LA-UR--85-2481

DE85 015705

CONF-8506125--6
AUG 07 1985

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

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SOLUTE BINDING IN BCC METALS

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SUBMITTED TO Proceedings of Eighth International Conference on
Internal Friction and Ultrasonic
Attenuation in Solids Urbana, IL.

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EVALUATION OF ANELASTIC EVIDENCE FOR INTERSTITIAL SOLUTE BINDING IN BCC METALS

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Résumé- Une nouvelle technique d'analyse directe des spectres (DSA) a été appliquée aux résultats cruciaux de frottement intérieur et de trainage mécanique invoqués dans la controverse sur l'existence d'une agglomération des interstitiels dans les métaux réfractaires. On trouve que, pour les concentrations de solutés interstitiels relativement élevées, une partie de l'élargissement du pic de Snoek est due à des relaxations distinctes de la relaxation principale. Ce résultat renforce l'idée d'une interaction de solutés qui conduit à la formation d'amas d'interstitiels.

Abstract- A Direct Spectrum Analysis (DSA) technique has been applied to key internal friction and elastic after-effect data which are involved in the controversy over the existence of interstitial clustering in the refractory metals. It is found that at relatively high interstitial solute concentrations some of the Snoek peak broadening is due to relaxations that are distinct from the main relaxation. This finding supports the view that interstitial solutes have an interaction that produces clusters of interstitials.

1- INTRODUCTION

In 1955 Powers /1/ published internal friction data showing that the oxygen Snoek peak is broadened asymmetrically as the oxygen solute concentration increases. In 1956 Powers and Doyle /2/ suggested that the broadened peak could be considered to be the sum of two single relaxation peaks; the main peak was assumed to be the regular Snoek peak due to single oxygen atoms and the smaller high-temperature peak was due to stress-induced reorientation of closely associated pairs of oxygen atoms (bound-pair model). Later Powers and Doyle /3/ published results of a more extensive investigation using elastic after-effect measurements which confirmed the bound-pair model and gave a value of roughly 0.09 eV for the binding enthalpy of oxygen atoms.

This work of Powers and Doyle has had a profound influence on our ideas about interstitial solid solutions and many other investigators have found similar results in various bcc metals. Now however, Weller et al /4/ have published new results for the Ta-O system which they claim show that the oxygen Snoek peak is symmetrically broadened as the oxygen concentration is increased and that there is no specific evidence for the existence of bound-pairs. In view of the importance of this question we decided to reanalyze the results reported by Weller and by Powers and Doyle using a newly-developed direct spectrum analysis (DSA) method which analyzes an internal friction peak to give an estimate of the spectrum of relaxation times (at constant temperature). The key reason for using the DSA method is that it does not make a priori assumptions about the form of the spectrum /5,6/. The results of the DSA method support the bound-pair model.

11- RESULTS

11a- INTERNAL FRICTION DATA OF WELLER et al

We analyzed Weller's data for samples containing 1200, 3400 and 5900 appm oxygen. The data were taken from his Fig. 2 /4/ using a high precision digitizer. The same corrections used by Weller et al /4/ for the variation of frequency and

Fig. 2. DSA relaxation time (or activation energy) distribution from Weller's data for oxygen concentrations 1200, 3400 and 5900 appm and from Powers' data for a sample containing 5900 appm. The solid curves show lognormal distributions fit to the histograms with parameters T_m and β given in Table 1. The vertical dashed lines give the spectral limits imposed on the calculation.

We also analyzed some of the elastic after-effect data of Powers and Doyle /3/ using DSA. Since these measurements were made at lower temperatures than the internal friction measurements the relative concentration of bound pairs is expected to be greater and the pair relaxation should show up at smaller oxygen concentrations. We analyzed the data for a sample containing 1900 appm oxygen and found two peaks in the spectrum with mean T values shown in Table 1.

Data Ref.	Oxygen appm	Temperature K	T_{m1}, s	β_1	T_{m2}, s	β_2	T_{m3}, s	β_3
Weller/4/	1200	423.7	.11	.34	*	*	*	*
	3400	423.7	.12	.35	.37	.28	*	*
	5900	423.7	.10	.35	.25	.70	2.2	.14
Powers/1/	4500	423.7	.09	.32	.18	.60	1.14	.24
Powers/3/	1900	349.9	60.6	.49	415	.36	*	*

* = component not present

III. DISCUSSION

Our analysis of the internal friction data of Weller et al shows that the spectral distribution of relaxation times agrees quite well with the distribution obtained from the older data of Powers for similar oxygen concentrations. At small oxygen concentrations a narrow (approximately lognormal) distribution of relaxation times is observed. As the concentration of oxygen increases, a shoulder appears on the high relaxation time side (or equivalently the high energy side) of the original distribution. This shoulder can be treated as a second lognormal distribution of relaxation times. At still higher concentrations of oxygen a third lognormal distribution of relaxation times appears at longer relaxation times. The general pattern is in agreement with Powers bound-pair model with the modification that the two discrete relaxations due to single oxygen atoms and pairs of oxygen atoms are replaced by two lognormal distributions of relaxation times. Physically such a modification appears reasonable since the lognormal distributions are very narrow and thus barely distinguishable from discrete relaxations. Since the distributions are so narrow we will discuss the spectra as though they composed of one, two or three single relaxation times, which are taken as the mean relaxation times of the corresponding lognormal distribution.

It is noteworthy that the first relaxation which is attributed to single oxygen atoms does not change position or width with increasing oxygen concentration. However, the second relaxation, which is attributed to oxygen pairs, shifts to lower relaxation times and increases in width as the oxygen concentration increases. This behavior might be explained by the superposition of a peak due to triplets or higher-order groups of oxygen atoms. According to the law of mass action the magnitude of the peak due to oxygen pairs should be proportional to the square of the magnitude of the peak due to single oxygen atoms. This relationship is not obeyed for the Weller data; the pair peak in the 5900 appm sample is too large relative to the pair peak in the 3400 appm sample. A possible explanation for the discrepancy is the presence of a substantial contribution from oxygen triplets or higher-order groups to the peak attributed to the pairs in the 5900 appm sample. Or it may be that because of the close proximity of the two relaxations the DSA method does not give a reliable estimate of the relative magnitudes of the two peaks.

The third distribution of relaxation times is centered at a mean relaxation time which corresponds well with the position of the oxygen-nitrogen interaction peak found by Powers and Doyle /3/. The Arrhenius equation given by Powers and Doyle predicts a relaxation time of 1.2 s at 423.7 K. Thus this peak may be due to residual nitrogen in the samples.

Powers and Doyle's model for the association of oxygen atoms in tantalum was derived primarily from elastic after-effect measurements rather than internal friction measurements. As shown in Table 1, the separation between the Snoek peak and the pair peak is greater for the elastic after-effect data than for the internal friction data. The relaxation times for these two peaks calculated from Powers and Doyle's equations are: 59 s and 361 s at 349.9 K, 0.10 s and 0.35 s at 423.7 K. These times agree well with the mean relaxation times determined by the DSA method for the three different sets of data.

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