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The Debye temperature of the Fe–Cr sigma-phase alloys

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Abstract

⁵⁷Fe Mössbauer spectra were recorded for microcrystalline and nanocrystalline samples of the σ -phase of Fe_{100-x}Cr_x alloys with x between 44.6 and 49.6 in the temperature range between 4.3 and 300 K. From the temperature dependence of the average centre shift derived from the spectra measured between 80 K and 300 K, Debye temperatures, θ_D , were determined. θ_D -values for the two types of sample show the same linear increase with x , namely ~ 15 K/at.%, which is faster than a similar trend observed for the α -phase Fe–Cr alloys.

1. Introduction

The σ -phase was discovered for the first time in a Fe–Cr–Ni alloy as a non-magnetic, brittle, and hard constituent [1]. Its crystallographic structure was definitely identified only 31 years later as close-packed tetragonal—space group $D_{4h}^{14}-P4_2/mnm$ —with 30 atoms in the unit cell [2], which are distributed over five crystallographically non-equivalent lattice sites: I, II, III, IV, and V with occupation numbers 2, 4, 8, 8, and 8, respectively. The sites have rather high coordination numbers—12 for sites I and IV, 14 for sites III and V, and 15 for site II—and quite different local symmetries. Since larger atoms go preferentially to the sites with the higher coordination numbers, a non-statistical distribution of the two constituent atoms on the different lattice positions is present. Therefore, the occupation numbers for iron are highest for sites I and IV ($\sim 90\%$), whereas for chromium they are highest for site II ($\sim 75\%$). On sites III and V both Fe and Cr are present with a predominance of chromium. This is confirmed by several neutron and x-ray investigations [2–6]. The σ -phase precipitates from the α -phase during an isothermal annealing in the temperature range of ~ 800 K $\leq T \leq \sim 1100$ K mostly at the grain boundaries and in the form of submicrometre-sized needles and/or particles [7, 8].

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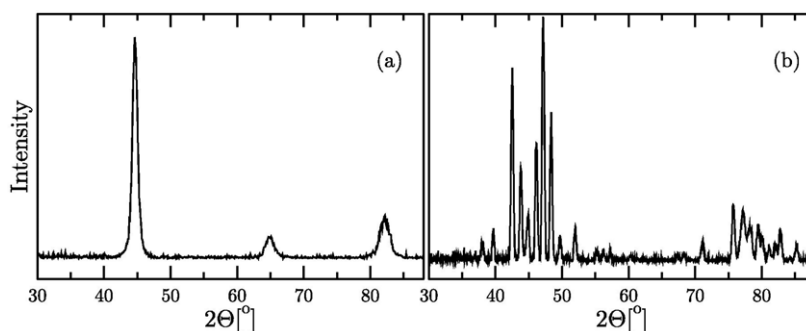


Figure 1. Typical XRD patterns as recorded at RT for nanocrystalline (a) α -Fe-Cr and (b) σ -Fe-Cr samples.

Despite a huge difference in crystallographic structure between α - and σ -phases, the volume available in a unit cell per atom is within the accuracy of 1% the same for the two phases. Also the average distances to the nearest neighbours are similar in the two phases (the one in the σ -phase being $\sim 5\%$ larger).

It is of interest to compare physical properties of the two phases in the Fe-Cr system, as it gives an opportunity to reveal the role the crystallographic structure plays. For this reason we started with a detailed investigation of the magnetic and dynamic properties of the σ -phase. In this paper we report on the concentration dependence of the Debye temperature of Fe-Cr alloys prepared in two ways, namely (a) by conventional arc melting, which resulted in a microrange size of grains, and (b) by mechanical alloying, which gave alloys with nanocrystalline grains. Preliminary results were already published elsewhere [9–12].

2. Experimental details

One series of $\text{Fe}_{100-x}\text{Cr}_x$ alloys, with $x = 46.2, 46.8, 48.0,$ and 49.0 , was prepared by melting the appropriate amounts of Fe (99.95% purity) and Cr (99.5% purity) in an arc furnace under argon atmosphere. The ingots obtained were heat treated for 72 h at 1273 K in vacuum, followed by fast cooling outside the furnace. Next the samples were cold rolled to a final thickness of 2–3 mm and transformed into the σ -phase by a second heat treatment at 973 K for 450 h. The alloys obtained in this way had grains in the micrometre range.

Another series of $\text{Fe}_{100-x}\text{Cr}_x$ alloys, with $x = 44.6, 46.6, 47.8,$ and 49.6 , was prepared by mechanical alloying using a planetary mill (Fritsch P-7), operated at a disc rotation speed of 640 rpm, equipped with hardened steel vials and balls (seven pieces), with mixtures of powders of Fe (99.9%, grain size $< 40 \mu\text{m}$) and Cr (99.2%, grain size $\sim 100 \mu\text{m}$).

Oxidation of the powder was prevented by performing the mechanical alloying in a protective atmosphere of argon. As the resulting nanostructural samples were in the form of agglomerates of an average grain size of $30 \mu\text{m}$, eventual surface oxidation could affect only a small fraction of all grains (10^9) included in the agglomerate.

The weight of the sample powder was 5 g and the powder-to-ball weight ratio was 1:20. The total milling time was 16 h, interrupted for 15 min every hour.

The samples as obtained were found to be 100% in the α -phase as determined by Mössbauer spectroscopy (MS) and x-ray diffraction (XRD) measurements carried out at room temperature. Their transformation into the σ -phase was successfully performed by isothermal annealing in vacuum at 973 K for 5 h. The verification of the α - to σ -phase transformation was

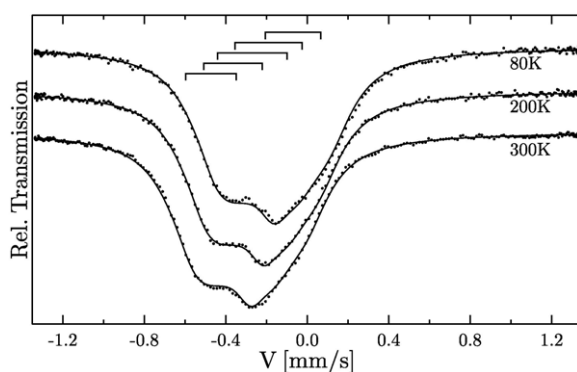


Figure 2. ^{57}Fe Mössbauer spectra recorded for the nanocrystalline $\sigma\text{-Fe}_{53.4}\text{Cr}_{46.6}$ alloy at various temperatures. The solid lines represent the best fits and the bars indicate the subspectra.

also done by recording room temperature MS spectra and XRD patterns. Both proved that the final phase was 100% sigma. The XRD technique using Cu $K\alpha$ radiation at room temperature was further used to determine the mean crystallite sizes and microstrains, obtained from the widths of XRD peaks which are shown in figures 1(a) and (b), for the $\alpha\text{-Fe-Cr}$ and $\sigma\text{-Fe-Cr}$ samples, respectively, using the Williamson–Hall method [13]. The results gave 6.5–8.9 nm and 0.30%–0.90% (α -phase) and 26–78 nm and 0.19%–0.9% (σ -phase) for mean crystallite sizes and microstrains, respectively. However, as revealed by a scanning electron microscopy (SEM) study, the $\sigma\text{-Fe-Cr}$ samples consist of aggregates with mean sizes of $\sim 30\ \mu\text{m}$ [10, 12]. The phase purity for both series was again checked using both x-ray diffraction and Mössbauer spectroscopy at room temperature.

^{57}Fe Mössbauer spectra were recorded in the transmission geometry using a standard spectrometer. The $^{57}\text{CoRh}$ source was moved with constant acceleration. Velocity was calibrated with both $\alpha\text{-Fe}$ and sodium nitroprusside. The samples were mounted in a continuous flow cryostat. Measuring temperatures between 4.3 and 298 K were controlled with an accuracy of 0.5 K.

3. Results

For determination of the Debye temperature, only the spectra measured between 80 and 300 K, i.e. in the paramagnetic phase, were used to avoid uncertainties resulting from the hf field distributions present below ordering temperatures.

In figure 2, typical spectra recorded at temperatures between 80 and 300 K are shown for the nanocrystalline $\sigma\text{-Fe}_{53.4}\text{Cr}_{46.6}$ alloy. The visual differences are minor, as in that range of temperatures the samples are in a paramagnetic state.

By Rietveld analysis of neutron diffraction measurements on some $\sigma\text{-Fe-Cr}$ samples, which were produced by the same preparation procedure as the micrometre-sized samples, it was shown that changes in the preparation conditions led only to small changes in the relative occupation of Fe and Cr on the five different sites [6]. Therefore the spectra for all samples were analysed, as in previous investigations on $\sigma\text{-Fe-Cr}$ alloys [10–12], via a superposition of five subspectra allowing different hyperfine parameters (quadrupole splitting and distribution of the centre shift). In the analysis of the spectra the quadrupole splitting was assumed to be small and independent of temperature. The average centre shift (CS) was calculated as the weighted one over all subspectra. Examples of the derived temperature dependence of (CS) are shown in figure 3.

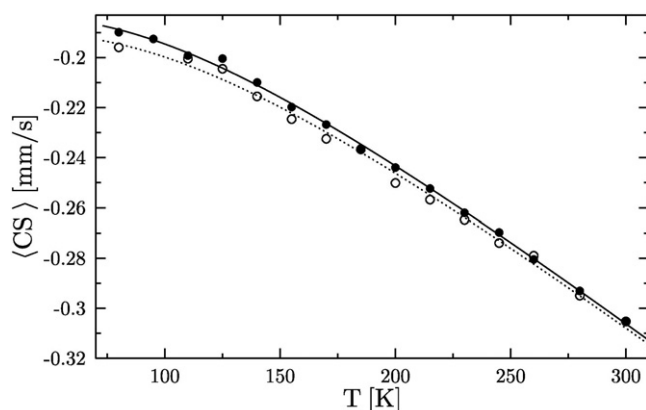


Figure 3. Average centre shift, $\langle CS \rangle$, versus temperature, T , for nanocrystalline samples of the σ -phase with $x = 46.6$ (full symbols) and $x = 49.6$ (open symbols). The solid and dotted lines indicate the best fit to the data in terms of equation (2).

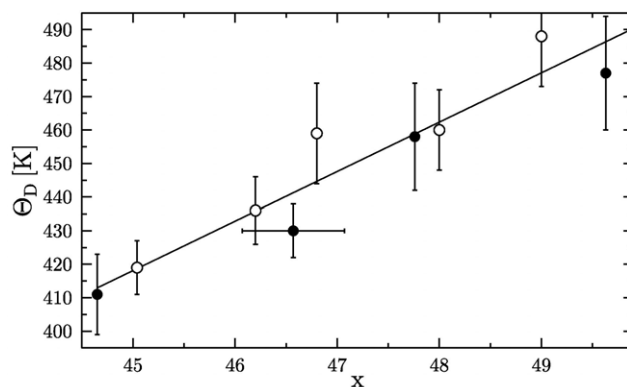


Figure 4. Debye temperature, Θ_D , versus Cr content, x , for microcrystalline (open symbols) and nanocrystalline (full symbols) $Fe_{100-x}Cr_x$ samples. The line represents a linear fit to the data.

Generally, the centre shift consists of two terms:

$$CS = IS + SOD \quad (1)$$

where IS is the isomer shift, which is proportional to the s-electron density at the Fe nucleus, and SOD is the second-order Doppler shift, which is related to the atomic mean square displacement and therefore strongly temperature dependent. Assuming that in first approximation the phonon spectrum can be described by the Debye model, and taking into account that the temperature dependence of IS can be neglected [14], the temperature dependence of CS can be related to the Debye temperature θ_D by

$$\langle CS(T) \rangle = -\frac{3kT}{2mc} \left(\frac{3\theta_D}{8T} + 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \right) \quad (2)$$

where m is the mass of the ^{57}Fe nucleus, k is the Boltzmann constant, c the speed of light, and $x = \hbar\omega/kT$.

In figure 4 the values obtained for the Debye temperature for both the micro-sized and the nano-sized samples of σ -Fe-Cr alloys are shown.

The Debye temperature, θ_D , seems to behave similarly for the two series, namely to increase linearly at the rate of ~ 15 K/at.% with increasing Cr content. The increase of θ_D with x supports the trend which is indicated by the values of the Debye temperature found for ^{57}Fe in $\alpha\text{-Fe}$ ($\theta_D = 331$ K [15]), in $\alpha\text{-Fe}_{55.9}\text{Cr}_{44.1}$ ($\theta_D = 400$ K [16]) and in Cr-rich Cr–Fe alloys ($\theta_D = 445$ K [17]), and reflects the hardening influence of chromium with $\theta_D = 600$ K. However, the rate of increase found here seems to be much faster than that in the α -phase. On the other hand, the θ_D -values determined for the nanocrystalline samples (average grain size between 26 and 78 nm) fit well to the concentration dependence obtained for the bulk Fe–Cr alloys. This may be a hint that surface-induced and/or interface-induced effects, which are known to decrease the Debye temperature [18–21], are of minor importance for the dynamics in these σ -phases. The reason could be either that the size of the nanograins in our samples is still too big or that the nanocrystalline samples form agglomerates consisting of, on average, 10^9 interacting grains, where the dynamic behaviour does not significantly differ from that of the bulk samples.

4. Summary

The Debye temperature, θ_D , was determined for (a) microcrystalline and (b) nanocrystalline series of the sigma-phase Fe–Cr alloys from the dependence of the isomer shift on the temperature. The θ_D -values found for the two series show similar linear composition dependences. The increase of θ_D with Cr content which amounts to ~ 15 K/at.% seems to reflect the hardening influence of chromium, but it is significantly stronger than the similar trend observed for alpha-phase Fe–Cr alloys. The nanosized samples are found to form agglomerates of 10^9 grains, on average.

Acknowledgments

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References

- [1] Bain E C 1923 *Chem. Met. Eng.* **28** 23
- [2] Bergman G and Shoemaker D P 1954 *Acta Crystallogr.* **7** 857
- [3] Algie S H and Hall E O 1966 *Acta Crystallogr.* **20** 142
- [4] Yakel H L 1983 *Acta Crystallogr. B* **39** 20
- [5] Kaspar J S and Waterstrat R M 1956 *Acta Crystallogr.* **9** 289
- [6] Steiner W, Reissner M and Cieslak J 2004 *ILL Report* 5-51-259
- [7] Blower R and Cox G J 1970 *J. Iron Steel Inst.* (August) 769
- [8] Sauthoff G and Speller W 1981 *Z. Metallk.* **72** 462
- [9] Cieslak J, Dubiel S M, Zukrowski J, Reissner M and Steiner W 2002 *Phys. Rev. B* **65** 212301
- [10] Cieslak J, Costa B F O, Dubiel S M, Reissner M and Steiner W 2004 *J. Phys.: Condens. Matter* **16** L345
- [11] Cieslak J, Reissner M, Steiner W and Dubiel S M 2005 *AIP Conf. Proc.* vol 765, p 357
- [12] Cieslak J, Costa B F O, Dubiel S M, Reissner M and Steiner W 2005 *J. Phys.: Condens. Matter* **17** 2985
- [13] Williamson G and Hall W H 1952 *Acta Metall.* **1** 22
- [14] Shrivastava K N 1985 *Hyperfine Interact.* **24–26** 817
- [15] Debrunner P and Morrison R J 1964 *Rev. Mod. Phys.* **4** 63
- [16] Hoare F E and Matthews J C 1958 *Proc. Phys. Soc.* **71** 220
- [17] Kuwano H and Morooka Y 1981 *J. Japan Inst. Met.* **45** 457
- [18] Harada J and Ohshima K 1981 *Surf. Sci.* **106** 51
- [19] Fukaya Y, Kawasuso A, Hayashi K and Ichimiya A 2004 *Appl. Surf. Sci.* **237** 29
- [20] Takeuchi W and Yamamura Y 2001 *Nucl. Instrum. Methods Phys. Res. B* **173** 344
- [21] Durkuanoglu S, Kara A and Rahman T S 2003 *Phys. Rev. B* **67** 235405