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The Influence of Interstitial Impurity Atoms on the Recovery Behaviour of Cold-Worked Vanadium

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Vanadium containing oxygen and nitrogen shows, after deformation at room temperature by rolling, two distinct recovery stages at annealing temperatures of about 450 and 550° K. Measurements of electrical resistivity and of low frequency damping were made. By variation of the gas content of the samples, it was established that the stage situated at 450° K is caused by the migration of oxygen atoms to dislocations, whereas at 550° K nitrogen atoms migrate to dislocations. Two small steps occurring at 340 and 400° K can be attributed to ordering of oxygen and nitrogen atoms in the dislocation stress fields.

1. Introduction

Usually, recovery experiments are carried out on deformed metals with the aim of investigating the annealing behaviour of intrinsic lattice defects such as vacancies, interstitials, and dislocations. There exists a large number of publications in the literature dealing with mainly the recovery of fcc metals. With the bcc metals of group Va of the periodic table, the stage occurring in niobium and tantalum around 420° K has been studied most extensively (for a review see references 1 and 2). Whereas in a number of publications [3-7] this stage has been ascribed to the annealing-out of intrinsic point defects, our measurements [2, 8, 9] showed that it is related to the migration of interstitially dissolved oxygen atoms and the associated strain-ageing phenomenon. When the metals have been degassed in ultra-high vacuum, one finds, instead of a well-defined step, a rather continuous resistivity decrease between room temperature and more than 600° K, in analogy to Cuddy's [10, 11] observations on iron with very low carbon content. Nitrogen influences the annealing behaviour of niobium and tantalum in a similar way to oxygen, if one takes into account its higher migration energy [9].

The three, group Va elements, vanadium, niobium, and tantalum, possess a relatively high solubility for oxygen and nitrogen. The tetragonal distortion of the host lattice produced by the dissolved interstitial impurity atoms causes a strong interaction with external and internal stress fields. For instance, the stress-induced rearrangement of the impurity atoms can be investigated by measurements of the mechanical damping or relaxation. If the relaxation time τ (depending on temperature in the form of an Arrhenius equation) for a particular impurity element is equal to the reciprocal of the frequency of the applied external stress, a maximum in internal friction is observed. Using this so-called Snoek effect [12], very accurate determinations of the diffusion rates of oxygen, nitrogen, and carbon in the three metals mentioned above have been performed [13]. Since the height of the Snoek peak is proportional to the number of atoms of the corresponding impurity element interstitially dissolved in the lattice, measurements of internal friction offer themselves for analytical purposes. Furthermore,

any observed decrease in the Snoek damping allows the conclusion that some of the impurity atoms have become rearranged in such a way that they no longer contribute to the mechanical relaxation. This is the case for precipitated atoms as well as for atoms segregated to dislocations.

When the recovery of deformed metals is studied by means of electrical resistivity measurements, a rearrangement of interstitial impurity atoms causes similar effects, as can be observed during the annealing of intrinsic point defects. To achieve further information, investigations on samples of various purity have to be done. Because of the aforementioned reasons, measurements of internal friction can give useful supplementary information. Such investigations have already been done with cold-worked niobium and tantalum [2, 8, 9].

Considering the striking similarities in physical properties among the group Va elements, one expects a resembling behaviour for vanadium. To our knowledge, there are no publications in the literature dealing with the recovery of deformed vanadium. Accordingly, the purpose of this work was to investigate the recovery of the electrical resistivity of cold-worked vanadium within the temperature range between room temperature and 650° K. In particular, it was to be established which of the stages observed can be ascribed to a rearrangement of interstitial oxygen and nitrogen atoms respectively.

2. Experimental Procedure

The experiments were performed with polycrystalline wires having a diameter of about 1.65 mm. The starting material was electron-beam zone-refined vanadium. A mass-spectrometric analysis is given in table I.

TABLE I Mass-spectrometric analysis of the vanadium used in this work.

Element	Concentration (ppm by wt)	Element	Concentration (ppm by wt)
Al	3	Ni	120
Ca	4	Si	300
Cr	15	Ta	50
Fe	170	Ti	20
Mg	4	W	2
Mo	300	Zr	200
Nb	40		

In order to reduce the impurity content further and to bring the samples to a standard condition, the wire samples were annealed in a vacuum of 2.10^{-6} torr by ohmic heating. Fig. 1 gives two measurements of the Snoek damping of such a sample prior to and after a heat treatment of 50 min at 1600° C, in the course of which the sample loses about a third of its initial mass by evaporation. Contrary to niobium and tantalum, which may be degassed almost quantitatively by heating in high vacuum [14], the oxygen content of the vanadium samples could only be reduced to some 70 ppm (from a starting value of 280 ppm), while the nitrogen content of 260 ppm in the as-received material remained unaltered. This is in agreement with results due to Hörz, Gebhardt, and Dürrschnabel [15].

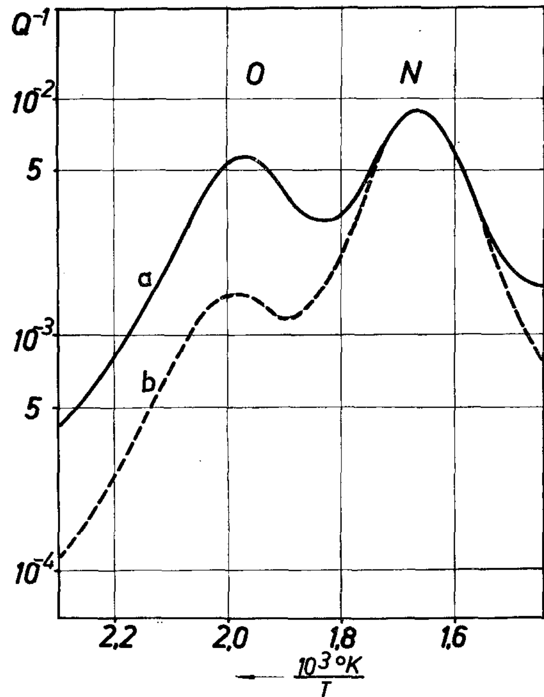

Figure 1 Oxygen (O) and nitrogen (N) Snoek damping of a vanadium sample, at a frequency of 13 c/sec: (a) as-received; (b) after annealing (50 min at 1600° C and 2.10^{-6} torr).

Because of this degassing problem, the content of interstitial impurities was varied by additional doping with oxygen and nitrogen. For the analysis of the concentrations, Snoek peak measurements and the vacuum fusion method were applied.

The samples were deformed by rolling at room temperature using reductions in thickness of 40%. The electrical resistivity was measured

at 77 and 273° K by a conventional potentiometric method. For the calculation of the additional residual resistivities, the data for the ideal resistivity of vanadium given by White and Woods [16] were employed, together with the assumption that Matthiessen's rule is valid. The annealed and undoped material had a resistivity of 19.8 $\mu\Omega$cm at 273° K.

Up to 520° K recovery anneals were carried out in a silicone oil bath, at higher temperatures in a vacuum of 5×10^{-6} torr.

3. Results

Because of the unfavourable degassing behaviour, no samples having a very small concentration of interstitial impurities could be prepared. Therefore the recovery measurements will always be influenced by the simultaneous presence of both oxygen and nitrogen. Thus, for clarity, some results obtained earlier with tantalum [8, 9] which can easily be degassed shall be briefly reviewed.

Fig. 2 shows some typical isochronal annealing curves of cold-worked tantalum containing various amounts of oxygen and nitrogen. The additional specific residual resistivity (as compared with a pure, undeformed dummy) is plotted versus annealing temperature. Temperature increments of 25° K and annealing times of 10 min were used.

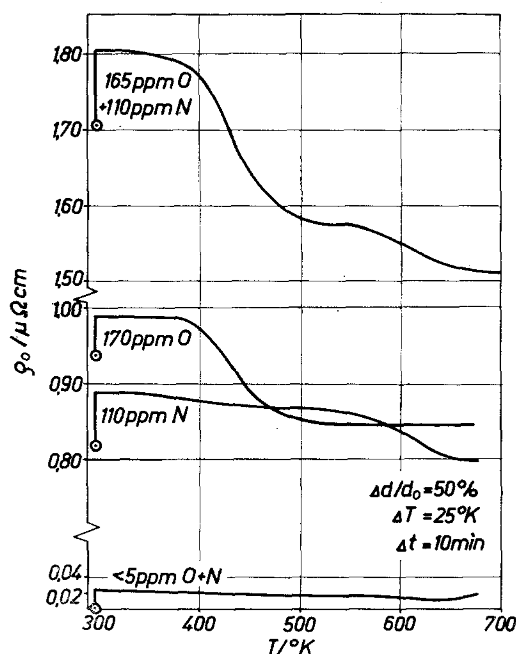

Figure 2 Isochronal recovery of electrical resistivity of deformed tantalum with various contents of oxygen and nitrogen.

The curve at the bottom of the diagram was obtained with a degassed sample having an overall content of interstitial impurities of less than 5 ppm. This sample exhibits only a small resistivity recovery. The resistivity of the sample prior to deformation (indicated by a small circle at the left-hand side) was not re-established within the covered temperature interval. The two curves in the middle of the diagram were measured on samples doped with 170 ppm oxygen and 110 ppm nitrogen respectively. With oxygen-containing tantalum, one finds a recovery stage centred at 420° K; for nitrogen-containing tantalum the corresponding stage is situated at 600° K. It has been shown that (keeping the degree of deformation constant) the resistivity drop in both cases varies linearly with the impurity concentration. The fact that the resistivity of the gas-containing samples drops below the values of the undeformed material leads to the conclusion that in the recovery stages mentioned no deformation-induced point defects anneal out (or at least this is not the only process taking place), but that a rearrangement of impurity atoms has occurred. Such an interpretation has also been given by Cuddy [10, 11] for the recovery of cold-worked iron containing carbon.

The upper curve of fig. 2 was obtained with a sample loaded at the same time with 110 ppm nitrogen and 165 ppm oxygen. Recovery curves of this type are to be expected with deformed vanadium.

Now the question arises: at what temperatures will the annealing stages caused by oxygen or nitrogen in vanadium occur? A rough estimate may be achieved by means of table II. In the third column of this table, the migration energies for oxygen and nitrogen in the three, group Va elements are listed. These values were obtained from the dependence of the Snoek damping on temperature and frequency [13] and they have an estimated accuracy in the order of ± 0.01 eV. For the relation between the activation energy E_D for the recovery of a defect and the mean temperature T_M of the associated stage, an approximate formula of the form $E_D \approx a \times kT_M$ (k is Boltzmann's constant) can be used. As for the factor a (which depends, for example, on the heating rate), our measurements with niobium and tantalum established a value of $a = 31 \pm 1$. Using this figure, one

TABLE II Annealing stages caused by oxygen and nitrogen in the group Va metals (see text).

Element	Interstitial impurity	Migration energy E_D (eV) [13]	Annealing stage at T_M (° K)
Ta	O	1.11	420
	N	1.64	600
Nb	O	1.17	425
	N	1.52	575
V	O	1.26	$\frac{E_D}{31k} \approx 470$
	N	1.48	$\frac{E_D}{31k} \approx 550$

estimates that in vanadium the stage caused by rearrangement of oxygen will appear around 470° K and that caused by nitrogen at about 550° K (table II, column 4). According to Edington *et al* [17] and Carlson and coworkers [18-20], the occurrence of strain-ageing phenomena due to interstitial oxygen and nitrogen respectively has been reported at comparable temperatures.

Fig. 3 gives the isochronals (measured with temperature increments of 5° K and annealing times of 5 min) taken from three vanadium samples having different concentrations of oxygen and nitrogen. In accordance with the estimation given in table II, one observes recovery stages around 450 and 550° K, which are obviously caused by a rearrangement of interstitial oxygen and nitrogen atoms respectively. It can be seen that the two stages rise with the concentration of the corresponding impurity element as indicated in the figure.

By analogy to earlier investigations on niobium and tantalum [2, 8, 9], the two main stages are interpreted as due to the migration of interstitial oxygen and nitrogen atoms to dislocations respectively.

This conclusion may be supported by a calculation of the mean numbers of jumps the impurity atoms have executed during the annealing treatment. In fig. 4, one of the isochronals of fig. 3 is shown together with the mean jump numbers calculated for oxygen and nitrogen by use of the diffusion coefficients given by Powers and Doyle [13] and in terms of the annealing conditions employed here. Just as for niobium and tantalum, the main stages occur between about 10^2 and 10^5 jumps of the impurity atoms.

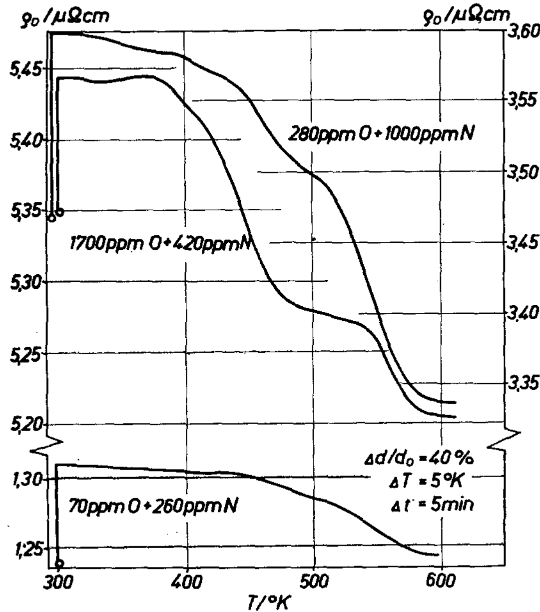

Figure 3 Isochronal recovery of electrical resistivity of deformed vanadium with various contents of oxygen and nitrogen.

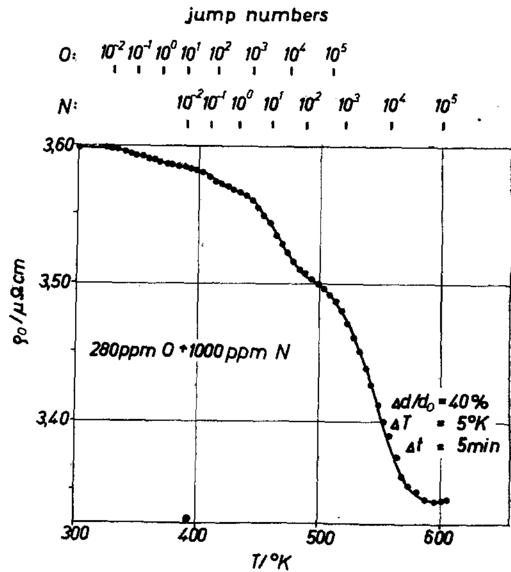

Figure 4 Calculated jump numbers of the oxygen and nitrogen atoms for the recovery of deformed vanadium.

Besides the stages discussed up to now, two further, small stages were observed around 340 and 400° K (fig. 3). These stages are believed to be due to so-called Snoek ordering [21, 22]

of oxygen and nitrogen atoms respectively. Here, the interstitial impurity atoms rearrange themselves within the dislocation stress fields in such a way that the dilated lattice sites will be preferentially occupied. This brings about a reduction in the internal stress of the sample and thereby causes a slight drop in the electrical resistivity. The corresponding small recovery stage requires only a single jump per impurity atom.

The oxygen-containing samples show a small resistivity increase near 350° K during the isochronal annealing; this was reproducible but has not yet been investigated in any detail.

Following cold work and low-temperature annealing, there was a diminution in the height of the oxygen and nitrogen Snoek peaks which amounted to a few per cent of the initial peak height. This is attributed to segregation of the impurities to dislocations. Furthermore, the internal-friction measurement exhibited, at about 720° K (with a frequency of 3.4 c/sec), a "cold-work peak" which could be annealed out by heating the samples to temperatures above 750° K. A similar cold-work peak observed in oxygen-containing tantalum has been discussed by Schöck and Mondino [23]. These peaks are due to linked movements of dislocations and impurity atoms.

4. Conclusion

It has been shown that, in analogy to tantalum and niobium, the recovery behaviour of deformed vanadium in the temperature range between room temperature and 700° K is strongly influenced by the presence of interstitial impurities. These impurity atoms give rise to a twofold recovery process, the first and smaller stage being caused by their Snoek ordering, the second and main stage by their migration to dislocations.

It should be mentioned that the possibility cannot be ruled out that, apart from these processes, some of the impurity atoms in the course of the annealing combine with deformation-induced point defects. In particular, the formation of complexes of vacancies with impurity atoms is conceivable.

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