

INVESTIGATION OF THE OXIDATION BEHAVIOUR OF FeTi ALLOY

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**ABSTRACT**

The FeTi intermetallic compound, when oxidised at various temperatures, exhibits some interesting properties. XRD analysis of the treated samples indicates the formation of FeTiO<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> phases at 973 K. ESR and DRS studies on the alloy sample treated at various temperatures in oxygen revealed that in the case of Ti, oxidation proceeds in a step-wise process forming the oxygen deficient phase and then the TiO<sub>2</sub> phase, which ultimately leads to the ternary FeTiO<sub>3</sub> phase. Iron first forms the ferric oxide phase which is then converted to the FeTiO<sub>3</sub> or the magnetic Fe<sub>3</sub>O<sub>4</sub> phase. Thus there is evidence for preferential oxidation of the two constituent elements leading to new catalytic systems.

**INTRODUCTION**

Hydrogen storage intermetallics like FeTi [1], LaNi<sub>5</sub> [2], CaNi<sub>5</sub> [3] have been shown to be susceptible to poisoning by oxygen, carbon monoxide or water vapour present in the stored hydrogen. It is known that the mechanism of poisoning by CO or CO<sub>2</sub> is different from that of oxygen, since CO or CO<sub>2</sub> interact with hydrogen to form hydrocarbons [2,4]. Increasing interest is being shown in the use of these intermetallics as catalysts for hydrogenation/dehydrogenation reactions [5,6]. It is known that the bulk and surface reactivity of the compounds play an important role in these properties. Other studies have shown

that oxidized intermetallic compounds are more active for hydrogenation reactions than the untreated compounds [7]. One of the important pretreatment procedures adopted for the use of such compounds as catalysts has been treatment with oxygen at elevated temperatures [8]. In view of the importance of activation procedures employed for hydrogen storage purposes a study on the oxidation behaviour of intermetallics has been attempted.

Studies on the oxidation of  $AB_5$  type intermetallics [9,10] and other nickel-based alloys [11] have led to some interesting observations like generation of supported metal catalyst systems and formation of ternary oxide phases. Extensive interest has been shown about the Fe/TiO<sub>2</sub> catalyst for the CO hydrogenation reaction [12,13]. In the present investigation, attempts have been made to evaluate the oxidation behaviour of an important hydrogen storage intermetallic namely FeTi.

#### **EXPERIMENTAL**

The FeTi intermetallic compound was obtained from Ergenics a division of the MPD Technology Corporation, USA as their commercial sample HYSTOR-101. The alloy particles were powdered in air before use. Oxidation at different temperatures was carried out in a tubular furnace and in a continuous flow of purified oxygen gas. X-ray diffractograms of the samples were recorded on a Philips Diffractometer (Model PW-1130) using CoK radiation at a scanning speed of 1 / min and a chart speed of 20 mm/min at room temperature.

The ESR studies for the powdered samples were carried out using quartz sample tubes on a Varian Spectrometer (Model-E112) at room temperature. The Diffuse Reflectance Spectra were obtained on a Perkin Elmer (Model-PE983) UV-VIS spectrophotometer with a special cell for the reflectance studies. For the DRS studies small amounts of magnesium powder was thoroughly mixed with a large amount of magnesium carbonate (diluent) and a pellet was made from the mixture on which the spectra were recorded.

#### **RESULTS AND DISCUSSION**

FeTi alloy was oxidised in presence of oxygen at various temperatures and the phase compositions obtained after oxidation at various temperatures were examined by X-ray diffraction. Typical diffractograms obtained after oxidation at temperatures

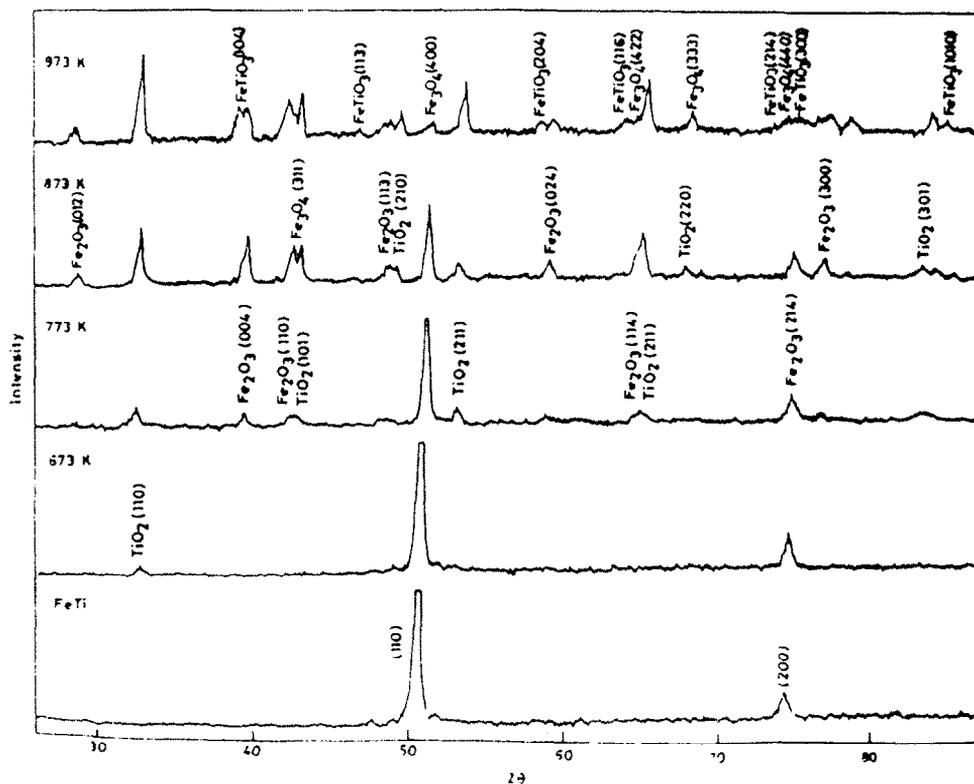


Fig.1. XRD of FeTi treated with oxygen at various temperatures.

of 673, 773, 873 and 973 K are given in Fig.1. It is seen that  $\text{TiO}_2$  formation takes place with oxygen treatment at 673 K itself while oxides of iron especially the fully oxidised phase ( $\text{Fe}_2\text{O}_3$ ) predominated only with oxygen treatment at 773 K and 873 K. However, oxygen treatment at still higher temperatures, *i.e.* above 873 K showed that the ternary phases are formed in addition to the formation of the magnetite phase ( $\text{Fe}_3\text{O}_4$ ). The reason for the formation of ferrous ferrite at higher temperatures could be associated with the energy involved in the crystallisation of the spinel phase. The importance of this parameter is evident, in that only in this temperature range is the perovskite phase of  $\text{FeTiO}_3$  also crystallised. It is interesting to note that the fully oxidised haematite phase is formed by oxidation at low temperatures while high temperature oxygen treatment is required for the formation of the magnetite phase. The essential X-ray data together with the corresponding phases for the systems after treatment with oxygen at various temperatures are summarised in Table.I.

It was also interesting to note that the alloy sample oxidised at temperatures showed a variation in its colour. Although the fresh compound was dark grey in colour with a metallic lusture, at 573 K the oxidised sample turned

Table I. Phases formed at various temperatures during the oxidation of FeTi.

Oxidation Temperature (K)	Physical appearance (colour & appearance)	Phases identified from XRD*
573	Brown, Metallic	FeTi
673	Bluish grey, Metallic	FeTi, TiO <sub>2</sub> (Rutile)
773	Dark Violet	FeTi, - Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>
873	Dark violet	Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , FeTi, (Fe <sub>3</sub> O <sub>4</sub> )
973	Violet	TiO <sub>2</sub> , FeTiO <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>

\* written in the order of abundance.

brown and the powder treated at 673 K was bluish grey in colour. Both these samples retained some of the metallic lusture of the alloy. The sample oxidised at higher temperatures became darker in colour losing the metallic lusture due to complete oxidation of FeTi.

From the above observations it is evident that, though there was no bulk transformation of the sample on oxidation upto 573 K (as seen from XRD), changes are occurring on the surface of the alloy particle (as evident from the colour of the treated sample), probably the formation of different oxides of the constituent elements. The observation of the ternary FeTiO<sub>3</sub> phase and the spinel Fe<sub>3</sub>O<sub>4</sub> phase in the sample treated at 973 K are similar to the results observed on the LaNi<sub>5</sub> system [9], though in the present case these phases begin to crystallise only at relatively higher temperatures. In order to unambiguously ascertain the nature of the species formed (mostly on the surface) on oxidation of the alloy sample at various temperatures and to have an insight into the order of formation of the various oxide phases, the samples were subjected to ESR and Diffuse Reflectance Spectroscopic analysis. In order to examine this oxidation behaviour more clearly, we have recorded the ESR spectra of the samples after oxygen treatments at various temperatures and the spectra obtained are given in Fig.2. The 'g' values of the ESR signals obtained and the identification of the phases responsible for the signals are summarised in Table II. It is seen the alloy shows two signals with g values equal to 9.18 and 2.17 corresponding to probably non-stoichiometric oxides of titanium and that of Fe<sub>2</sub>O<sub>3</sub> respectively. However, with oxygen treatment at higher temperatures up to 673 K, one could observe the signal with g = 2.2 due to the haematite type of phase. However, a new signal appears around g = 5.0 and this signal alone is observed after oxygen treatment above 623 K. It is known that the experimental g value for stoichiometric Fe<sub>3</sub>O<sub>4</sub> is around 4.0 and it increases with increase in temperature

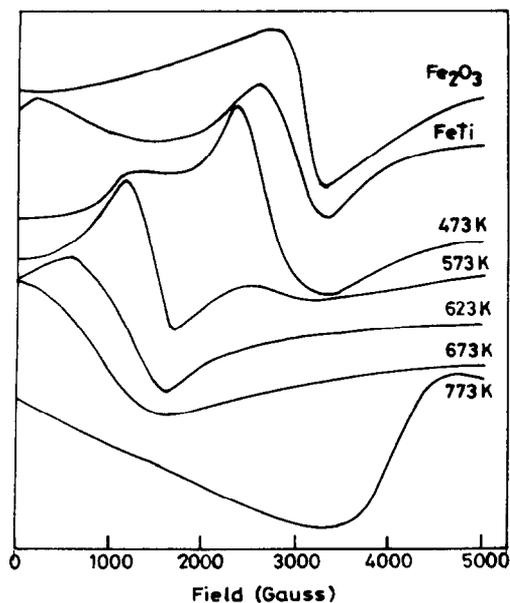


Fig. 2. ESR spectra of FeTi treated with oxygen at various temperatures.

Table II. Results of ESR Studies.

Sample	Oxidation Temperature(K)	g Value	Phases Responsible
Fe <sub>2</sub> O <sub>3</sub>	Fresh	2.17	Fe <sub>2</sub> O <sub>3</sub>
FeTi	Fresh	9.18	non-stoichiometric oxides of Ti
		2.17	Fe <sub>2</sub> O <sub>3</sub>
	473	5.1	Fe <sub>3</sub> O <sub>4</sub>
		2.2 (broad)	Fe <sub>2</sub> O <sub>3</sub>
	573	4.6	Fe <sub>3</sub> O <sub>4</sub>
		2.2	Fe <sub>2</sub> O <sub>3</sub>
	623	5.7	Fe <sub>3</sub> O <sub>4</sub>
	673	5 (broad)	Fe <sub>3</sub> O <sub>4</sub>
	5 (broad)	Fe <sub>3</sub> O <sub>4</sub>	
	1.6	Ternary Tioxides	

as well as lattice parameter [14]. The increase in lattice parameter could be achieved by treatment with oxygen at higher temperatures. It is therefore deduced that the ferric oxide initially formed at low temperatures interacts and oxidises the non-stoichiometric titanium oxides to form the ternary

perovskite phase namely,  $\text{FeTiO}_3$ , which is covered with an overlayer of  $\text{Fe}_3\text{O}_4$  arising out of oxygen diffusion inside the bulk of the material to form the core ternary oxide phase.

If this model were to be correct for the oxidation behaviour of FeTi alloy then one should have observed the formation of oxygen deficient titanium oxide phases like  $\text{TiO}$  or  $\text{Ti}_2\text{O}_3$  by XRD. Since we have failed to observe such phases by XRD, probably due to the low percentage of these phases (<5%) in the system we have attempted to identify their presence by diffuse reflectance spectroscopy. It is known [15] that  $\text{TiO}$  phase gives an absorption peak around 3.57 eV (transition from  $t_{2g}$  to  $e_g^*$  levels) while  $\text{Ti}_2\text{O}_3$  phase gives peaks at 2.25 and 3.4 eV since the oxide ions form a field of distorted trigonal symmetry. The reflectance spectra of rutile and anatase  $\text{TiO}_2$  show sharp absorptions beginning at 3.0 and 3.23 eV respectively. The DR spectra obtained for the samples heated at different temperatures are given in Fig.3 together with those of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . It is seen that the sample heated in oxygen at 523 K showed an extended absorption from 2.15 eV. This could have arisen

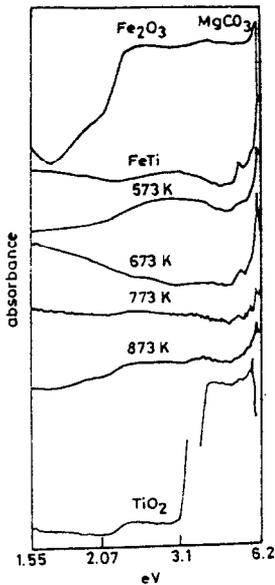


Fig. 3. DRS of FeTi treated with oxygen at various temperatures.

from  $\text{Fe}_2\text{O}_3$  or  $\text{Ti}_2\text{O}_3$  or both. The intensity of this absorption decreases for samples prepared at 673 K and 773 K, while absorption is discernable even at lower energy values (<1.65 eV) for the sample prepared at 873 K. This shows that the amount of either  $\text{Fe}_2\text{O}_3$  or  $\text{Ti}_2\text{O}_3$  or both decreased with increase of temperature of oxidation, while the formation of  $\text{Fe}_3\text{O}_4$  is discernable by oxidation at higher temperatures (>873 K) because of the shifting of the absorption peak to lower energy values.

## CONCLUSION

It is interesting to note that the oxidation of an intermetallic like FeTi gives rise to a sequence of oxidation of the two constituent elements. In the case of Ti, the oxidation proceeds by a stepwise process forming the oxygen deficient phases first and then the  $TiO_2$  phase, which ultimately reacts with  $Fe_2O_3$  to yield the ternary oxide phase. In the case of iron, the initial stages of oxidation produce the ferric oxide phase, which is subsequently transformed to the ternary phase or to the magnetic oxide phase. This type of preferential oxidation of the two constituent elements can give rise to some interesting feasibility wherein one can generate new catalytic systems with preferred oxidation states of the elements. This interesting possibility has however, to be further explored and exploited.

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