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THE α-PEAK IN VANADIUM

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Introduction

A model for the α-peak in the bcc metals has been extremely elusive. This peak, observed over a wide range of conditions, has been assumed by most authors to have its origin in dislocation damping, but many associated details are not well understood. Such factors as amount of deformation, the role of interstitials, irradiation effects, and effects of annealing have been difficult to evaluate.

The α-peak has been reported for several of the bcc metals, among them Nb, Ta, Mo, V and W (1-6). The damping peak, seen between 100°K and 200°K for usual frequencies of observation, initially increases in height with degree of deformation, but decreases again after a certain point. This behavior has usually been interpreted in terms both of the density of dislocations and their loop length. Most writers have, in fact, interpreted their results in terms of the Bordoni mechanism; a concise review has been given by Nowick and Berry (7). Their review does not consider impurity effects, however, and does not attempt an explanation of annealing effects.

The role of hydrogen seems important since it diffuses rapidly in the metals at usual temperatures of observation. Bruner indeed attributed the peak as being caused by an interaction of hydrogen atoms with dislocations (8). Later work supported that view (9), Cannelli and Mazzolai proposed that the peak in Ta, Nb, and V was the Snoek-Köster peak due to hydrogen (10). Other authors have doubted this view (11,12).

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The present study had three goals:

To deduce the effect of interstitials on the α-peak.
2. To deduce the effects of annealing on the α-peak.
3. To relate a peak caused by the precipitation of hydrides to the α-peak.

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Material Used

The vanadium used in the work was wire drawn from rod of initial purity out 99.9%. It was annealed and outgassed by a high temperature vacuum treatment. The details of the experimental method are outlined in an earlier publication (13).

The α-Peak

The α-peak in the annealed and outgassed vanadium shows the characteristic behavior with deformation. Data for four levels of deformation are shown in Fig. 1. Three features are apparent: (1) The peak initially increases with deformation, then levels off. (2) The peak temperature shifts appreciably with increase in deformation. (3) The peak broadens markedly at high deformation. The first two of these features show the peak to have two regions of behavior -- one below 20% deformation, the other above, see Fig. 2.

Measurements of activation energies emphasize the difference between the regions of low and high deformation. For the low region the activation energy is about 3400 cal/mole, for the high, 6750. Thus the region of high deformation has an activation energy a little higher than those reported for other bcc metals, the low region a little lower, see Table I. For both peaks in V, the frequency factor is much lower than for Nb, Ta, Mo and W (7,14).

Effect of Hydrogen on the α-Peak

Hydrogen additions modify the α-peak. Data are shown in Fig. 3 for a specimen deformed 14% and subsequently charged with hydrogen to various levels. Clearly the relaxation spectrum is altered appreciably -- the peak shifts to higher temperatures and increases in height; both effects saturate at about 1000 at. ppm of hydrogen. We label this altered peak the Type I

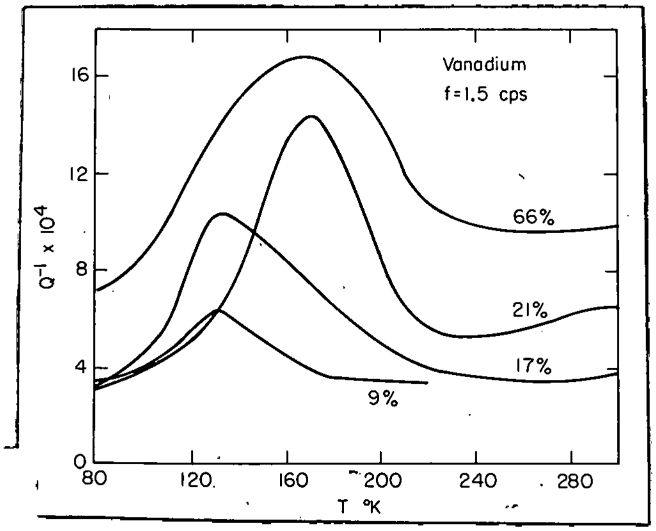

FIG. 1
The α-peak in vanadium.

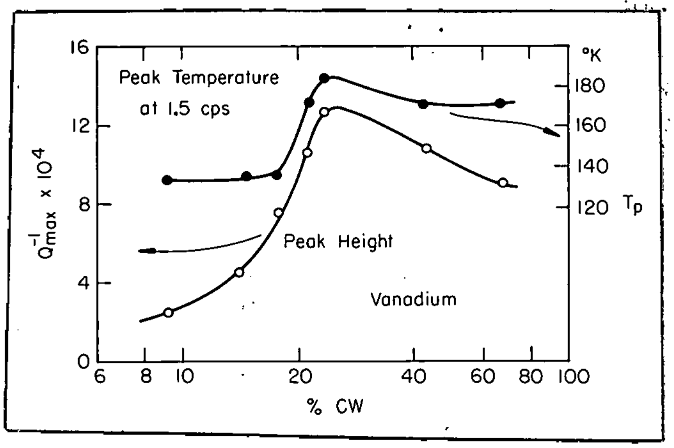

FIG. 2
Peak heights and position for α-peak as a function of deformation.

TABLE I
Parameters for the α-Peak in the bcc Metals. $= f_o e^{-Q/RT}$. First Four Entries Are from Reviews of Nowick and Berry (7) and of Chambers (14).

Metal	f_o (sec^{-1})	Q (ev)
Nb	10^{12}	0.25
Ta	10^{12}	0.25
Mo	10^{11}	0.18
W	10^{10}	0.21
V (14%CW)	10^{6}	0.15
V (23%CW)	10^{8}	0.29

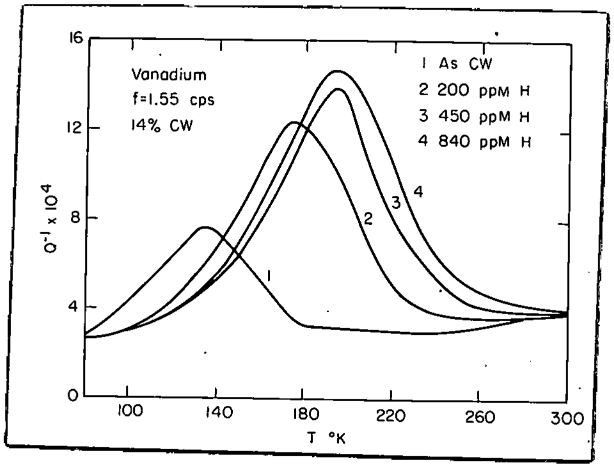

FIG. 3
Effect of hydrogen on α-peak.

Snoek-Köster peak. It has the relaxation equation (for curve 3 at 450 at. ppm H)

$$f = 1.3 \times 10^{10} \exp (0.38 \text{ ev}/RT).$$

Effect of Interstitial Oxygen and Nitrogen

The α-peak for both the low and high regions is suppressed by the presence of oxygen and nitrogen in solution. The effect for oxygen is shown in Fig. 4. (The symbols VXO or VXH signify vanadium with X000 at. ppm of oxygen or hydrogen.) Clearly the α-peak is nearly suppressed by the presence of 12,000 at. ppm of oxygen; nitrogen in the amount of 8000 at. ppm also suppresses the peak at this level of deformation. Data for the suppression of the peak for 14%CW may be seen in earlier publications (13,15).

Materials for which the α-peak is suppressed by the presence of oxygen and nitrogen display a peak if hydrogen is added. An example is shown in Fig. 5 for a specimen containing 5000 at. ppm of oxygen and cold worked 14%. The initial measurement with no hydrogen addition is shown by curve 1; the peak is suppressed. Hydrogen addition causes a peak to appear, the height of which saturates at about 2000 at. ppm of hydrogen (curves 2-5). We designate this restored peak as the Type II Snoek-Köster hydrogen peak. Measurement of the frequency dependence of this peak yields the parameters (for 520 at. ppm, i.e., curve 3) $f_o = 3 \times 10^{16}$ and $Q = 0.55$ ev. This is an extremely large frequency factor, but not unique.

An effect similar to this has been reported by Cannelli and Mazzolai (10). They observed no α-peak after deformation but a peak developed after rogen addition. Their values of f_o and Q were 3×10^{17} per sec and 0.52 ev, values fairly close to ours. They called this peak the "hydrogen cold work peak" and concluded that no α-peak exists after deformation unless hydrogen is present. We conclude that their specimen contained enough dissolved

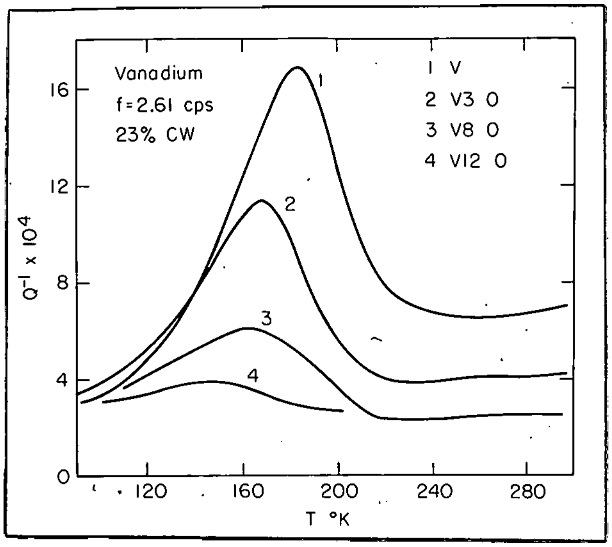

FIG. 4
Suppression of α-peak by oxygen.

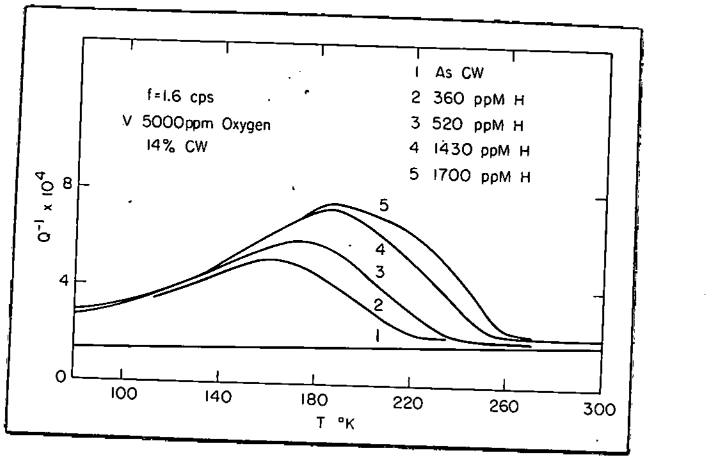

FIG. 5
Growth of a Snoek-Köster peak by addition of hydrogen.

oxygen and nitrogen to suppress the α-peak initially (16) and that hydrogen addition produced the same peak we show in Fig. 5, a Snoek-Köster peak due to hydrogen.

Annealing Away of the α-Peak

The annealing of deformed vanadium in the temperature range 200°C to 300°C causes the α-peak to disappear. An example is shown in Fig. 6 for a specimen containing a small amount of oxygen. We believe that annealing in this temperature range causes segregation of oxygen to the dislocations, pinning them firmly. Bruner showed this also for the annealing of deformed niobium (8). We find, furthermore, that hydrogen additions do not, in this instance, cause development of a Type II Snoek-Köster peak.

Peak Caused by Precipitation of Hydride

A peak caused by the precipitation of hydrides has been observed for V (as well as for Nb). It is thought to have its origin in the dissipation of energy by dislocations generated in the metal during formation of incoherent hydrides. Thus the peak should have the same features as the Type I Snoek-Köster peak.

A set of measurements showing the peak for different hydrogen levels is shown in Fig. 7. These are all cooling measurements; the abrupt increase in damping shows the temperature of the solvus line at that compo- ion. The height increases with hydrogen content, but levels off at the higher hydrogen contents. Activation energy measurements as have been attempted by us, by Owen and Scott (17) and by Butera and Kofstad (18) yield values around 0.4 ev. This value is about the same as that found by us for the Snoek-Köster peak of Type I.

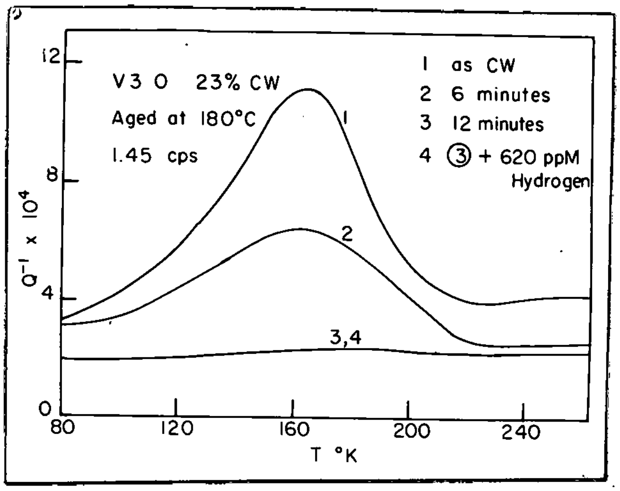

FIG. 6
Effect of annealing on α-peak.

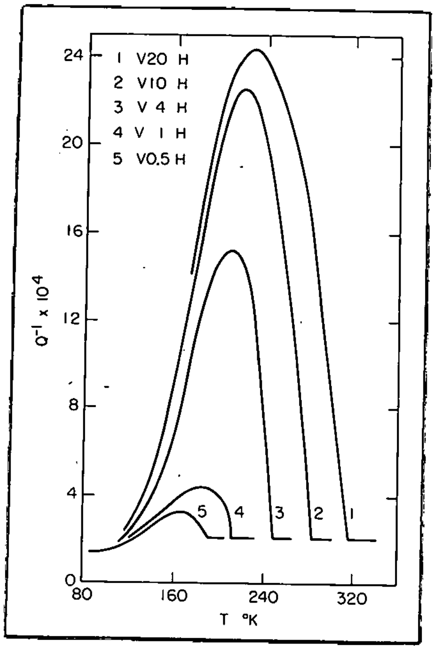

FIG. 7
Precipitation peak.

We have found differences in the solvus temperatures determined by us, by Westlake (19) by Scott and colleagues (17,20) and by Cannelli and Mazzolai (10). We attribute these differences to variation in dissolved oxygen and nitrogen impurities between the several studies; a paper describing our interpretation is in press (21).

Summary and Discussion

We believe that the α-peak (as described in many earlier papers) is not a single, unique peak. Instead it may vary with the presence of hydrogen, oxygen and nitrogen. We see from the preceding observations and references to the literature that many of the previous discrepancies can be reconciled if careful control is established of the impurity levels.

The peak in deformed vanadium of the highest purity we could achieve we call the α-peak. Two regions of deformation seem to exist for this peak. Frequency factors and activation energies for these two regions are shown by the first two lines of Table II.

The presence of immobile interstitials (oxygen and nitrogen) in solid solution suppresses the α-peak, apparently by locking the dislocations. Only a small concentration of randomly dispersed interstitial is required -- ≈ thousand atomic ppm. A damping peak can be restored by low temperature drogen addition, a peak whose damping mechanism seems likely to be the dragging of a hydrogen atmosphere in the small motion left to the pinned dislocations. This damping peak -- termed the Snoek-Köster peak of Type II -- has a much higher frequency factor and a large activation energy, see lines 4 and 5 of Table II.

Annealing of deformed specimens in the temperature range 200°C to 300°C permits large scale diffusion of interstitial oxygen or nitrogen to the dislocations. These interstitials pin the dislocations so firmly at low temperature that they not only suppress the α-peak but also inhibit the formation of a Type II Snoek-Köster peak when hydrogen is added. Thus the anomalous annealing behavior referred to by earlier authors is explained.

The precipitation peak can now readily be explained. The formation of incoherent hydrides causes the generation of many dislocations. These are, of course, in the atmosphere of hydrogen in thermodynamic equilibrium with the hydride at the peak temperature. Consequently the damping peak originating from these dislocations should be the Snoek-Köster peak Type I. Indeed it seems to be; the rate parameters listed in Table II lines 6 and 7 agree well with those of the line 3 of Table II.

Finally, we caution against annealing of the bcc metals in the temperature range 1000°C to 1200°C. Even in the best vacuums available, oxygen and nitrogen pick up is inevitable. If these interstitials at levels of a few thousand ppm influence the property to be observed, the result of the annealing treatment may be to complicate interpretation of the observations.

TABLE II

Parameters for Various Peaks Observed in Vanadium

	Peak Designation	f_o (sec^{-1})	Q (ev)	
1)	α-peak 14% CW	10^{6}	0.15	
2)	α-peak 23% CW	10^{8}	0.29	
3)	Type I S-K peak	10^{10}	0.38	
4)	Type II S-K peak	10^{16}	0.55	
5)	Type II S-K peak	10^{17}	0.52	Ref. 17
6)	Precipitation peak	10^{9}	0.36	
7)	Precipitation peak	10^{10}	0.41	Ref. 10

Acknowledgment

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