Journal of Thermal Analysis, Vol. 36 (1990) 2593-2599

STUDIES ON THE THERMAL STABILITY OF IRON CHROMITE IN AIR

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(Received March 12, 1990; in revised form May 14, 1990)

Studies on the thermal stability of $FeCr_2O_4$ in air show that surface oxidation preceeds bulk oxidation. Electrical resistivity and thermoelectric power measurements show that above 47 K, Fe^{2+} ions are oxidised by the oxygen adsorbed on the surface and above 523K diffusion of the ions into the bulk occur. DTA and TG show that the bulk oxidation starts above 673 K and the change from the defect spinel phase to the rhombohedral phase occurs during oxidation and is not a sharp transition.

The thermal stability of finely grained ferrous spinels in air and oxygen has been extensively studied by Gillot *et al.* [1-5]. From their studies on aluminium and chromium substituted magnetite, they reported that these compounds are completely oxidised on heating in air or oxygen and suggested that during oxidation, the adsorbed oxygen on the grain surface becomes ionized by acquiring electrons from Fe^{2+} ions and diffuse through the crystal. This leads to a concentration gradient which cause diffusion of Fe^{3+} ions and vacancies into the interior of the grain, and Fe^{2+} and M^{3+} ions from the interior. The simultaneous presence of Fe^{2+} and Fe^{3+} ions in the sample, during oxidation, was shown by electrical conductivity measurements [6]. The present work attempts to investigate the oxidation process by thermal analysis, electrical resistivity and thermoelectric power measurements on $FeCr_2O_4$ heated in air.

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Experimental

$FeCr_2O_4$ was prepared following the method of Lotgering [7]. Stoichiometric amounts of AR grade ferric nitrate and chromium nitrate were decomposed, the resulting oxides were mixed and pressed into disc pellets. The pellets were sintered at 1524 K for 36 hrs and slowly cooled at a rate of 2 deg/minute to obtain $Fe_{1/2}Cr_{3/2}O_3$ (corundum structure) by the following reaction step

$$Fe_2O_3 + 2\,Cr_2O_3 \rightarrow Fe_{1/2}Cr_{3/2}O_3$$

To this intermediate, powdered Fe was added in the ratio 1:4 and mixed by grinding for 6-7 hrs. The pellets of this mixture were heated in vacuum in a sealed quartz tube, at 1323 K for 48 hrs and slowly cooled to room temperature. $FeCr_2O_4$ was obtained by the following reaction

$$Fe + 4\,Fe_{1/2}Cr_{3/2}O_3 \rightarrow 3\,FeCr_2O_4$$

X-ray diffraction analysis of the samples were carried out using a Philips X-ray diffraction unit model PW1F10/00 using copper target and nickel filter.

Thermal analysis was carried out in air with a Stanton Redcroft instrument between 300 to 1273 K at a heating rate of 10 deg/min.

Electrical resistivity of the sample was determined upto 500 K using a two probe technique. The resistivity variation with time was carried out at various temperatures. The experimental set up is described elsewhere [8].

Thermoelectric power measurements were carried out upto 650 K. The experimental set up is described elsewhere [9].

Results and discussion

In Fig. 1 the DTA curve shows a sharp exothermic peak at 526 K which is not accompanied by any weight change as shown in the TG curve. On further heating, two small peaks at 723 and 743 K respectively, appear on a broad exothermic hump which extends upto about 1073 K and is accompanied by weight gain. From kinetic studies [1] and DTG measurements [6], Gillot *et al.* have shown that $FeCr_2O_4$ oxidizes between 603 and 723 K respectively and hence the peak at 723 K (Fig. 1) could be due to oxidation of $FeCr_2O_4$. Another peak around 923 K, showing the transformation of the defect spinel phase to the rhombohedral phase, has been reported [1]. This is however, at a higher temperature than the DTA peak at 743 K (Fig. 1) and hence cannot be attributed to phase change of the oxidized spinel from the γ-form to the α-form. Moreover, the weight gain continues much above this temperature (Fig. 1, TG curve) and hence oxidation of $FeCr_2O_4$ is not complete at 743 K. Two consecutive peaks in the temperature region where oxidation occurs have been found in chromium substituted magnetite samples due to the oxidation of Fe^{2+} (tetrahedral) and Fe^{2+} (octahedral) at different temperatures. In $FeCr_2O_4$ however, all the Fe^{2+} ions are present on the tetrahedral sites and hence, oxidation is expected to occur in a single step. Thus the two peaks at 723 K and 743 K do not represent oxidation of Fe^{2+} ions on two different sites of the spinel lattice. As mentioned earlier, the peak at 723 K is due to oxidation and the peak at 743 K probably represents the onset of the defect spinel phase formation during oxidation.

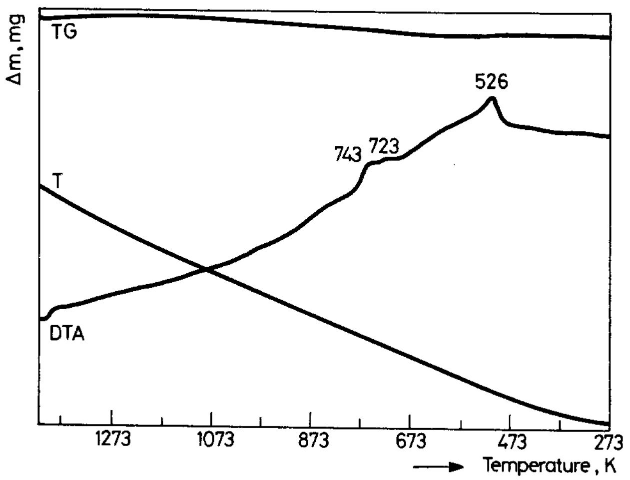

Fig. 1 DTA and TG of $FeCr_2O_4$

The present results do not show the change of γ-$Fe_2Cr_4O_9$ to α-$Fe_2Cr_4O_9$ to be a rapid process as the DTA curve has no sharp peak upto 1273 K. The TG curve shows that the oxidation of $FeCr_2O_4$ is completed by 1073 K and the X-ray diffractogram of the sample heated to this temperature shows the presence of only the rhombohedral phase, implying that the phase change occurs along with the oxidation process. From these results it appears that the γ-$Fe_2Cr_4O_9$ → α-$Fe_2Cr_4O_9$ is not a sharp transition and occurs during oxidation, covering a wide temperature range. This is manifest as a broad hump in the DTA peak which is accompanied with weight gain as shown in the TG curve.

The sharp DTA peak at 526 K is, neither accompanied by any weight change (Fig. 1, TG curve), nor is it due to any crystallographic change as the X-ray diffractogram of the sample heated to 693 K shows the lines of the original spinel phase only (Fig. 2).

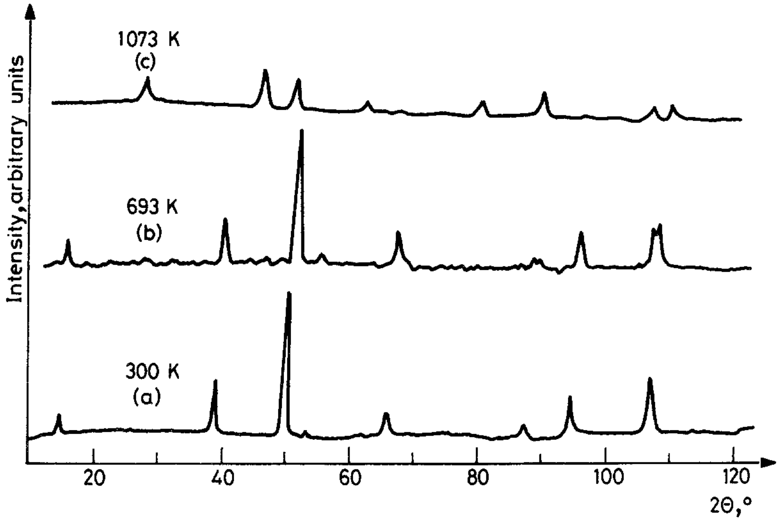

Fig. 2 X-ray diffractogram of $FeCr_2O_4$ at 300 K (a), 693 K (b), 1073 K (c)

It was proposed by Gillot *et al.* that during oxidation of $FeCr_2O_4$ in air or oxygen, oxygen atoms adsorbed on the grain surface become ionized by acquiring electrons from Fe^{2+} ions, and diffuse through the crystal. The resulting concentration gradients thus cause the diffusion of Fe^{2+} ions and vacancies into the interior of the grain, and diffusion of Fe^{2+} and M^{3+} ions from the interior. If such a process preceeds bulk oxidation then the DTA peak at 526 K (Fig. 1) could be due to ionization of adsorbed surface oxygen. To determine, if diffusion of ions occur prior to bulk oxidation, as suggested by Gillot *et al.*, electrical resistivity measurements and thermoelectric power measurements were carried out on $FeCr_2O_4$ heated in air. The $\log \rho \rightarrow 1/T$ plot (Fig. 3) shows that the heating and cooling curves upto 500 K are not reversible implying that the sample undergoes an irreversible

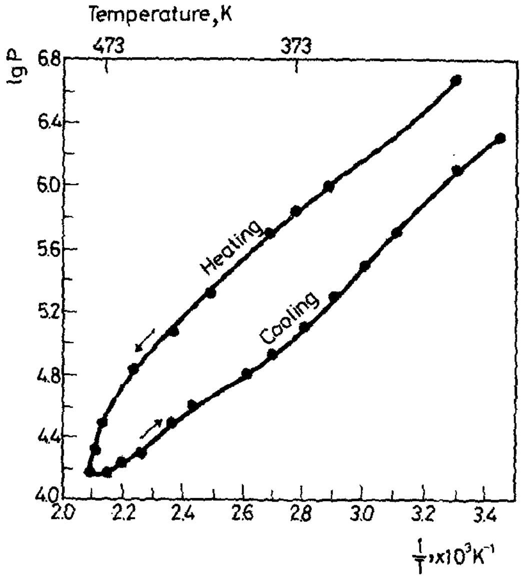

Fig. 3 Variation of resistivity with temperature

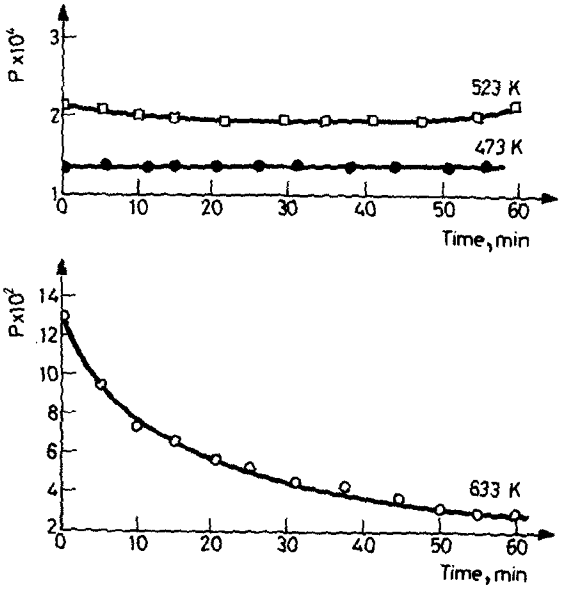

Fig. 4 Variation of resistivity with time

change on heating in air which is not recorded in either the DTA or TG curves. The $\rho \rightarrow$ time plots in Fig. 4 show that above 523 K conduction is by diffusion of ions but below this temperature there is no ionic diffusion. The $\alpha \rightarrow 1/T$ plot in Fig. 5 shows that upto about 473 K the sample is p-type and the magnitude of 'α' does not change on heating the sample in air. However, on further heating, the sample becomes *n*-type and a rapid change in the α-value is observed above 523 K. A change in the sign of the charge carriers i.e. *p*-type to *n*-type, is probably brought about by oxidation of Fe^{2+} ions to Fe^{3+} ions and the subsequent rapid change in α-values could be due to the diffusion of the Fe^{3+} ions into the bulk.

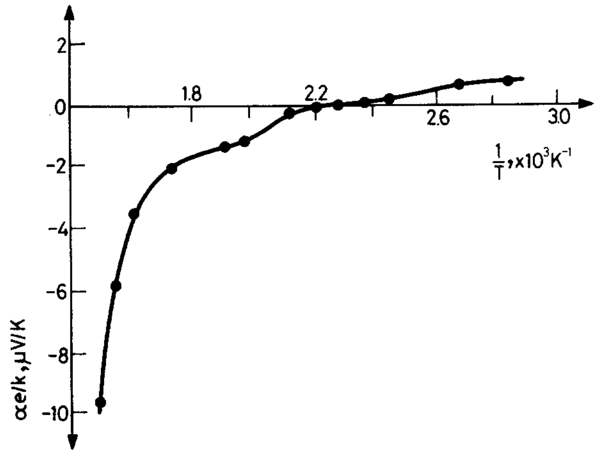

Fig. 5 Variation of thermoelectric power with temperature

From these results it may be concluded that on heating $FeCr_2O_4$ in air the adsorbed oxygen on the surface are ionized by accepting electrons from Fe^{2+} ions whereby *p*-type $FeCr_2O_4$ is changed into *n*-type. On further heating above 473 K, diffusion of these ions into the bulk occurs and the magnitude of the thermoelectric power increases very rapidly. Above 673 K $FeCr_2O_4$ undergoes bulk oxidation followed by a change into the α-rhombohedral phase.

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The authors wish to thank DST for some financial help.

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Zusammenfassung — Untersuchungen der thermischen Stabilität von $FeCr_2O_4$ in Luft zeigen, daß der Masseoxidation eine Oxidation an der Oberfläche vorangeht. Messungen des elektrischen Widerstandes und der thermo-elektromotorischen Kraft zeigen, daß die Fe^{2+}-Ionen oberhalb 47 K durch den an der Oberfläche adsorbierten Sauerstoff oxidiert werden und daß oberhalb 523 K eine Diffusion der Ionen in das Innere abläuft. DTA- und TG- Untersuchungen zufolge setzt die Masseoxidation oberhalb 673 K ein und während der Oxidation verläuft ein unscharfer Übergang von der defekten Spinellphase in die rhomboedrische Phase.