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THE ZENER RELAXATION IN SOME HIGH PURITY IRON-VANADIUM ALLOYS

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Résumé. — La relaxation de Zener a été étudiée dans trois alliages Fe-V de haute pureté, contenant 12, 16 et 20 % en poids de vanadium. Les mesures ont été faites en pendule de torsion inversé sous vide, dans une gamme de fréquence allant de 0,1 à 10 Hz.

Les temps de relaxation \( \tau_r \), dans le domaine de température 650-720 °C, peuvent être représentés par les équations suivantes:

\[
\begin{align*}
\text{Fe-12 % V} & \quad \tau_r = 1.1 \times 10^{-22} \exp(93500/RT) \\
\text{Fe-16 % V} & \quad \tau_r = 1.6 \times 10^{-23} \exp(95500/RT) \\
\text{Fe-20 % V} & \quad \tau_r = 1.9 \times 10^{-24} \exp(96700/RT).
\end{align*}
\]

On suppose l'existence d'une relation entre les paramètres de relaxation \( \tau_0 \) et \( \Delta H_r \) et les paramètres de diffusion correspondant au mécanisme le plus rapide ; il a été trouvé que les vitesses de diffusion croissent avec le pourcentage de vanadium. Les résultats sont discutés à partir des théories habituelles de la relaxation de Zener et on donne des explications pour les hautes énergies d'activation du processus de diffusion.

Abstract. — The Zener relaxation has been studied in three high purity iron vanadium alloys containing 12, 16 and 20 wt. % vanadium. The measurements have been made in an inverted torsion pendulum under high vacuum in the frequency range 0.1-10 Hz.

The relaxation time \( \tau_r \) in the temperature range 650 to 720 °C can be described by the equations:

\[
\begin{align*}
\text{Fe-12 % V} & \quad \tau_r = 1.1 \times 10^{-22} \exp(93500/RT) \\
\text{Fe-16 % V} & \quad \tau_r = 1.6 \times 10^{-23} \exp(95500/RT) \\
\text{Fe-20 % V} & \quad \tau_r = 1.9 \times 10^{-24} \exp(96700/RT).
\end{align*}
\]

A relation between the relaxation parameters \( \tau_0 \) and \( \Delta H_r \) and the diffusion parameters of the faster diffusing specie is assumed, it is found that diffusion rates increase with increasing vanadium content. The results are discussed in terms of current theories of the Zener relaxation and reasons for the high activation energy of the diffusion process are given.

Introduction. — The Zener relaxation provides a potentially powerful method for diffusion studies at low temperatures compared with normal radioactive tracer studies. In a recent review Wert [1] has compared diffusion and Zener relaxation data for both f. c. c. and b. c. c. systems. For the f. c. c. systems the relaxation activation energy is observed to be lower than that for the faster diffusing specie in the alloy. Recent work on the f. c. c. Ag-Cd and Ag-In systems [2, 3, 4] where accurate diffusion data are available has confirmed that relaxation occurs with a lower activation energy than diffusion.

The present work was carried out to investigate the effect of vanadium content on the Zener relaxation and relate this to diffusion in the alloys. The Zener relaxation in Fe-V alloys was first observed by Stanley and Wert [5]. For an Fe-18 % V alloy they found that diffusion in the ferromagnetic region is about 100 times lower than would be indicated by extrapolation from the paramagnetic region. The present work on Fe-12, 16 and 20 % V alloys has been carried out in the transition temperature range between the ferromagnetic and paramagnetic states. In this range of anomalous diffusion it is found that diffusion rates increase with increasing vanadium content and the diffusion process has a high activation energy compared with diffusion at higher temperatures.

Experimental Procedure. — Zone refined iron (*) and zone refined vanadium were used for alloy production. The zone refined iron had a typical impurity content in atomic parts per million of: C, 50 ; Si, 10 ; S, 6 ; P, < 1 ; Ni, 7 ; Cr, 7 ; Cu, < 10 ; Co, 8. The zone refined vanadium had a composition better than 99.9 pure and was supplied by Metals Research Limited. The alloys were melted under vacuum to 5 mm diameter and swaged to 0.70 mm diameter. The wire specimens were then annealed under a high purity hydrogen atmosphere at 1 200 °C for 8 hours to produce a large grain size. This heat treatment effectively eliminated contributions to damping from grain boundary relaxations.

Measurements of logarithmic decrement (\( \delta \)) were made by free decay of a 100 mm long specimen.

(*) The zone refined iron was kindly supplied by Dr. C. M. Sellars, Metallurgy Department, University of Sheffield, England.
0.70 mm diameter in an inverted torsion pendulum under a vacuum of better than $10^{-5}$ mm of Hg. Low inertial damping ($\delta < 10^{-5}$) was achieved by using a rigid balance arm supported by a low damping quartz fibre. The maximum shear strain on the specimen was $1.5 \times 10^{-5}$.

**Results.** — The Fe-12, 16 and 20 % V alloys used are b. c. c. up to the melting temperature, figure 1 [6].

![Fig. 1. The Iron-Vanadium equilibrium diagram [6].](image1)

A typical series of damping against temperature curves are shown in figure 2 for an Fe-12 % V alloy. Subtraction of the estimated background damping gave a symmetrical peak, such a Zener peak is shown in figure 3 for a specimen tested at a frequency of 0.575 Hz. The background damping is believed to be due to dislocation and grain boundary effects. In order to obtain these peaks it was necessary to eliminate magnetoelastic effects, this was achieved by applying a high tensile stress to the wire specimens during testing. For a particular value of the activation energy the peaks should have a characteristic width, the present peaks are about 12 % too wide indicating a distribution of relaxation centres having different local relaxation times. By plotting $\log(\tau_r)$ against the reciprocal of the peak temperature for the three alloys, figure 4, we obtain by a least squares analysis of the data the following equations for $\tau_r$:

- Fe-12 % V: $\tau_r = 1.1 \times 10^{-22} \exp(93,500/RT)$
- Fe-16 % V: $\tau_r = 1.6 \times 10^{-23} \exp(95,500/RT)$
- Fe-20 % V: $\tau_r = 1.9 \times 10^{-24} \exp(96,700/RT)$

![Fig. 2. The Zener internal friction peak in Fe-12 % V. The vibration frequencies shown are those at the peak temperature.](image2)

![Fig. 3. A Zener internal friction peak in Fe 12 % V with background damping subtracted, frequency, 0.575 Hz.](image3)

**Theory.** — In substitutional solid solutions a relaxation occurs which is associated with substitutional atomic moments and is known as the Zener relaxation. Zener's explanation was that it was caused by reorientation under stress of pairs of solute atoms [7]. The relaxation is also present in concentrated alloys where the concept of isolated pairs is not valid. LeClaire and Lomer [8] suggested a directional short range order theory which is applicable to concentrated solid
The Zener relaxation occurs by vacancy diffusion, consequently the jump time and relaxation time are related, \( \tau = \alpha \tau_r \).

Therefore
\[ D = \frac{d^2}{6 \alpha \tau_r}. \] (1)

For the Zener relaxation it is well established experimentally that
\[ \tau_r = \tau_{ro} \exp(\Delta H_e/RT). \]

We may write
\[ D = \frac{d^2}{6 \alpha \tau_{ro}} \exp(-\Delta H_e/RT). \] (2)

Eq. (2) will be used to obtain diffusion data.

**Discussion.** — For an Fe-18 % V alloy Stanley and Wert [5] obtained the following expression for the relaxation time, \( \tau_r \),
\[ \tau_r = 4.15 \times 10^{-22} \exp(-85,000/RT). \]

They assumed a value for \( \alpha \) in eq. (2) to calculate diffusion data. For the b. c. c. alloys Fe-27 % Al and \( \beta \) brass Wert [1] showed that \( \alpha \) is approximately 0.1 and 1 respectively. For the present system we assume a value of 0.5 for \( \alpha \). It seems reasonable to assume that the Zener relaxation measures the diffusion of the faster diffusing specie vanadium. Correcting the relaxation data using eq. (2) we obtain the following expressions for diffusion of vanadium over the temperature range 650 to 720 °C.

Fe-12 % V
\[ D = 1.9 \times 10^6 \exp(-93,500/RT) \text{cm}^2 \text{s}^{-1}. \]
Fe-16 % V
\[ D = 1.3 \times 10^7 \exp(-95,500/RT) \text{cm}^2 \text{s}^{-1}. \]
Fe-20 % V
\[ D = 1.1 \times 10^8 \exp(-96,700/RT) \text{cm}^2 \text{s}^{-1}. \]

In calculating the above equations a value of \( 2.5 \times 10^{-9} \) cm has been used for the interatomic spacing. The results are plotted in figure 5, together with the relaxation data.
with the results of Stanley and Wert [5] on an Fe-18 V alloy. Figure 6 shows the present data together with data for diffusion of vanadium in Fe-18 % V and low temperature strain relaxation data for this vanadium content, figure 1. Near the Curie temperature the diffusion rate falls off, this decrease occurs at lower temperatures as the vanadium content increases. Such an explanation satisfactorily describes the present observations, figure 7.

![Figure 6](image1)

**FIG. 6.** Comparison of present diffusion data with radiotrace
er diffusion of V in Fe-18 % V and low temperature strain relaxation data.

![Figure 7](image2)

**FIG. 7.** The relation between diffusion and the Curie temperature in Fe-V alloys.

The diffusion coefficient can be described experimentally as

\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]

where

\[ D_0 = d^2 \nu \exp(\Delta S_f/R + \Delta S_m/R) \]

and

\[ Q = \Delta H_f \times \Delta H_m ; \]

where \( \Delta H_f \) and \( \Delta H_m \) are the formation and movement enthalpies of a vacancy respectively; \( \Delta S_f \) and \( \Delta S_m \) are the formation and movement entropy of a vacancy respectively; \( \nu \) is the vibrational frequency, \( d \) is the jump distance.

The high activation energy in this transition region may be attributed to an increase in formation enthalpy and movement enthalpy. Borg et al. [12] attributed an excess enthalpy of formation to the presence of short range spin ordering near the Curie temperature. An alternative approach by Hirano et al. [13] explained the decrease in diffusivity by supposing a vacancy leads to a local demagnetisation requiring additional energy, hence an increase in vacancy formation energy. In terms of the elastic constants Borg [14] suggested that the movement enthalpy increases because of a change in the elastic properties of iron near the Curie temperature. In order to explain the large change in activation energy of the present data it seems that both \( \Delta H_f \) and \( \Delta H_m \) would have to be increased significantly. Such a
large increase cannot be explained satisfactorily in terms of the above theories. Similarly the large $D_0$ value can only be explained by a large change in the entropies of formation and movement of vacancies. At present no satisfactory theory is available to explain these significant changes of the diffusion constants.

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