Growth of $Co_{1-x}Fe_xTiO_3$ single crystals

H. TAKEI, Y. SYONO
Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

K. KITAMURA
National Institute for Researches in Inorganic Materials, Sakura-mura, Ibaraki 305, Japan

A. ITO
Department of Physics, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

Single crystals of $Co_{1-x}Fe_xTiO_3$ ($1 \geqslant x \geqslant 0$) solid-solution were grown by the floating-zone method using a lamp-heated furnace. Boules averaged 7 mm diameter and 40 to ~ 70 mm long and were found to be homogeneous as to the value of x in 80 to $\sim 90\%$ of the total length. Atmosphere control, employing a mixed gas flow of CO_2 and H_2, was essential for obtaining high-quality cyrstals.

1. Introduction

Ilemites, whose general formula is $RTiO_3$ in which R can represent Mn, Fe, Co or Ni, exhibit interesting physical properties at low temperatures. In particular, $FeTiO_3$ and $CoTiO_3$ undergo an antiferromagnetic transition at 55 and 38 K, respectively, below which the magnetic spin axis of the former compound is along the hexagonal c-axis, whereas that of the latter is in the c-plane. In recent years, there has been considerable interest in the solid-solution consisting of $FeTiO_3$ and $CoTiO_3$ because a mixture of such antiferromagnets having orthogonal spin axes is sxpected to have a new type of magnetic ordering [1, 2].

In order to elucidate the magnetic properties of this series more exactly, large and high-quality single crystals are essential. Floating-zone (FZ) growth has been the favoured method of producing homogeneous solid-solution single crystals. $(Mg_{1-x}Fe_x)_2SiO_4$ [3], $(Mn_{1-x}Mg_x)_2SiO_4$ and $Mn_{1-x}Mg_xSiO_3$ [4] have been successfully crystallized using the FZ method over the whole range of x. Those experiments indicated that the method is suitable for obtaining crystals with a homogeneous composition along the growth direction.

This paper describes the growth of $Co_{1-x}Fe_xTiO_3$ solid-solution crystals by the FZ method under a controlled atmosphere of oxygen fugacity. The crystals are also described based on analysis by X-ray, EPMA and Mössbauer methods.

2. Crystal growth

Powders of three chemicals were used as starting reagents: $FeC_2O_4 \cdot 2H_2O$ (99.5% pure, Kantō Chemical Co), CoO (99.9% pure, High-Purity Chemical Co) and TiO_2 (99.5% pure, Merck). They were mixed in the desired proportions and heated in a resistance furnace at $1000°C$ for 4 h in a mixed gas flow of Ar, CO_2 and H_2, where the flow rates were fixed at 100, 100 to ~ 120 and 2.0 to ~ 5.0 ml min^{-1}, respectively. The pre-heated powders were pressed hydrostatically into the shape of rods about 10 mm diameter and 100 mm long. The rods were sintered at $1200°C$ for 4 h in an H_2/CO_2 mixed gas flow. The values of x in the rods were 0.0, 0.35, 0.425, 0.45, 0.475, 0.50, 0.60, 0.65, 0.75, and 1.0.

The crystal growth apparatus was an FZ furnace of Nichiden Machinery Co, in which infrared radiation from a 1.5 kW halogen lamp was used as a heat source. Details of the furnace have been reported elsewhere [5, 6]. The atmosphere in the furnace was also controlled by an H_2/CO_2 mixed gas flow using a thermal mass-flow type gas-flow controller. Typical growth conditions are listed in Table I.

3. Analyses of Crystals

The boules were analysed by the usual means of back-reflection Laue photography, reflection microscopy and the SEM-EPMA technique. The

TABLE I Growth conditions of $Co_{1-x}Fe_xTiO_3$ solid-solution crystals

Atmosphere	Ar	$100\,ml\,min^{-1}$
	CO_2	100 to $\sim 120\,ml\,min^{-1}$
	H_2	2.0 to $\sim 5.0\,ml\,min^{-1}$
Zone travelling rate		$3\,mm\,h^{-1}$
Nutrient and seed rotation rate		30 rpm (opposite)
Max. power of lamp		750 W
Growth direction		$\perp[00\cdot1]$
Crystal size		7 mm diameter, 40 to ~ 70 mm long

lattice parameters were determined by the X-ray powder diffraction method using $FeK\alpha$ radiation filtered by Mn, where Si powder was used as an internal standard. The results were computed using the U-CELL-II program [7]. Single-crystal analyses were also performed by the Buerger precession method using Zr-filtered Mo-radiation.

The composition of the boules was determined colorimetrically: Fe was analysed using orthophenanthroline, Co by using 1 nitroso-2 naphtol and Ti by using H_2O_2.

Microprobe analyses were also performed on cut and polished sections of the boules, where single crystal specimens of $FeTiO_3$ and $CoTiO_3$ were used as standards. The Mössbauer technique was used to analyse pulverized specimens of crystals with a constant-acceleration spectrometer in a transmission arrangement between room temperature and 4.2 K. Some results of this study have been reported elsewhere [1, 2].

4. Results and discussion

The boules obtained were black and opaque, typically 7 mm diameter and 40 to ~ 70 mm long, as shown in Fig. 1. They were often cracked when the zone-travelling rate was too great. Two tiny facets of $(00\cdot1)$ were found on the side of the

Figure 1 Single crystal of $Co_{0.525}Fe_{0.475}TiO_3$ grown by the floating-zone method.

boules grown perpendicular to $[00\cdot1]$. X-ray Laue photography revealed that the boules were single crystals over the whole range of x.

The uniformity of the composition of the boules was checked with EPMA employed on a cross-section along the growth direction. Fig. 2 shows a typical plot of $FeTiO_3$ concentration as a function of the boule length, Z. At the initial stage of growth, x increases with an increase in Z, and reaches a constant concentration at $Z > 8$ mm. This means that the steady-state condition at which x in the growing crystal becomes equal to that in the nutrient rod, is realized at $Z > 8$ mm. By using the zone-refining theory [8], the effective distribution coefficient, κ_{eff}, for $FeTiO_3$ is between 0.8 and 0.9.

Table II gives the results of chemical analysis of specimens chosen from a part longer than 8 mm. The data indicate that the compositions of the crystals are very close to those of the nutrient (sintered) rods. This fact is also confirmed by the EPMA results, as shown in Fig. 3, where the analytical composition is proportional to the nominal one. Mössbauer analysis at room temperature showed that oxidation from ferrous to ferric

TABLE II Composition of $Co_{1-x}Fe_xTiO_3$ crystals determined by chemical analysis

Crystal no.	x	CoO (mol %)	FeO (mol %)	TiO_2 (mol %)
FCT-1-2C	0.35	31.9	18.2	49.9
		(32.5)	(17.5)	(50.0)
FCT-2-2C	0.425	28.1	22.5	49.9
		(28.75)	(21.25)	(50.0)
FCT-3-5C	0.50	21.6	27.1	50.0
		(25.0)	(25.0)	(50.0)
FCT-4-2C	0.60	18.3	31.5	49.9
		(20.0)	(30.0)	(50.0)
FCT-5-2C	0.75	11.2	39.3	50.0
		(12.5)	(37.5)	(50.0)

The composition in the nutrient (sintered) rods is also given in parentheses.

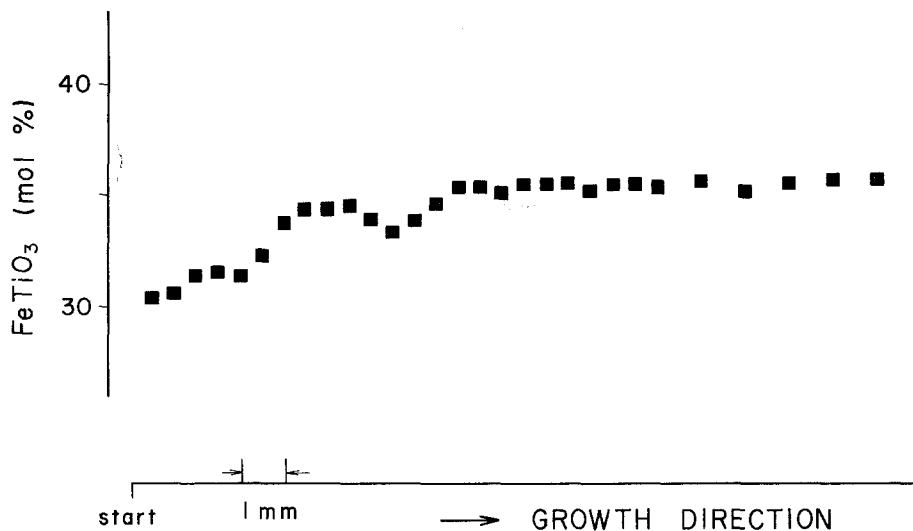*Figure 2* FeTiO$_3$ concentration of Co$_{0.65}$Fe$_{0.35}$TiO$_3$ crystal as a function of growth length.

ion was not remarkable. Antiferromagnetic Néel points were determined as a function of x using a change in the Mössbauer spectra. The results have already been reported elsewhere [1, 2]. As shown in Fig. 4, the lattice parameters increase linearly with an increase of x. The pseudobinary system FeTiO$_3$–CoTiO$_3$ exhibits a perfect solid-solution over the whole range of x. Johnson *et al.* have reported the formation of a perfect solid-solution consisting of FeTiO$_3$ and MgTiO$_3$ [9]. With an increase of Mg^{2+} concentration in the melt, Fe^{2+} ions are proportionally replaced by Mg^{2+} ions,

whose octahedrally coordinated ionic radius is 0.072 nm, at the Fe^{2+} site (0.078 nm). In the present system, it is apparent that Co^{2+} substitutes more readily than Mg^{2+} because the ionic radius of Co^{2+} (0.0745 nm) is closer to that of Fe^{2+} (0.078 nm) than that of Mg^{2+} (0.072 nm).

It became clear that atmosphere control is very important for obtaining inclusion-free crystals. As shown in Fig. 5, precipitated lamellar structure was found as inclusions on cross-sections when the boules were grown under reducing or oxidizing conditions greater than those listed in Table I. The
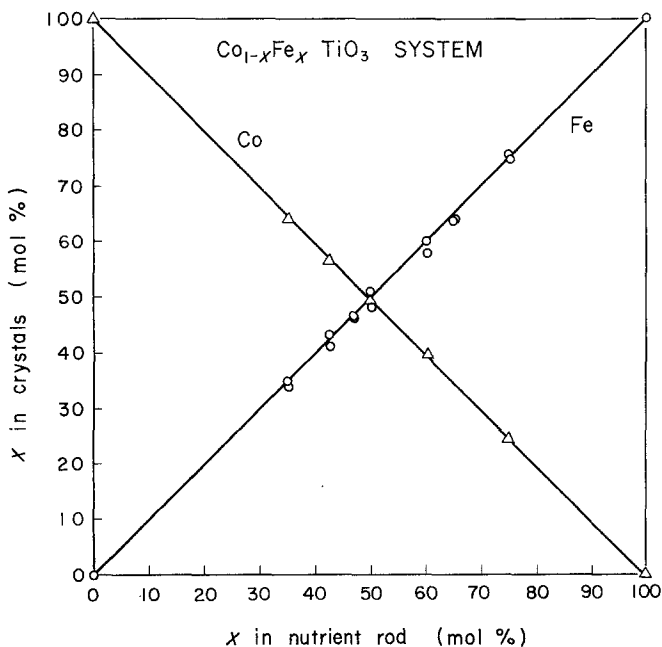

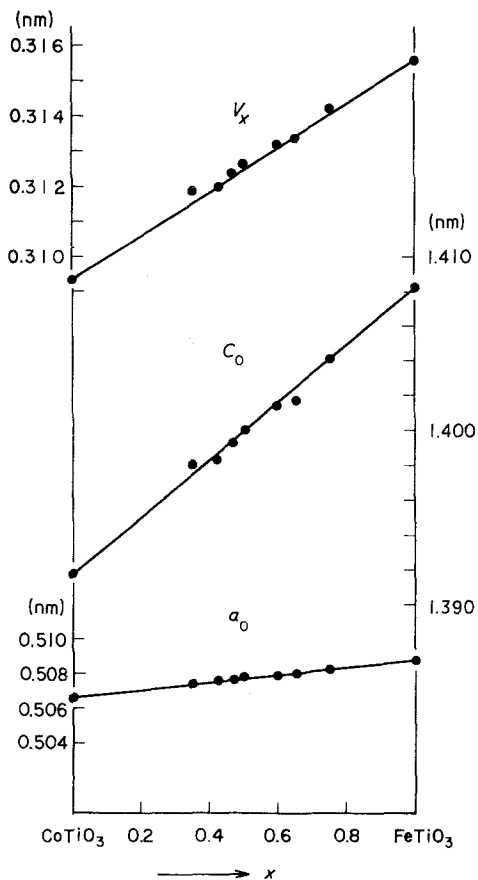*Figure 3* Nominal and analytical data of Fe- and Co-contents. EPMA was used.

Figure 4 Lattice parameters of $Co_{1-x}Fe_xTiO_3$ solid-solution crystals.

X-ray analysis showed that the precipitation which appeared in the reduction atmosphere was of the spinel phase and that in the oxidation atmosphere was of the pseudobrookite phase. The results of EPMA confirmed the X-ray results, as shown in Fig. 6 and Table III. A slight increase in Co con-
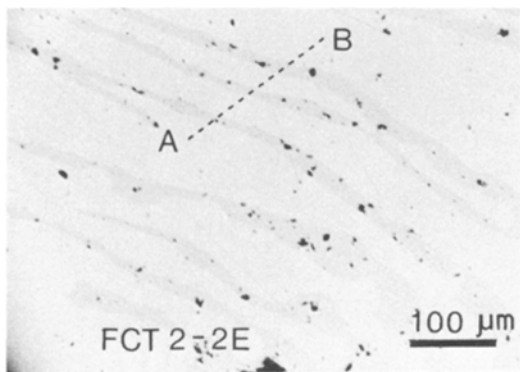

Figure 5 Precipitated lamellae of spinel phase in the ilmenite matrix. The dotted line is a trace of the electron beam in EPMA. $Co_{0.425}Fe_{0.575}TiO_3$ crystal was used.
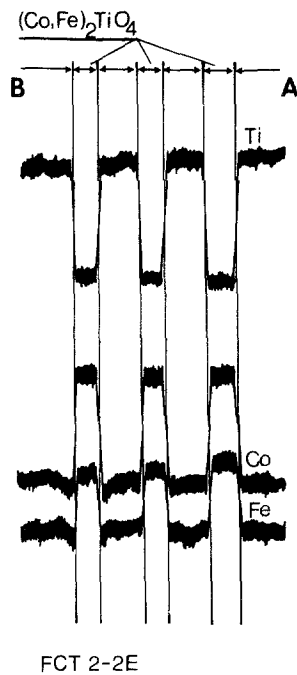

FCT 2-2E

Figure 6 EPMA results of precipitated lamellae in Fig. 5. A to B represents the trace of the electron beam. The X-ray intensities are arbitrary.

tent and a slight decrease in Fe content were observed in the precipitated spinels. For the $Co_{0.5}Fe_{0.5}TiO_3$ $(x = 0.5)$ specimen, for example, the precipitation of spinel was found under a gas flow of $H_2/O_2 > 0.05$. Contrary to this, the pseudobrookite precipitation was observed in $H_2/CO_2 < 0.018$. Webster and Bright [10] reported that the ilmenite-stable region in the system $Fe-Ti-O$ at $1200°C$ was very narrow with a range between 10^{-11} and 10^{-12} atm in oxygen partial pressures, and that the spinel and pseudobrookite phases appeared below and above this region, respectively. The present study suggests that the ilmenite region in the $Fe-Co-Ti-O$ system is also very narrow with variation of oxygen partial pressure.

The X-ray precession analyses revealed that the precipitated spinel and pseudobrookite were single crystals with preferential orientation relations to the ilmenite matrix as follows:

X: $[h0\cdot0]^*_{ilmenite} \| [hh0]^*_{spinel}$,

Y: $[hh\cdot0]^*_{ilmenite} \| [2hhh]^*_{spinel}$,

Z: $[00\cdot l]^*_{ilmenite} \| [hhh]^*_{spinel}$,

and

X: $[h0\cdot0]^*_{ilmenite} \| [00l]^*_{pseudobrookite}$,

$Y: [hh \cdot 0]^*_{\text{ilmenite}} \| [0k0]^*_{\text{pseudobrookite}},$

$Z: [00 \cdot l]^*_{\text{ilmenite}} \| [h00]^*_{\text{pseudobrookite}},$

where * indicates a reciprocal cell. Such a precipitation is often found in a single large grain in natural minerals such as "the exsolution textures" [11, 12]. In this experiment, the spinel or pseudobrookite phases precipitated from the Fe—Co—Ti—O melts during solidification with the preferential orientation stated above.

5. Conclusions

(1) Single cyrstals of Co$_{1-x}$Fe$_x$TiO$_3$ solid-solution were prepared by using a lamp-heated type floating-zone furnace for the whole range of x.

(2) The value of x in the crystal was homogeneous along 80% to ∼90% of the total length;

(3) X-ray analyses showed that this sytem resulted in crystallization of a perfect solid-solution over the whole range of x.

(4) Atmosphere control was important for obtaining inclusion-free crystals because spinel or pseudobrookite precipitations were observed when the atmosphere was, respectively, more oxidizing or reducing than that of the ilmenite-stable region.

(5) The inclusions were related to the ilmenite matrix.

Acknowledgements

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