Metallographic Characterisation of Twinning and Other Microstructure Defects of Fe_4Al_{13}

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The metallographic characterisation of alloys is a fundamental technique for the evaluation of the microstructure with respect to homogeneity or arrangement of phases to get information on phase formation and equilibria. The microstructures are mainly investigated by light- and scanning electron microscopy. Energy and wavelength dispersive X-ray analysis systems are often used to determine the chemical composition of phases even in multi phase samples. Furthermore, the metallographic characterisation is essential because microstructure properties generally have significant influence on physical properties and other macroscopic behaviour. Also, grain size effects are important for the phase formation in the solid state [1].

In case of the complex metallic phase Fe_4Al_{13}, multiple twinning is a characteristic feature of the microstructure. Here we present an overview of the results of our extensive metallographic investigations by means of light optical and transmission electron microscopy. The twins are characterized on micro and nano scaling.

Metallographic preparation and microstructure characterisation

The crystal structure of Fe_4Al_{13} [2] shows monoclinic symmetry (Pearson code *mC*102) and is formed by four atomic layers within one periodic unit of 0.8078 nm along the monoclinic *b* axis. The monoclinic angle $\beta = 107.69° \approx 3 \times 36°$ and the lattice parameter ratio $c/a = 0.805 \approx \tau/2$ (with $\tau = 1.6180\ldots$ golden mean) indicate the relation to tenfold symmetry. Indeed, a similar atomic arrangement within the layers and geometric properties of the unit cell motivate to describe Fe_4Al_{13} as a crystalline approximant to quasi-crystalline phases with decagonal symmetry. All atomic positions are completely occupied at the nominal composition $Fe_{23.5}Al_{76.5}$ and the existence of a small homogeneity range of 2 at. % [3] is related to the partial occupation of one aluminum position. Nevertheless, the phase always shows a large number of defects because twinning is almost always observed as fine lamellae in the microstructure of Fe_4Al_{13}. Three different kinds of twins with reflec-

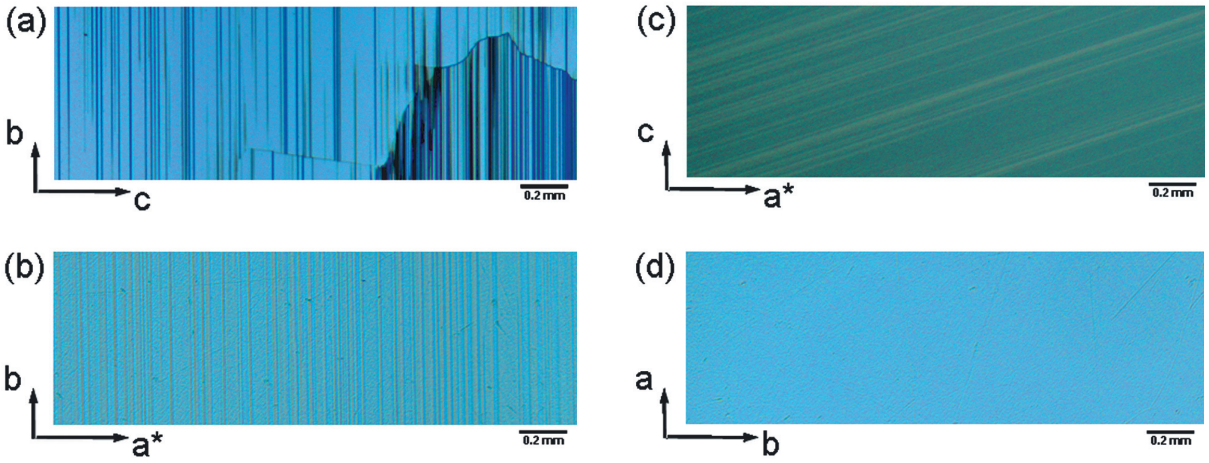

Fig. 1: Etched microstructures with different crystallographic orientation of the same Fe_4Al_{13} crystals grown by Czochralski method. The microstructures **a)** (100) and **b)** perpendicular to [001] reveal (001) twins with the relief evolved by chemical etching (bright field image, light optical microscope). **c)** Microstructure of (010) (polarised light contrast). Lamellae and *c* axis enclose an angle of 72° consistent with (001) twinning planes. Here, etching has no significant effect on the surface topography. **d)** etched microstructure of (001); (polarized light contrast).

tion planes (100), (001) and (20 – 1) are known [4]. These planes are strongly related to the tenfold symmetry because they include angles which are multiples of 36°. In fact, quasi-crystalline domains as well as multiple twins of Fe_4Al_{13} with tenfold symmetry were found in rapidly quenched Fe-Al alloys by means of high resolution electron microscopy and electron diffraction [5]. Slow cooling rates suppress the formation of metastable decagonal phase but slowly pulled crystals of Fe_4Al_{13} often also contain twins and other defects. For our investigations, rods were extracted from a large cone shaped crystal with a height of 15 mm and a basal diameter of 25 mm which was prepared by Czochralski method [6]. Crystal growth was initiated by pulling parallel to the *a**-direction with a constant rate of 0.05 mm h^{-1} – 0.15 mm h^{-1} from the Al rich melt ($Fe_{19}Al_{81}$). Rods with dimensions of 5 × 3 × 2 mm^3 were cut along crystallographic axes using a wire saw that minimizes surface damage and avoids the formation of twins by surface deformation. The specimens were mounted in epoxy resin for metallographic preparation which was performed by grinding on SiC paper followed by diamond paste polishing with 9 µm down to ¼ µm grain size. Final polishing with colloidal silica (50 nm, pH = 10) significantly improves the surface quality of the microstructure. All samples show single phase microstructure in the material contrast of the scanning electron microscope. The polarized light contrast showed very fine lamellae parallel to the crystallographic *b* axis in the planes (100) and perpendicular to [001]. Additionally, the lamellae in the (010) enclose an angle of ca. 72° with the crystallographic *c* axis in (010). The orientation of the lamellae in these planes (Fig. 1a – c) and the absence of lamellae in the microstructure of (001) (Fig. 1d) are consistent with twins on (001) planes.

A strong relief develops in the planes (100) and perpendicular to [001] during the treatment with dilute etchant (etchant according to Fuss: 7.5 ml HF, 2.5 ml HCl, 8 ml HNO_3 and 980 ml H_2O). But the same etchant has no effect on the microstructures of (010) and (001). It seems that the twinning enhances the chemical reaction with the etchant for the planes (100) and perpendicular to [001] because untwinned areas in these planes are hardly attacked by the etchant. Repeated metallographic preparations with the complete removing of upper surface layers confirm these results. Especially, simultaneous mounting, preparation and etching of different crystallographic planes clearly shows the anisotropic behavior.

TEM preparation and TEM investigation

The crystallographic orientations of selected twins have been studied with transmission electron microscopy (Tecnai 10, 100 kV) by means of bright field imaging and selected area electron diffraction (SAED). These investigations have been performed on slices which were prepared from the Fe_4Al_{13} rods presented in Figure 1a and 1c. The orientations of the slices are perpendicular to the polished surface of the particular Fe_4Al_{13} plate and also perpendicular to the twinning planes. For TEM preparation the samples with initial thickness of 300 µm have been fixed on a Tripod sample holder and manually thinned down to 30 µm on diamond grinding foils with grain sizes between 15 µm and ¼ µm. Final thinning was performed by ion beam polishing using Argon ions with energies between 5 keV and 1 keV (Precision Ion Polishing System PIPS 691, Gatan). Typically, a total preparation time of 6 hours is necessary to get electron transparent areas suitable for TEM investigations (Fig. 2). It should be mentioned that the material removal depends on the orientation of the ion beam with respect to the twin lamellae, thus generating a relief along the twinning planes in case of parallel orientation.

The crystallographic orientation of the twins in the (010) plane was determined by means of bright field TEM images and SAED patterns of both domains (Fig. 3). The diffraction pattern clearly shows that both domains are connected via common planes (001). The superposition of both diffraction patterns leads to split reflection spots observed clearly at larger diffraction angles. In the

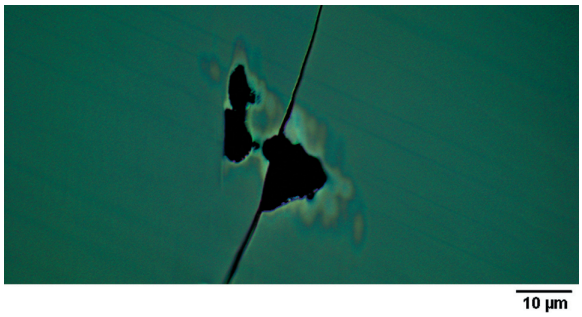

Fig. 2: Light optical microscope image (polarized light) of thin region around a hole in a TEM sample – polished and finally thinned with argon ion beam polishing technique (PIPS).

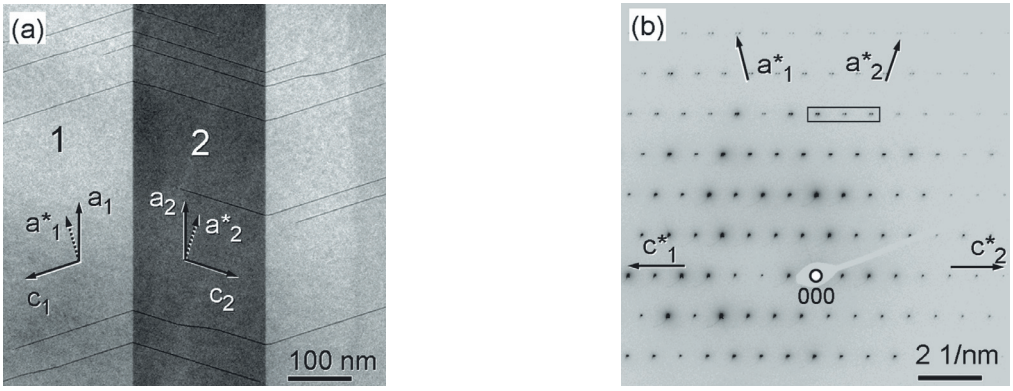

Fig. 3: **a)** TEM image (bright field modus) of regions with (001) twin domains as viewed along [010] (the thin darker domain is nearer to the Bragg diffraction condition). **b)** Part of selected area diffraction (SAED) along [010] from twin domains 1 and 2 together.

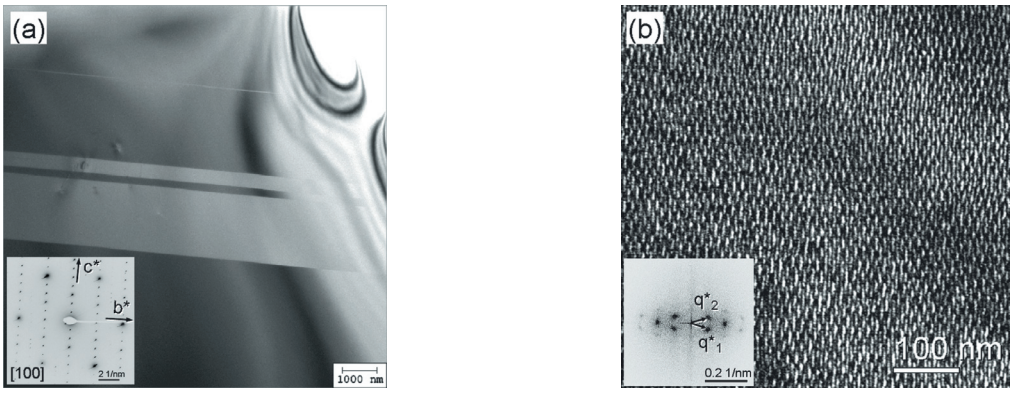

Fig. 4: **a)** TEM image (bright field) of region with (001) twin domains as viewed along [100] (darker domains are nearer to the Bragg diffraction conditions; inset: corresponding SAED pattern). **b)** Middle resolution TEM image of one domain (slightly tilted from [100] zone axis) showing a quasi 2D modulation (with magnitudes of $q_1 = q_2 = 116$ Å; inset: corresponding FFT image).

bright field image of (010), defects are observed which extend from domain to domain following the changes in [001]. Similar analysis of the twins on the plane perpendicular to [100] also confirms the twinning on (001) (Fig. 4a). Middle resolution TEM image of one domain shows a 2D modulation (Fig. 4b). The evaluation of this image by fast Fourier transformation (FFT) results in a periodicity of 116 Å. This kind of modulation is verified in several other domains and also in samples prepared by means of the focus ion beam technique (FIB, Quanta 3D, FEI). It seems that the modulations represent a special kind of intrinsic defect of the Fe_4Al_{13} microstructure.

Conclusions

The investigation of the Fe_4Al_{13} phase shows that the microstructure of very slowly grown Fe_4Al_{13} crystals is yet dominated by twins with preferred twinning on (001). Moreover, 2D modulations have been identified and characterized by TEM analyses. Chemical etching of the twinned microstructures reveal a significant anisotropy and indicate on a twin enhanced etching effect in planes parallel [010].

References

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