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Etch-pit investigations of deformed stoichiometric and non-stoichiometric Mn–Zn ferrite single crystals

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Etching solutions both for stoichiometric and non-stoichiometric Mn–Zn ferrite crystals have been developed. The hot phosphoric acid method is suitable for nearly stoichiometric compositions and shows an etch memory effect for dislocations nearly parallel to the crystal surfaces. From the etch-pit arrays the slip system of Mn–Zn ferrite crystals is concluded to be of $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ type independent of the chemical composition and the Schmid factor.

1. Introduction

Crystalline Mn–Zn ferrite, $(MnO)_x(ZnO)_{1-x} \cdot nFe_2O_3$, is a well-known material for magnetic recording heads. Its use as a high-temperature structural material is also anticipated because it has the same crystal structure as spinel crystal, $MgO \cdot nAl_2O_3$, which shows excellent high-temperature characteristics as a structural material. The etch-pit method is a useful way to characterize crystal perfection, but a general etchant suitable for Mn–Zn ferrite crystals of various chemical compositions, i.e. for different n, is not known. Hanke and Burger [1] first tried an etch-pit observation of manganese ferrite crystals, but a one-to-one correspondence of the etch pits and dislocations could not be confirmed. Mizushima [2] used 10% H_2SO_4 and zinc powder for manganese ferrite and obtained etch pits corresponding to dislocations. This method was applied to Mn–Zn ferrite with a composition of $n = 1.17$ by Kawado [3]. By comparing the etch-pit patterns with X-ray topographic images it was confirmed that the etch pits have a one-to-one correspondence with dislocation lines.

We tried to apply this method for the investigation of plastically deformed Mn–Zn ferrite crystals with various chemical compositions. However, etch pits could not be obtained for crystals having nearly stoichiometric compositions ($n \simeq 1$). We therefore tested hot phosphoric acid for the etching of these crystals, as used as an etchant of sapphire (Al_2O_3) [4] and spinel ($MgAl_2O_4$) [5]; clear etch pits and etch lines, both corresponding to dislocations, could be obtained. Combining Mizushima's method and the hot phosphoric acid method, an etch-pit study of Mn–Zn ferrite crystals became possible for a wide range of chemical compositions. In this report etch-pit patterns obtained with these methods and the slip systems determined from the etch-pit observations are presented.

2. Experimental details

Chemical compositions of the specimen crystals used in this work are shown in Table I. Ingot crystals grown by the Bridgman method were cut into square rods having $\{1\,0\,0\}$ and $\{1\,1\,0\}$ flanks and $[0\,0\,1]$ or $[1\,1\,0]$ axes and were subjected to compressive deformation at high temperatures. To observe etch pits the surfaces of as-grown and deformed specimens were ground with No. 1500 emery paper until they became glossy, and the surface damage layers were removed by chemical polishing with phosphoric acid at 120 to 190° C for 0.5 to 2 min, for non-stoichiometric crystals at high temperatures. After the chemical polishing the specimens were dipped in phosphoric acid at 80 to 100° C for several seconds to avoid fracture by thermal stresses and then were rinsed with running tap or pure water. The remaining surface strains of $FePO_4$, if they existed, were removed by phosphoric acid at room temperature. Chemically polished

TABLE I Compositions of specimen crystals, $MnO_x(ZnO)_{1-x} \cdot n(Fe_2O_3)$

Crystals	x	$1-x$	n
A	0.60	0.40	1.02
B	0.65	0.35	1.05
C	0.52	0.48	1.13
D	0.51	0.49	1.57
E	0.56	0.44	1.76
F	0.47	0.53	1.86

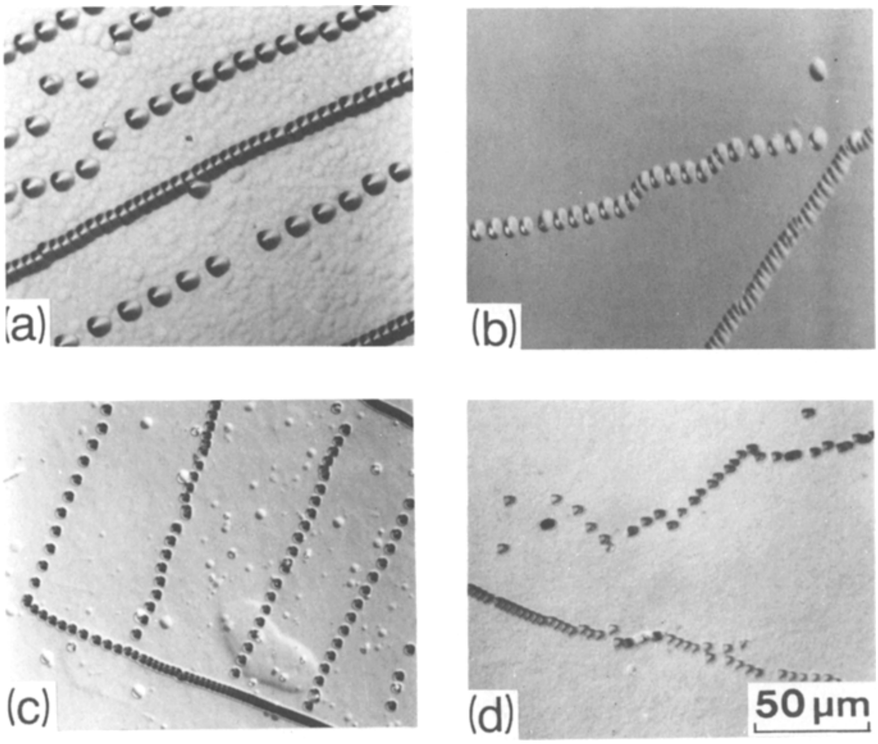

Figure 1 Etch-pit patterns of as-grown crystals. (a) Crystal B (1 0 0), (b) Crystal C (1 1 0), (c) Crystal D (1 0 0) and (d) Crystal E (1 1 0).

specimens of $1.57 \leqq n \leqq 1.76$ were etched by the method of Mizushima [2] (10% H_2SO_4 + zinc powder) and those of $1.05 \leqq n \leqq 1.13$ were etched with phosphoric acid at 60 to 130° C for 0.5 to 10 min. In the latter case the specimens were held normal to the liquid surface and were slowly moved up and down repeatedly. Etch-pit patterns were observed by a Nomarksi-type optical microscope. Compressive deformations of the square-rod specimens were produced at 1000 to 1300° C in air, mostly by creep.

3. Results and discussion

3.1. As-grown crystals

Fig. 1 shows etch-pit patterns of as-grown crystals of various chemical compositions. Figs. 1a and b were obtained with the hot phosphoric acid method, and

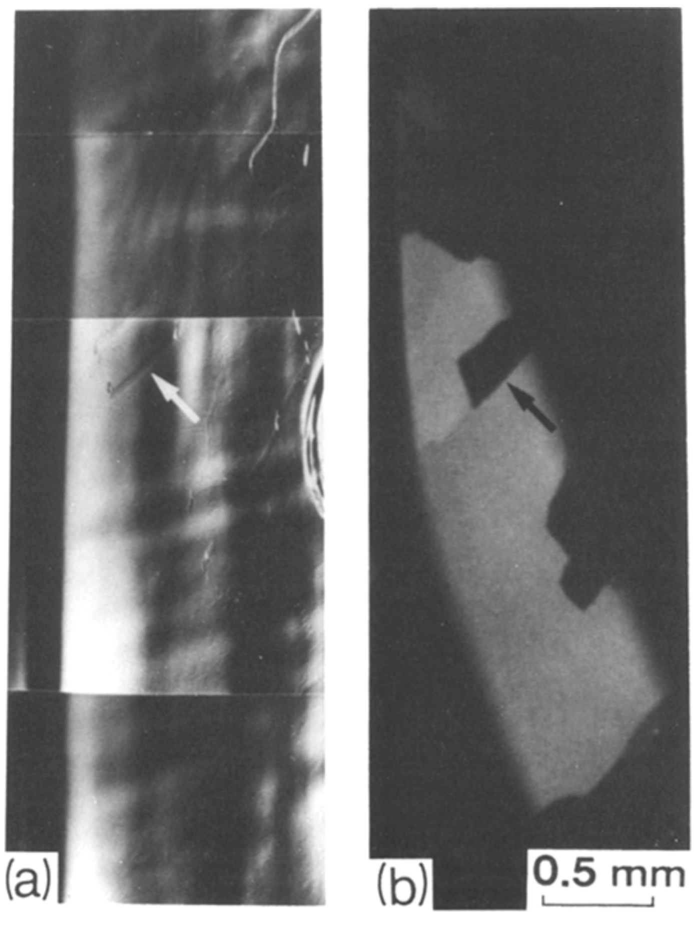

Figure 2 Comparison of (a) an etch pattern and (b) the X-ray topographic image of Crystal C. The arrows indicate the same position of the crystal.

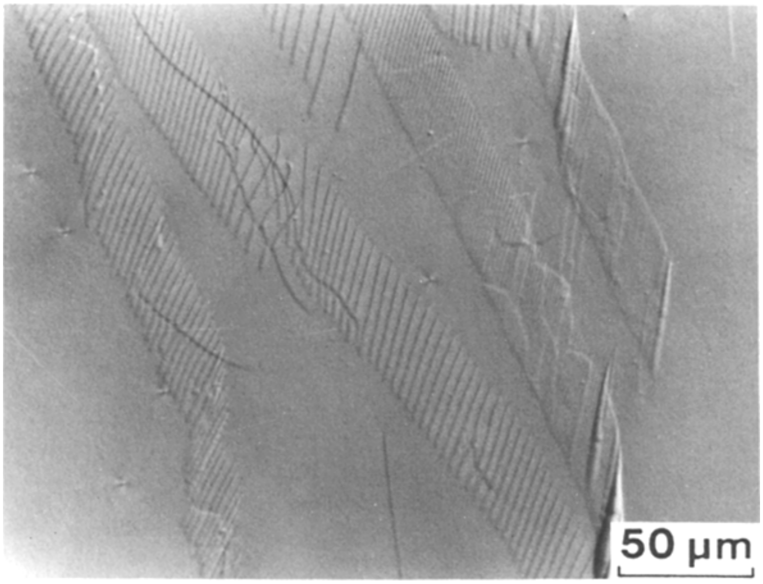

Figure 3 Enlarged etch bands in Crystal C.

Figs. 1c and d with Mizushima's method [2]. The etch-pit arrays in every figure correspond to the dislocations forming the subgrain boundaries which appear frequently in crystals grown by the Bridgman method. The mean etch-pit density (except at subgrain boundaries) is $8 \times 10^4 cm^{-2}$. With hot phosphoric acid some etch bands are observed as shown in Fig. 2a for the same crystal as in Fig. 1b. X-ray topography of the same part of the specimen (Fig. 2b) reveals that the etch bands correspond to subgrain boundaries, one of which is indicated by an arrow. In Fig. 3 etch bands appearing in the other part of the crystal are enlarged, which shows that an etch band is composed of a regular array of etch lines. Fig. 4 shows an electron micrograph of a dislocation network at a small-angle boundary. Comparing Figs. 3 and 4, an individual etch line in an etch band corresponds to a bundle of dislocations in a small-angle boundary lying near the crystal surface. An etch line is supposed to be the projection of a dislocation bundle caused by a difference in etching velocities between the neighbourhood of dislocations and the matrix. This type of etch memory effect has been reported also for etchants of silicon [6] and GaAs [7].

3.2. Deformed crystals

Compressive creep tests were performed for the square-rod specimens in the temperature range 750 to 1150° C, and afterwards a surface layer of more than 1 mm depth was removed from a flank by mechanical polishing. Etch-pit observations were made for the polished flanks in the same manner as in the as-grown crystals, but as the etch-pit density is high in a deformed specimen the etching period was somewhat shortened. Etch pits were uniformly distributed in the inner part of the specimen (Fig. 5a), but in the surface region of the flank they aligned in a definite direction. Fig. 5b shows an etch figure of $(0 1 \bar{1})$ for a specimen with $n = 1.13$ which was deformed by compressive creep in the [0 1 1] direction. The dark broad lines are hematite (α-Fe_2O_3) precipitated on $\{1 1 1\}$ near the specimen surface during the cooling process after deformation. Etch pits align along the $\langle 1 1 2 \rangle$ direction near the hematite precipitates, and this means that the operating slip system is $\{1 1 1\} \langle 1 \bar{1} 0 \rangle$.

Two slip systems are known in crystals having the spinel structure, that is $\{1 1 1\}\langle 1 \bar{1} 0 \rangle$ and $\{1 1 0\}\langle 1 \bar{1} 0 \rangle$. In the spinel crystal ($MgO \cdot Al_2O_3$, $n \geqq 1$), one of these slip systems is activated depending

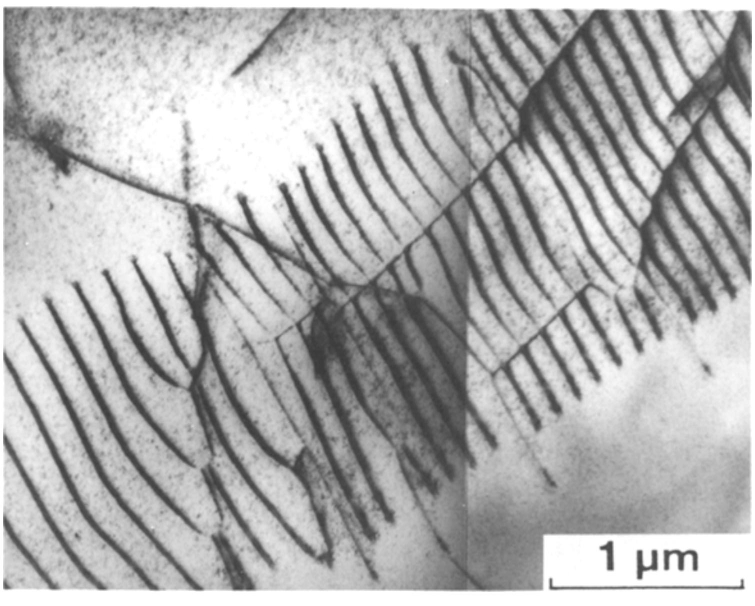

Figure 4 An electron micrograph of a small-angle boundary in a Mn–Zn ferrite crystal.

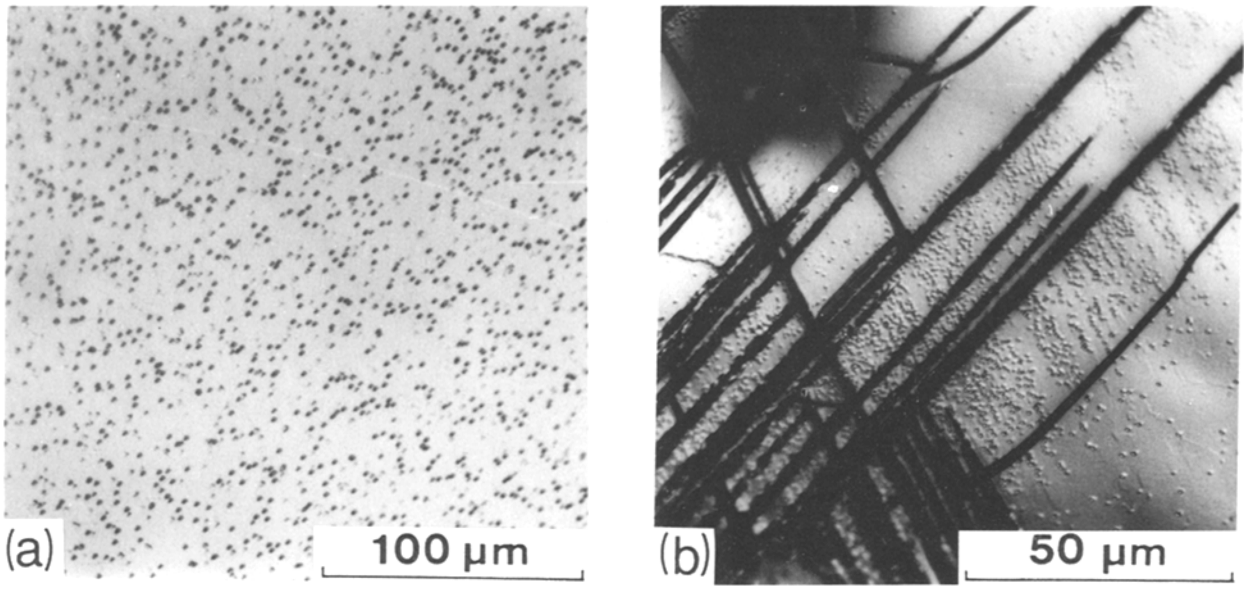

Figure 5 Etch-pit patterns of deformed Crystal C: (a) uniformly distributed etch pits in the inner part of the specimen, (b) etch-pit arrays appearing near the specimen surface.

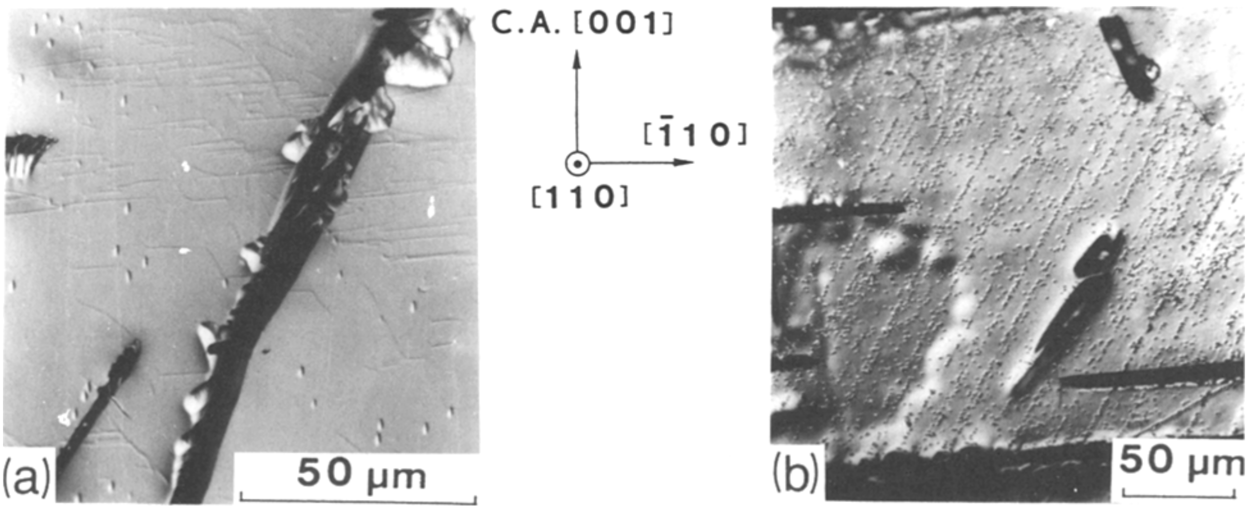

Figure 6 Etch-pit patterns of deformed crystals with different chemical compositions. (a) Nearly stoichiometric crystal (Crystal B), (b) non-stoichiometric crystal (Crystal E). C.A. denotes the compression axis.

both on its deviation from stoichiometry and on the Schmid factor for the compression direction, and in a Mn–Zn ferrite crystal a $\{1\,1\,0\}\ \langle 1\,\bar{1}\,0\rangle$ system may also be activated. Therefore specimens having a Schmid factor for $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ which is 1.2 times higher than that of $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ were subjected to compressive creep along [0 0 1] and were examined by the etch-pit method. Fig. 6a shows etch lines and pits on the (1 1 0) surface obtained by hot phosphoric acid for a specimen with $n = 1.05$. The etch lines parallel to $[1\,\bar{1}\,0]$ have short segments along $[1\,\bar{1}\,2]$. Thus the etch lines correspond to dislocations extending in the $[\bar{1}\,1\,0]$ and $[1\,0\,1]$ directions on $(1\,1\,\bar{1})$. Fig. 6b shows an etch figure obtained with Mizushima's method for a non-stoichiometric specimen ($n = 1.76$) deformed along [0 0 1]. Etch-pit arrays along $[\bar{1}\,1\,2]$ on (1 1 0) are observed and the slip dislocations are on $(1\,\bar{1}\,1)$. Therefore, the slip system in Mn–Zn ferrite crystals can be concluded to be of the $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ type, and this depends neither on the composition nor on the Schmid factor of the compression direction. Further investigations on the deformation of Mn–Zn ferrite crystals will be reported in a forthcoming paper [8].

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