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DIFFUSION MECHANISM OF IRON IN VANADIUM AT HIGH TEMPERATURE

1. Introduction.- Studies of diffusion in refractory BCC metals have shown that some of these metals deviate from the so-called "normal diffusion behaviour", in particular by the appearance of non-linearity in the Arrhenius plots Log D = f(T) /1/, /2/.

Such a non-linear Arrhenius curve for self-diffusion /3/ or impurity diffusion in vanadium /4/, /5/ results in two distinct straight lines Log D = f (T). This striking anomalous feature was confirmed by different authors /6/, /7/, /8/, /9/ even if the temperature of the crossing point and the slopes of the two straight lines sometimes vary significantly from investigator to investigator. Among the various explanations offered to account for the behaviour observed in vanadium, impurity effect remains the most plausible one /6/ along with changing in the mechanism of atomic transport.

In a recent study /10/ it was possible to measure simultaneously the activation energy E_a for self diffusion in the "low" temperature region (up to about 1300°C) and the actual concentration C_i of interstitial impurities (O, N, ...). This was done in NMR experiments through measurements of spin-spin relaxation time T_2 (motional narrowing effect) and of the dipolar T_1 and quadrupolar T_1Q contributions to spin-lattice relaxation time (the asymptotic slopes of T_1 and T_2 versus temperature give E_a and the amplitude of the T_1Q peak is proportional to C_i). Thus, the activation energy E_a in the low temperature region was found to vary from 2.5 eV to 3.2 eV, the last being the upper limit obtained with progressively improved sample purity. This confirms the strong influence of extrinsic effect and suggests that, up to about 1400°C, single vacancies associated to interstitial impurities could be the defects involved in the mechanism of self-diffusion in vanadium.

The purpose of this paper is to present Mössbauer data, compared to diffusion coefficient values obtained by microsectioning techniques /11/, in order to contribute to the explanation of the non-linear behaviour in the V - Fe system.

2. Experimental Method.- Experiments intended to measure the diffusion broadening of the Mössbauer resonance have been tempted for a long time, especially in metallic system /12/, /13/ up to about 1000°C. Because of their high melting point, vanadium based alloys have to be investigated up to the 2000K region and this is not an easy achievement, first to manufacture the proper furnace able to heat a sample and keep constant its temperature in such circumstances, second to carry our Mössbauer spectroscopy in presumably very low recoilless fraction conditions.

This has been overcome by using:

1) a special furnace as described in figure 1, built in a compact geometry, with an external double-wall for cooling by circulating water, a direct current low voltage power supply, a complex system for radiation screening, a cylindrical tungsten resistor and two beryllium windows;

2) a source experiment geometry with a V - 57Co source of about 54 mCi, obtained by electrodeposition followed by annealing in hydrogen. Thus, the sample is kept the same for all series of measurements, that is a 1 cm x 1 cm x 2 mm vanadium polycrystalline ingot containing about 50 ppm of 57Co and 57Fe;

3) an electron conversion technique with both standard absorber (pure iron foil or stainless steel)
and detector moved by the Mössbauer transducer (see Fig. 1).

Fig. 1: Furnace and Mössbauer arrangement.

In such a way, Mössbauer spectra were measured up to temperatures never reached before. As typically shown in figure 2, the ratio of signal over background is still about 2 at 940 K and 0.10 at 1824 K with a stainless steel absorber, and very nice spectra can be obtained up to 1600 K with a pure iron absorber.

Unfortunately, the diffusion broadening measurements had to be restricted to only a few values of the temperature in the narrow range 1473 K to 1824 K because of unmeasurable broadening at lower temperature and drastic evaporation of the source.

The diffusion broadenings $\Delta \tau$ were directly deduced from the line widths and are given in the second column of table I. As it is well known /12/, this can be considered as an absolute determination of the average atomic jump frequency:

$$\frac{1}{\tau} = f \frac{\Delta \tau}{c \cdot 2k}$$

($f_c$ is the so-called correlation coefficient).

A diffusion coefficient $D(<1^2>)$ can be calculated from $1/\tau$, provided that the average length $<1^2>$ of the elementary jump is known, by the relation:

$$D(<1^2>) = \frac{1}{6} \cdot \frac{<1^2>}{f_c} = \frac{\Delta \tau}{12k} \cdot <1^2>$$

In the third column of table I, $D(a_o)$ has been calculated assuming a nearest neighbour distance for the elementary jump. The fourth column reports the macroscopic data $D^*$ obtained by classical microsectioning techniques /11/ for the diffusion of iron impurity in vanadium and the last column gives the ratio $\sqrt{<1^2>/a_o}$ obtained by adjusting $D(<1^2>)$ to $D^*$. 

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not be invoked neither since they would suppose $\sqrt{\langle l^2 \rangle}/a_0 = 1.16$ which is still too small. In a divacancy mechanism, the jumping atom would perform two successive displacements, each of them corresponding to a distance $a_0$; but actually there is no stop between them and this will account for one jump in Mössbauer spectroscopy, with a $\sqrt{\langle l^2 \rangle}/a_0 = 1.66$. The experimental value at 1550°C being about 1.3 means contribution to diffusion from both single and divacancies. Then, the measured diffusion broadening $\Delta \Gamma$ and the total diffusion coefficient $D_{\text{total}}$ can be expressed by:

$$D_{\text{total}} = D_{1v} + D_{2v}$$

where the subscripts $1v$ and $2v$ refer to single and divacancies respectively.

3. Discussion and Conclusion.- Up to about 1400°C it is clear that diffusion coefficients calculated from the Mössbauer line broadening can be reasonably adjusted to the microsectioning data, within experimental accuracy, assuming elementary jumps between nearest neighbour sites. This is consistent with a diffusion mechanism in which single vacancies are involved and confirms both macroscopic /11/ and NMR data /10/. The ratio $\sqrt{\langle l^2 \rangle}/a_0$ being a little smaller than one, just account for the well known existence of a migration volume.

At higher temperature diffusion coefficients obtained from Mössbauer spectroscopy and microsectioning techniques can be adjusted to each other only if the elementary jump distance is supposed larger than $a_0$. Thus, the data cannot be analysed any longer in terms of a single vacancy mechanism. Direct jumps between next nearest neighbour sites can be expressed by:

$$\Delta \Gamma_{\text{total}} = \Delta \Gamma_{1v} + \Delta \Gamma_{2v}$$

$$D_{\text{total}} = D_{1v} + D_{2v}$$

The various possible exchange processes of an impurity atom with a divacancy in a BCC metal.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta \Gamma$(mm/s)</th>
<th>$D(a_0)$ cm$^2$/s</th>
<th>$D^*$ cm$^2$/s</th>
<th>$\sqrt{\langle l^2 \rangle}/a_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473</td>
<td>2x10^{-3} to 4x10^{-2}</td>
<td>(5.3) 10^{-11}</td>
<td>1.53x10^{-11}</td>
<td>0.42 to 0.95</td>
</tr>
<tr>
<td>1573</td>
<td>0.026 to 0.036</td>
<td>(1.3±0.2) 10^{-10}</td>
<td>0.8x10^{-11}</td>
<td>0.52 to 0.72</td>
</tr>
<tr>
<td>1673</td>
<td>0.100 to 0.200</td>
<td>(6.4±0.2) 10^{-10}</td>
<td>3x10^{-11}</td>
<td>0.60 to 0.84</td>
</tr>
<tr>
<td>1683</td>
<td>0.080 to 0.100</td>
<td>(3.4±0.2) 10^{-10}</td>
<td>3x10^{-15}</td>
<td>0.92 to 0.97</td>
</tr>
<tr>
<td>1824</td>
<td>0.252 to 0.320</td>
<td>(1.2±0.2) 10^{-9}</td>
<td>2x10^{-9}</td>
<td>1.21 to 1.36</td>
</tr>
</tbody>
</table>

Fig. 2: Typical Mössbauer spectra at high temperature measured with a stainless steel absorber.

Fig. 3: The various possible exchange processes of an impurity atom with a divacancy in a BCC metal. A : 1 = 2a_0, weight : 1 ; B : 1 = $\sqrt{3}$a_0 = 1.63 a_0, weight : $\frac{1}{2}$ ; C : 1 = $\sqrt{2}$a_0 = 1.16 a_0, weight : $\frac{1}{4}$.

with the following relations:

$\Delta \Gamma_{\text{total}} = \Delta \Gamma_{1v} + \Delta \Gamma_{2v}$

$D_{\text{total}} = D_{1v} + D_{2v}$
Using the data from table I at 1550°C results in calculating the equations:

\[
\begin{align*}
D_{\text{total}} &= \frac{(1.3a_0)^2}{12m} \Delta \Gamma_{\text{total}} \\
D_{1V} &= \frac{a^2_0}{12m} \Delta \Gamma_{1V} \\
D_{2V} &= \frac{(1.66a_0)^2}{12m} \Delta \Gamma_{2V}
\end{align*}
\]

Taking into account the classical expressions of the diffusion coefficients as obtained from thermodynamics,

\[
\frac{a^2_0}{12m} \left( \Delta \Gamma_{1V} + 2.76 \Delta \Gamma_{2V} \right) = 2 \times 10^{-9}
\]

\[
\frac{a^2_0}{12m} \left( \Delta \Gamma_{1V} + \Delta \Gamma_{2V} \right) = 1.2 \times 10^{-9}
\]

or:

\[
D_{1V} = 0.75 \times 10^{-9} \text{ cm}^2/\text{s} \\
D_{2V} = 1.26 \times 10^{-9} \text{ cm}^2/\text{s}
\]

\[
\Delta \Gamma_{2V} = 0.61 ; \quad D_{2V} = 1.7
\]

As pointed out by Kimura /11/, the migration energy should be larger than the formation energy in V, Nb, Ta and \(E_B\) is expected to be of the order of \(E_{\text{F}}^1/3\), say:

\[
\begin{align*}
E_{\text{F}}^1 &= 1.5 \text{ eV} \\
E_{\text{m}} &= 1.7 \text{ eV} \\
E_B &= 0.5 \text{ eV}
\end{align*}
\]

Then, the Mössbauer data at 1550°C would correspond to:

\[
\begin{align*}
\frac{C_{2V}}{C_{1V}} &= 2 \times 10^{-3} \\
\Delta E_m &= 0.6 \text{ eV} \\
\Delta E_m &= 2.5 \text{ eV}
\end{align*}
\]

which is both reasonable and in acceptable agreement with recent macroscopic data for diffusion of iron impurities in vanadium /11/.

References

/2/ Ablitzer, D., Philos. Mag. 36 (1977) 1239.
/10/ Chabre, Y., Private Communication.
/11/ Ablitzer, D., Private Communication.