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GROWTH OF $\text{Fe}_y\text{Mn}_{1-y}\text{O}_{1+x}$ SINGLE CRYSTALS BY
CHEMICAL VAPOR TRANSPORT⁺

by

C. A. Goodwin* & H. K. Bowen

Ceramics Division

Department of Metallurgy and Materials Science

Massachusetts Institute of Technology

Cambridge, Massachusetts

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ABSTRACT

The closed tube chemical vapor transport technique was employed to grow single crystals of $\text{Fe}_y\text{Mn}_{1-y}\text{O}_{1+x}$ on MgO substrates. Single crystalline films of 1-250 μm thickness were obtained for $y = 0.25-1.00$. MnO concentration gradients were found in the grown layers resulting from time dependent compositional changes during growth so that near the substrate the composition is nearly FeO_{1+x} and at the vapor-crystal interface is richest in MnO; the concentration gradients are proposed to have resulted from differences in the partial pressure gradients of the metal chlorides. Oxidized phases were found in some cases, especially when the source material had been exhausted.

Introduction

The closed tube chemical vapor deposition technique has been utilized to prepare single crystals of the iron group transition metal monoxides^{1,2} and compositions in the series $\text{Ni}_y\text{Co}_{1-y}\text{O}$.³ This procedure has now been extended to the growth of single crystalline $\text{Fe}_y\text{Mn}_{1-y}\text{O}_{1+x}$. Here x represents the deviation from stoichiometry at 1000°C and may vary from 0.05 to 0.15 for y = 1 and from ~ 0.00 to 0.02 for y = 0.

Chemical transport was assumed to occur according to the reaction:

In a temperature gradient the forward reaction proceeds at the higher temperature which leads to gaseous transport to the cooler zone where the reverse reaction occurs. The partial pressure gradients of FeCl_2 and MnCl_2 which are functions of the chemical potential of Fe and Mn in the solid solution source material are the thermodynamic driving forces for transport.³

Experimental

Growth takes place in a sealed fused quartz ampoule which contained a MgO substrate (cleaved 1 mm x 1 cm x 1 cm, (100) faces, polished in hot (150°C) orthophosphoric acid) and the solid solution source material of specified composition in the form of either a powder pellet or a melted button prepared in a

tri-arc Czochralski furnace similar to that described by Reed and Pollard.⁵ The ampoule was evacuated (10^{-5} torr), back filled with HCl (10 torr) and then placed in a gradient furnace. Details of the encapsulation system and the crystal growth furnace are discussed elsewhere.³

Results and Discussion

It was found that when a pressed pellet of greater than 10 mole percent MnO was used as the source material, very poor growth was obtained; that is, either no growth occurred or a dull black Fe_3O_4 coating grew in a configuration of crystallographically oriented, faceted bars. However, the use of dense melted buttons containing 25-100% FeO as a source resulted in uniform single crystal monoxide films having compositions of 25-100% FeO with highly specular surfaces and thicknesses in the range of 1-250 μm . Growth of MnO was also successful, although deposition was in the form of pyramids which grew together to form an epitaxial layer with no crystallographic misorientation. For $\Delta T = 715-700^\circ\text{C}$, growth rates varied from 5.50×10^9 cm/sec for MnO-rich compositions to 1.4×10^{-7} cm/sec for FeO-rich compositions.

X-ray diffraction measurements revealed an MnO concentration gradient through the thickness of the as-grown crystal with the highest MnO concentrations near the external growth surface. It was also found that short time growth runs (1 hr) using practically any composition as the source, yielded pure FeO_{1+x} growth. As growth times lengthened, the MnO content of the surface layers of the deposited crystal increased toward the composition of the source. As a result the final average composition was time dependent. This behavior may be a result of a large difference in the partial pressure gradients for FeCl_2 and MnCl_2 . Since the pressure difference for each metal chlorine across the transport zone is determined by the chemical potential of the corresponding oxide in the solid solution source,³ the observed concentration gradient in the grown crystal suggests that the activity of each component is not ideal: that is, the activity of "FeO" in the solid solution source exhibits a strongly positive deviation from ideality which is reflected by the large chemical potential gradient of FeCl_2 relative to MnCl_2 . This observation has now been substantiated by the discovery of a region of solid-solid immiscibility in the FeO-MnO system at 900°C.⁴

X-ray diffraction measurements (Debye-Scherrer, diffractometer and Laue) indicated that as-grown monoxide solid solution crystals were single crystalline ((100) orientation) possessing

the NaCl structure; however, the MnO concentration gradient present in most samples was evidenced by rather wide and diffuse diffracted lines on the x-ray patterns. After annealing samples in controlled oxygen atmospheres ($P_{O_2} = 3 \times 10^{-19}$ atm) at 800°C for 10 hr, these diffuse lines become sharp and distinct. The phase separation which occurs in this system is on a scale of 100-500 Å which is not observable by typical x-ray measurements and is similar to that observed in the $Ni_xCo_{1-x}O$ system.³ The composition of each sample was determined by comparing the measured lattice parameter to standardized curves such as in Figure 1. These curves were derived from x-ray data of pressed pellets which had been annealed under the same conditions as the deposited crystals. As shown in Figure 1, the lattice parameter varies with composition according to Vegard's Law for 20-100% MnO: the negative deviation near FeO is a result of an increasing cation defect content.

An excess of source material (more than ~ 2 gm) in the transport system was necessary to maintain a low partial pressure of oxygen such that the monoxide phases were stable. It was found that the O/M ratios for single crystal deposits were usually greater than that of the original source material, especially when the source was expected. In most cases, all or part of the residual source pellet was magnetic (Fe_3O_4 , as determined by x-ray powder patterns) indicating that oxidation had occurred.

Figure 2 and 4 and Table 1 depict results of an electron microprobe analysis performed on two samples which gave evidence of oxidation during growth. In both cases the source material had been exhausted. In Figure 2 a cross-sectional cut of a sample (40% MnO source) is shown. Brightly reflecting precipitated regions are evident in a matrix of the monoxide single crystal. The electroprobe results suggest that these regions may be Fe_3O_4 . Figure 3 depicts a top view of a sample (80% MnO source) where non-uniform growth layers were found. Deposition was in the form of irregular deposits and faceted bars. The latter also appear to be Fe_3O_4 .

For several of the pure MnO growth runs, dull-brownish growth occurred, consisting of oriented, faceted bars grown together in an intermeshed arrangement. The bars were Mn_3O_4 as determined from Debye-Scherrer analysis. The residual source material after had a redish Mn_3O_4 coating.

Several experiments were performed to determine the source of the excess oxygen in the system. Small ampoules containing only MnO (no HCl) were evacuated and placed in the growth furnaces in exactly the same manner as were the crystal growth ampoules but there was no temperature gradient. No oxidation occurred; thus the oxidation in the growth runs was probably a result of the reactions involving the transport gas. Similar experiments with small ampoules containing HCl and MnO or FeO but with no temperature gradient resulted in a slight oxidation of the powder.

Several experiments were performed to determine both the source of excess oxygen in the system and the whereabouts of the manganese for runs similar to that described above. Results eliminated the possibility of leakage of air into the ampoule. It was found, however, that the presence of HCl gas was a necessary condition for oxidation to occur. For all growth runs, a greenish or brownish silicate deposit (e.g. Fe_2SiO_4 or Mn_2SiO_4) was found on the inside ampoule wall. The following two reactions inside the ampoule were assumed to occur for the case of wustite transport:

Reaction (2) proceeds in the reverse direction at the growth zone, where the excess oxygen produced is recombined during the growth of the nonstoichiometric crystal. However, in reaction (3) iron and oxygen are used in an equimolar ratio to form Fe_2SiO_4 , leaving $\frac{x}{2}$ moles of free oxygen in the system per mole of FeO_{1+x} initially reacted. A similar process is expected for MnO and intermediate solid solution compositions, although the deviation from stoichiometry, x , is smaller. The excess oxygen formed in this manner would increase the oxygen partial pressure inside the ampoule resulting in oxidation of the deposited crystal and the residual source material. These silicate reaction problems are more serious for MnO and $\text{Fe}_{1-y}\text{Mn}_y\text{O}_{1+x}$ growth than for pure FeO growth;¹ this is probably because of the larger growth rates for wustite. No attempts were made to employ a different ampoule material since the primary focus of this investigation

was simply to achieve the satisfactory preparation of samples.

Conclusions

The closed tube chemical vapor transport technique has proven successful in preparing single crystals in the series $\text{Fe}_{1-y}\text{Mn}_y\text{O}_{1+x}$. Films with specular surfaces having compositions in the range of 25-100% FeO were prepared. A temperature gradient of $\Delta T = 715-700^\circ\text{C}$ gave growth rates of 5.5×10^{-9} cm/sec for MnO-rich compositions and 1.4×10^{-7} cm/sec for FeO-rich compositions. MnO concentration gradients were found in the grown crystals with the layers richest in MnO located at the vapor-crystal interface. An excess of source material was necessary to maintain the monoxide phases within the growth ampoule.

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TABLE 1

Results of Electron Microprobe Analysis

<u>Sample</u>	<u>Area</u>	<u>Mole % Metal</u>	
		<u>Mn</u>	<u>Fe</u>
40 a (Figure 2)	1	5	45-50
	2	0-5	75-80
	3	5	30-40
	4	4	50-60
80 a (Figure 3)	1	0	30-35
	2	1-5	80
	3	0	0 (MgO)

Figure 1 Lattice parameter of $\text{Fe}_{1-y}\text{Mn}_y\text{O}_{1+x}$ solid solutions annealed at 800°C , $\text{CO}_2/\text{CO} = 1.0$ ($P_{\text{O}_2} = 3 \times 10^{-19}$ atm).

Figure 2 Photograph of two cross-sectional views of a CVD grown $\text{Fe}_y\text{Mn}_{1-y}\text{O}_{1+x}$ film (as cleaved). Compositions of numbered regions are listed in Table 1.

Figure 3 As grown surface of an $\text{FeMn}_{1-y}\text{O}_{1+x}$ sample. Compositions of numbered regions are listed in Table 1.