Relaxation Mechanisms in Fe-Al-C Alloys

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The relaxation spectrum of Fe-Al alloys has been studied as a function of Al content and ordering reaction in Fe-Al. Three types of relaxation peaks are observed, with activation energies between 0.8 and 3 eV. Snoek-type relaxation is studied in Fe-(0 to 50 at. pct)Al and compared with the Snoek relaxation in pure iron (C in α-Fe), chromium (C in Cr), and niobium (O in Nb). The snoek-type relaxation peak in iron (at 314 K for 1 Hz) shifts to higher temperatures with increasing Al content in iron. Significant changes in the peak parameters occur when α-Fe is alloyed with Al, because of the ordering reaction in Fe-Al. Peculiarities of the carbon-atom distribution in ordered and disordered Fe-Al alloys are discussed using an atom-interaction model, in which the elastic interaction is supplemented by the chemical C-Al interaction. Two other peaks are observed only when a certain Al content is exceeded: a Zener peak for Fe-(>10 pct)Al and an X peak for Fe-(>26 pct)Al. Parameters of these peaks are discussed with respect to alloy structure. Three hypotheses are discussed for the X-peak mechanism with an activation energy about 1.7 eV. A map of relaxation peaks in the Fe-Al system is constructed.

I. INTRODUCTION

IRON-RICH alloys of the Fe-Al system are widely used because of their favorable combination of mechanical, magnetic, and dissipative properties. Besides their application as a functional material, Fe-Al alloys are attractive for structural applications because they show higher strength than iron, high corrosion resistance, and are relatively inexpensive. Binary Fe-Al alloys containing sufficient Al content may produce long-range ordering of two types: D03 (Fe3Al) and B2 (FeAl). The Fe3Al phase is stable at lower temperatures, while the FeAl phase is stable at higher temperatures for Al < 35 pct. At high temperatures, Fe-Al is a disordered bcc solid solution (designated A2). In contrast to the many studies of long-range ordering in binary Fe-Al alloys (e.g., References 1 through 4), a limited number of articles have examined carbon-atom short-range ordering accompanying D03 or B2 ordering[5,6,7] and the corresponding dissipative properties. The use of an internal-friction method allows a study of the parameters of carbon-atom diffusion and short-range order caused by the Fe-Al order-disorder transition.[8−11] The loss maximum (Q−1) for the relaxation peak and, in particular, for stress-induced jumps of interstitial atoms in bcc metals (known as Snoek relaxation[12]), is described by the Debye equation:[13]

\[ Q^{-1} = \Delta \cdot \frac{\omega \tau}{1 + (\omega \tau)^2} \]  

where \( \Delta \) is the relaxation strength, \( \omega = 2\pi f \), and \( f \) is the measuring frequency. In practice, it is usual to measure \( Q^{-1} \) vs \( T \) (T being the temperature). The jump of carbon (C) atoms under stress in Fe-based alloys is the elementary step of carbon diffusion, and its temperature dependence is described by the well-known Arrhenius equation:

\[ \tau = \tau_0 + \exp \left( \frac{H k_B T}{k_B T_{m}} \right), \]

where \( H = 0.84 \pm 0.04 \) eV was determined by magnetic after-effect spectroscopy.[16] A Zener peak caused by stress-induced reorientation of solute metallic atom pairs in solid solution is observed in Fe-Al alloys, with an activation energy of about 2.5 eV (\( H \) depends on the percentage of Al). Another relaxation peak between the Snoek and the Zener effects has been recently reported in the literature, but its origin is not well explained. All relaxation peaks in Fe-Al are broader than the single Debye peak.[5−11]

In Fe-Al, as in other alloys, there is a set of nonequivalent energy positions for the interstitial (e.g., carbon) atoms because of their interaction with substitute atoms. In such a case, the lognormal spectrum of the relaxation-time (\( \tau \)) distribution for continuous spectra is almost always used.[13,17–19] In that case, the Snoek peak measured at different temperatures for a fixed frequency is described as[18,19]

\[ Q^{-1}(T) = Q_{m}^{-1} \cosh^{-1} \left( \frac{H}{k_B \tau_2(\beta)} \left( \frac{1}{T} - \frac{1}{T_m} \right) \right) \]

where \( Q_{m}^{-1} \) is the peak height, \( T_m \) is the peak temperature, \( B \) is the width of the relaxation-time distribution, \( \tau_2(\beta) = \Delta T^{-1}(\beta)/\Delta T^{-1}(\beta = 0) \) is the width of a single Debye peak in terms of temperature. Broadening of the Snoek peak with respect to a Debye peak with a single relaxation time (for a single relaxation time of \( \beta = 0 \) and \( \tau_2(\beta = 1) \) is calculated on the assumption that symmetrical broadening is caused by a lognormal distribution of relaxation times[13]
due to a distribution of C atoms in different positions in solid solution. For an analytical description of the broadened relaxation peak, one should know the activation energy, peak height, and width parameter. The methods used for evaluation of C-atom energies and distribution on the basis of Snoek relaxation have been discussed.[11–16]

The purpose of this article is to bring the results on internal friction together with structural study and computer simulations for specimens with different compositions in binary Fe-Al alloys that undergo different order-disorder reactions on heating. The aim is to explain quantitatively the parameters of the relaxation peak observed by corresponding short-range atom distributions. Special attention is paid to the question of peak stability during measurement. In addition, the experimental results of this article are compared with available data from the literature.

### II. MATERIALS, EXPERIMENTAL TECHNIQUE, AND CALCULATION METHOD

Most of the Fe-Al specimens used this article (Table I, all concentrations are given in atomic percent) were vacuum melted in an induction furnace using refined iron and A99-grade aluminium, annealed, and spark machined. Then, the specimens were water quenched* after tempering for 60 minutes in a protective atmosphere at different temperatures between 720 °C and 1100 °C, followed by aging at different temperatures (200 °C to 560 °C, depending on Al content). The specimens used might be roughly divided into three groups, namely, 12 and 16 pct Al with an A2 structure and short-range ordering at low temperatures (so-called K1 state); 20 to 22 pct Al with an A2-D03 ordered structure; and 28 to 35 pct Al with A2-B2(D2-D03) transitions, depending on temperature. "Pure" chromium and niobium specimens were also used for comparison with Fe-Al alloys.

Internal-friction measurements were carried out by means of low-frequency free-decay vibration in (1) an inverted torsion pendulum (f = 1 to 4 Hz, magnetic field of 2 · 10^4 A/m, pressure of ≈3 Pa, and heating rate of 2 K/min) using thin bars measuring 80 × 1 × 1 mm^3 under a surface deformation of γ₀ ≈ 3 × 10^-5; and in (2) a torsion pendulum (f = 30 to 90 Hz, magnetic field of 2.4 · 10^4 A/m, pressure of ≈0.01 Pa, and heating rate of 2 to 4 K/min) using double-blade-shaped specimens with a working diameter of 2.5 mm and working length of 18 to 25 mm, under a surface deformation of γ₀ ≈ 5 × 10^-5. Activation energies of relaxation peaks were determined by the temperature-frequency (Tf) shift:

\[ H = (RT_m T_m ln (f_n/f_m))/(T_m - T_{m1}) \]  \[ \text{[3a]} \]

and by the Marx–Wert equation:

\[ H = RT_m ln (k_b T_m / h f_m) + T_m \Delta S \]  \[ \text{[3b]} \]

where R and h are the universal gas and Planck constants, respectively.

Equation [3a] is used to deduce the activation energy only in the case where the peak-temperature shift caused by change in frequency does not change the specimen microstructure. This is not always true for the Fe-Al system.

The Snoek relaxation is treated in terms of an atom-interaction model, in which a long-range strain-induced interatomic interaction according to the Khachaturyan method[20] is supplemented by a short-range "chemical" C-Al interaction and a screened Coulomb C-C repulsion.[21–24] This approach is helpful for internal-friction studies when the "first-principle" calculations of energy distribution are absent. This has been applied for an internal-friction application in different bcc[19,25–27] and fcc[22,28,29] alloys by Blanter and Golovin. Coupling effects from C-C atom interaction, considered in References 30 and 31, are neglected because of the low carbon content in the present alloys. The C-Al interaction influences the distribution of C atoms and creates a short-range order around the Al atoms. This changes the energy of C atoms in the octahedral interstices. A short-range chemical interaction, i.e., the interatomic chemical forces, must be assumed, because it is not known for real materials. For this reason, the Lennard–Jones potential (the pairwise-additive interaction potential \( U(r_{min}) \sim r^2 \) where \( r_{min} \) is the distance between C and Al atoms) is employed as the best simple potential for qualitative insight into the phenomena,[32] and the value of the C-Al chemical interaction in the first shell \( (H_{ch}(1)) \) is the single fitting parameter of this model. Energies of strain-induced (elastic) pair interactions were computed for five coordination shells in Reference 24. The atom energies and distribution in the lattice are calculated by the Monte Carlo method. The change in the energies of dissolved atoms in a solid solution caused by atom interactions influences the diffusion and relaxation parameters. Interstitial atoms (in our case, C atoms) create a distortion field of tetragonal symmetry in octahedral interstices in the bcc lattice, which are characterized by the values \( \lambda_1 \) and \( \lambda_2 \), used for internal-friction simulations.[13]

Transmission electron microscopy (TEM) samples were prepared from 3 mm discs punched out from thin slices (150 µm) cut from the specimen. The discs were electrochemically thinned by twin-jet polishing using an electrolyte containing 640 ml methanol, 300 ml glycerine, and 600 ml perchloric acid. Thinning was carried out at -20 °C at a voltage of 27 V. Specimens were examined in a PHILIPS* CM12 microscope operating at 120 kV. Dark-field imaging with [111] reflections in the (110) beam direction was used to image the ordered domains of Fe₃Al. The thermal analyses were done using a Perkin-Elmer DSC7 differential scanning calorimeter with a heating-cooling rate of 5 K/min in the temperature range up to 700 °C.

### Table I. Al and C Content in Different Fe-Al Alloys

<table>
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<tr>
<th>At. pct Al</th>
<th>11.7</th>
<th>16.3</th>
<th>19.6</th>
<th>21.7</th>
<th>22.5</th>
<th>28.4* (+2.7 pct Cr)</th>
<th>31.5</th>
<th>35.0</th>
<th>40.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>At. pct C</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.16</td>
<td>0.075</td>
<td>0.03</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Al28.44, Cr2.65, Mn0.40, and Ce0.02 (at. pct).