Measurement of the Zener Relaxation in High-Purity FeCr Single Crystals

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In binary alloys the measurement of the so-called Zener relaxation may be used as a non-destructive method to determine the activation enthalpy of self diffusion. High-purity FeCr single crystals with a Cr content of 53 at% were prepared by containerless inductive zone melting under Ar atmosphere. The internal friction was measured between temperatures of 300 to 1200 K using an inverted torsion pendulum in the frequency range between 2 and 80 Hz. A strong damping is observed below the Curie temperature of about 600 K due to domain wall motion. Above the ferromagnetic transition temperature a relaxation maximum occurs at about 920 K. The relaxation strength and the activation parameters were determined for single crystals with (100), (110) and (111) orientation. The relaxation can be assigned to the stress-induced reorientation of short-range ordered Fe and Cr atoms, respectively. An analysis yielded an effective activation enthalpy of (2.95 ± 0.3) eV showing no significant dependence on the crystal orientation. The orientation dependence of the relaxation strength and shear modulus indicates that jumps between nearest and next-nearest neighbor sites are involved. These results are compared with results of self-diffusion measurements.

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1. Introduction

Zener¹⁾ discovered that α -brass single crystals exhibit a well-defined internal friction maximum at about 673 K at a frequency of 620 Hz. A few years later, Zener²⁾ proposed that the relaxation is due to a stress-induced reorientation of solute atom pairs in the solute solution. Indeed, this relaxation is a quite general property, which is observed in many alloys of fcc, hcp, and bcc structure (*e.g.* Ref. 3)), and is commonly referred to as the Zener relaxation. Studies of the kinetics of the Zener relaxation provide valuable information on both atomic mobility and microstructural behaviour of binary alloys. In an alloy the rate of atom migration can be determined by the Zener relaxation and since such internal friction measurements are typically performed at lower temperatures than conventional diffusion experiments, the diffusion data may be extended to lower temperatures.

The iron-chromium system, which represents a model system for disordered bcc alloys, is of enormous technical importance due to its use in stainless steels. This also explains why previous work has been concentrated on the Fe-rich side.⁴⁻⁷⁾ In particular, no internal friction measurements on single crystals are available for FeCr alloys with a nearly equiatomic composition, where the Zener effect is expected to be most pronounced. An increase of the Cr content over 35 mass% reduces the ductility due to the formation of the σ phase. Nevertheless, Cr-rich steels may be technologically interesting since high-purity FeCr alloys containing 50 mass%Cr exhibit excellent corrosion resistance.⁸⁾

In the present work, a slightly Cr-rich (53 at%) composition was chosen in order to avoid the formation of the brittle σ phase during thermal cycling and to reduce the Curie temperature.

2. Experimental Procedure

The FeCr alloy was produced by induction melting of Fe and Cr with 99.998% purity in an Al_2O_3 crucible under Ar

atmosphere and casting into Cu molds. After cleaning the surface of the polycrystalline rods, high-purity single crystals were prepared by containerless inductive zone melting under Ar atmosphere (for details of the apparatus see Ref. 9)). Seed crystals with (100), (110), and (111) orientations were used to grow well-oriented long single crystals. The single crystals were cut by spark erosion into suitable shapes for the internal friction measurements (diameter 3 mm, length 40 mm).

The composition of the specimens was determined by chemical analysis to be 47 and 53 at% for Fe and Cr, respectively, with an accuracy of ± 0.5 at%. The content of interstitial impurities of C, N, O, and S was analysed by hot extraction to be very low (Table 1). The bcc structure was proved by powder X-ray diffraction in Bragg-Brentano geometry using Cu $K\alpha$ radiation and a secondary monochromator. Figure 1

Table 1 Contents of interstitial impurities as determined by hot extraction.

Element	C	N	O	S
C (mass ppm)	<10	24 ± 2	<10	7 ± 3

Fig. 1 X-ray diffraction pattern of Fe₄₇Cr₅₃ using Cu $K\alpha$ radiation and a secondary monochromator.

shows the diffraction pattern yielding only the peaks for a bcc structure with a lattice parameter of about 0.288 nm and no indication of any σ phase. Laue micrographs indicated that the deviation of the crystal orientations with respect to the cylindrical axis of the specimens were lower than 2° .

Internal friction measurements were done in an inverted Kê pendulum¹⁰) applying the resonance method. The internal friction Q^{-1} of the sample was determined from the damping of the torsional oscillation with an experimental uncertainty of smaller than 5×10^{-5} . For measuring the internal friction from room-temperature up to 1600 K a specially designed high temperature pendulum was used, which is operated with a radiation heater and a specimen holder of a molybdenum alloy (commercial brand name TZM).

3. Experimental Results

Figure 2 shows the internal friction and modulus defect of a $\langle 110 \rangle$ oriented $\text{Fe}_{47}\text{Cr}_{53}$ single crystal in the temperature range from 500 to 1200 K. At low temperatures a strong

Fig. 2 Internal friction and modulus defect of a $\text{Fe}_{47}\text{Cr}_{53}$ single crystal with torsion axis in $\langle 110 \rangle$ direction.

Fig. 3 Shift of the maximum temperature in dependence of the oscillation frequency for a $\text{Fe}_{47}\text{Cr}_{53}$ single crystal with torsion axis in $\langle 110 \rangle$ direction.

damping is observed, which decreases sharply at about 600 K. This marks the Curie temperature of $\text{Fe}_{47}\text{Cr}_{53}$. Below 600 K the specimen is in the ferromagnetic state accompanied by the division into domains with different directions of the spontaneous magnetization. Owing to the magnetoelastic coupling, the applied external stresses lead to motion of the domain walls and therefore to the large damping observed. Above the ferromagnetic transition temperature a relaxation maximum occurs between 850 and 1050 K. The relaxation maximum is reversible, *i.e.* the maximum appears during heating and cooling cycle and no annealing occurs up to temperatures of 1250 K. For a resonance frequency of 4.7 Hz the maximum is located at about 920 K and this maximum shifts to higher temperature with increasing oscillation frequency (Fig. 3). The relaxation strength of the maximum depends on the crystal

Fig. 4 Internal friction versus temperature for $\text{Fe}_{47}\text{Cr}_{53}$ single crystals with different orientations, $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ for similar oscillation frequencies of about 10 Hz.

Fig. 5 Arrhenius plot of the maximum temperatures determined for different frequencies (see Fig. 3) of a $\text{Fe}_{47}\text{Cr}_{53}$ single crystal with torsion axis in $\langle 110 \rangle$ direction.

Fig. 6 Arrhenius plot of the maximum temperatures determined for different frequencies of a $\text{Fe}_{47}\text{Cr}_{53}$ single crystal with torsion axis in $\langle 111 \rangle$ direction.

Fig. 7 Arrhenius plot of the maximum temperatures determined for different frequencies of a $\text{Fe}_{47}\text{Cr}_{53}$ single crystal with torsion axis in $\langle 100 \rangle$ direction.

orientation with respect to the torsion axis, whereas the maximum temperature shows no difference within the experimental uncertainty. Figure 4 shows the relaxation maximum for three different single crystals possessing $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ orientations measured under the condition of a resonance frequency around 10 Hz. The relaxation strength of the maximum shows the highest value for the $\langle 111 \rangle$ orientation and the lowest for the $\langle 100 \rangle$ orientation.

For all crystal orientations a similar frequency dependence of the maximum temperature is observed, which is characteristic for a thermally activated process. An evaluation assuming an Arrhenius law is shown in Figs. 5 to 7 for the $\langle 110 \rangle$,

$\langle 111 \rangle$, and $\langle 100 \rangle$ orientation, respectively. Within the experimental uncertainty, the activation enthalpy yields the same value of $H = (2.95 \pm 0.3) \text{ eV}$ and the pre-exponential factor possesses a value of $\tau_0 = 3 \times 10^{-18 \pm 1} \text{ s}$.

4. Discussion

4.1 Zener relaxation and self diffusion

Above the Curie temperature high-purity $\text{Fe}_{47}\text{Cr}_{53}$ single crystals exhibit a characteristic relaxation maximum at about 920 K (frequency 4.7 Hz). This maximum is reversible and thermally activated indicating its intrinsic nature. In binary alloys forming a substitutional solute solution, the Zener relaxation is a quite common feature in single crystals, where no interfering grain boundary relaxations occur. In $\text{Fe}_{76.2}\text{Cr}_{23.8}$ Tanaka^{6,7} observed a relaxation maximum at about 850 K (frequency 1 Hz) by internal friction measurements, which he attributed to the Zener relaxation. Therefore, the observed relaxation maximum in $\text{Fe}_{47}\text{Cr}_{53}$ is assigned to the stress-induced reorientation of short-range ordered Fe and Cr atoms, *i.e.* the Zener relaxation. This reorientation occurs with vacancies as vehicles. A comparison with self-diffusion data is of particular interest, as the vacancy-assisted reorientation of atom pairs represents the same elementary process as for self diffusion in metals and disordered alloys. With the Zener relaxation involving only one or two atomic jumps, internal friction measurements provide an access to the diffusion properties at temperatures lower than accessible by tracer techniques, which involve long-range migration.

The pre-exponential factor for diffusion is given by $D_0 = \alpha a^2 \omega_0$, where α is a numerical constant, a the lattice parameter, and ω_0 the pre-factor of the diffusional jump rate between specific sites.³⁾ For substitutional diffusion in the bcc lattice $\alpha = 1$. For a relaxation process $\tau_0^{-1} = \beta \omega_0$, where τ_0 denotes the period of the Zener relaxation and β a numerical factor involving the number of equivalent diffusion paths to achieve reorientation. The weak orientation dependence indicates that different defect symmetries are involved in the relaxation process and thus the value of β can only be estimated to be of the order of 10, which is a typical value for point defect relaxations. Therefore, the experimental results yield an estimated pre-exponential factor for diffusion of $D_0 = 4 \times 10^{-3 \pm 1} \text{ m}^2/\text{s}$.

In the case of the present work on single crystalline $\text{Fe}_{47}\text{Cr}_{53}$, both the activation enthalpy H and the pre-exponential factor D_0 show no significant difference to self-diffusion data for ^{59}Fe and ^{51}Cr tracers in $\text{Fe}_{49}\text{Cr}_{51}$ ¹¹⁾ (see Table 2).

4.2 Relaxation strength and defect symmetry

While the activation enthalpy H shows no noticeable dependency on the crystal orientation (see Figs. 5 to 7), the relaxation strength of the maximum shows the highest value for the $\langle 111 \rangle$ orientation and the lowest for the $\langle 100 \rangle$ orientation (Fig. 4). A quantitative analysis of the relaxation strength Δ was done by a numerical fit with the assumption, that the broadening of the relaxation maximum is due to a superposition of Debye maxima (for detail see Ref. 12)). For $\langle 111 \rangle$ orientation the relaxation strength Δ is 2.5 times larger than the value for the $\langle 100 \rangle$ orientation (Table 3).

Table 2 Comparison of activation enthalpy H and pre-exponential factor D_0 determined by Zener relaxation in Fe₄₇Cr₅₃ (present work) and by self-diffusion experiments using ⁵⁹Fe and ⁵¹Cr tracers in Fe₄₉Cr₅₁.¹¹⁾

Composition	Technique	H (eV)	D_0 (m ² /s)
Fe ₄₇ Cr ₅₃	Zener rel.	2.95 ± 0.3	$4 \times 10^{-3 \pm 1}$
Fe ₄₉ Cr ₅₁	⁵¹ Cr tracer	3.05	4.0×10^{-3}
Fe ₄₉ Cr ₅₁	⁵⁹ Fe tracer	3.24	2.5×10^{-3}

Table 3 Experimental results of the relaxation strength Δ , the relative shear modulus $G/G_{(111)}$, and the relative relaxation amplitude $\delta G^{-1}/\delta G_{(100)}^{-1}$ for Fe₄₇Cr₅₃ single crystals with different orientations. Theoretical predictions for the relaxation amplitude δG^{-1} of defects possessing trigonal and tetragonal symmetry^{3,13)} (given in arbitrary units).

Orientation	(100)	(110)	(111)
Experimental results			
Δ	6×10^{-3}	13×10^{-3}	15×10^{-3}
$G/G_{(111)}$	1.7	1.1	1.0
$\delta G^{-1}/\delta G_{(100)}^{-1}$	1.0	1.4	1.5
Theoretical predictions			
Trigonal: δG^{-1} (a.u.)	1.00	0.54	0.33
Tetragonal: δG^{-1} (a.u.)	0.00	0.69	1.00

The torsional shear modulus G shows an inverse behavior in comparison to the relaxation strength $\Delta = \delta G^{-1}/G^{-1}$, as indicated by a noticeable shift of the accessible frequency range to lower values in case of the (111) specimen orientation. The shear modulus G is directly proportional to the square of the resonance frequency, therefore the shear moduli of different specimens possessing the same geometry may be compared by measuring the resonance frequency for an identical mechanical setup of the internal friction apparatus. For the single crystals with (100), (110), and (111) orientation a comparison of the resonance frequency $f_{\max}$ at the maximum temperature was performed in this manner for three different configurations of the setup yielding each an estimated ratio of $G_{(100)} : G_{(110)} : G_{(111)} = 1.7 : 1.1 : 1.0$ (Table 3). These ratios between the different orientations are very similar to the findings of Masumoto and Kikuchi⁵⁾ on single crystals of Fe_{80.6}Cr_{19.4}. No significant change of the torsional shear modulus G is expected for different levels of Cr content, as the bcc structure and the lattice parameters remain practically unchanged.

With the relaxation strength Δ and the torsional shear modulus G showing an inverse tendency in relation to the crystal orientation of the Fe₄₇Cr₅₃ single crystals, the relaxation amplitude δG^{-1} shows only a weak orientation dependency with relative values of $\delta G^{-1}/\delta G_{(100)}^{-1} = 1.0, 1.4$ and 1.5 for the (100), (110) and (111) orientations, respectively (Table 3).

Zener²⁾ assumed in his nearest-neighbor pair model only these reorientations, however, the reorientation of next-nearest-neighbor pairs may as well contribute to the relaxation. The defect symmetries for nearest-neighbor and next-nearest-neighbor pairs in the bcc lattice are trigonal and tetragonal, respectively.³⁾ A comparison of the dependence of the relaxation strength on the orientation parameter between the experimental results and theoretical predictions for trig-

Fig. 8 Change of the relative relaxation amplitude $\delta G^{-1}/\delta G_{(100)}^{-1}$ versus the orientation parameter for Fe₄₇Cr₅₃ single crystals with different orientations (upper part) and theoretically expected orientation dependence of the relaxation amplitude δG^{-1} for defects possessing trigonal and tetragonal symmetry^{3,13)} (lower part).

onal and tetragonal defect symmetries^{3,13)} (see Table 3 and Fig. 8) indicates that both nearest-neighbor and next-nearest-neighbor pair reorientations are contributing to the relaxation process.

5. Conclusions

High-purity Fe₄₇Cr₅₃ single crystals with (100), (110) and (111) orientation were prepared by containerless inductive zone melting. No indication of any σ phase was found by X-ray diffraction measurements. Above the Curie temperature of about 600 K, internal friction measurements exhibit a Zener relaxation maximum at about 920 K (frequency 4.7 Hz), which is due to the stress-induced reorientation of short-range ordered Fe and Cr atoms. The activation enthalpy of $H = (2.95 \pm 0.3)$ eV and the pre-exponential factor of $D_0 = 4 \times 10^{-3 \pm 1}$ m²/s are comparable to measurements of self diffusion in Fe₄₉Cr₅₁.¹¹⁾ The weak orientation dependence of the relaxation amplitude indicates that jumps between nearest and next-nearest neighbor sites are involved in the relaxation process.

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