Extraordinary Snoek Damping in an Fe-Mn-N Alloy

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Extraordinary Snoek damping was examined in an Fe-2 pct Mn-0.01 pct N alloy over a temperature range of -50°C to 290°C. The complex damping spectrum is composed of a relatively small nitrogen Snoek peak and a series of at least four extraordinary Snoek peaks that lie between 7°C and 135°C at 1 Hz. The low-temperature peak (at 7°C for 1 Hz) was investigated in some detail by varying the frequency between 0.19 and 2.5 Hz and by analyses of the peak shape. The peak-shift analyses give an activation energy of 17.1 kcal per mole, which is 2 to 3 kcal per mole more than that given by the peak-shape analyses. Therefore, the low-temperature peak is not characterized by a single relaxation time. Furthermore, analyses of a series of synthetic curves indicated that the low-temperature peak can be characterized by two relaxation times with the strength of one relaxation being about 15 pct of the other. The activation energy of 17.1 kcal per mole is in excellent agreement with the previously proposed proportionality between peak temperature and activation energy of relaxation peaks. The present findings are in general consistent with the model for the low-temperature peak that envisions a nitrogen atom jumping about a pair of manganese atoms.

INTERSTITIAL elements in solution strongly affect many properties of bcc metals. The most reliable method of determining the type and amount of interstitials in solution is Snoek damping. However, damping investigations have revealed complex interactions between interstitial and substitutional elements in ternary bcc alloys. It is logical to suspect that such interactions will affect the properties of these alloys and, in fact, it has been shown that the strain aging of Fe-Mn-N alloys is affected by the interaction between manganese and nitrogen. As a step toward a more complete understanding of substitutional-interstitial systems in general, and Fe-Mn-N in particular, we shall in this paper consider in detail a part of the damping spectrum of Fe-2 pct Mn-N.

Snoek damping, which is caused by the stress-induced ordering of interstitial atoms in bcc metals, is satisfactorily described by the Debye equation:

\[ \Delta = 2\Delta_m \left( \frac{T_p}{T} \right) \omega T / [1 + (\omega T)^2] \]  

or, alternatively, since one can assume \( \tau = \tau_0 \exp (H/RT) \)

\[ \Delta = \Delta_m \left( \frac{T_p}{T} \right) \cosh \left[ \frac{H}{R} \left( \frac{1}{T} - \frac{1}{T_p} \right) \right] \]  

where \( \Delta \) is Snoek damping, \( \Delta_m \) is maximum Snoek damping, which occurs at \( \omega T = 1 \), \( \omega \) in angular frequency of vibration, \( \tau \) is a relaxation time, \( \tau_0 \) is a constant, \( H \) is the activation energy of the relaxation (which is caused by interstitial diffusion), \( R \) is the gas constant, \( T \) is the absolute temperature, and \( T_p \) is the temperature at the peak. Eq. [3] has proved useful analytically because \( \Delta_m \) is proportional to the number of interstitial atoms in solution.

Complex damping spectra with additional damping peaks called extraordinary Snoek peaks have been observed in a number of interstitial-substitutional ternary bcc alloys. It is generally believed that the extraordinary peaks are caused by the interstitial atoms jumping into and out of special sites adjacent to the substitutional atoms.

Several investigators of Fe-Mn-N and other systems have been partially successful in resolving the complex spectra into a series of perfect Debye peaks, that is, by the equation,

\[ \Delta = \sum_i \Delta_i \left( \frac{T_p}{T} \right) \cosh \left[ \frac{H_i}{R} \left( \frac{1}{T} - \frac{1}{T_p} \right) \right] \]  

In their approach, \( H_i, T_i \), and the number of peaks, \( i \), are essentially adjustable parameters that are taken as independent of chemical composition. Eq. [4] implies that the partition of nitrogen among the various sites (e.g., zero, one or two manganese near neighbors) is independent of temperature, but recent work suggests that this partition is quite probably temperature dependent.

In Fe-Mn-N alloys with greater than 1.5 pct Mn the low-temperature peak is predominant, and its \( H \) can be obtained by the shift of the peak with a frequency change, as well as by peak-shape analysis. Table I summarizes the published data on the low-temperature peak in Fe-Mn-N alloys. Not only is the reported

<table>
<thead>
<tr>
<th>Reference</th>
<th>( T_p ), °C</th>
<th>( H_p ), kcal per mole</th>
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<tr>
<td>Enrietto 9</td>
<td>7</td>
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<td>Gladman</td>
<td>11</td>
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<td>2</td>
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<td>Jancke et al. 10</td>
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<tr>
<td>Ritchie and Rawlings 11</td>
<td>7</td>
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<td>Ritchie 13</td>
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<td>17.5</td>
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<td>Cooper</td>
<td>7</td>
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<td>and Kennedy 22</td>
<td>7</td>
<td>17.0</td>
<td>Peak-shape analysis</td>
</tr>
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*\( T_p \) adjusted to one Hz by Eq. [3] with given \( H_p \).
†Low-temperature peak composed of two discrete relaxations of about equal strength.
range in $H_i$ rather large, but previous investigators have variously characterized the low-temperature peak as resulting from a single $\tau$\textsuperscript{11,12} two $\tau$ values,\textsuperscript{11,16} and a continuous distribution of $\tau$\textsuperscript{11,17}.

The purpose of the present investigation was to determine the activation energy of the extraordinary Snoek peak that occurs at about 7°C and 1 Hz in a Fe-2 pct Mn-N alloy. This purpose necessitated establishing whether the low-temperature peak would be better characterized as a single-$\tau$ peak or in some other manner. The $H_i$ and $T_2$ were estimated by the shift of the peak with frequency and by several peak-shape analysis methods. The results were compared with previous results from other systems to find out whether the Wert-Marx Rule\textsuperscript{18} applies to extraordinary Snoek peaks. In addition, an estimate was made of the minimum number of peaks required to characterize the damping spectrum of an Fe-2 pct Mn-N alloy, and the effect of a temperature dependence in the partition of nitrogen among various sites was considered.

**EXPERIMENTAL**

Wire specimens were prepared from a vacuum-melted ingot of the following composition in wt pct: 0.015 C, 2.0 Mn, 0.002 P, 0.005 S, 0.004 Al, 0.004 Ti, 0.001 Sn, and less than 0.01 of Si, Ni, Cr, Mo, Cu, and V. The ingot was hot rolled to $\frac{3}{8}$ in. plate, machined to a $\frac{3}{8}$ in. diam cylinder, and then swaged and drawn to 0.037 in. diam wires. The wires were decarburized by annealing in wet hydrogen at 700°C for 8 hr, and were subsequently nitrided at 700°C for 3 days in a Vycor capsule with a small amount of ammonia. This treatment yielded about 0.01 wt pct N. The wires were resealed in evacuated Vycor capsules, solution-treated at 700°C, and brine quenched.

Several wires were treated in the above manner. All data reported in this paper were obtained from one wire. However, the main characteristics of the damping spectrum were reproducible. Damping was measured from −50° to about 10°C above the low-temperature peak. In the testing sequence a low-frequency test was alternated with a high-frequency test and the specimen was again solution-treated after each high-frequency test. Finally, after measuring the damping at nine frequencies between 0.19 and 2.50 Hz, a final test was made over the temperature range −50° to 290°C at 1.02 Hz.

The specimens were tested in a K~ pendulum. The logarithmic decrement, $\Delta$, was measured by the lamp-and-scale technique, which limited the maximum frequency to about 2.5 Hz. The minimum frequency of 0.19 Hz was determined by consideration of the temperature change during one damping measurement. The heating rate was $\frac{1}{2}$ deg per min, as measured by a calibrated thermocouple suspended near the specimen. Measurements with a dummy specimen indicated that the average specimen temperature lagged the thermocouple by about 1 deg and that the temperature gradient along the specimen was about 1°C. All damping tests were made in a longitudinal magnetic field of 400 oe. The maximum surface strain was less than $4 \times 10^{-5}$ and the amplitude-dependent damping was negligible.

**THEORETICAL ANALYSES OF ACTIVATION ENERGY**

Assuming a single $\tau$, Eqs. [1], [2], and [3] can be rearranged to yield several experimentally different methods for calculating $H$. These methods can be applied to the high- and low-temperature peaks in a complex damping spectrum, if the peaks are separated from the next nearest peaks by, say, 10°C.\textsuperscript{19-21}

The most reliable analysis\textsuperscript{11,18} is the peak-shift method. Consideration of Eqs. [1] and [2] indicates that the Snoek peak shifts to higher temperatures for increasing frequencies. For a constant $T_d/T_p\Delta_m$,

$$\ln \left( \frac{f_1}{f_2} \right) = -\frac{H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where $T_1$ and $T_2$ are the positions of a given value of $T_d/T_p\Delta_m$ at the frequencies $f_1$ and $f_2$.

Activation energy can be calculated from peak shape by three methods, which are all based on Eqs. [1] and [2] and thus are theoretically identical but treat the data in different manners. The peak breadth, in reciprocal degrees Kelvin, can give an activation energy. Rearranging Eq. [1], solving the resulting quadratic equation, and substituting Eq. [2] yields

$$\ln \left( \frac{T_p\Delta m}{T_d} \right) = \ln \left( \frac{T_p\Delta m}{T_d} \right) + \sqrt{\left( \frac{T_p\Delta m}{T_d} \right)^2 - 1}$$

where $T$ is temperature at $\Delta\Delta_m$. Eq. [6] can be applied to the low-temperature peak in complex damping spectra if $T_p$ can be estimated accurately and if overlapping peaks are insignificant.

Another activation-energy analysis based on peak shape follows directly from Eq. [3], which can be rewritten as

$$\left| \frac{H(1/T - 1/T_p)}{R} \right| = \cosh^{-1} \left( \frac{T_p\Delta m}{T_d} \right)$$

Consequently, plots of $\cosh^{-1} (T_p\Delta_m/T_d)$ vs $1/T$ can give the activation energy. This method, which has the advantage that it uses all the available data from a peak, has been applied to complex damping.\textsuperscript{20}

The last method of activation-energy analysis that we shall consider is based on the approximation derived from Eqs. [1] and [2] that for the lower third or so of the peak

$$\ln \left( \frac{H(1/T - 1/T_p)}{R} \right) = \ln \left( \frac{2T_p\Delta m}{T_d} \right)$$

K~\textsuperscript{21} used Eq. [8] to determine whether a peak was a single relaxation, but it must be borne in mind that this method uses only part—the least accurate part—of the available data.

**RESULTS AND ANALYSIS**

Fig. 1 shows the measured damping as a function of temperature over the complete temperature range. The damping spectrum is obviously complex. Casual examination of Fig. 1 and similar spectra from companion specimens suggested that the complex damping is composed of a series of at least four extraordinary peaks. Peaks at about 7°, 35°, and 135°C were rather well resolved, while the shape of the spectra between 50° and 100°C strongly suggested the presence of at