Al₄(Cr, Fe): single crystal growth by the Czochralski method and structural investigation with neutrons at FRM II

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Abstract. A single crystal of Al₄(Cr,Fe) with composition $Al_{78}Cr_{19}Fe_3$ grown by the Czochralski method was studied by neutron diffraction for the first time. As a preliminary result the neutron diffraction experiment suggests a body-centered orthorhombic space group *Immm* with $a = 1.24985(3)$ nm, $b = 1.25500(3)$ nm and $c = 3.0512(2)$ nm as found by Deng *et al.* (Pearson symbol: *oI*366-59.56) [1] using single crystal X-ray diffraction. Additionally, more or less diffuse maxima at positions with $k = \dfrac{n}{2}$ ($n = $ odd) are clearly observable.

1. Introduction

During the last decade there have been several publications on different structure models of Al₄(Cr,Fe) found either in alloys with a nominal composition of $Al_{12}CrFe_2$ or $Al_{12}Cr_2Fe$. Sui *et al.* (1995) [2] reported on an orthorhombic phase (o-AlCrFe) found in an $Al_{12}Cr_2Fe$ alloy. Using electron diffraction methods, the space group was determined to be *Immm* with $a = 1.23$ nm, $b = 1.24$ nm and $c = 3.07$ nm. Based on the appearance of streaking and weak spots in the [100] electron diffraction pattern of the orthorhombic phase also a monoclinic phase was mentioned which is supposed to be an ordered super-structure of the body-centered orthorhombic phase reducing the symmetry to C-centered monoclinic with the following lattice parameter relationship: $a_M = c_O / \sin\beta = 3.31$ nm, $b_M = a_O = 1.24$ nm, $c_M = 2b_O = 2.48$ nm and $\beta = 112°$ ([2], [5]). Later the structural model of an orthorhombic phase with space group *Imm*2 ($a = 1.234$ nm, $b = 1.241$ nm, $c = 3.071$ nm) was derived from comparing high-resolution electron microscopy images [3] and the structure of μ-Al₄Mn [4]. But from this model the composition was calculated to be $Al_{5.103}$(Cr,Fe) rather than Al₄(Cr,Fe). Palm [6] studied the isothermal section at 1000 °C of the Al-rich part of the

Al–Cr–Fe system. No ternary phases were found, but certain solubilities for the third element in the binary subsystems. Al₄Cr dissolves up to 11.9 at.% Fe. The given existence region of the Al₄(Cr,Fe) phase suggests an isoconcentration behaviour with respect to the Cr content of the solid phase. Therefore, Fe would substitute for Al instead of Cr, and the formula should be written as (Al,Fe)₄Cr rather than Al₄(Cr,Fe). But the question regarding the structure of the binary or the quasi-ternary phase remains open in this publication. In 1999, Sui *et al.* [7] found a new hexagonal compound with a composition of $Al_{81}Cr_{11}Fe_8$, which was called h-AlCrFe, in alloys of nominal composition $Al_{12}Cr_2Fe$ as well as $Al_{12}CrFe_2$. Using electron diffraction the space group $P6_3/m$ was suggested. This structure was investigated further by using a combination of transmission electron microscopy and X-ray single crystal diffraction by Mo *et al.* (1999) [8]. A single crystal with $Al_{80.61}Cr_{10.71}Fe_{8.68}$ (called ν-Al₄(Cr, Fe)) was used and the space group ($P6_3/m$) found earlier by Sui *et al.* (1999) was confirmed. Later in 2004, Deng *et al.* [1] determined an orthorhombic structure for a single crystal of Al₄(Cr,Fe), with the composition of $Al_{80.6}Cr_{10.7}Fe_{8.7}$, using single crystal X-ray diffraction. The space group *Immm* rather than *Imm*2 [3] was confirmed. In all the structure solutions up to now the positions of the almost isoelectronic transition metals Cr and Fe could not be distinguished by X-ray diffraction and electron diffraction methods. A series of crystals starting from initial melt compositions from $Al_{88}Cr_{11}Fe_1$ to $Al_{87}Cr_6Fe_7$ were grown and analyzed by electron probe microanalysis (EPMA). Contrary to Palm [6], the Al-rich limit of the existence region indicates an Al-isopleth behaviour confirming the Al₄(Cr,Fe) formula with Fe substituting for Cr. To judge the question whether Fe alloyed to Al₄Cr enters Al or Cr sites, a single crystal neutron diffraction measurement was performed, where the scattering power Fe : Cr exihibits a scattering contrast of roughly 7 : 1.

2. Crystal growth

The Czochralski method has been proven to be a powerful tool for growing crystals from off-stoichiometric melts, due to a good mixing of the melt and the possibility to

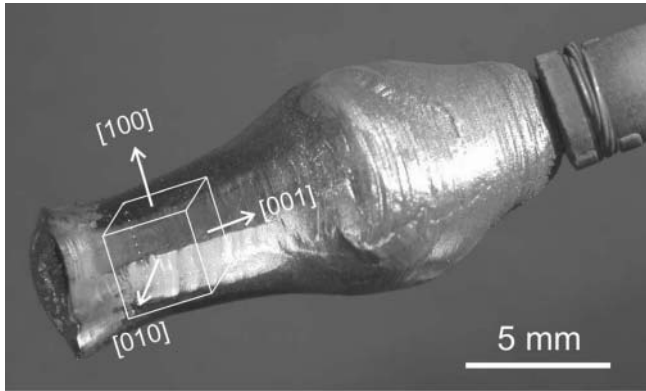* Correspondence author (e-mail: birgitta.bauer@lrz.uni-muenchen.de)

Fig. 1. $Al_{78}Cr_{19}Fe_3$ as-grown single crystal with the sketched position of the sample used in the neutron diffraction study.

Fig. 2. Instrument RESI at FRM II.

observe the crystal during seeding and growth. Crystals with various Cr and Fe content were grown starting from melts with initial compositions between $Al_{88}Cr_{11}Fe_1$ and $Al_{87}Cr_6Fe_7$. The typical ingot charges were about 17 g and were ex-situ synthesized by using a RF heating facility. In order to prevent the Al-rich melts from any traces of oxygen during growth a fully metal-sealed growth chamber was used. For seeding native seeds from former crystal growth experiments were used, oriented along all three main axis of the orthorhombic system. Due to kinetic reasons pulling rates as low as 0.05 mm/h have proved to be necessary. The composition of crystals grown from off-stoichiometric melts differs from the initial melt. Since the amount of Al that is incorporated into the growing crystal is lower than in the melt its concentration in the remaining melt increases during growth resulting in a decreasing liquidus temperature. This temperature change has to be compensated by using a progressive temperature ramp in order to keep the diameter of the growing crystal constant. The ramp usually varied in the range of 0.1 K/h to 0.5 K/h. The starting crystallization temperature was about 1050 °C. The grown crystals were investigated by electron probe microanalysis and revealed a rather homogenous composition within each particular crystal in radial as well as in axial direction in the limit of the measurement error.

For the neutron experiment a cube of $3 \times 3 \times 3\,mm^3$ was cut from an as-grown crystal using a wire saw. The crystal's composition was $Al_{78}Cr_{19}Fe_3$ (values are rounded to the closest integer) grown from an initial melt composition of $Al_{88}Cr_9Fe_3$ (Fig. 1).

3. Experimental setup

The single crystal neutron diffraction experiment was carried out at room temperature using the instrument RESI (REciprocal Space Investigator) at the FRM II research reactor in Garching. RESI is a thermal single crystal diffractometer designed to record both strong and weak scattering simultaneously covering large portions of the reciprocal space with high resolution [9]. The detector is an imaging plate detector system (MAR345, marresearch) with a standard FUJI BAS-ND-type image plate containing 50% Gd_2O_3 [9] (Fig. 2). The sample was mounted on
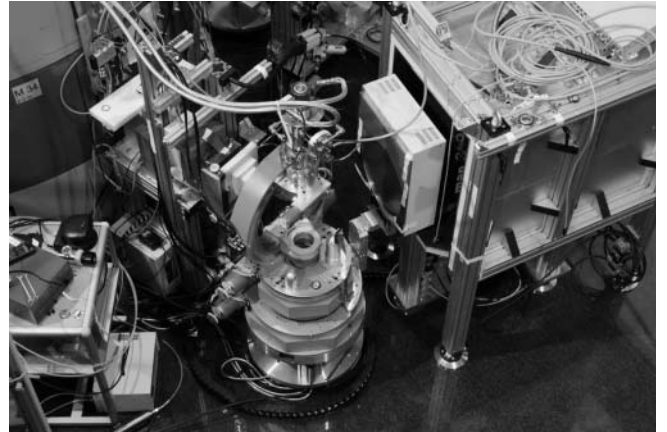
a Bruker–Nonius Mach3 Kappa-goniometer. A Ge(511) monochromator was used, providing a wavelength of 0.15391 nm. The distance between detector and sample was 273 mm. To check the crystal quality short φ-scans were used. No twinning was observed. φ-scans (from $\varphi = 0°$ to $\varphi = 180°$) for different θ-positions ($\theta = -10.0°$, $-27.0°$ and $-44.0°$) were performed. The oscillation range per frame was $0.5°$ and the exposure time 900 sec. A total of 8303 reflections was recorded.

4. Results and discussion

As a first result the neutron data suggests a body-centered space group *Immm* with $a = 1.24985(3)$ nm, $b = 1.25500(3)$ nm and $c = 3.0512(2)$ nm as proposed by Deng *et al.* [1] obtained from a single crystal X-ray diffraction experiment. Nevertheless a renewed analysis of the structure (= "substructure" cf. below) was carried out taking care of the individual distribution of Fe and Cr atoms. Although the structure refinement has not been completed yet, a few insights can already be gained. Taking the structure model derived by Deng *et al.* [1], the iron seems to occupy the positions TM 10 and the sites Al/TM 5 and Al/TM 15 (notation according to [1]) with significant contributions (Occ.$_{Fe10}$ = 0.26, Occ.$_{Cr10}$ = 0.36, Occ.$_{Al15/Cr5}$ = 0.24, Occ.$_{Fe5}$ = 0.12, Occ.$_{Al15/Cr15}$ = 0.0, Occ.$_{Fe15}$ = 0.2). Due to the almost identical scattering lengths, Al and Cr were restricted to the same occupancy on the triply mixed sites. Most of the other TM-sites contain only a few percent Fe. However, the R1-value of 10% is not satisfactory for further discussions of the structure. Additionally, more or less diffuse maxima at positions with $k = \frac{n}{2}$ ($n =$ odd) are clearly observable (Figs. 3 and 4). As this result is unknown from XRD data, we relate it to the origin of a chemical (Fe−Cr) superorder with doubling of the period along the *b*-axis ("superstructure") and reducing the overall body-centering to a primitive space group. Concerning the diffuseness of the "$k = \frac{n}{2}$ ($n =$ odd)" reflections one may discern two contributions: (i) faint diffuse streaking extended along *l*, and (ii) a broadening also along the *k*-direction. In fact, the fwhm's of these superstructure reflections along *k* is twice as compared to those of the "main"
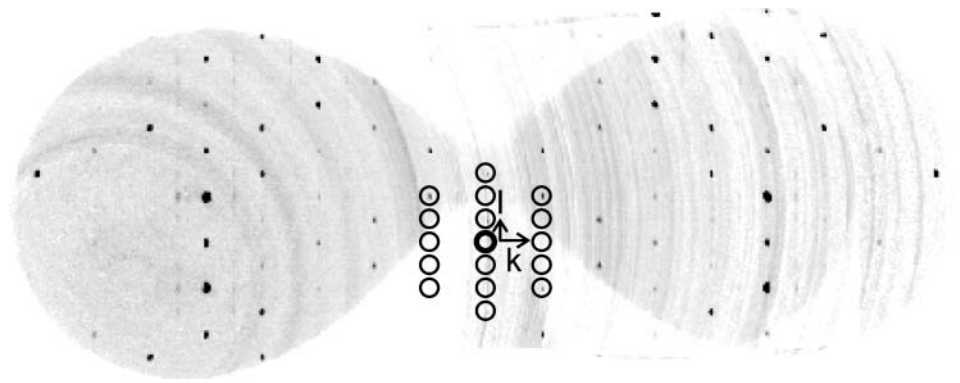
Fig. 3. Reconstructed 3kl-layer with the orthorhombic cell overlayed.
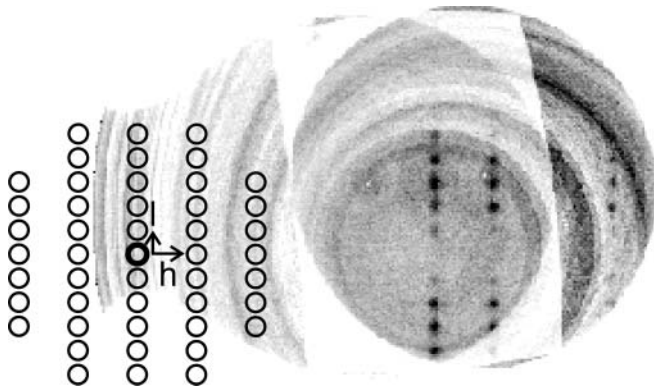

Fig. 4. Reconstructed h1.5l-layer showing only the additional reflexions.

peaks due to the substructure. Integrating the intensities of the superstructure reflections and use it in a conventional way an averaged superstructure model irrespective the true Fe−Cr distribution can be derived. In other words, the model neglects the diffuseness along k (and also along l) which might be due to some kind of chemical short range order or domain like chemical order in layers but indicates the absence of a true long-range Fe−Cr related superorder. An analysis of the extension and anisotropy of the diffuseness (cf. (ii)) of these superstructure reflections would give more information about the kind of disordering. This is, however, beyond the scope of this paper. The elongation and intensity modulations of the diffuse peaks along l (cf. (i)) must be discussed in more detail: For example, fluctuations of c-spacings must be taken into account, which relate to platelike chemical domains extended perpendicular to the c-directions. However, other explanations might also be valid.

5. Conclusion

For the first time the structure of a single crystal of Al$_4$(Cr,Fe) with a composition of Al$_{78}$Cr$_{19}$Fe$_3$ was investigated in a neutron diffraction experiment. The substructure remains body-centered, as determined by single crystal X-ray diffraction, but a preferential site occupancy for iron could be determined. Taking also the diffuse peaks into account ("superstructure") the symmetry was found to be reduced to primitive very likely due to the ordering of Cr and Fe atoms. A single crystal X-ray diffraction experiment on the same crystal is planned. The final interpretation of the data is an ongoing subject of discussion and will be published soon.

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