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α-Fe_2O_3 Ceramics as Negative Temperature Coefficient Thermistors

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Abstract

The electrical behaviour of negative temperature coefficient (NTC) thermistors can be expressed by the relationship $\rho = \rho_{25} \exp[\beta(1/T - 1/298)]$. *Good thermistors are thus obtained through the adequate control of the parameters* β *and* ρ_{25}, *which has been achieved in* α-Fe_2O_3 *ceramics by a convenient processing. Reducing in nitrogen and then reoxidizing in air has lead to thermistors with good values for* β *and reasonable ones for* ρ_{25}. *The samples consisted then of two phases of polycrystalline ceramics, one of hematite the other of magnetite.*

Der elektrische Widerstand von Thermistoren mit negativem Temperaturkoeffizienten kann durch folgende Gleichung beschrieben werden: $\rho = \rho_{25} \exp[\beta(1/T - 1/298)]$. *Thermistoren mit guten Eigenschaften können demnach erhalten werden, wenn die Parameter* β *und* ρ_{25} *in adäquater Weise kontrolliert werden. Bei* α-Fe_2O_3*-Keramiken konnte dies durch eine prozeßtechnische Anpassung erreicht werden. Reduzieren in Stickstoff und ein erneutes, sich anschließendes Oxidieren an Luft führte zu Thermistoren mit guten Werten für* β *und ausreichenden Werten für* ρ_{25}. *Die polykristallinen Proben bestehen dann aus zwei keramischen Phasen: Hämatit und Magnetit.*

Le comportement électrique des thermistances à coefficient de température négatif (CTN) peut être décrit par l'expression: $\rho = \rho_{25} \exp[\beta(1/T - 1/298)]$. *De bonnes thermistances sont donc obtenues par le contrôle adéquat des paramètres* β *et* ρ_{25}, *ce qui a été réalisé dans des céramiques à base de* α-Fe_2O_3 *par un processus d'élaboration bien adapté. Une réduction dans l'azote suivie d'une réoxydation dans l'air a conduit à des thermistances présentant de bonnes valeurs de* β *et des* ρ_{25} *acceptables. Les échantillons étaient constitués de céramiques polycristallines biphasées: hématite et magnétite.*

1 Introduction

Negative temperature coefficient (NTC) thermistors are electrical resistors which exhibit a negative thermal coefficient for the electrical resistance.[1] Their behaviour can be well characterized through the relationship

$$\rho = \rho_{25} \exp[\beta(1/T - 1/298)]$$

where ρ is the resistivity at the absolute temperature T and ρ_{25} is the resistivity at 25°C. The parameter β is related to the sensitivity of the thermistor in relation to the temperature, where $(\mathrm{d}\rho/\rho)/\mathrm{d}T = -(\beta/T^2)$. The greater β is, the better the response to temperature variations. In this sense, β is called a temperature coefficient. Other characteristics of interest for a thermistor are the resistivity at 25°C, ρ_{25}, the heat dissipation factor and the thermal time constant.[1]

2 Experimental

The samples of α-Fe_2O_3 were fabricated using the conventional methods. The starting material was α-Fe_2O_3, powder, purity 99·9%, Fluka, without any additive, which was subjected to a treatment suggested by Johnson *et al.*[2] The samples were subjected to a thermal cycle consisting of three periods. Initially, they were heated up and sintered in air, then reduced in nitrogen atmosphere and lastly reoxidized in air. The green samples were introduced slowly, over 15 min, into the oven which was previously heated up to 800°C. They were calcined at this temperature for 1 h, and then the temperature was increased up to 1300°C at a rate of 7·5°C/min. The reduction was performed at a constant temperature of 1300°C for 3 min, in a dynamic atmosphere of nitrogen with a flow rate of 420 cm^3/min. The reoxidation took place in air at temperatures of 800,

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1000, 1100 and 1300°C, for periods which varied from 1 to 900 min.

All the samples were taken out of the oven within a short time (around 15 min), in order to prevent reoxidation or phase transition during cooling.

The average value of the density of the samples is equal to 93% of the theoretical value, and that of the grain size equal to 7 μm, which are rather better than those obtained by de Wit.[3]

To improve the homogeneity of the samples, the surface layers were removed by polishing. Good electrical contacts were obtained by depositing silver over the plane faces of the discs. The electrical conductivity measurements were carried out by a two-probe method. The voltage used was as low as possible to prevent Joule heating followed by eventual runaway.

3 Results

Some of the results obtained with the α-Fe_2O_3 samples are presented in Figs 1, 2, 3 and 4. Figure 1 shows the relation between resistivity and temperature for the samples which have been reduced at the same temperature (1300°C) for different times: 0, 1, 2 and 3 min. In Fig. 2, the same relation, $\rho = \rho(T)$, resistivity versus temperature, can be seen for two samples which were reoxidized at 1100°C for 30 and 100 min, respectively. The values of the temperature coefficient, β, are shown near the curves in the corresponding temperature range.

Figure 3 illustrates the relation $\rho = \rho(T)$, for three samples which were reoxidized at the same temperature (1300°C) for different reoxidation times: 3, 5 and 10 min. Similar behaviour was observed for temperatures of reoxidation equal to 800 and 1000°C. As was to be expected, longer reoxidation times for

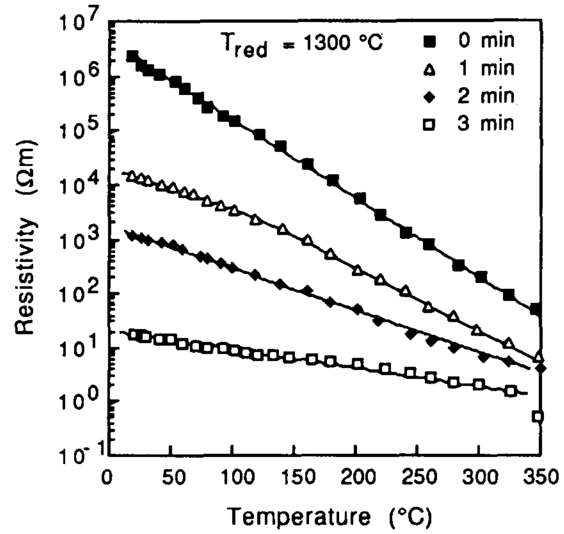


Fig. 1. Resistivity versus temperature for different times of reduction at a temperature of 1300°C.

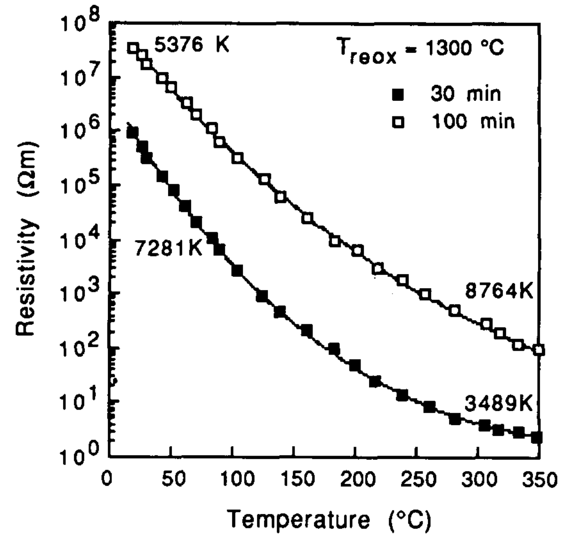


Fig. 2. Resistivity versus temperature for 30 and 100 min of reoxidation at a temperature of 1100°C.

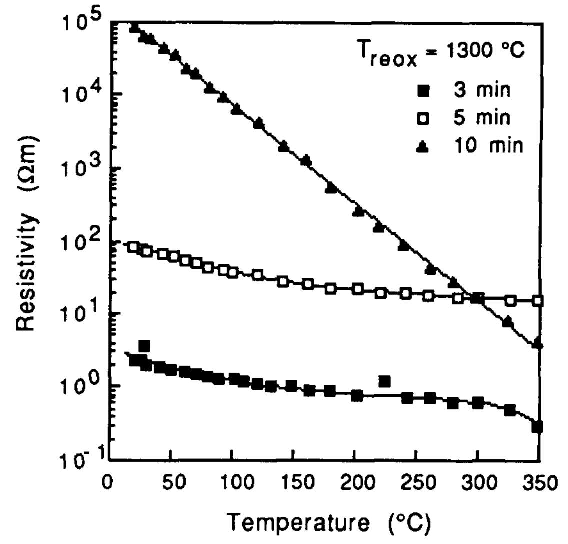


Fig. 3. Resistivity versus temperature for different times of reoxidation at a temperature of 1300°C.

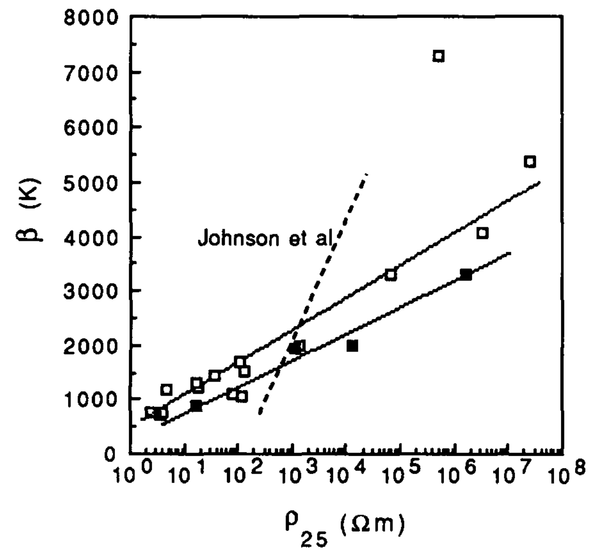


Fig. 4. Plot of the temperature coefficient β versus resistivity at 25°C for (■) samples reduced for different times at a temperature of 1300°C and for (□) samples reoxidized at 800, 1000, 1100 and 1300°C for different times. (- - - -) Obtained by Johnson *et al.*[2]

lower temperatures were needed to obtain the same results.

In Fig. 4 the temperature coefficient β versus the resistivity at 25°C, ρ_{25}, is shown for all the samples previously referred to. For the samples which were obtained by reduction of those shown in Fig. 1, the relation β/ρ_{25}, between the temperature coefficient, β, and the resistivity at 25°C, ρ_{25}, is approximately equal to 4×10^{-5} K/Ωm. A slightly higher value for the same relation β/ρ_{25} is observed in the case of the reoxidized samples. The dashed straight line, corresponding to the thermistor fabricated by Johnson *et al.*,[2] exhibits a steeper slope for β/ρ_{25} of $1{\cdot}5 \times 10^{-2}$ K/Ωm.

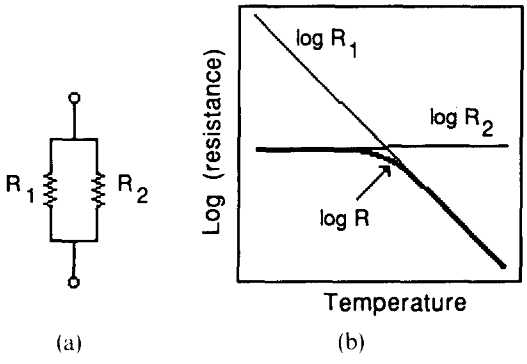
4 Discussion

Let us consider a sample composed of two solid phases. If R is the total resistance of the sample and R_1 and R_2 are the resistances of phases 1 and 2 distributed according to the equivalent electric circuit of Fig. 5(a), then

$$R = \frac{R_1 R_2}{R_1 + R_2}$$

Supposing the temperature coefficient of R_1, β_1, is much greater than that of R_2, β_2, then at low temperature $R_1 \gg R_2$ and $R \approx R_2$. At high temperatures, $R_2 \gg R_1$ and $R \approx R_1$. The variation of these resistances with the temperature T is shown in Fig. 5(b).

This type of behaviour has been obtained with α-Fe_2O_3 samples which were submitted to a reduction treatment in a nitrogen atmosphere.[3] In the corresponding model of the structure, shown in Fig. 6, the hexagons represent the grains, and was based on microscopic observations, such as the one exhibited in Fig. 7, and on the FeO–Fe_2O_3 phase diagram.[4] Fe_3O_4 was observed in a thin layer around the cylindrical area of the discs. The *n*-type semiconducting Fe_3O_4 grains at the surface are electrically in parallel with the α-Fe_2O_3 insulating grains within the bulk. It follows that the α-Fe_2O_3 (hematite) and the Fe_3O_4 (magnetite) grains are well represented by the resistances R_1 and R_2 of Fig. 5.[5,6]



(a) (b)

Fig. 5. (a) The equivalent electrical circuit for the parallel R_1/R_2. (b) Total resistance variation for the parallel R_1/R_2 in function of temperature.

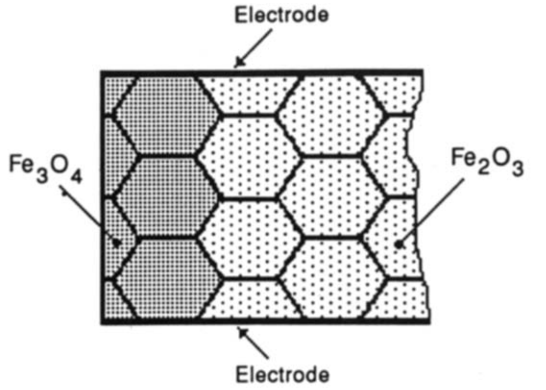


Fig. 6. Schematic structure of α-Fe_2O_3 samples which were reduced.

The four curves of Fig. 1, corresponding to the reducing times of 0, 1, 2 and 3 min, can be explained on the basis of the partial resistances of the two phases with the same slope as those of Fig. 5(b) but translated in relation to each other. In Fig. 8, three cases are considered for the reducing times: (a) low, (b) intermediate and (c) high values. R_m and R_h are the magnetite and hematite resistances, respectively. For the intermediate case, at low temperatures, $R_m \ll R_h$, and then the approximation $R \approx R_m$ can be made. At high temperatures $R_h \ll R_m$, from which it follows that the approximation $R \approx R_h$ is legitimate. Thus, the behaviour exhibited in Fig. 1 can in that way be explained.

For the samples which, after the reduction in nitrogen, have been reoxidized (see Figs 2 and 3) the model of Fig. 9(a) has been proposed. This model was suggested not only by the one already adopted for the reduced samples (Fig. 6) but also by the FeO–Fe_2O_3 phase diagram[4] and by microscopic observations such as the one presented in Fig. 10. The reoxidation transforms again into Fe_2O_3 the outer part of the Fe_3O_4 layer previously obtained by reduction. Thus the bulk remains apparently

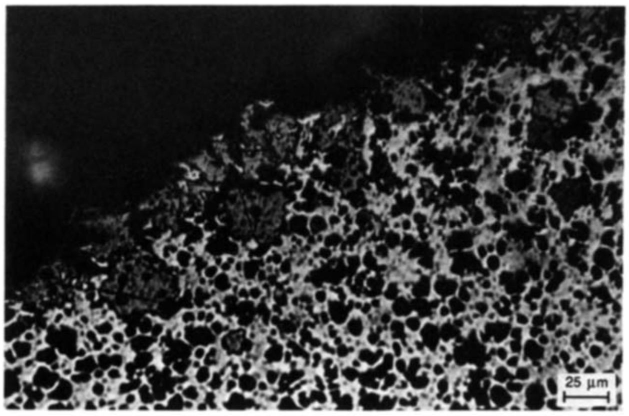


Fig. 7. Photomicrograph of the surface of a sample reduced for 3 min at 1300°C. H indicates α-Fe_2O_3 phase and M indicates Fe_3O_4 phase.

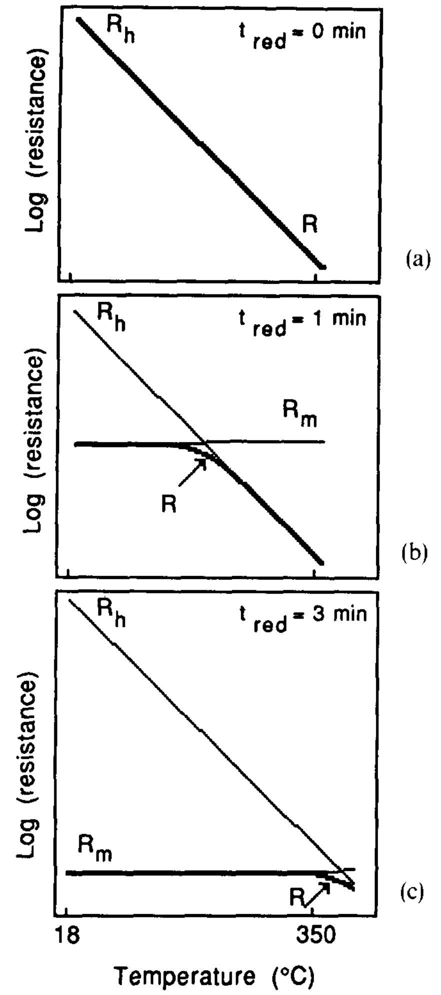
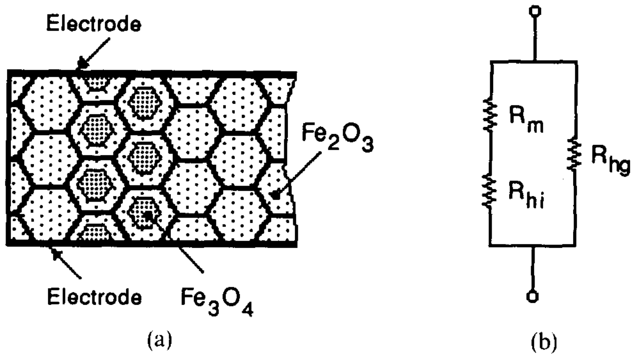


Fig. 8. Plot showing the approximate result of the combination of two phase resistances at 1300°C for reducing times: (a) 0 min (low), (b) 1 min (intermediate) and (c) 3 min (high).

unchanged and the remaining *n*-type semiconducting Fe_3O_4 grains are covered by an insulating layer of α-Fe_2O_3. Figure 9(b) represents its equivalent electrical circuit, where R_m is the resistance of the magnetite, R_{hg} is the total resistance of the grains of the phase α-Fe_2O_3 and R_{hi} is the α-Fe_2O_3 intergranular layer resistance. The total resistance will be given by

$$R=\frac{1}{\dfrac{1}{R_{hg}}+\dfrac{1}{R_m+R_{hi}}}$$



(a) (b)

Fig. 9. (a) Schematic structure of the samples of Figs 2 and 3 which were reoxidized. (b) The equivalent electric circuit.

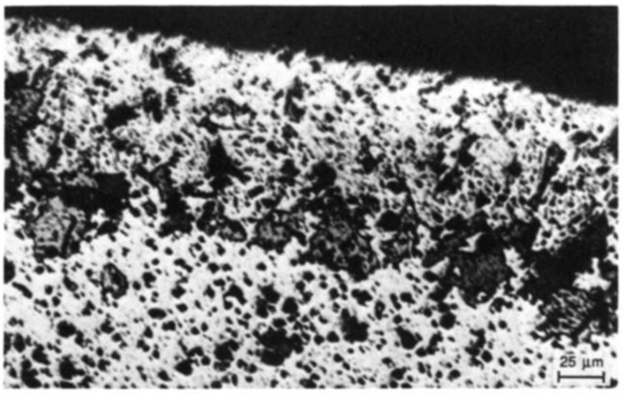


Fig. 10. Photomicrograph of the surface of a sample reoxidized for 30 min at 1300°C after being reduced for 3 min at the same temperature. H indicates α-Fe_2O_3 phase and M indicates Fe_3O_4 phase.

Firstly, let us consider low reoxidation times (Fig. 11(a)). At low temperatures, with $R_m<R_{hi}<R_{hg}$, then $R\approx R_{hi}$. At intermediate temperatures, $R_{hi}<R_m<R_{hg}$, which implies $R\approx R_m$. At high temperatures, with $R_{hi}<R_{hg}<R_m$, it follows that $R\approx R_{hg}$.

The increase of the reoxidation time (Fig. 11(b)) makes the curves $\log R=\log R(T)$ go up and to the

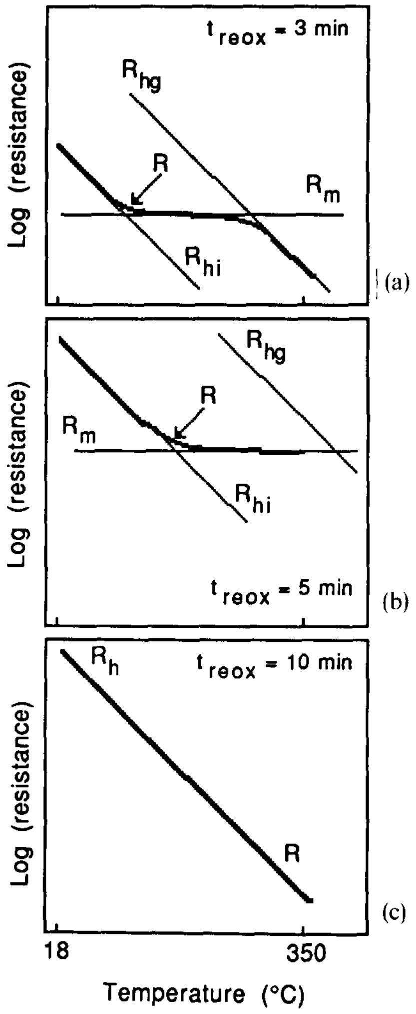


Fig. 11. Plot showing the approximate results of the combination of the two phase resistances at 1300°C for reoxidation times: (a) 3 min (low), (b) 5 min (intermediate) and (c) 10 min (high).

right. The third regime, typical of the high temperatures, does not appear in the present temperature range. The equivalent electrical circuit is appropriate if all the resistances increase. The decrease of the Fe_2O_4 phase causes the increase of R_m and R_{hi}. The increase of R_{hg} can be due to the disappearance of non-stoichiometric α-Fe_2O_3 formed during the reduction process, which had a higher conductivity than the stoichiometric one. For longer reoxidation times (Fig. 11(c)) again only one phase is obtained, the α-Fe_2O_3 one, and the curve again becomes a straight line. So, the curves of Figs 2 and 3 can be explained through this model.

A negative temperature coefficient (NTC) thermistor must have a high temperature coefficient β at low temperatures, with low values at high temperatures. This is the case for some of the samples of α-Fe_2O_3, first reduced in nitrogen, then reoxidized. Figure 2 shows two of them, with the following pairs of parameters (β, R_{25}): (5400 K, 1500 MΩ) and (7300 K, 33 MΩ). The least resistive of the samples shows those characteristics. These ceramics exhibit good values for β,[1] although those observed for ρ could be better.[2] The slope of the relation β/ρ_{25} is almost constant in all of them, not allowing a great possibility of choice for R_{25}.

5 Conclusion

α-Fe_2O_3 ceramics, without any additives, submitted to thermal treatments in different atmospheres can be used as NTC thermistors with good values for β. They can be used in applications which require high values of resistance with a high value for β.

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