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Germany
Email: gdz@sub.uni-goettingen.de

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Changes of Structure, Phase Composition and Electric Conductivity Under High-Temperature Oxidation of Titanomagnetites

V. Kropáček and M. Laštovičková

Geophysical Institute, Czechoslovak Academy of Sciences, Boční II/1401, 141 31 Praha 4, Czechoslovakia

Abstract. Temperature dependence of electrical conductivity in the temperature range from 200 to 900° C has been measured on a set of 17 magnetic fractions separated from Tertiary and Quaternary basaltic rocks of the Bohemian Massif. Under partial oxygen pressure of 0.1–1.0 Pa and temperatures over 600° C, conditions under which the sample can oxidize, and phase and structural changes occur in the specimens. Generally the electrical conductivity σ was found to decrease with increasing degree of oxidation z. A possible mechanism of electrical conductivity and the corresponding distribution of cations is proposed to explain the results. For $z<0.4$, the mechanism of valence transfer predominates, whereas for $z>0.4$ the mechanism of controlled valency is most important.

Key words: Titanomagnetic – Thermal treatment – Electric conductivity.

Introduction

The process of oxidation of titanomagnetites $Fe_{3-x}Ti_xO_4$, changes in the distribution of cations, and phase changes in the representation of individual spinel and other phases connected with this process, have been studied by a number of authors (Readman and O'Reilly 1970, 1972; Bleil 1971, 1975; O'Donovan and O'Reilly 1978). In most of these papers magnetic measurements were used to obtain an idea of the distribution of the cations into sublattices. However, direct use of magnetic measurements in restricted by the highest Curie temperature of titanomagnetite, about 500° C. Therefore, in this paper an attempt has been made to use another structurally sensitive physical parameter, electrical conductivity, to characterize the process of oxidation at temperatures up to 900° C.

Experimental Methods

Seventeen titanomagnetite specimens separated from Tertiary and Quaternary basaltic rocks of the Bohemian Massif (Kropáček 1974, 1977) were used. Specimens of the magnetic fractions were obtained by repeated magnetic separation in an A.C. field and by cleaning with the aid of heavy fluids. The resultant purity of the magnetic fractions was between 90 and 95%. These powdered fractions were used to prepare specimens for measuring electrical conductivity. The specimens were of cylindrical shape, 8 mm i.d. and 6 mm high. They were compressed under a pressure of 300 MPa in a fixture of Ti-bronze. A 5% admixture of talc was used as a plasticizer. The effect of the low-conductivity talc on the electrical conductivity σ and on the activation energy E_0 was checked in a series of measurements using specimens with different concentrations of talc (from 1.0 to 75%). These measurements (Laštovičková and Kropáček 1979) were used to determine corrections ($\Delta \log \sigma(200° C) = -0.25$ and $\Delta E_0 = -0.12$ eV) which are practically constant in the temperature interval 200°–900° C, for the content of talc 2–5%. Electrical contacts were of 'silver pain' paste which was not contaminated by the specimens. A two-electrode connection with a source of stabilized voltage and a continuous record of the electrical conductivity and temperature were used. Specimens were heated in a flow-through Ar-atmosphere with a partial oxygen pressure $P_{O_2} \sim 0.1$–1.0 Pa.

Structures and phase composition of the specimens were determined by means of a X-ray difractometer DRON 2.0 with Co radiation (Fe filter) and in some cases with a graphite or quartz monochromator. Calibration was carried out with the aid of NaCl p.a. Diffraction intensities were recorded over an angular range of $2\vartheta = 20°$–$80°$, for selected sections using a scanning interval of $2\vartheta = 0.05°$ and an integration time of 40–200 s. High temperature X-ray measurements were made in a UPVT-1500 diffractometric chamber in a vacuum of 10^{-5} Pa. Reflections were evaluated by means of a three-point parabola with correction for the Lorentz polarization factor, and lattice parameters were determined by the least-squares method (Azároff and Buerger 1958).

The degree of oxidation of titanomagnetites z is defined by the following relation (O'Reilly and Banerjee 1966):

$$Fe^{2+} + 1/2\,z\,O \rightarrow z\,Fe^{3+} + (1-z)\,Fe^{2+} + 1/2\,z\,O^{2-}.$$

First, z was determined by conventional chemical analysis from the relation

$$z = [2(1+x)(M+3L+2K) - 8M] \times [(1+x)(3M+6L+4K)]^{-1},$$

where x is the content of ulvöspinel in the titanomagnetite, $(1-x)\,Fe_3O_4 \times Fe_2TiO_4$ M is the content (mol%) of FeO, L the content of Fe_2O_3, K the content of TiO_2 (Ozima et al. 1974); and secondly by X-ray analysis using the intensities of reflection 111 (Readman and O'Reilly 1972) and from the intensities of reflections 110, 210, 211, 310, 321 (Gendler and Kropáček 1979).

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Table 1. Composition parameters of magnetic fractions and its changes during the thermal treatment; MT titanomagnetite, HI hemoilmenite, PB pseudobrookite, R + A rutile and anatase

Group	Specimen no.	Natural state											After heating up to 900° C					
		Fe^{2+}	Fe^{3+}	Ti^{4+}	□	x	z	a [nm]	MT	HI	PB	R + A	z	a [nm]	MT	HI	PB	R
I	201	1.38	0.85	0.68	0.09	0.68	0.15	0.8465	92	–	–	–	0.10	0.8470	80	10	–	–
	206	1.11	1.13	0.60	0.16	0.62	0.28	0.8447	85	10	–	–	0.25	0.8434	80	10	5	–
	227	1.04	1.38	0.43	0.13	0.44	0.25	0.8427	96	–	–	–	0.05	0.8459	80	6	–	10
	249	0.13	1.96	0.46	0.45	0.48	0.90	0.8376	92	–	–	–	0.40	0.8427	90	–	–	–
	256	0.97	1.90	0.09	0.04	0.09	0.10	0.8398	83	–	–	10	0.06	0.8423	85	–	–	5
	257	0.96	1.91	0.09	0.04	0.09	0.11	0.8433	93	–	–	–	0.08	0.8431	93	–	–	–
	259	1.38	0.88	0.65	0.09	0.65	0.15	0.8468	93	–	–	–	0.12	0.8472	90	5	–	–
	298	0.46	1.70	0.50	0.34	0.50	0.66	0.8373	92	–	–	–	0.34	0.8405	92	–	–	–
II	202	1.58	0.69	0.69	0.04	0.70	0.06	0.8467	94	–	–	–	0.70	0.8378	40	15	20	20
	218	0.93	1.35	0.52	0.20	–	–	0.8436 0.8425	90	–	–	–	1.00	0.8342	28	42	23	–
	220	0.15	2.40	0.12	0.33	0.14	0.85	0.8349	80	–	8	7	0.80	0.8377	45	20	20	5
	230	0.94	1.92	0.09	0.05	0.10	0.13	0.8398	85	5	3	–	0.30	0.8386	52	30	6	7
	235	0.20	1.88	0.49	0.43	0.50	0.85	0.8366	90	3	–	–	0.80	0.8377	55	20	12	5
	238	0.40	2.07	0.24	0.29	0.25	0.65	0.8336	90	5	–	–	0.66	0.8376	42	20	30	–
	263	1.22	1.10	0.60	0.08	0.60	0.15	0.8443	85	7	–	–	0.65	0.8357	72	15	–	5
	288	1.23	1.14	0.53	0.10	–	–	0.8445 0.8388	90	–	4	–	1.00	0.8345	50	15	23	5
	297	0.10	1.90	0.58	0.42	0.60	0.90	0.8348	80	12	2	–	0.93	0.8351	30	58	–	6

The number f of vacancies per formula unit of titanomagnetite was determined from known values of the parameter x and z as follows:

$$f=[3z(1+x)][8+z(1+x)]^{-1},$$

assuming the formula of titanomagnetite to be

$$Fe_b^{2+}Fe_c^{3+}Ti_d^{4+}\,\square_f\,O_4^{2-}.$$

Amounts of the individual phases (titanomagnetite, hemoilmenite, pseudobrookite, rutile, anatase) were determined by X-ray quantitative phase analysis with an accuracy of ±2.5%. For low contents (2–5%) the existence of these phases was determined only qualitatively. From conventional chemical analysis only FeO, Fe_2O_3, TiO_2 were determined.

The temperature dependence of specific heat c_p was measured using a DSM-2 differential scanning microcalorimeter in the temperature range of 20°–500° C. Differential thermic analysis (DTA) and thermogravimetric analysis (TG) were obtained with a Derivatograph instrument in air in the temperature range of 20°–1,000° C and a rate of 10° C/min.

Experimental Results

X-ray measurements indicated that titanomagnetite at various stages of oxidation constituted the largest part of the magnetic fractions beside other phases such as hemoilmenite, pseudobrookite, and rutile, as indicated in Table 1.

Composition of titanomagnetites $Fe_{3-x}Ti_xO_4$ varies over the range $x=0.08$–0.70, and the oxidation parameter z varies between 0.06–0.90. The lattice constant of the cubic phase in our samples was within the interval $a=0.8336$–0.8468 [nm] (Table 1).

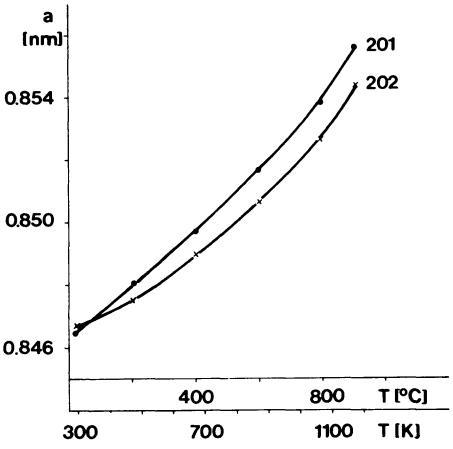


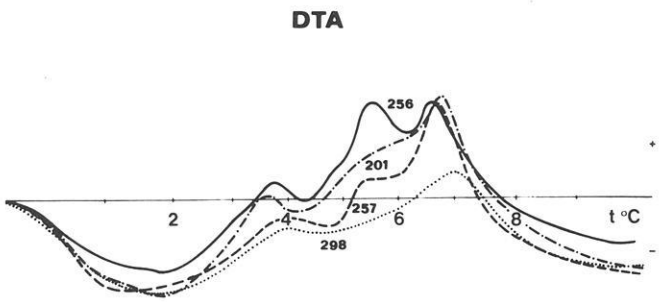
Fig. 1. Temperature dependence of lattice parameter a [nm] for the specimens 201 and 202 in vacuum

For two specimens (Nos. 201 and 202) the dependence $a(t)$ of the lattice constant a on temperature t [°C] was measured in the range 20°–900° C (Fig. 1). $a(t)$ can be described by the relations

$$a=0.8465+6.082\times10^{-6}t+4.283\times10^{-9}t^2 \quad \text{for No. 201}$$

$$a=0.8467+2.733\times10^{-6}t+6.035\times10^{-9}t^2 \quad \text{for No. 202.}$$

From high-temperature X-ray measurements we determined that no phase changes took place in specimen No. 201, whereas in specimen No. 202 3–5% hemoilmenite and rutile appeared above 700° C. The working vacuum was $\sim10^{-4}$ Pa. Curves from differential thermoanalysis (DTA) and thermogravimetry (TG) have been used for determining titanomagnetite oxidation states during heating in air (Figs. 2 and 3). From the DTA curves it is



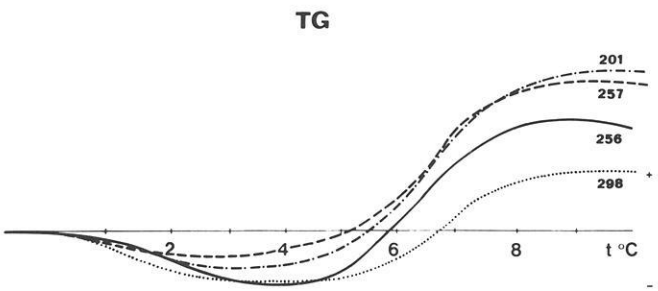
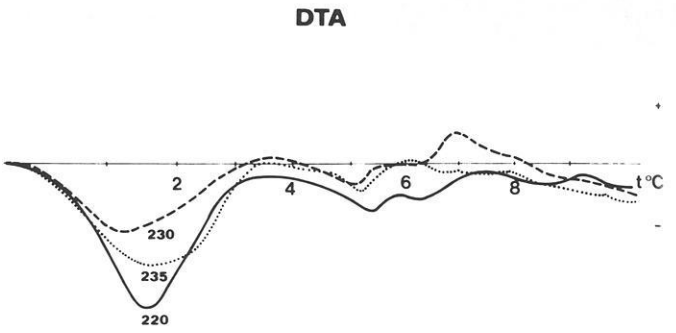


Fig. 2. Thermogravimetric (*TG*) and differential thermic curves for the specimens Nos. 201, 256, 257, 298. Heating in air, temperatures are in units of 100° C, *TG* and *DTA* curves in arbitrary units



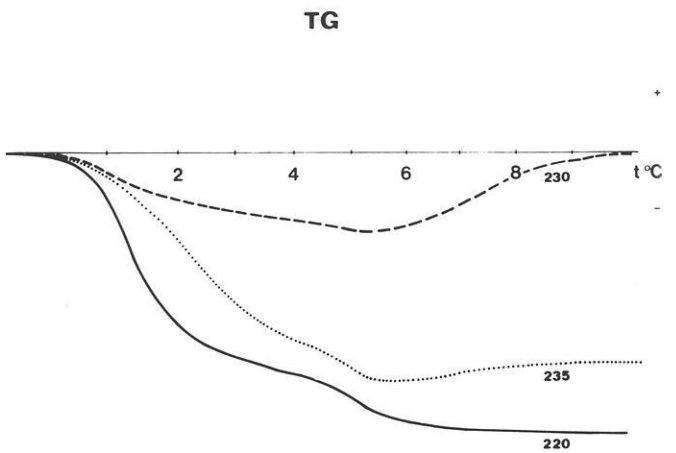


Fig. 3. *TG* and *DTA* curves for specimens Nos. 220, 230, and 235. Heating in air, temperatures are in units of 100° C

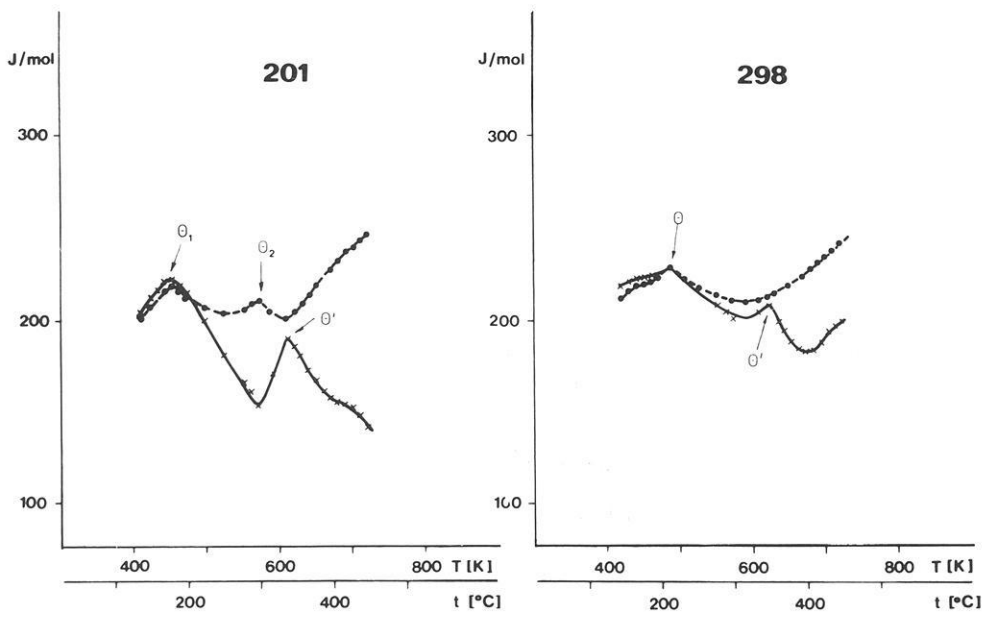


Fig. 4. Temperature dependence of specific heat $c_p = c_p(t)$. ●: Heating in nitrogen; ×: heating in air. θ, θ_1 are Curie temperature of the primary titanomagnetites and θ_2, θ' are Curie temperatures of secondary titanomagnetites produced during the heating

apparent that the first stage of oxidation produces exothermic effects in the temperature range 450° to 800° C with the greatest changes occuring between 600° and 700° C. At higher temperatures of 800° to 1,000° C the changes are endothermic. Similar results have been found from the thermogravimetric analysis (TG), where the oxidation processes also resulted in an increase of sample mass. The maximum rate of oxidation has again been found between 600° to 700° C, whereas above 800° C the mass of the samples has remained constant. X-ray phase analysis yielded the results that after heating the samples to 1,000° C in air the cubic phases had transformed into hemoilmenite, rutile, pseudobrookite and anatase.

The temperature dependence of the specific heat c_p (Fig. 4), determined in nitrogen and air, suggests formation of states with lower enthalpy $\Delta H = \int_{T_1}^{T_2} c_p \, dT$ during oxidation of titanomagnetites, that is formation of more stable phases at normal oxidizing condition. After heating to 900° C at a rate of 10° C/min and cooling in a Ar-atmosphere with $P_{O_2} \sim 0.1$–1.0 Pa (for the conductivity measurements) marked changes occurred in the structure and phase composition of the specimens. These changes can be divided into two categories and the specimens, depending on these changes, into two groups.

The first group of specimens (Nos. 201, 206, 227, 249, 256, 259, and 298) is characterized by a moderate decrease of the values of the oxidation parameter z (i.e., the stoichiometry of the specimens increases), and no other detectable phases are created. The average value of $\bar{z}$ is 0.32 in the natural state and $\bar{z} = 0.18$ after thermal treatment. Accordingly the value of the lattice constant $\bar{a}$ is found to have increased slightly, from 0.8423 to 0.8443 nm, after the thermal cycle. The content of any newly generated phase in this group is minimal and does not exceed 10 % on the whole (Table 1).

As regards the second group of specimens (Nos. 202, 218, 220, 230, 235, 238, 263, 288, and 297) very marked changes take place under thermal treatment. A whole series of other phases is generated (hemoilmenite, pseudobrookite, rutile, and anatase) and the content of the spinel phase decreases as much as to 28 % of the original value. The lattice constant also decreases from $\bar{a} = 0.8495$ nm in the initial state to $\bar{a} = 0.8365$ nm after thermal treatment. Correspondingly, the oxidation parameter z increases markedly from the original $\bar{z} = 0.48$ to about 0.83. Therefore, intensive oxidation associated with the generation of new phases takes place in the second group of specimens under thermal treatment with the following average proportion of phases: non-stoichiometric titanomagnetite 40–50 %, hemoilmenite 20–25 %, pseudobrookite 15–20 %, rutile and anatase 7–15 %.

Average values of the electrical conductivity at $t = 200°$ C of the specimens of the first group ($\log \sigma_I = -6.343\,[\Omega m]^{-1}$) are distincly higher the the average values of the second group ($\log \sigma_{II} = -7.942\,[\Omega m]^{-1}$); a smaller difference is preserved at a temperature of 600° C ($\log \sigma_I = -2.956\,[\Omega m]^{-1}$, $\log \sigma_{II} = -3.546\,[\Omega m]^{-1}$) (Table 2). Statistically significant relations, for which the correlation coefficient $r > r_{crit} = 0.71$ (for $N = 8$ and a 95 % probability) at a temperature of 200° C, are only observed in the first group:

$$\log \sigma(200°\,C) = -9.45 + 2.935\,b \quad (r = +0.74), \tag{1}$$

$$\log \sigma(200°\,C) = -5.02 - 7.960\,f \quad (r = -0.78), \tag{2}$$

$$\log \sigma(200°\,C) = -7.35 + 1.77\,b - 4.49\,f \quad (r = 0.84),$$

if we express titanomagnetite formula unit as

$$Fe_b^{2+} Fe_c^{3+} Ti_d^{4+} \square_f O_4^{2-}.$$

At a temperature of 600° C in the first group of the specimens attain statisticaly significant values of the coefficients of correlation for other relations:

$$\log \sigma(600°\,C) = -1.76 - 7.16\,f \quad (r = -0.80), \tag{3}$$

$$\log \sigma(600°\,C) = -5.45 + 2.50\,b \quad (r = +0.75), \tag{4}$$

$$\log \sigma(600°\,C) = -3.29 + 1.16\,b - 4.88\,f \quad (r = 0.78).$$

Table 2. Electrical conductivity σ at temperatures 200° C and 600° C, activation energy E_0 in the temperature intervals 200°–400° C, 600°–700° C and 800°–900° C

Group	Specimen no.	$\log \sigma$ (200° C) $[\Omega m]^{-1}$	$\log \sigma$ (600° C) $[\Omega m]^{-1}$	E_0 [eV] 200°–400° C	E_0 [eV] 600°–700° C	E_0 [eV] 800°–900° C
I	201	−5.717	−2.550	0.79	0.76	1.58
	206	−6.745	−2.594	1.08	1.51	1.70
	227	−7.092	−4.250	0.45	1.20	1.15
	249	−9.007	−5.264	0.58	1.25	1.32
	256	−6.430	−2.695	1.52	0.53	0.11
	257	−4.614	−1.303	0.75	1.30	–
	259	−4.309	−1.441	0.69	0.48	1.72
	298	−6.230	−3.523	0.98	1.39	0.85
II	202	−8.030	−3.625	1.41	2.01	1.88
	218	−7.114	−1.354	1.16	1.34	0.46
	220	−8.283	−5.143	0.48	0.86	2.44
	230	−8.827	−4.701	0.50	1.57	–
	235	−7.991	−3.251	0.88	0.71	3.00
	238	−8.551	−4.229	1.01	1.12	2.50
	263	−7.577	−4.126	0.55	1.16	1.91
	288	−6.538	−1.399	1.28	0.80	0.42
	297	−6.230	−3.523	0.98	1.39	0.95

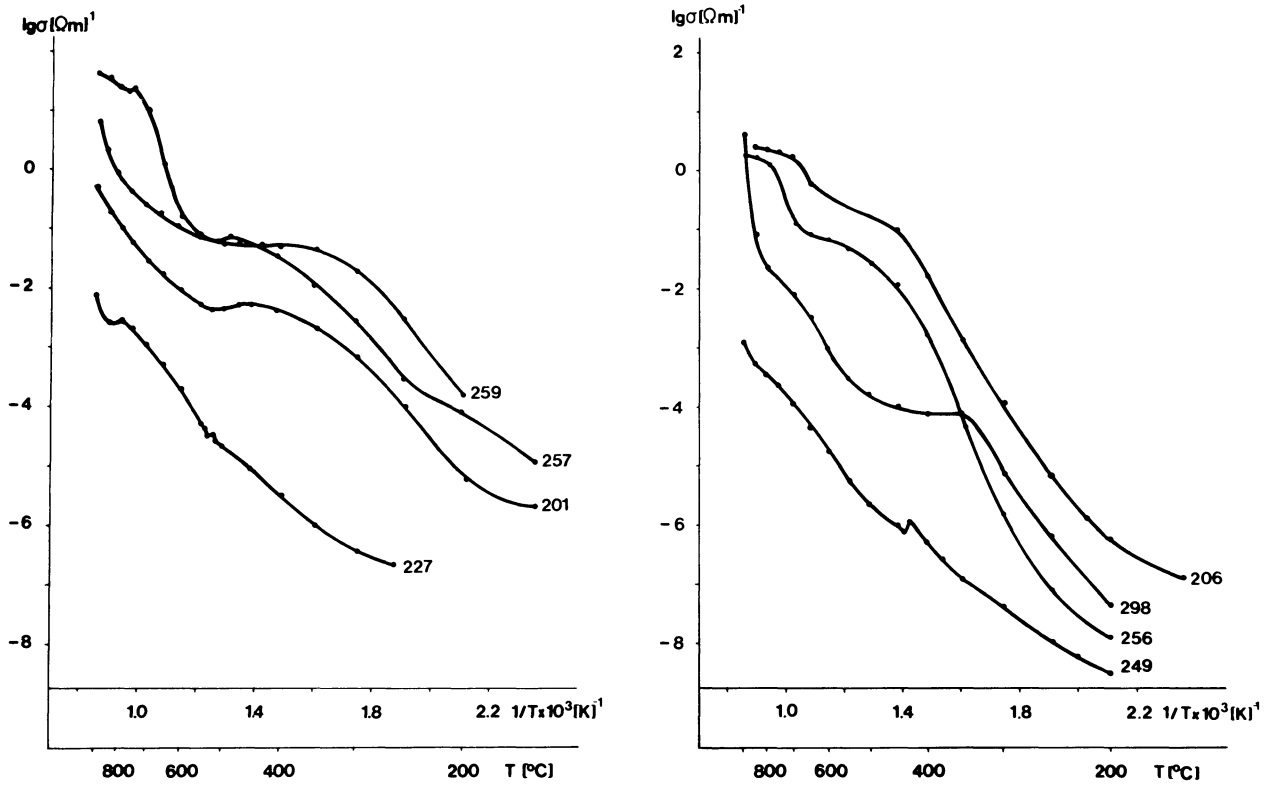


Fig. 5. Electrical conductivity $\sigma\,[\Omega m]^{-1}$ as a function of temperature for the first group of samples (see text)

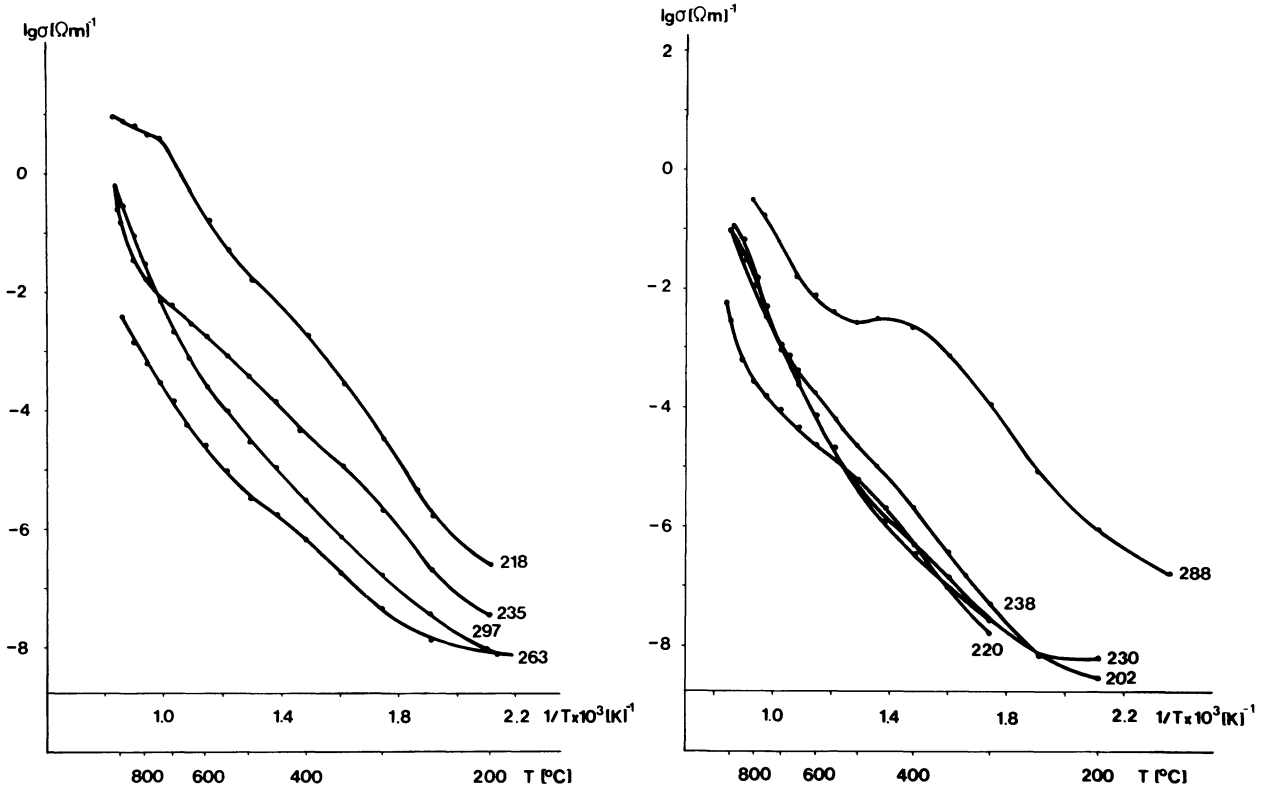


Fig. 6. Electrical conductivity $\sigma\,[\Omega m]^{-1}$ as a function of temperature for the second group of samples

For the second group there is no statistically significant correlation between $\log\sigma$ and any of the other parameters considered; higher values were only observed for $r_{\log\sigma(200),b} = 0.56$ and $r_{\log\sigma(200),f} = -0.40$.

Temperature dependence of the electrical conductivity for the specimens of the first group is shown in Fig. 5 and for those of the second group in Fig. 6. The comparison of Figs. 5 and 6 indicates that specimens of the first group display a relatively low increase of σ with temperature. The second group displays a high increase of σ with temperature, particularly above 600° C. To describe the dependence of the electrical conductivity on temperature we used

$$\sigma = \sigma_0 \exp(-E_0/kT),$$

where E_0 is the activation energy, k Boltzmann's constant and T the absolute temperature.

Values of E_0 for the individual temperature intervals derived from the above relation differ considerably between specimens of groups I and II (Table 2). For specimens of group I, with the exception of the temperature interval of 400°–600° C, activation energies between specimens are practically constant, and probably one type of electric conductivity predominates. For specimens of the second group, values of E_0 tend to be considerably higher above 600° C than those of the first group; we may, therefore, assume the existence of other types of electric conductivity.

Discussion

According to Verwey et al. (1947) the generation of electric current in ferrites can be envisaged as a process of an electron transition between ions according to the following general pattern:

$$M_{(1)}^{q+} + M_{(2)}^{r+} \rightleftarrows M_{(1)}^{(q+1)+} + M_{(2)}^{(r-1)+}. \qquad (5)$$

According to this model of valence transfer, if ions of the same element exist in a crystal at equivalent locations and differ in valency by unit, transition of electrons will be easy and the electrical conductivity will be high. Values of the activation energy E_0, on the other hand, will be low.

In titanomagnetites Fe^{2+} and Fe^{3+} ions may exist in octahedral (B), as well as tetrahedral (A) positions. Valence transfer will be posible only between ions in either (A–A) or (B–B) positions. These measurements (Tables 1 and 2) have shown that the value of $\log\sigma(200°\,C)$ is small dependent on parameter x and more dependent for temperature $t = 600°$ C. Therefore, it is probable that part of the Fe^{2+} ions will be located in the tetrahedral (A) positions and the cations will be distributed as

$$Fe_k^{3+} Fe_l^{2+} [Fe_m^{3+} Fe_n^{2+} Ti_d^{4+} \square_f] O_4^{2-},$$

where $k+m=(2-2x+p)/L$, $l+n=(1+x)(1-z)/L$, $d=x/L$, $f=3p/8L$ and $p=z(1+x)$, $L=1+p/8$.

As indicated by Eqs. (2) and (3), $\log\sigma$ reflects the effect of the degree of oxidation z expressively, i.e., with increasing non-stoichiometry the electrical conductivity decreases markedly. This can be explained by a decrease of Fe^{2+} ions with increasing value of the number of vacancies f (or of z), and consequently a decrease of $Fe^{2+} - Fe^{3+}$ pairs, because the created vacancies do not contribute to the conductivity. The decrease of $\log\sigma$ with decreasing content of Fe^{2+} ions is determined by Eqs. (1) and (4). For specimens of the second group, the tendencies observed are very similar; however, values of the correlation coefficients are lower than the critical values for a 95 % probability.

It is clear that the content of Ti^{4+} ions which distinctly prefer octahedral positions will also play a role in the mechanism of electrical conductivity because one may assume rearrangements of the type

$$\beta Fe^{3+} + \gamma Fe^{3+} + \delta Ti^{3+} \rightleftarrows \delta Ti^{4+} + \gamma Fe^{2+} + \beta Fe^{3+}, \qquad (6)$$

$\beta \gg \gamma, \delta$, i.e., the mechanism of controlled valence with the aid of admixture ions (Krupička 1969). In this case current carriers will be electrons localized on Fe^{2+} cations and generated by ionization of the $Ti^{4+} - Fe^{2+}$ pairs, which represent donor centres. The number of carriers will be proportional to the number of Ti^{4+} cations, i.e., to the value x. The energy required to ionize the $Ti^{4+} - Fe^{2+}$ pair will be higher than that required to ionize the $Fe^{2+} - Fe^{3+}$ pair, but it will be markedly lower than for pure maghemite ($\gamma - Fe_2O_3$), where transitions between levels $Fe^{3+} + Fe^{3+} \rightleftarrows Fe^{2+} + Fe^{4+}$ mainly occur to preserve the condition of electron neutrality. With the titanomagnetites the value of $\log\sigma$ should be proportional to the concentrations of Ti^{4+} cations.

Also the values for selected specimens are: No. 220 ($x=0.14$, $f=0.33$; $\log\sigma(200°\,C) = -8.283\,[\Omega m]^{-1}$) and No. 298 ($x=0.50$, $f=0.34$; $\log\sigma(200°\,C) = -6.230\,[\Omega m]^{-1}$) which differ significantly only in the x-value and not in concentration of vacancies.

The observed smaller mean values of the activation energy E_0 for the first group as compared to the second group (Table 2) in all temperature intervals also can be explained on the basis of these mechanism of electrical conductivity.

Conclusion

1. In the process of high-temperature oxidation of titanomagnetites at temperatures of up to 900° C and partial oxygen pressure of 0.1–1.0 Pa two types of changes occur:

   (a) Increase of the degree of stoichiometry without the generation of other phases;

   (b) oxidation of titanomagnetites with the generation of new phases of hemoilmenite, pseudobrookite, rutile and anatase.

2. The electrical conductivity of titanomagnetites dependends on the degree of oxidation z. For $z<0.4$ and $x<0.7$ the mechanism of valence transfer ($Fe^{2+} + Fe^{3+} \rightleftarrows Fe^{3+} + Fe^{2+}$) with low values of the activation energy predominates. For $z>0.4$–0.5 and $x>0.7$ the mechanism of controlled valency [Eq. (6)]. The activation energy is higher.

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