Curie temperature for x=0.4 (TM40) and x=0.6 (TM60) compositions and found the temperature dependence of $\lambda_s(T)$ to be $\propto M_s^{3.5}(T)$ and $M_s^{2.8}(T)$ respectively. Halgedahl (1990) estimates similar results in synthetic TM60 based on analysis of wavy wall domain patterns.

Naturally occurring titanomagnetites often contain impurity cations. Electron microprobe analysis of titanomagnetites in oceanic and continental basalts indicates that aluminum, with an average content of 4% by weight, is the most abundant impurity cation [Creer and Ibbetson, 1970]. The present work investigates the temperature dependence of magnetostriction in synthetic polycrystalline aluminum-substituted titanomagnetites (ATM60) and is the first reported measurements of magnetostriction of ATM60 at elevated temperatures.

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Experimental

The polycrystalline titanomagnetites $Fe_{2.4-\delta}\ A\ell_\delta\ Ti_{0.6}\ O_4$ (δ=0.05, 0.1, 0.15 and 0.2), were synthesized in double firings at 1300°C using partial self-buffering [Özdemir and O'Reilly, 1981a]. After each firing, the unit cell dimension was determined from Debye-Scherrer (Fe-Kα radiation) X-ray powder photographs and the Curie temperature T_c was found from the high-field thermomagnetic curves determined with an automatically recording vertical Curie balance. In all cases, after the second firing, cell-edges and Curie points were those of single-phase spinels [Özdemir and O'Reilly, 1978]. Curie temperature and X-ray cell edge decreased with increasing aluminium substitution (Table 1). The former is as expected for the replacement of paramagnetic by diamagnetic $A\ell^{3+}$ ions. Saturation magnetization, M_s, was determined at room temperature with a vibrating-sample magnetometer. M_s fell linearly with increasing $A\ell^{3+}$ substitution.

Polycrystalline magnetostriction constants (λ_s) were measured with a recording rotating-field magnetostrictometer in the temperature range between 25°C and the Curie temperatures of the titanomagnetites. The magnetostrictometer consists primarily of a strain-gauge bridge and two rotating $SmCO_5$ permanent magnets [Moskowitz, 1992]. The two permanent magnets produce a constant field of 170 mT in the centre of a 3 cm gap where the sample is positioned. A metal strain gauge (Micromeasurement type WK-06-031CF-350), bonded to the sample, is used to measure magnetostriction. The change in gauge resistance ΔR_g is related to the change in length of the sample along the gauge axis by the equation

$$\frac{\Delta R_g}{R_g} = g\frac{\Delta \ell}{\ell} \qquad (1)$$

where g is the gauge factor and R_g is the gauge resistance. The permanent magnets rotate at a frequency of about 30 Hz and the magnetostriction is detected at twice this frequency with a lock-in amplifier and measurement sensitivity of $\lambda \approx 10^{-7}$. Magnetostriction is recorded continuously as the sample is slowly heated and cooled in an inert atmosphere. Measurements were made on thin disks of polycrystalline samples of titanomagnetites (~10 mm in diameter and 1-2 mm thick). The absolute magnitude of λ for the sintered polycrystalline samples may be lower than for single crystals due to porosity, but the compositional and thermal dependence of λ_s should be unaffected for a suite of samples produced under identical conditions. The magnetostrictometer has been described in detail by Moskowitz [1992].

The thermal dependence of $\lambda_s(T)$ between room temperature and Curie temperature, was measured three

TABLE 1. Various experimental parameters for the ATM60 series. T_c is obtained from high-temperature thermomagnetic curves, a, is the cell-edge parameter determined from Debye Scherrer powder pictures. M_s is measured by using a VSM. n is the index parameter in the expression $\lambda_s(T)=M_s(T)^n$.

Composition δ	T_c (°C)	a (Å°)	M_s (Am²/kg)	λ_s (x10⁻⁶)	n ($\lambda_s(T)=M_s(T)^n$)
0.05 (ATM60/5)	149	8.474±0.005	23.39	95.70	2.72±0.03
0.10 (ATM60/10)	128	8.467±0.004	20.8	70.60	3.16±0.01
0.15 (ATM60/15)	99	8.462±0.004	17.46	52.90	3.35±0.03
0.20 (ATM60/20)	75	8.456±0.003	14.34	25.20	3.61±0.11

(δ=0.1), ATM60/15 (δ=0.15) and ATM60/20 (δ=0.2) (Figure 1). The λ_s–T curves were reversible with heating and cooling and reproducible among the three separate runs. Average values of $\lambda_s(T)$ were determined by first averaging the two λ_s values at each temperature along the heating and cooling curves. This was done for each of the three separate runs and then all three runs were averaged. The magnetostriction constant decreases very rapidly with temperature and becomes zero close to the Curie temperature.

Discussion

Composition Dependence of λ_s

Figure 2 shows the variation of room temperature λ_s with the degree of $A\ell^{3+}$ substitution. The magnetostriction constant decreases with increasing $A\ell^{3+}$ content. Extrapolating back to δ=0, we obtain $\lambda_s \approx 119 \times 10^{-6}$ for TM60, which agrees well with the value measured by Moskowitz [1992]. Although λ_s decreases with increasing $A\ell^{3+}$ substitution at room temperature, it must be remembered that room temperature is not, even approximately, a magnetic isotherm. In Figure 3 we replot the data as a function of reduced temperature, T/T_c. Now the variation of λ_s with T/T_c is very steep for all $A\ell^{3+}$ substituted samples and when extrapolated back to $T/T_c=0$ give giant value of λ_s. However, within the temperature range studied ($T/T_c>0.75$), magnetostriction decreases only slightly with $A\ell^{3+}$ content for constant value of T/T_c.

Özdemir and O'Reilly [1981b] studied high-temperature hysteresis properties of slightly non-stoichiometric SD-titanomagnetites of composition $Fe_{2.4-\delta}A\ell_\delta Ti_{0.6}O_4$ (δ=0, 0.1, 0.2) and found that the coercive force at room temperature decreases with increasing $A\ell^{3+}$ substitution. However, replotting the data in terms of T/T_c show that while the coercive force decreases rapidly with T/T_c, it actually changes little with composition between δ=0.1 and 0.2 for $T/T_c>0.75$. This is consistent with the magnetostriction results in Figure 3 if the coercivity in the SD particles is due to stress anisotropy.

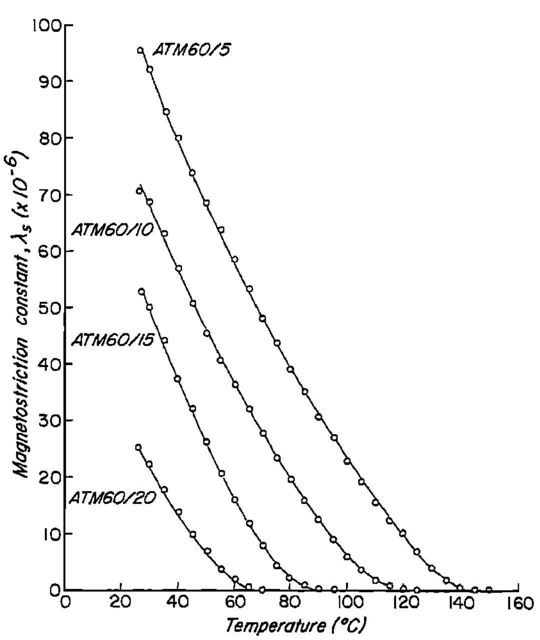

Fig. 1. Variation with temperature of the magnetostriction constants in the ATM60 series.

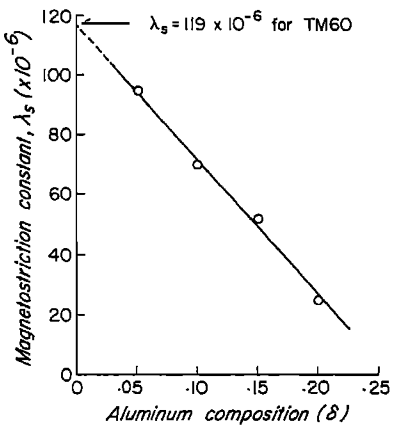

Fig. 2. Variation with aluminium composition of the room temperature magnetostriction constant.

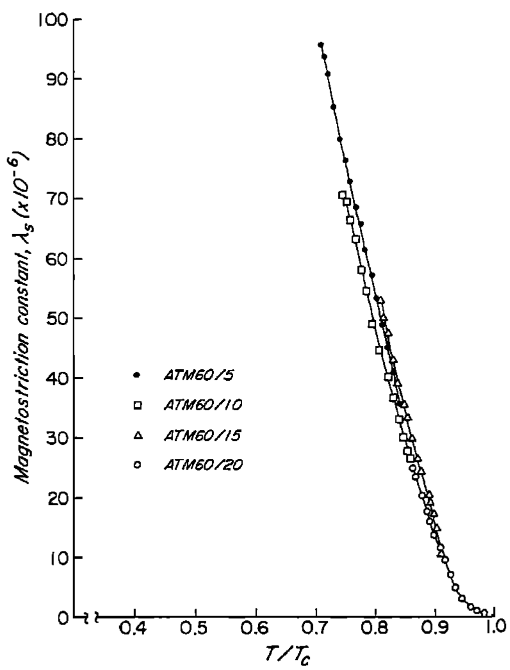

Fig. 3. Replot of the data of Figure 1 in terms of "magnetic isotherms" T/T_c.

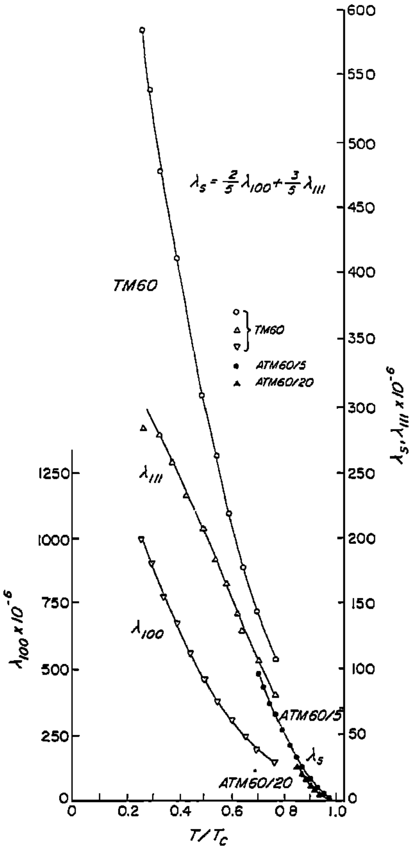

Fig. 4. The magnetostriction constants of ATM60/5 (closed circles) and ATM60/20 (closed triangles) compared with TM60. λ_{100} (inverse open triangles), λ_{111} (open triangles) and λ_s (open circles) of TM60 are taken from Klerk et al. [1977].

Studies of $A\ell$-substituted magnetite suggest that the $A\ell^{3+}$ is located predominantly on octahedral sites and that an equal quantity of Fe^{2+} is transferred from octahedral to tetrahedral sites [Gillot et al., 1977]. In spinel oxides like titanomagnetite, a consequence of tetrahedral Fe^{2+} is that all tetrahedral sites are expanded by an equal displacement of the four oxygen ions outward along the body diagonals of the cube, resulting in a trigonal distortion of the cubic geometry of the octahedral sites [e.g., Smit and Wijn, 1959]. According to Banerjee et al. [1967], large values of magnetostriction and magnetocrystalline anisotropy in titanomagnetites at low temperatures are caused by the indirect effects associated with a negative trigonal distortion of the octahedral Fe^{2+} geometry resulting in a twofold degenerate groundstate for Fe^{2+} rather than a model that attributes high anisotropy to the direct effect of tetrahedral Fe^{2+} [Syono, 1965]. This is an important distinction and means that it is octahedral ferrous ions that are responsible for the magnetostriction in titanomagnetites. In our case, the decrease in λ_s with increasing $A\ell^{3+}$ substitution in TM60 is consistent with this hypothesis. As the $A\ell^{3+}$ content increases, the concentration of octahedral Fe^{2+} decreases while tetrahedral Fe^{2+} increases, thus, producing the observed decrease, rather than an increase, in λ_s. However, because of the limited temperature range studied, exact confirmation must await single crystal measurements at very low temperatures.

Room Temperature λ_s

The uniaxial anisotropy constant, K_u, which is the major contributor to the total anisotropy for the present titanomagnetites, can be determined form the experimental value of λ_s by using the expression

$$K_u = \frac{3}{2}\lambda_s \sigma_i \tag{2}$$

where σ_i is residual stress. An indirect way of obtaining K_u is from the work done to magnetically saturate an assemblage of SD grains, using two aspects of the hysteresis loop. The first is to measure the approach to saturation in the high-field region [Bozorth, 1951, p.484]. The approach of magnetization to saturation in high fields can be written as

$$M = M_s\left(1 - \frac{B}{H^2}\right) \tag{3}$$

where

$$B = \frac{1}{M_s^2}\left(\frac{4}{15}K_u^2 + \frac{8}{105}K_1^2\right). \tag{4}$$

In (3) and (4), H is the applied field and K_1 is the first-order cubic magnetocrystalline constant. The terms in B arise from the magnetic crystal forces which oppose the action of H and are proportional to square of both cubic and uniaxial anisotropy constants. The B values are obtained from the slope of M versus H^{-2} curves [Özdemir and O'Reilly, 1981b].

The second method is to measure the work done against anisotropy torques to ascend the reversible portion of the hysteresis loop, of an assemblage of randomly aligned SD grains, from the remanent state to saturation. The work done, for the cubic case, is $K_1/5$ when $K_1>0$ and for the uniaxial case, $K_u=2K_1/3$. In the case of combined cubic and uniaxial anisotropies, the total work done will be

$$A = \frac{K_1}{5} + \frac{2K_u}{3}. \tag{5}$$

The work is equal to the area A between the descending branch of the hysteresis loop, the vertical M axis and the horizontal line $M=M_s$. Özdemir and O'Reilly [1981b] determined K_u and K_1 from equations (3) to (5) and obtained $K_u=1.2 \times 10^5$ and 0.82×10^5 erg/cm^3 for ATM60/10 and ATM60/20 respectively. Using the experimental λ values of 71×10^{-6} and 25×10^{-6} for these two compositions and equation (2), we calculate that σ_i=100–200 MPa for the SD particles. This is a typical value of residual stress for ball-milled, ultrafine particles. In contrast, Moskowitz et al. [1988] estimated residual stresses approximately ten times less for coarse grained (50–100μm) samples of similar compositions ($Fe_{2.2}A\ell_{0.1}Mg_{0.1}Ti_{0.6}O_4$) based on magnetic domain observations.

Temperature Dependence of λ_s

The magnetostriction constant λ_s is strongly dependent upon temperature. This dependence can be expressed as a power law dependence upon the spontaneous magnetization or the reduced temperature. Bilogarithmic plots of $\lambda_s(T)$ versus $M_s(T)$ for the ATM60 samples are reasonably linear and give values of the index n in $\lambda_s(T) \propto M_s(T)^n$ of 2.72, 3.16, 3.35 and 3.6 for δ=0.05, 0.1, 0.15 and 0.20 respectively. The values are close to the results obtained by Moskowitz [1992] for TM40, TM60, and an aluminum-magnesium substituted TM60. All of the results agree well with the theoretical value of n=3 based on the phenomenological single-ion theory of Callen and Callen [1966] even though the theory is strictly applicable only at low temperatures.

The observed high-temperature values of n for the ATM60 samples are in the range 2.7-3.6 and increase with increasing aluminium content. This increase is probably an artifact due to the decrease in Curie temperature with increasing $A\ell^{3+}$ substitution. The bilogarithmic fits are sensitive to the variation of M_s near T_c where the magnetization changes most rapidly [e.g., Moskowitz, 1992]. The less aluminium substituted titanomagnetites have higher Curie temperatures, providing a large variation in relative temperatures at which λ_s and M_s were measured. Therefore, we calculate lower n values for ATM60/5 and ATM60/10. To remove some of this effect, the magnetostriction data were fit to $\lambda(T) \propto (T-T_c)^m$ using a nonlinear least squares procedure that included T_c as an adjustable parameter (see Moskowitz [1992] for details). Over the entire temperature range of 25°C to $T_c-10°$, the index m was 1.48±0.02, 146±0.02, 1.43±0.03, and 1.43±0.06 for δ=0.05, 0.1, 0.15, 0.20. These values are larger than the m=1.3 value observed for TM40 and TM60 [Moskowitz, 1992] and may indicate a real compositional dependence.

Figure 4 is a comparison of λ_s data for ATM60/5 and ATM60/20 with low-temperature, single crystal, results for TM60 by Klerk et al. [1977]. The magnetostriction constants λ_{111}, λ_{100} and λ_s are plotted in terms of T/T_c. λ_{111}, λ_{100} and $\lambda_s=2/5\lambda_{100}+3/5\lambda_{111}$ for TM60 are all positive and decrease with increasing temperature in the range 77 to 300 K. The temperature dependencies of λ_s for the ATM60 and TM60 samples have similar aspects. It seems likely that λ_{111} and λ_{100} for our samples are also positive and very large at low temperatures.

Conclusions

The magnetostriction constants λ_s of aluminium-substituted titanomagnetites $Fe_{2.4-\delta}\, A\ell_\delta\, Ti_{0.6}\, O_4$ are strongly dependent on composition and temperature. The room-temperature λ_s values are linearly dependent upon aluminium concentration δ; the values are 95.7, 70.6, 52.9 and 25.2 x 10^{-6} for δ=0.05, 0.1, 0.15 and 0.20 respectively. Our results support the hypothesis of Banerjee et al. [1967] that the source of the large magnetostriction and magnetocrystalline anisotropy in titanium-rich titanomagnetites is octahedral Fe^{2+} with a twofold degenerate groundstate. The thermal dependence of λ(T) is well approximated by a power-law equation in terms of $M_s(T)^n$, where the index n =2.72 (ATM60/5), 3.16 (ATM60/10), 3.35 (ATM60/15), and 3.60 (ATM60/20). In terms of T/T_c, $\lambda_s(T)$ varies approximately as $(1-T/T_c)^{1.5}$ for all ATM60 compositions. The variation of magnetostriction of aluminium-substituted titanomagnetites at elevated temperatures is here determined for the first time. The present study has provided data which should help in theoretical and experimental studies of magnetic domains and coercivity. Such data are needed in modelling TRM and discussing the effect of stress on remanent magnetization.

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