Composition Dependence of the Zener Relaxation in High-Purity FeCr Single Crystals

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High-purity FeCr single crystals with Cr contents between 34 at% and 60 at% and orientations close to the (111) direction 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 due to domain wall motion. Above the ferromagnetic transition temperature a relaxation maximum occurs at about 950 K. This relaxation can be assigned to the so-called Zener relaxation which is due to the stress-induced reorientation of short-range ordered Fe and Cr atoms, respectively. An analysis yielded an effective activation enthalpy of $3.1 \pm 0.3$ eV showing no significant dependence on the composition. The relaxation strength shows a maximum value near the equiatomic composition and decreases for lower and higher Cr contents. Furthermore, the influence of the $\sigma$ phase on the internal friction and the dynamic torsional shear modulus was studied on a single crystal with a Cr content of 48 at%. After annealing for 24 h at 973 K the torsional shear modulus increases with temperature up to over 1000 K, indicating a hardening due to precipitates of the $\sigma$ phase.

Keywords: FeCr, internal friction, diffusion, Zener relaxation, single crystals

1. Introduction

Many alloys of fcc, hcp, and bcc structure exhibit a well-defined internal friction maximum which is due to a stress-induced reorientation of solute atom pairs in the solid solution (e.g. Ref. in 1)). Owing to its discovery and first interpretation by Zener this relaxation 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.2–5) An increase of the Cr content over 35 mass % reduces the ductility due to the formation of the $\sigma$ phase. Nevertheless, Cr-rich steels may be technologically interesting since high-purity FeCr alloys containing 50 mass %Cr exhibit excellent corrosion resistance.6) Recently, we presented first internal friction measurements on Fe$_{47}$Cr$_{53}$ single crystals exhibiting the Zener relaxation.7)

In the present work, the composition dependence of the Zener relaxation was studied on high-purity FeCr single crystals with a Cr content between 34 at% and 60 at%. Additionally, the influence of the $\sigma$ phase on the internal friction and the dynamic torsional shear modulus was studied on a single crystal with a Cr content of 48 at%.

2. Experimental Procedure

The FeCr alloy was produced by induction melting of Fe and Cr with 99.998% purity in an Al$_2$O$_3$ 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. 8)). Well-oriented long single crystals were grown using seed crystals with (111) orientation. The single crystals were cut by spark erosion into suitable shapes for the internal friction measurements (diameter 3 mm, length 40 mm).

The Fe and Cr composition of the specimens was determined by chemical analysis utilizing X-ray florescence spectroscopy (XRF) and inductive-coupled plasma optical-emission spectroscopy (ICP-OES). The typical accuracy is about ±0.5 at% and the results are shown in Table 1. The content of interstitial impurities of C, N, O, and S was analysed by hot extraction to be very low (Table 2). For all compositions the bcc structure was proved by powder X-ray diffraction in Bragg-Brentano geometry using Cu Kα radiation and a secondary monochromator. In the as-grown state the diffraction pattern yielded only peaks for a bcc structure and no indi-

<table>
<thead>
<tr>
<th>Cr (at%)</th>
<th>33.8</th>
<th>40.2</th>
<th>47.9</th>
<th>53.4</th>
<th>59.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (at%)</td>
<td>66.2</td>
<td>59.8</td>
<td>52.1</td>
<td>46.6</td>
<td>40.2</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>878</td>
<td>835</td>
<td>763</td>
<td>668</td>
<td>536</td>
</tr>
</tbody>
</table>

Table 1 Results of the Fe and Cr content gained by chemical analysis and the Curie temperature, $T_c$, determined by magnetization measurements using the kink-point method.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (mass ppm)</td>
<td>&lt; 10</td>
<td>24 ± 2</td>
<td>&lt; 10</td>
<td>7 ± 3</td>
</tr>
</tbody>
</table>

Table 2 Content of interstitial impurities as determined by hot extraction.
cation of any σ phase. Laue micrographs indicated that the deviation of the crystal orientation with respect to the cylindrical axis of the specimens was smaller than 2° to the (111) direction showing that the orientation of the seed crystal could be preserved during the growth process.

Additionally, the Curie temperature was determined by magnetization measurements using the kink-point method with a magnetic field of 0.1 mT applied perpendicular to the (111) direction. The Curie temperature, $T_C$, is decreasing with increasing Cr content as shown in Table 1.

Internal friction measurements were done in an inverted Ké pendulum\(^9\) 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 $5 \times 10^{-5}$. 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 and Discussion

#### 3.1 Zener relaxation and self diffusion

Figure 1 shows the internal friction and modulus defect of a (111) oriented Fe\(_{40}\)Cr\(_{60}\) single crystal in the temperature range from 400 to 1200 K. At low temperatures a strong damping is observed, which decreases sharply at about 500 K. This marks the Curie temperature of Fe\(_{40}\)Cr\(_{60}\). Below 500 K the specimen is in the ferromagnetic state accompanied by the division into domains with different directions of the spontaneous magnetization. Owing to the magnetoeelastic 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 1250 K. For a resonance frequency of 12 Hz the maximum is located at about 940 K and this maximum shifts to 1250 K. For a resonance frequency of 12 Hz the relaxation maximum is reversible, and the relaxation strength shows a maximum near the equiatomic composition and decreases for lower and higher Cr contents. An analysis of the activation parameters yields the values given in Table 3, which show no dependence on the composition of the alloy. The average over all compositions measured gives an activation enthalpy of $H = (3.04 \pm 0.3)$ eV and a pre-exponential factor of $\tau_0 = 1.4 \cdot 10^{-18} \text{s}$.

With increasing Fe content of the alloy, the internal friction spectrum looks similar. The decrease of the strong domain wall damping in the ferromagnetic state shifts to higher temperatures according to the higher Curie temperature with increasing Fe content (see Table 1). The characteristic relaxation maximum occurs in the same temperature range independent of composition, whereas the relaxation strength shows a maximum near the equiatomic composition and decreases for lower and higher Cr contents. An analysis of the activation parameters yields the values given in Table 3, which show no dependence on the composition of the alloy. The average over all compositions measured gives an activation enthalpy of $H = (3.1 \pm 0.3)$ eV and a pre-exponential factor of $\tau_0 = 2 \cdot 10^{-19} \text{s}$.

This characteristic relaxation maximum, occurring in high-purity FeCr single crystals, is reversible and thermally activated indicating its intrinsic nature. In binary alloys forming a substitutional solid solution, the Zener relaxation is a quite common feature in single crystals, where no interfering grain boundary relaxations occur. In Fe\(_{76.2}\)Cr\(_{23.8}\) Tanaka\({}^4,5\) 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 is assigned to the stress-induced reorientation of short-
range ordered Fe and Cr atoms, i.e. the Zener relaxation. Figure 3 shows the relaxation strength for the different alloy compositions exhibiting a maximum near the equiatomic composition. According to the theory of the Zener relaxation by LeClaire and Lomer, the relaxation strength is proportional to $X^2(1 - X)^2$, where $X$ is the mole fraction of solute atoms. Owing to the few compositions measured and the experimental errors, the functional dependence on the concentration could not be analysed; however, a maximum of the relaxation strength is observed near the equiatomic composition as predicted. Furthermore, this reorientation could not be observed, and the difference in the relaxation strength is observed near the equiatomic composition as predicted. Therefore, the experimental results yield an estimated pre-exponential factor for diffusion of $D_0 = 4.4 \times 10^{-2} \text{m}^2/\text{s}$.

The results obtained by internal friction measurements on high-purity FeCr single crystals are comparable to results measured by self-diffusion experiments using $^{59}\text{Fe}$ and $^{51}\text{Cr}$ tracers (see Table 4).

### 3.2 Formation of $\sigma$ phase

Figure 4 shows the internal friction spectrum of a (111) oriented Fe$_{52}$Cr$_{48}$ single crystal in the as-grown state, after a heat treatment at 973 K for 24 h and after a further annealing at 1273 K for 24 h.

The pre-exponential factor for diffusion is given by $D_0 = a \alpha^2 \tau_0$, where $\alpha$ is a numerical constant, $a$ the lattice parameter, and $\tau_0$ the pre-factor of the diffusional jump rate between specific sites. For substitutional diffusion in the bcc lattice $\alpha = 1$. For a relaxation process $\tau_0^{1/2} = \beta \omega_0$, where $\tau_0$ denotes the period of the Zener relaxation and $\beta$ a numerical factor involving the number of equivalent diffusion paths to achieve reorientation. In a previous paper only a weak orientation dependence of the relaxation strength on the crystal orientation was observed, indicating that different defect symmetries are involved in the relaxation process and thus the value of $\beta$ 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 $D_0 = 4.4 \times 10^{-2} \text{m}^2/\text{s}$.

The results obtained by internal friction measurements on high-purity FeCr single crystals are comparable to results measured by self-diffusion experiments using $^{59}\text{Fe}$ and $^{51}\text{Cr}$ tracers (see Table 4).

### Table 4 Comparison of activation enthalpy $H$ and pre-exponential factor $D_0$ determined by Zener relaxation in high-purity single crystals with compositions ranging from Fe$_{66}$Cr$_{33}$ to Fe$_{40}$Cr$_{59}$ (present work) and by self-diffusion experiments using $^{59}\text{Fe}$ and $^{51}\text{Cr}$ tracers in Fe$_{49}$Cr$_{51}$ and Fe$_{48.5}$Cr$_{51.5}$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Technique</th>
<th>$H$ (eV)</th>
<th>$D_0$ (m$^2$/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{66}$Cr$</em>{33}$</td>
<td>Zener rel.</td>
<td>3.13 ± 0.3</td>
<td>$4.4 \times 10^{-2}$</td>
<td>this work</td>
</tr>
<tr>
<td>Fe$<em>{49}$Cr$</em>{51}$</td>
<td>$^{51}\text{Cr}$ tracer</td>
<td>3.05</td>
<td>$4.0 \times 10^{-3}$</td>
<td>11</td>
</tr>
<tr>
<td>Fe$<em>{49}$Cr$</em>{51}$</td>
<td>$^{59}\text{Fe}$ tracer</td>
<td>3.24</td>
<td>$2.5 \times 10^{-3}$</td>
<td>11</td>
</tr>
<tr>
<td>Fe$<em>{48.5}$Cr$</em>{51.5}$</td>
<td>$^{51}\text{Cr}$ tracer</td>
<td>2.60</td>
<td>$5.4 \times 10^{-5}$</td>
<td>12</td>
</tr>
<tr>
<td>Fe$<em>{48.5}$Cr$</em>{51.5}$</td>
<td>$^{59}\text{Fe}$ tracer</td>
<td>2.52</td>
<td>$3.0 \times 10^{-5}$</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 3 Composition dependence of the relaxation strength of the Zener relaxation in FeCr single crystals with torsion axis in (111) direction.
ing with temperature up to over 1000 K. After annealing at 1273 K the temperature dependence of the modulus is again very similar to the one in the as-grown state.

According to the phase diagram, for a Cr content of 48 at% the $\sigma$ phase is formed below a temperature of about 1093 K. Owing to the low atomic mobility at these temperatures far below the melting point of about 1850 K, the formation of the $\sigma$ phase is very slow. This is especially in high-purity single crystals the case due to the low number of defects acting as nucleation sites. Nevertheless, after 24 h heat treatment in this temperature region, i.e. at 973 K, the internal friction measurements give evidence for the formation of precipitates of the $\sigma$ phase. In the ferromagnetic region the domain wall damping is reduced due to Bloch wall pinning by these precipitates. The increase of the dynamic torsional shear modulus with temperature up to over 1000 K clearly indicates a precipitation hardening.

After further annealing 24 h at temperatures above the existence region of the $\sigma$ phase, i.e. 1273 K, the internal friction spectrum and the temperature dependence of the dynamic shear modulus are again almost similar to the as-grown single crystal indicating the dissolving of the precipitates of the $\sigma$ phase. The increasing damping at temperatures above 1000 K may be due to dislocation climb since after formation and dissolving of the $\sigma$ phase the dislocation density may be higher.

4. Conclusions

High-purity FeCr single crystals with Cr contents between 34 at% and 60 at% and orientations close to the (111) direction were prepared by containerless inductive zone melting under Ar atmosphere. Below the Curie temperature internal friction measurements show a strong damping due to domain wall motion. Above this transition temperature the internal friction exhibits a Zener relaxation maximum, which is due to the stress-induced reorientation of short-range ordered Fe and Cr atoms. The relaxation strength shows a maximum value near the equiatomic composition and decreases for lower and higher Cr contents. The effective activation enthalpy of $(3.1 \pm 0.3)$ eV is nearly independent of the alloy composition and comparable to self diffusion measurements. Furthermore, annealing the crystal with a Cr content of 48 at% at 973 K for 24 h leads to the formation of the $\sigma$ phase and to precipitation hardening as indicated by the increase of the torsional shear modulus with increasing temperature.

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REFERENCES