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Domain state of Ti-rich titanomagnetites deduced from domain structure observations and susceptibility measurements

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Abstract. Domain structure observations and measurements of the temperature dependence of susceptibility on synthetic and natural titanomagnetites are reported. At room temperature Ti-rich titanomagnetite particles ($x \approx 0.6$) of MD grain size normally develop a very complicated domain structure. The experimental results of our investigations, in addition to simple theoretical calculations, indicate that internal stress is the dominant cause of the observed anomalous domain patterns. Part of the results have already been published by Appel and Soffel (1984). The paper presented here, however, is a far more extended summary of the actual state of our research.

Key words: Rock magnetism – Titanomagnetites – Domain structure

Introduction

The acquisition and high stability of thermoremanent magnetization (TRM) in single domain (SD) particles is theoretically well explained by the theory of Néel (1949). In basaltic rocks, however, the volume fraction of SD particles is, in general, negligible (e.g. Winhard, 1983). Therefore, the micromagnetic structure of the larger multidomain (MD) particles is of fundamental interest for the understanding of magnetization processes in rocks. There is already a broad spectrum of explanations of the pseudo-single domain (PSD) behaviour, especially the high stability of TRM: SD moments caused by dislocations (Verhoogen, 1959), subregions with submicroscopic grain boundaries (Ozima and Ozima, 1965), Barkhausen discreteness (e.g. Stacey, 1963), surface domains and subdomains (e.g. Banerjee, 1977), domain wall moments (e.g. Dunlop, 1977), absence of domain structure at all (e.g. Radhakrishnamurty et al., 1982) and domain wall nucleation (e.g. Halgedahl and Fuller, 1980). However, none of the theories is really satisfying and the problem of stable PSD remanence is still an open question in rock magnetism.

In ocean floor basalts the ferrimagnetic mineral phase normally consists of Ti-rich titanomagnetites $Fe_{3-x}Ti_xO_4$ with x around 0.6 (TM60) and some amounts of other cations, mainly Al and Mg. The typical composition is given by

$Fe_{2.27}Ti_{0.60}Al_{0.08}Mg_{0.05}O_4$

(Appel and Moll [1980], calculated from microprobe analysis of Petersen et al. [1979], other cations neglected). For this reason, our studies were concentrated on Ti-rich compositions (partly substituted with Al, Mg). Domain structure observation provides the most direct analysis of the domain state. Earlier reported experiments (e.g. Soffel et al., 1982) proved the existence of domain structures on titanomagnetites up to TM75, but all studies have been carried out only with particles showing a nearly classical domain structure (constant specific wall energy, dominance of magnetocrystalline anisotropy as the source of anisotropy). However, such particles have rarely been observed. Non-classical, very complicated domain configurations – by far the most frequently occurring on surfaces of Ti-rich titanomagnetites – have generally been disregarded because of the assumption of incomplete removal of the irregular strained surface layer (Beilby layer) due to mechanical polishing. The latest investigations, however, provide good arguments for the existence and dominance of internal stress, suggesting that these anomalous domain structures are in fact the typical ones in Ti-rich titanomagnetites. This new view of stress-controlled domain state is based on the following experiments and calculations:

- qualitative domain structure observations,
- domain wall behaviour in external magnetic fields,
- domain wall behaviour under external uniaxial pressure,
- balancing of magnetocrystalline and magnetostrictive energies,
- measurements of the temperature dependence of susceptibility.

The possible origin and amount of internal stress in titanomagnetite particles are discussed in a later section.

Sample description

Most of the experiments were carried out with synthetic titanomagnetites (sintered at 1,300° C in an equilibrium oxygen atmosphere near the spinel – spinel + wüstit phase boundary). The polycrystalline specimens were tested with optical methods, X-ray analysis, Curie temperatures, dependence of saturation magnetization J_s on temperature and hysteresis measurements. According to the results of the tests, all synthetic samples are homogeneous and stoichiometric. The Curie temperature T_C, cell edge a_0 and coerciti-

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Table 1. Curie temperature T_C, cell edge a_0 and coercitivity H_C of the analysed synthetic and natural titanomagnetite samples

Composition	T_C, °C	a_0, Å	H_C, Oe
Synthetic titanomagnetites			
$Fe_{2.90}Ti_{0.10}O_4$ (TM10)	499	8.404	6
$Fe_{2.76}Ti_{0.24}O_4$ (TM24)	424	8.421	4
$Fe_{2.74}Ti_{0.26}O_4$ (TM26)	411	8.424	10
$Fe_{2.60}Ti_{0.40}O_4$ (TM40)	314	8.442	4
$Fe_{2.48}Ti_{0.52}O_4$ (TM52)	234	8.461	6
$Fe_{2.40}Ti_{0.60}O_4$ (TM60)	154	8.476	5
$Fe_{2.28}Ti_{0.72}O_4$ (TM72)	58	8.491	2
$Fe_{2.25}Ti_{0.75}O_4$ (TM75)	40	8.492	10
$Fe_{2.18}Ti_{0.62}Al_{0.20}O_4$ (ATM20/62)	56	8.450	4
$Fe_{2.18}Ti_{0.62}Mg_{0.20}O_4$ (MTM20/62)	127	8.472	10
$Fe_{2.315}Ti_{0.62}Al_{0.04}Mg_{0.025}O_4$ (AMTM4/2.5/62)	120	8.475	4
$Fe_{2.075}Ti_{0.60}Al_{0.20}Mg_{0.125}O_4$ (AMTM20/12.5/60)	46	8.451	10
Basalt			
$Fe_{2.26}Ti_{0.52}Al_{0.06}Mg_{0.13}Mn_{0.03}O_4$ (Basalt of Triebendorf TR)	220		65

vity H_C data are listed in Table 1. For experiments with small isolated particles, the polycrystalline material was crushed and embedded in a nonmagnetic matrix.

Further observations were carried out with natural Ti-rich titanomagnetites in a basaltic rock specimen. $J_s(T)$ measurements and optical analysis indicate that the titanomagnetite grains are unexsolved and only moderately oxidized. The composition was determined by microprobe analysis. Values of T_C and H_C are given in Table 1.

Domain structure studies

Observation technique

Domain structure observations were carried out with the Bitter pattern technique. The domain walls near the observed surface are represented by dark lines (accumulation of colloid particles). An ester-based magnetite colloid ("Ferrofluid") was used, enabling us to observe the dynamics of magnetization processes (domain wall displacements) directly. Strain-free surfaces were achieved by ionic polishing (Soffel and Petersen, 1971).

Qualitative domain structure observations

As already pointed out, recent domain observations were concentrated on the complicated non-classical domain structures which are seen, as a rule, on the major parts of the surfaces of Ti-rich titanomagnetite grains.

Following Syono (1965), the magnetocrystalline anisotropy constant K_1 at 290 K is negative for Ti-poor titanomagnetites and changes sign for $x > 0.65$ (linear interpolation of Syono's data). $K_1 < 0$ means that the spontaneous magnetization is orientated in the [111] direction and, therefore, a subdivision into domains with 180°, 109° and 71° domain walls is expected if a classical domain structure (Fig. 1) exists.

On synthetic Ti-poor titanomagnetites (up to TM26) classical domain structures comparable to Fig. 1 partially occur if the observed surface is nearly a (110) plane (Fig. 2). Typical closure domains (as already know from nickel) are developed if the observed surface is slightly inclined (perhaps about 10°) to a (110) plane (Fig. 2). If the angle between the directions of the spontaneous magnetization and the observed surface increases, more complicated surface domain patterns occur. In most cases the Bitter lines on Ti-poor titanomagnetites are nearly straight, not interrupted in the crystal's interior and fully developed up to the particle edges. However, some differences from the classical concept were observed: more strongly bent domain walls and weak and varying distinctness of Bitter lines. Furthermore, domain walls seem to dissolve inside the particles.

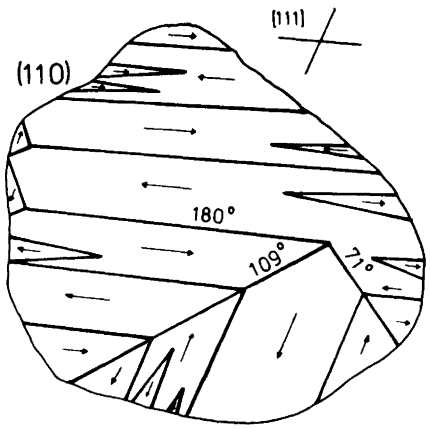

Fig. 1. Classical domain structure on a (110) plane for $K_1 < 0$ (71°, 109° and 180° domain walls, closure domains and spike domains)

Synthetic Ti-rich titanomagnetites around TM60 (compositions of greatest importance for rock- and palaeomagnetism) exhibit quite different domain structure configurations. The above-mentioned non-classical features partially occurring on Ti-poor titanomagnetites are typical for the Ti-rich compositions (examples are shown in Fig. 3):

- 180° domain walls with large domain spacing,
- narrowly spaced, more complicated domains,
- faint fine structures,
- zones without visible domain structures,
- bent domain walls,
- varying intensity of Bitter lines, dissolution of Bitter lines near the particle edges and even inside the crystal.

Naturally occurring Ti-rich titanomagnetites show similar domain structure characteristics. The examples of Fig. 4, however, represent domain configurations still of simple form. Normally, extremely complicated domain configurations (Fig. 5) were observed.

All observed features can be explained by an inhomogeneous anisotropy field caused by internal stress. Apart from the width of the domains, similar domain structures have been reported from metallic glasses (e.g. Kronmüller et al., 1979; Salzmann and Hubert, 1981). Metallic glasses are characterized by the absence of magnetocrystalline anisotropy. Stress is believed to be responsible for the local anisotropy.

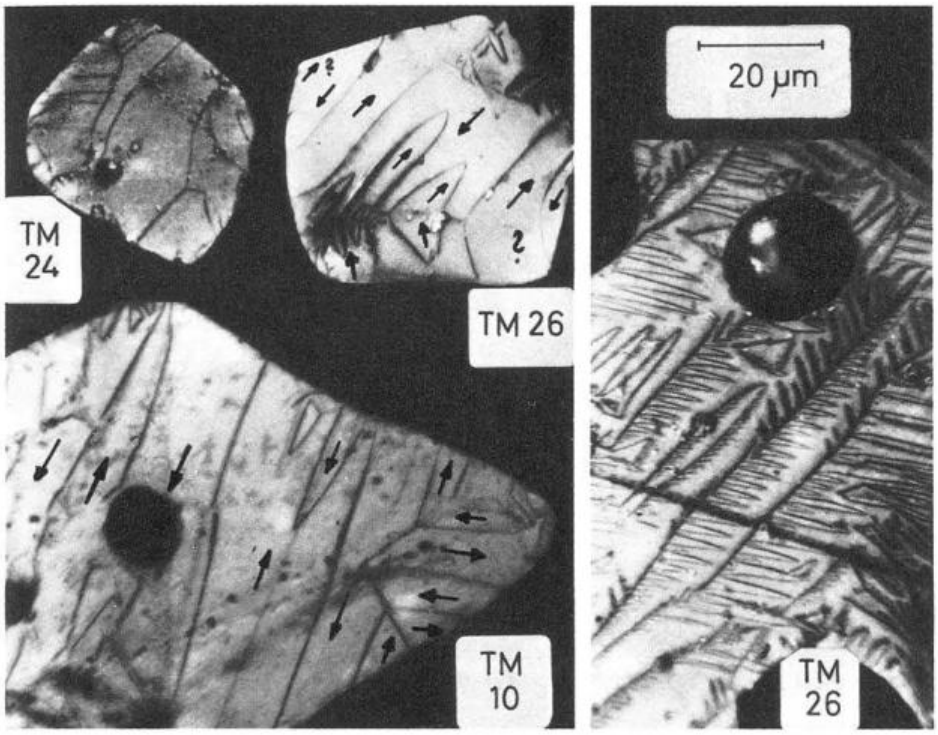

Fig. 2. Domain structures on synthetic polycrystalline Ti-poor titanomagnetites (on surfaces near to (110) plane)

Domain wall behaviour in external magnetic fields

A coil system was attached to the microscope allowing external fields H up to 500 Oe (40,000 A/m). The domain wall displacements were observed directly on small isolated synthetic MD particles showing simple domain configurations (Fig. 6). There are good reasons to assume that these particles are in a nearly strain-free state (see discussion section).

The example of Fig. 7 documents two characteristics:
– With increasing external field, the Bitter line (on the right side of the particle) is getting faint and finally disappears without changing its position. This may be explained by spin rotations inside the domains associated with reduced stray field variations. If the stray field variations are too low, the colloid particles cannot be attracted and the Bitter pattern technique becomes inadequate for the analysis of the real domain structure.
– Small external fields of only 10 Oe (800 A/m) or even less are able to change the domain pattern of the isothermal remanence (IRM) state drastically.

Coercivities of isolated Ti-rich particles were determined from balancing the domain areas while undergoing hysteresis (magnetic field H parallel or antiparallel to the assumed direction of spontaneous magnetization). The following basic suppositions were made for the method:
– Only particles with nearly straight and parallel domain walls (e.g. Fig. 6) were selected for the experiments.
– The observed Bitter lines represent the volume domains.
– The spontaneous magnetization of the domains is homogeneous and antiparallel in neighbouring domains.
– Domain wall displacements are the only magnetization process; spin rotations do not occur (the external magnetic field is parallel to the domain walls).

Assuming that $\Delta A/A=[A-A']/[A+A']$ (where A, A' are the total areas of the domains with antiparallel orientation of the spontaneous magnetization) is identified with the normalized magnetization of the particle J/J_s (J_s spontaneous magnetization), we get hysteresis curves $\Delta A/A\,(H)$. An example is given in Fig. 8. Values of coercitivity H_c can be determined from these curves and allow at least an estimate of H_c. Nine particles of different grain sizes (8.5–35 µm) of the Ti-rich compositions TM72 and AMTM4/2.5/62 were tested. All values of H_c are below 10 Oe (Fig. 9). They are about 10 times smaller than H_c of TM40 of the same grain size (taken from macroscopic hysteresis measurements of Day [1977]). The difference is probably even more evident in a comparison of specimens of the same composition because the critical diameter of the SD-MD transition is smaller for TM40 than for TM72 (e.g. Butler and Banerjee, 1975).

As the minimum statement we can conclude that Ti-rich titanomagnetite particles with simple domain structure (lamellae-shaped domains) cannot provide high coercitivity by domain wall blocking.

Domain structure behaviour under external uniaxial pressure

Earlier domain structure observations on titanomagnetites with applied pressure are known only for pure magnetite (Bogdanov and Vlasov, 1966; Soffel, 1966; Kean et al., 1976). These experiments proved that preferentially orientated domains grow with increasing uniaxial pressure or, if not previously existing, preferentially orientated domains nucleate. No domain rotations were observed up to a pressure of about 850 bar. The amount of internal stress of the Beilby layer was determined to be $\sigma_{pol}\approx 2.5$ kbar by Soffel (1966).

Pressure experiments of the present work were carried out with synthetic polycrystalline and natural Ti-rich titanomagnetites. A pressure apparatus attached to the microscope was used. The value of σ was measured with a ma-

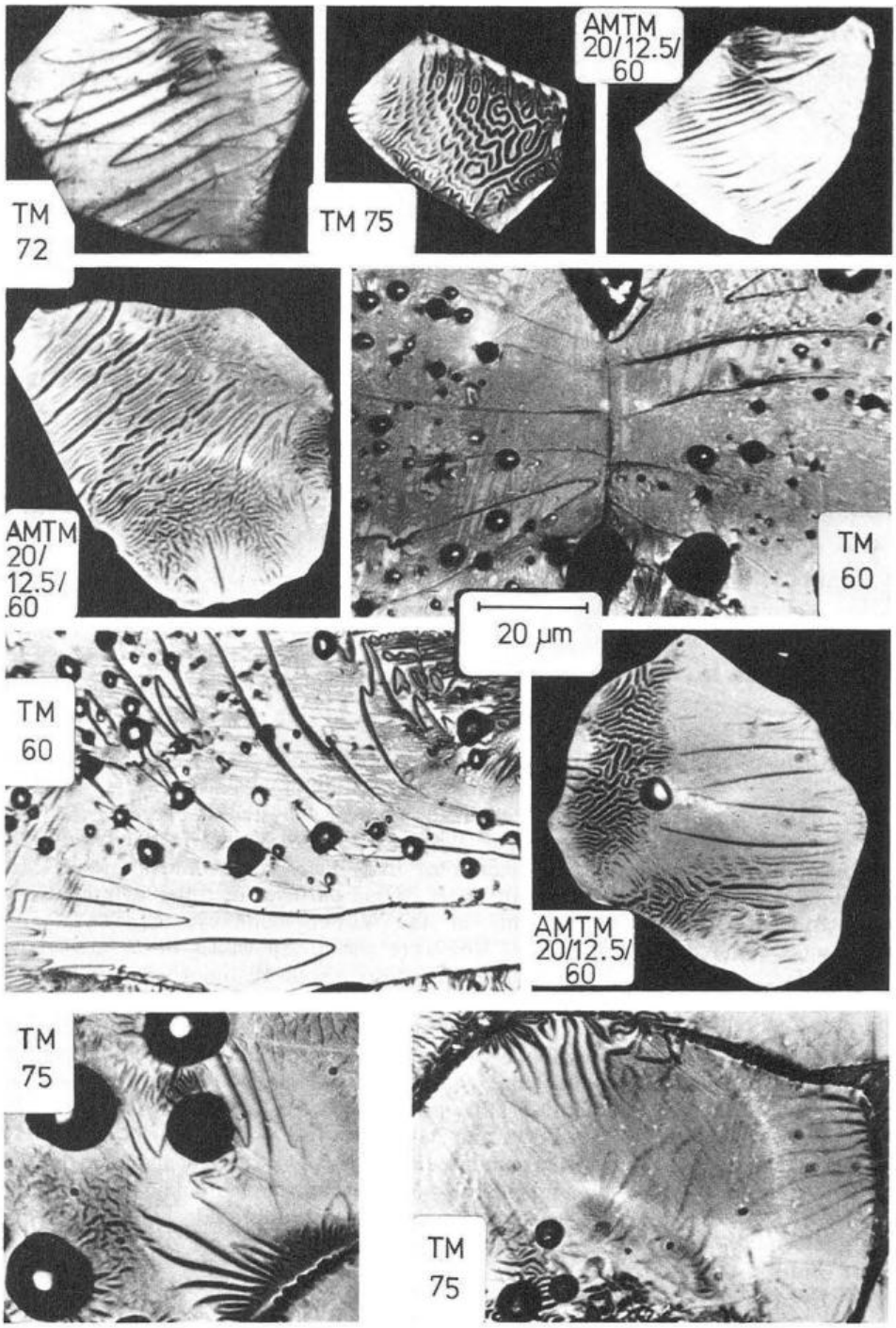

Fig. 3. Domain structures on Ti-rich synthetic polycrystalline titanomagnetites (partially + Al, Mg)

nometer. Problems arise from the porosity of the synthetic polycrystalline samples because the direction of the external pressure σ_a might be changed by the pores.

What kind of transitions of the domain configuration appear with increasing σ_a? First of all, only domain structures with wide domain spacing (volume parts assumed to be free of high internal stress or high inhomogeneity of stress) will be ragarded. Three principal processes are possible (Fig. 10):

– dissolution of the primary domain walls and re-formation of prefentially orientated domains (spin rotation or reduction of anisotropy?, Fig. 10a),
– domain rotation as a whole (Fig. 10b),
– nucleation of preferentially orientated domains growing with increasing σ_a (Fig. 10c).

For Ti-rich titanomagnetites (and probably for Al, Mg substituted Ti-rich samples too) the magnetostriction constants λ_{111}, λ_{100}, λ_s are positive (Syono, 1965). This means that the prefered orientation of the spontaneous magnetization is perpendicular to the direction of pressure. Nuclea-

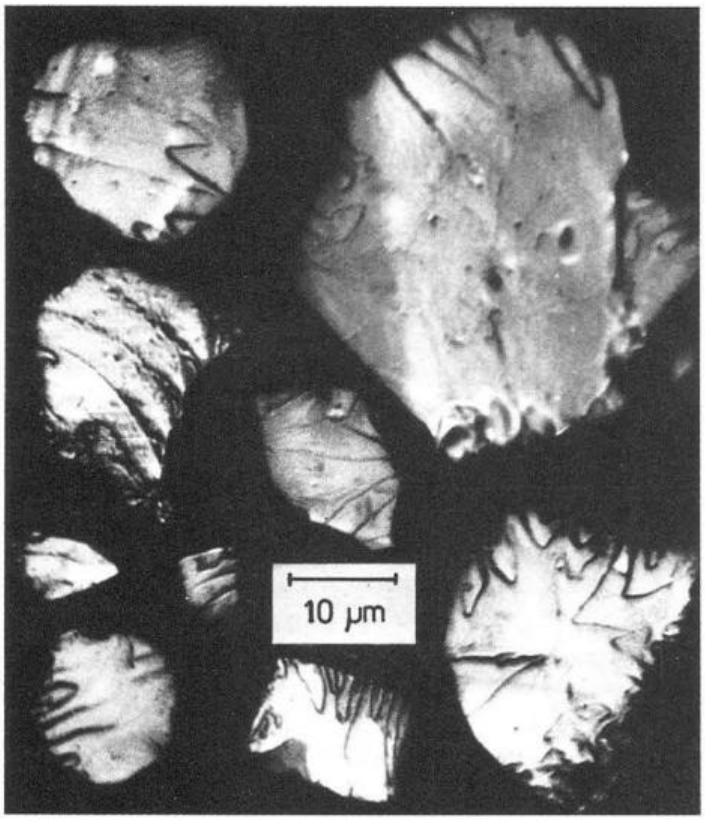

Fig. 4. Domain structures on natural Ti-rich titanomagnetite particles in the Basalt TR of composition $Fe_{2.26}Ti_{0.52}Al_{0.06}Mg_{0.13}Mn_{0.03}O_4$

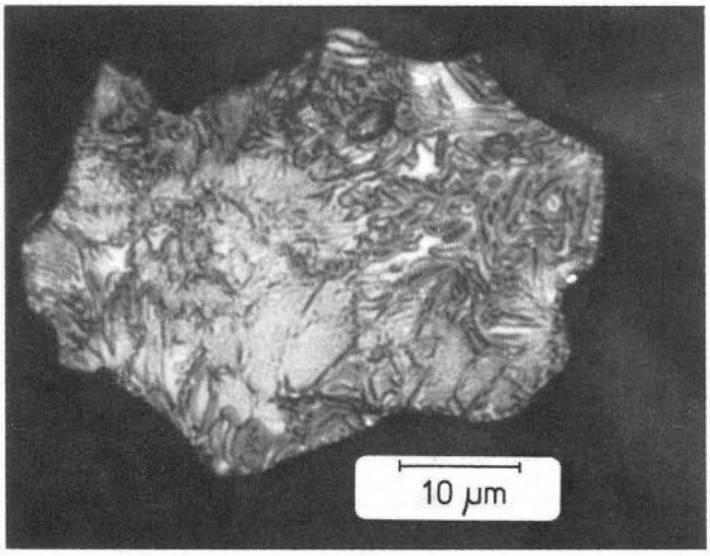

Fig. 5. Typical domain structure on natural Ti-rich titanomagnetite (Basalt TR)

tion was never observed on Ti-rich titanomagnetites, but previously existing preferentially orientated domains grow with increasing σ_a. On the contrary, both dissolution and re-formation of preferentially orientated domains (Fig. 11, left side), as well as domain rotation (Fig. 11, right side), were observed frequently.

Further attention was focussed on the transition of extremely complicated domain patterns induced by an inhomogeneous anisotropy field (presumably caused by internal stress σ_i). Applied uniaxial pressure σ_a superposes the original anisotropy and reduces the inhomogeneity of the resulting total intrinsic anisotropy. This will be associated with the transition of the complicated domain structures into simpler ones (if σ_a is high enough). For $E_{\sigma,a}$ lower than E_i ($E_{\sigma,a}$ stress anisotropy energy caused by external pressure, E_i intrinsic anisotropy energy), no drastic changes of the domain pattern are expected. For $E_{\sigma,a}$ exceeding E_i, an almost complete reorganization of the domain structure should occur. An example is shown in Fig. 12. Appel and Soffel (1984) demonstrated the variation of the amount of the intrinsic anisotropy. In most cases, low σ_a ($\sigma_a \approx 0.1$–0.2 kbar) changes the domain configuration drastically and

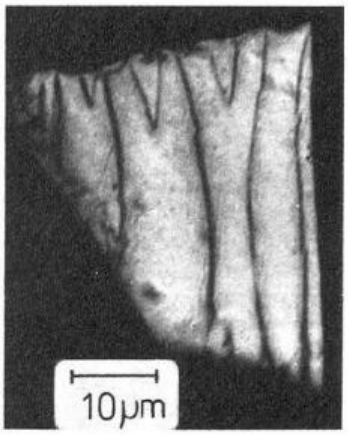

Fig. 6. Domain structure on an isolated synthetic particle of AMTM4/2.5/62

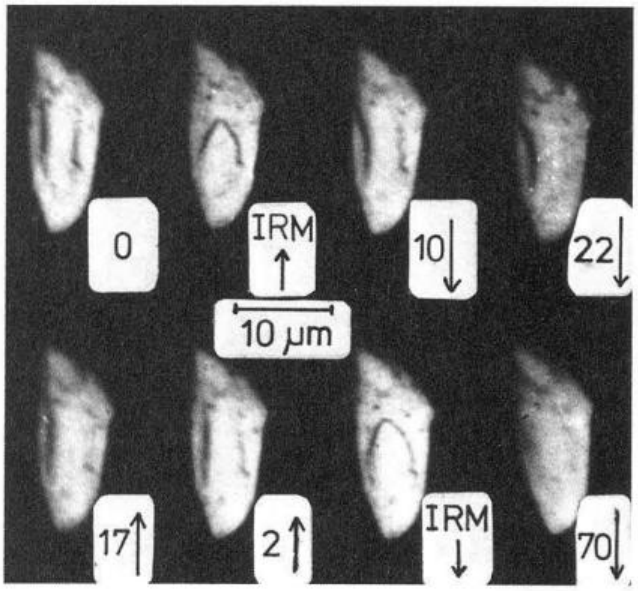

Fig. 7. Domain structures on an isolated synthetic TM72 particle under external magnetic fields H parallel to the observed surface. Values of H are given in Oe

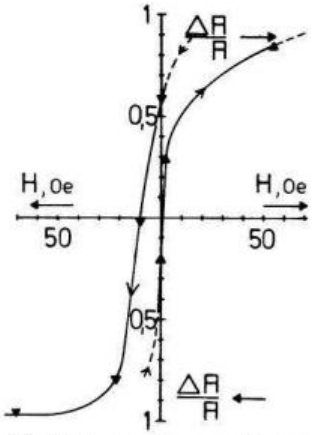

Fig. 8. Hysteresis curve from planimetry of the total domain areas with antiparallel magnetization. ▲ Magnetic field from $H_{max}\leftarrow$ to $H_{max}\rightarrow$; ▼ Magnetic field from $H_{max}\rightarrow$ to $H_{max}\leftarrow$

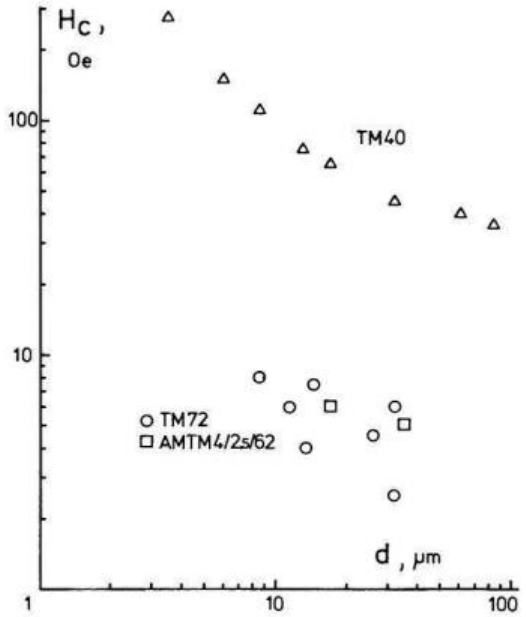

Fig. 9. Coercivity H_C as a function of grain diameter d. Values of TM72 and AMTM4/2.5/62 are from domain area hysteresis, whereas H_C of TM40 are from macroscopic measurements of Day (1977)

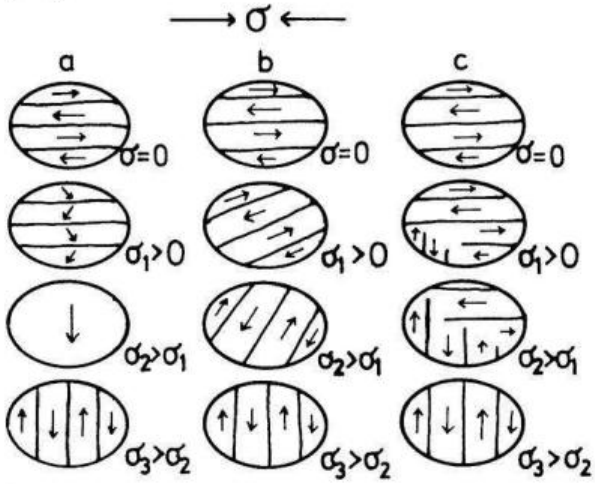

Fig. 10. Possible transitions of domain structures with increasing external uniaxial pressure $\sigma(\lambda>0)$. The spontaneous magnetization is marked by *arrows*

only on a minor part of the grain surface does the domain pattern remain complicate up to almost 1 kbar. The essential result is the high stress sensitivity of the material.

On natural Ti-rich titanomagnetites the observed processes are principally the same, but usually higher σ_a values are required to obtain a simple domain configuration. Frequently, $\sigma_a = 1$ kbar does not simplify the complicated domain pattern substantially. The particle shown in Fig. 13 represents an example for presumably low intrinsic anisotropy (lamellae-shaped domain pattern for $\sigma_a >$ 0.5 kbar).

Temperature dependence of susceptibility ($\chi - T$) – inference of domain state

$\chi(T)$ curves of synthetic MD titanomagnetites (powders with particle sizes of about 10–100 µm) were measured between liquid nitrogen and Curie temperature using an AC

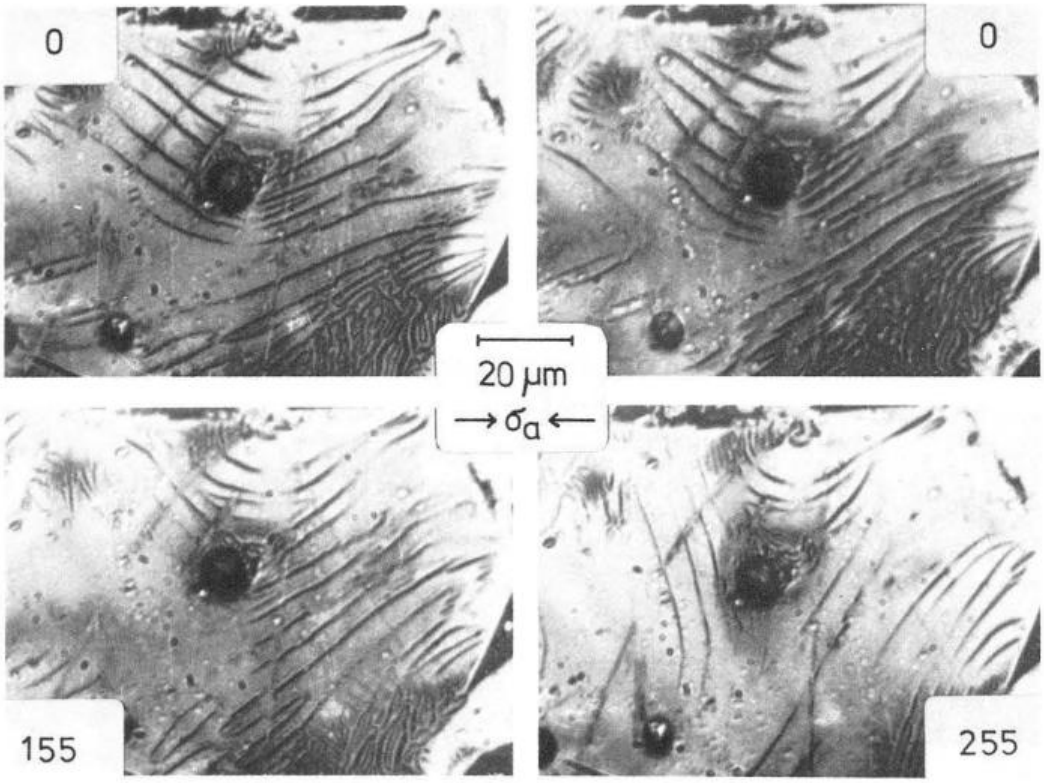

Fig. 11. Domain structure transition under external uniaxial pressure σ_a on synthetic polycrystalline ATM20/62. Values of σ_a are given in bar

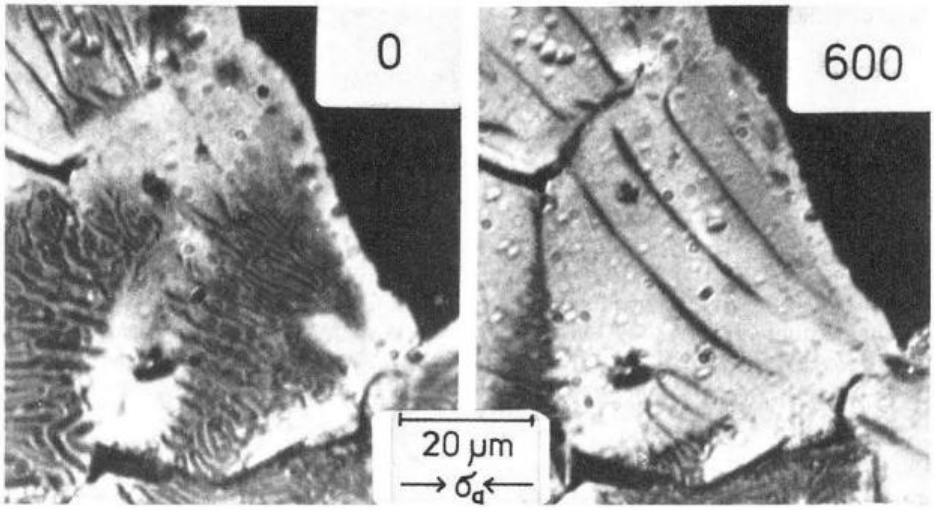

Fig. 12. Domain structure transition of complicated domain configurations into simpler ones by external uniaxial pressure σ_a on synthetic polycrystalline MTM20/62. Values of σ_a are given in bar

bridge with a frequency of 1 kHz and a magnetic field amplitude of 1.5 Oe (120 A/m).

The measured $\chi_0(T)$ curves (Fig. 14) show some systematic variations with the composition of the samples. The first one is the increasing enhancement of the Hopkinson peak with increasing Ti content. However, more important for the inference of the domain state is the peak (or change in the steepness of the curve) at low temperature, which is quite distinct for TM10 and TM24, less pronounced for TM40, only very weak for TM52 and no longer recognizable for the Ti-rich TM60 and TM75 samples. The peaks of TM10, TM40 and TM52 are in rather good agreement with $T(K_1=0)$ (interpolation of the data of Syono [1965]) and only in the case of TM24 is there a discrepancy (but this is probably a consequence of the insufficiency of the interpolation of Syono's data for TM18 and TM31).

Interpolating Syono's data shows that K_1 of TM60 should be zero at about $-30°$ C. The disappearance of the magnetocrystalline anisotropy, however, is not expressed in the measured $\chi_0(T)$ curve of TM60. For this reason, we suppose that there is no essential influence of the magnetocrystalline anisotropy in Ti-rich (around TM60) MD titanomagnetite particles.

For comparisons of theoretical and experimental $\chi_i(T)$

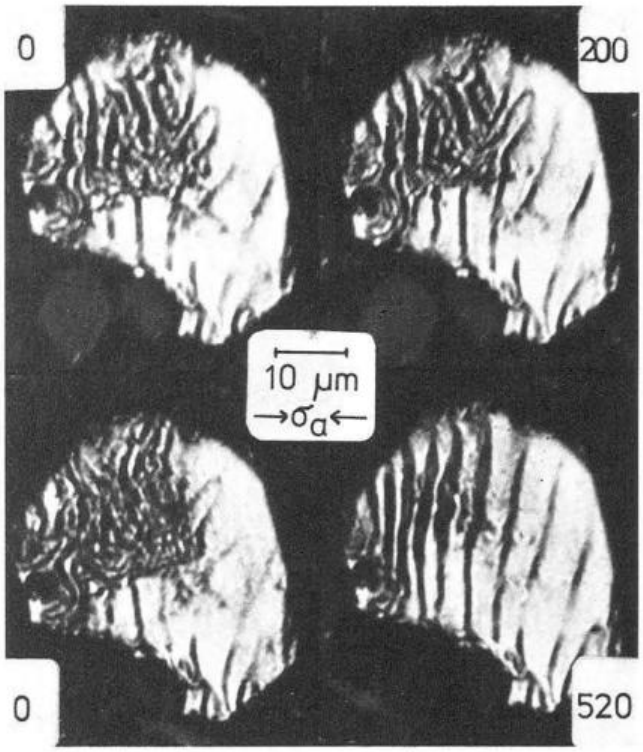

Fig. 13. Domain structure transition under external uniaxial pressure σ_a on natural titanomagnetite $Fe_{2.26}T_{0.52}$-$Al_{0.06}Mg_{0.13}Mn_{0.03}O_4$. Values of σ_a are given in bar

curves, the intrinsic susceptibility χ_i must be calculated from χ_0 with the equation

$$\chi_i = \frac{\chi_0}{1 - N\chi_0}, \tag{1}$$

where N is the demagnetizing factor. The shape of $\chi_i(\chi_0, N) - T$ is strongly dependent on the value of N. Unfortunately, the demagnetizing factor N is unknown. N of MD particles is not only a function of the particle size but strongly dependent on the domain configuration. For MD particles of cubic size, values of N between about 1.6 and $4\pi/3$ are possible (Dunlop, 1983). The maximum value N_{max} can be drived from the maximum value $\chi_{0,\,max}$ of the measured susceptibility with the equation $N_{max} = 1/\chi_{0,\,max}$ ($\chi_i \to \infty$).

Theoretical normalized $\chi_i(T)$ curves were calculated from the relation

$$\chi_i \sim \frac{J_s^2}{f_1(K_1, \lambda_s) + f_2(N, J_s)}. \tag{2}$$

$f_1(K_1, \lambda_s)$ arises from the magnetocrystalline and magnetostriction anisotropy, $f_2(N, J_s)$ from the shape anisotropy. Neglecting f_2, we get (Träuble, 1966) for SD processes (spin rotations):

$$\chi_i \sim \frac{J_s^2}{K_1} \tag{3}$$

in the case of dominance of magnetocrystalline anisotropy

$$\chi_i \sim \frac{J_s^2}{\lambda_s} \tag{4}$$

in the case of dominance of stress, and for MD processes (domain wall displacements):

$$\chi_i \sim \frac{J_s^2}{K_1^{7/4}} \tag{5}$$

in the case of dominance of magnetocrystalline anisotropy

$$\chi_i \sim \frac{J_s^2}{\lambda_s K_1^{1/4}} \tag{6}$$

in the case of dominance of stress.

Figures 15 and 16 show the theoretical $\chi_i(T)$ curves for TM52 and TM60. The expected peaks at low temperatures (caused by $K_1 \to 0$) are partly suppressed by stress and shape anisotropy (see also Clark and Schmidt [1982]). The peak of $\chi_i(T)$ from relation (6) is only weakly pronounced (weak dependence with $\chi_i \sim K^{-1/4}$) and may not be detected in measurements of $\chi_0(T)$. For this reason, SD and MD behaviour cannot be distinguished in the case of dominance of stress. But, in any case, it is possible to diagnose the dominance of stress or magnetocrystalline anisotropy. The theoretical $\chi_i(T)$ curves calculated from relation (4), of both TM52 and TM60, are in good agreement with the $\chi_i(T)$ curves determined from $\chi_0(T)$ with $N = 2.0$ (TM60) and $N = 2.8$ (TM52), respectively (Figs. 15 and 16). The small values of N are confirmed by the values of N_{max} (≈ 3) derived from the $\chi_{0,\,max}$ values.

Consequently we infer, as the essential result of this section, the dominance of stress for magnetization processes in small magnetic fields (at least in the temperature range around $K_1 \to 0$).

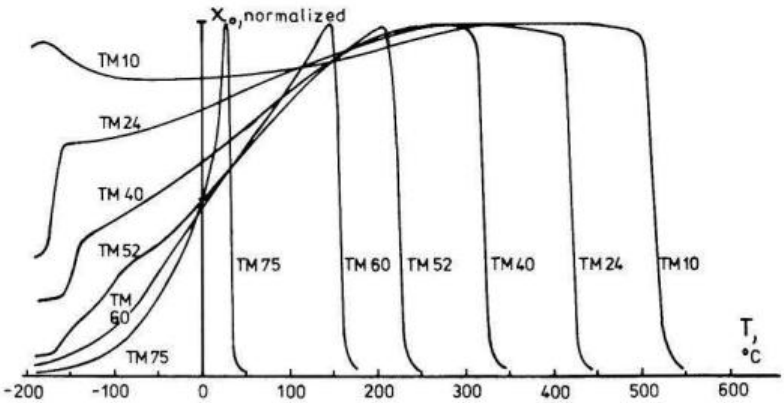

Fig. 14. Temperature dependence of susceptibility χ_0 of synthetic MD titanomagnetites TM10, TM24, TM40, TM52, TM60 and TM75 (grain size 10–100 µm)

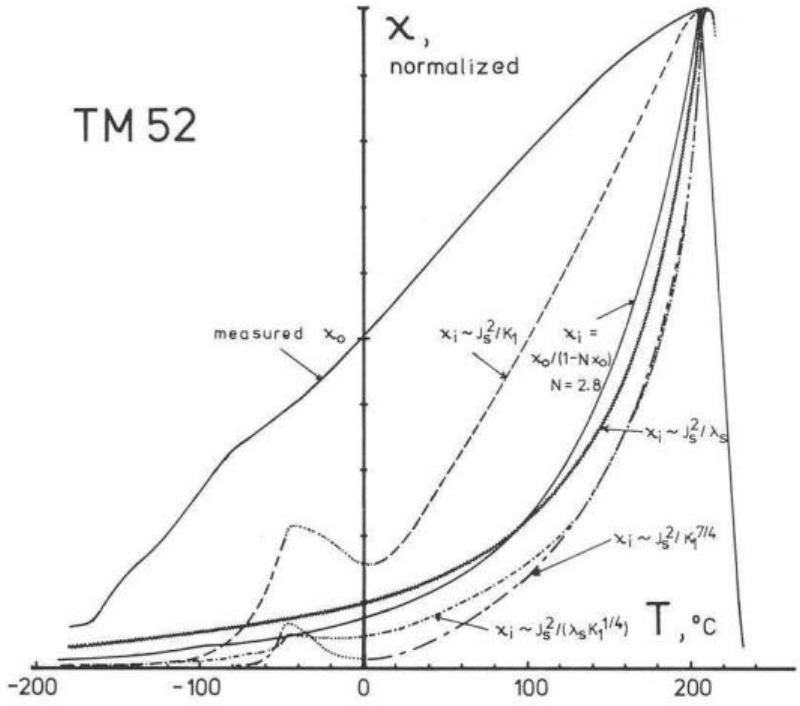

Fig. 15. Theoretical and experimental $\chi_i(T)$ curves of TM52. For details, see text

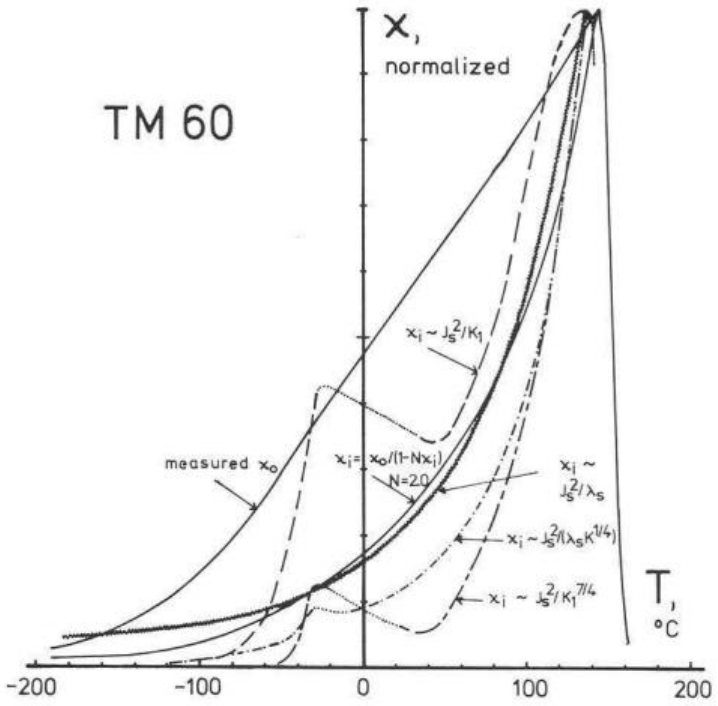

Fig. 16. Theoretical and experimental $\chi_i(T)$ curves of TM60. For details, see text

Comparisons of theoretical and experimental $\chi_i(T)$ curves are not possible for compositions TM10, TM24 and TM40 because $(1-N\chi_0)\rightarrow 0$ for temperatures near T_c (plateau of $\chi_0 - T$ because of high χ_i-value). For TM75, only a extremely rough extrapolation of λ_s would be possible from Syono's data and no comparison was made for this reason.

Discussion and conclusions

Domain structure observations showed that at room temperature Ti-rich titanomagnetites normally develop a non-classical domain structure characterized by a very complicated domain pattern. Possible explanations are:

- mineralogical inhomogeneity of the specimens,
- inhomogeneous anisotropy field, causing a locally varying preferential direction of the spontaneous magnetization. Possible sources of anisotropy are stress, magnetocrystalline and shape anisotropy.

Mineralogical inhomogeneity was not detected by the various analysis methods.

The general occurrence of bent domain walls, the varying intensity of the Bitter lines and the local sensitivity on external stress indicate the existence of an inhomogeneous

anisotropy field, in amount and in direction. Consequently, the preferential direction of the spontaneous magnetization and the specific domain wall energy should fluctuate and prevent the development of a classical domain configuration. Complicated domain patterns will arise from the locally varying anisotropy conditions. Mainly, the spontaneous magnetization should be orientated in the direction defined by the local anisotropy (apart from the domain walls). Depending upon certain anisotropy conditions, the development of true domain structures may even be impossible in part of the crystals.

The most probable cause for the formation of complicated domain patterns is the existence of an inhomogeneous stress field. Of course, the magnetocrystalline and shape anisotropy will not vanish, but superposes the stress anisotropy. However, from the pressure experiments we can derive the dominance of stress because of

– the high difference of sensitivity on external stress between natural and synthetic titanomagnetites (of about the same composition) and

– the usually low sensitivity on external stress in natural Ti-rich titanomagnetities.

Magnetocrystalline anisotropy and anisotropy of magnetostatic origin are limited by material constants. The maximum values of the magnetostatic anisotropy energy E_M and magnetocrystalline anisotropy energy E_K can be calculated from the equations

$$E_K = |K_1|/3 \quad \text{(for cubic anisotropy with } K_1 < 0) \tag{7}$$

$$E_M = 0.5\,(N_1 - N_2)\,J_s^2 . \tag{8}$$

Taking values for TM60 (magnetocrystalline constant K_1 from Syono [1965], saturation magnetization J_s from Akimoto et al. [1957]) and $(N_1 - N_2) = 2\pi$, we obtain $E_K \approx 0.1 \times 10^5$ erg/cm^3 and $E_M \approx 0.6 \times 10^5$ erg/cm^3. Both are too low to explain the frequently observed stability of the complicated domain structures in natural specimens up to 1 kbar because, with the equation

$$E_\sigma = 1.5\,|\lambda_s \sigma|, \tag{9}$$

the stress anisotropy energy E_σ becomes several times higher ($\approx 2 \times 10^5$ erg/cm^3, λ_s from Syono [1965], $\sigma = 1$ kbar). It seems that anisotropy of magnetostatic origin cannot explain the amount of observed intrinsic anisotropies, although it might contribute considerably to the total anisotropy. Magnetocrystalline anisotropy is even lower.

Considering only E_K and E_M we cannot find a satisfactory explanation for the difference of sensitivity to external stress in natural and synthetic specimens. Strong specific differences of mineralogical or crystalline and geometrical structure would be required. Stress-controlled anisotropy, however, agrees with our observations because E_σ depends not only on material constants but high and low state of intrinsic anisotropy can be easily interpreted by varying σ_i.

Calculations balancing the maximum energies E_K and E_σ (Eqs. 7 and 9) confirm the importance of stress. E_σ exceeds E_K for ≈ 100 bar (290 K) in the case of TM60 (Fig. 17). Stress becomes dominant above this value. Only in the case of very low stress (or more precisely, stress inhomogeneity) a simple domain structure (like Figs. 6 and 7) is possible. In Fig. 18 ($E_K = E_\sigma$) is plotted against temperature for TM56. Above $\approx -50°$ C, stress below 200 bar is sufficient for $E_\sigma > E_K$. With decreasing temperature E_K becomes more and more dominant for TM56.

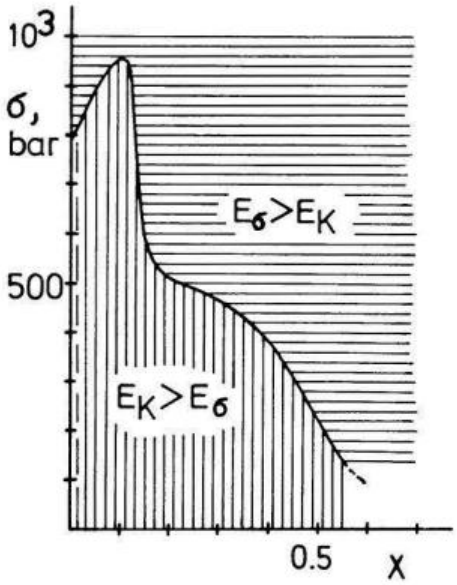

Fig. 17. Required stress σ for $E_K = E_\sigma$ of titanomagnetites (composition x) at 290 K

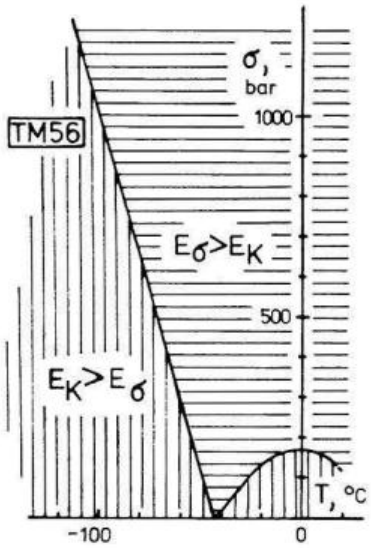

Fig. 18. Required stress σ for $E_K = E_\sigma$ of TM56 at various temperatures

The stress control of magnetization processes in Ti-rich titanomagnetites near room temperature is indicated by the hysteresis experiments – if we identify almost classical domain structures with low internal stress – and by the measurements of temperature dependence of susceptibility. The dominance of stress is also inferred from Hodych (1982a, 1982b) by measuring coercivity. The author finds that H_C is well correlated with the magnetostriction constant λ_s in the case of large (≈ 200 μm) natural MD titanomagnetites ($x \approx 0.6$, 295 K to 190 K) but also for natural MD magnetite (2.7 – 65 μm, 300 K to 130 K).

The existence of internal stress σ_i up to several hundred bars and the inhomogeneity of the amount and direction of internal stress is plausible. Internal stress might arise from:

– Crystallization pressure: there is only poor knowledge about the amount of crystallization pressure.

– Magnetoelastic energy: when basaltic rock is cooling below the Curie temperature of the titanomagnetites the minerals are already crystallized. Therefore, no free deformation (due to magnetostriction) is possible and internal stress will be produced. The amount of σ_i can be approximately calculated from

$$1.5|\lambda_s \sigma_i| = E'_K(c_{ij}, \lambda) \tag{10}$$

(E'_K magnetoelastic energy, c_{ij} elastic constants). For TM60 a maximum value $\sigma_i \approx 140$ bar is calculated (c_{ij} from interpolation of values for magnetite and ulvospinel, after Hearmon [1956] and Ishikawa and Syono [1971]).

– Vacancies in the spinel lattice caused by oxidation: the cell parameter a_0 decreases with oxidation. Based on a model of an inner sphere with degree of oxidation z and a surrounding shell with $z + \Delta z$, σ_i (radial stress) can be calculated from

$$\sigma_i = 0.03\, k \Delta z \tag{11}$$

(k bulk modulus) with $\Delta a_0/a_0 \approx -0.01 \Delta z$ (Readman and O'Reilly, 1972; Moll, 1980). For $\Delta z = 0.01$ (very small value) σ_i becomes 310 bar ($k \approx 10^{12}$ dyn/cm^2 is calculated from c_{ij}). High values of σ_i from oxidation are confirmed by the occurrence of shrinkage cracks.

– Dislocations: the maximum mean value of σ_i around dislocation can be estimated from

$$\sigma_i = (2Gb)/(\pi d) \tag{12}$$

(G shear modulus, b Burger's vector, d critical diameter for the superparamagnetic–single domain transition). $d = 0.1$ μm (Butler and Banerjee [1975], for TM60), leads to $\sigma_i \approx 1.1$ kbar ($G \approx 0.6 \times 10^{12}$ dyn/cm^2 from c_{ij}, $b \approx 3 \times 10^{-8}$ cm). However, the range width of σ_i caused by dislocations is probably too small for creating PSD behaviour.

Crystallization pressure and magnetoelastic stress cause internal stress with inhomogeneous direction because of the irregular shape of the particles, whereas the degree of oxidation itself is locally varying (and therefore causes internal stress with locally varying direction). The consequence is an inhomogeneous direction of anisotropy.

A preliminary simple model for the domain state of Ti-rich titanomagnetites has been published by Appel and Soffel (1984). Following the idea of the model, particles of MD grain size should consist of multidomain, single domain and spin cluster regions. The consequence is the decrease of the "effective grain size" (division into subvolumes) and an enhanced importance of spin rotation processes. The micromagnetic state will be comparable with the conditions in magnetic sponges (cold-pressed and partially sintered magnetic powders: e.g. Weil [1953]).

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