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ATOMIC-DEFECT MECHANISMS FOR DIFFUSION IN REFRACTORY BCC METALS[*]

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ABSTRACT

Despite a number of recent investigations into the nature and properties of equilibrium atomic defects in the refractory bcc metals, the mechanisms responsible for the high-temperature mass transport in these materials are not clear. The observed strong high-temperature enhancement in self-diffusion appears to be unexplainable in terms of divacancies, but might result from the presence of small equilibrium concentrations of highly-mobile self-interstitials. Recent vacancy formation measurements in Cr appear to support this view. However, recent studies of diffusion in Nb(W) alloys and high-temperature vacancy migration in W have raised new issues to be considered.

INTRODUCTION

Investigations of the nature and properties of atomic defects in the Group V-B and VI-B refractory bcc metals, and their relationship to atomic transport, have been performed during the last several years using a variety of techniques (e.g., [1-4]). Although these studies have resulted in a better understanding of the atomic-defect mechanisms for diffusion in refractory metals, problems still remain [5]. Below about half the melting temperature, self- and solute-diffusion appear to be controlled by atomic exchange with mono-vacancies. However, at higher temperatures, diffusion is strongly enhanced above that normally associated with monovacancies. This enhancement, which is much stronger than that found in fcc metals, is apparently not due to diva-cancy formation, but might result from the presence of small equilibrium concentrations of highly-mobile self-interstitials. This suggestion, raised previously for W [1,2] and Mo [5], has been supported by recent positron annihilation spectroscopy (PAS) measurements of equilibrium vacancy formation in Cr [6], which indicate that vacancies are not responsible for the measured self-diffusion behavior over the complete temperature range in which such measurements are presently possible.

RESULTS AND DISCUSSION

The radiotracer self-diffusion data for the refractory bcc metals, shown schematically in Figure 1, are typified by an enhancement at the melting temperature of about a factor of ten over that extrapolated from the low-temperature diffusion behavior [5]. Based upon a simple two-defect diffusion model, a consistent set of temperature independent diffusion parameters can be obtained from these data [7]. For tungsten, the most extensively studied of these metals, post-quench resistivity measurements [1] of the vacancy formation (3.6 eV) and migration (1.8 eV) enthalpies have confirmed that the low-temperature diffusion mechanism (with activation enthalpy 5.45 eV [8]) is atomic exchange with monovacancies, and have further suggested that the strong high-temperature enhancement in the self-diffusion coefficient may be a result of atomic transport via an interstitialcy mechanism. This description has gained additional support from combined post-quench resistivity and field ion microscopy (FIM) measurements [2], which yielded a value for the divacancy binding enthalpy (about 0.7 eV) and, in combination with the previous quench-ing results [1], indicated that the nearest-neighbor divacancies observed by FIM have a mobility that is slightly less than or about equal to that for the monovacancy. This combination of a rather low divacancy concentration (no more than 1-10% of the total vacancy concentration at T_m) and low (or at least not enhanced) divacancy mobility cannot explain the strong high-temperature enhancement of self-diffusion. Equilibrium PAS results [3,4] lend further support to this picture, while confirming the results from the nonequilibrium quenching studies on tungsten. The equilibrium value of $H_v^F = 3.8 \pm 0.4$ eV
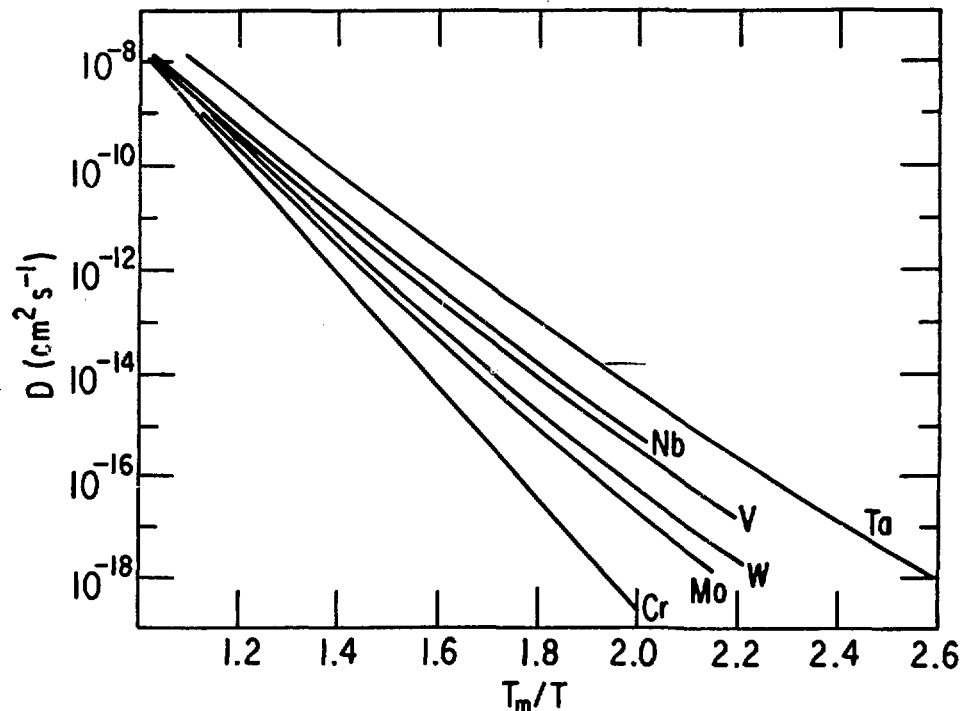

Fig. 1. Radiotracer-diffusion coefficients for the refractory bcc metals as a function of reciprocal temperature normalized to the respective melting temperatures, T_m [7].

Table 1. Fitted values of the diffusion parameters for the refractory bcc metals according to the equation $D = D_{01} \exp(-Q_1/kT) + D_{02} \exp(-Q_2/kT)$. The values in parenthesis for Cr are suggested in accordance with the value of Q_2/Q_1 for the other metals [7].

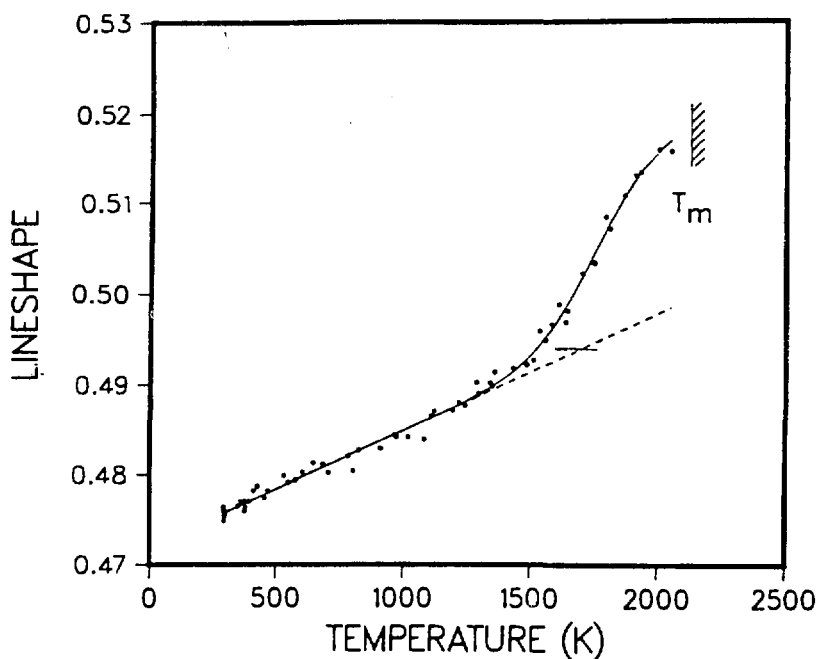| Metal	D_{01} $(10^{-3}\ cm^2\ s^{-1})$	Q_1/T_m $(10^{-3}\ eV\ K^{-1})$	D_{02} $(cm^2\ s^{-1})$	Q_2/T_m $(10^{-3}\ eV\ K^{-1})$	Q_2/Q_1
Ta	1.3	1.2	1.0	1.4	1.24
Nb	8.0	1.3	3.7	1.7	1.24
V	14	1.3	7.5	1.7	1.28
W	40	1.5	46	1.9	1.28
Mo	130	1.6	139	2.0	1.27
Cr	(~900)	(1.7)	1280	2.2	(1.26)

Fig. 2. Positron annihilation Doppler-broadening lineshape for Cr as a function of temperature between 296 and 2049 K. The two-state trapping model fit to the data up to near the melting temperature (T_m = 2130 K) is shown, along with a dashed-line extension of the Bloch-state fit [6].

obtained from temperatures between 300 K and 3633 K [4] agrees within experimental precision with that from the quenching studies [2,3], 3.6 ± 0.1 eV, but would allow for at most a small divacancy contribution at the highest temperatures consistent with the FIM results [2].

The equilibrium vacancy ensemble observed recently [6] by PAS in Cr, as shown in Figure 2, does not seem to be responsible for the diffusion behavior measured by radiotracer techniques [7], which after all appears to be dominated by a high-temperature mechanism by comparison with the results for other refractory bcc metals [5,7]. The value found for H_v^F(2.0 eV) could only be consistent with a vacancy model for the observed diffusion (with activation enthalpy 4.58 ± 0.03 eV [7]), if the vacancy migration enthalpy were about 2.6 eV. However, this value would indicate vacancy migration at temperatures well above those found by PAS for the complete annealing of any vacancy defects introduced by electron irradiation in Cr [9], unless H_v^M were strongly temperature dependent. Indeed, a comparison of the observed temperature (550 K) for the dominant post-irradiation vacancy annealing stage [9] and an empirical correlation between such temperatures and vacancy migration enthalpies would indicate a vacancy migration enthalpy in Cr of ~1.4 eV. Furthermore, if it is assumed that the measured self-diffusion activation enthalpy for Cr, 4.58 eV, is characteristic of a high-temperature mechanism by analogy with the results for the other refractory bcc metals (see Table 1), then the empirical rule observed by Mundy et al. [7], $Q_2/Q_1 \simeq 1.26$, could be used to estimate a self-diffusion activation enthalpy representative of monovacancies, $Q_1 \simeq 3.6$ eV. Using this and the PAS result for H_v^F, a monovacancy migration enthalpy can be estimated as $H_v^M = Q_1-H_v^F = 1.6 ± 0.2$ eV, which is consistent with that deduced above from the electron-irradiation results [9]. The inability to explain the measured diffusion behavior in Cr in terms of the equililbrium vacancy ensemble observed with PAS, therefore, seems clear. Whether an interstitialcy mechanism, as suggested for the other Group VI-B metals W and Mo [5], is responsible for the observed diffusion behavior remains to be seen; more direct experiments to attempt to answer this question are required.

In an effort to further elucidate this problem, a series of self- and solute-diffusion measurements on Nb(W) alloys was carried out [10] within the high-temperature (enhanced) diffusion regime. The results were surprising in that the observed dehancement factors for [95]Nb,[95]Zr, and [185]W were all of similar magnitude (~5), indicating that whatever diffusion mechanism pertains in this regime, the effects of tungsten alloying of the Nb were essentially non-local in nature. Such a constraint would have to be satisfied by any appropriate diffusion model for high-temperature diffusion.

The question of whether strong temperature dependences of the atomic-defect properties (particularly H_v^M) relevant to diffusion could explain the observed high-temperature diffusion enhancement has recently been raised [11] on theoretical grounds, and an experimental study of this in W has now been completed [12]. It was experimentally determined that H_v^M varies between about 1.7 eV at 1550 K and 2.0 eV at 2600 K, indicating a rather strong temperature dependence, but one that would be insufficient in itself to explain the observed Arrhenius-plot curvature for W self-diffusion [8]. A similarly strong temperature dependence for H_v^F would also have to be invoked to explain the observed curvature. While such a temperature dependence for H_v^F has not been observed, it might conceivably be accommodated within the uncertainties of previous measurements [1-4]. The case of Cr, however, raises more difficulty

with such an explanation. In this case, not only would H_v^M and H_v^F have to be strongly temperature dependent, but their temperature dependences would have to be such that the Arrhenius plot for $D(T)$ could still remain straight over about ten orders of magnitude in D [7]. Also, such an explanation would necessarily lead to the conclusion that $H_v^M > H_v^F$ in Cr, opposite to the situation pertaining in other metals.

CONCLUSIONS

Within the context of our present knowledge, it would appear that the most straightforward explanation of the strong high-temperature diffusion enhancement observed for the refractory bcc metals is in terms of the presence of small equililbrium concentrations of highly-mobile self-interstitials, with formation enthalpies about twice that for the respective monovacancy [5]. Such a model leads to no apparent inconsistencies with data presently available, and would provide a consistent description for the diffusion parameters of the refractory bcc metals presented in Table 1. However, the strong temperature dependence in H_v^M for W recently observed [12] would suggest that at least part of the Arrhenius-plot curvatures for $D(T)$ may be a result of inherent temperature dependences in the relevant vacancy-defect properties. Further experimental and theoretical research will be required to clarify this situation.

A type of experiment that should be able to clearly differentiate between vacancy and self-interstitial contributions to high-temperature mass transport would be a transient diffusion experiment which could take advantage of the very different response times for these two types of defects to come to equilibrium. Rapid cyclic variation of the sample temperature during diffusion should be able to suppress contributions arising from vacancy defects, while affecting contributions from self-interstitals rather little. Such an experiment is within present capabilities and should be performed.

Finally, if the high-temperature diffusion in the refractory bcc metals is indeed dominated by mass transport via an interstitialcy mechanism, it is interesting to consider how this fits in with diffusion mechanisms in other elemental solids. It appears that, while low-temperature self-diffusion via atomic exchange with monovacancies is ubiquitous, the dominant atomic defect for high-temperature self-diffusion may vary from divacancy to interstitial as the interatomic bonding varies from free-electron like to increased covalent character. Thus, an interstitialcy high-temperature diffusion mechanism in the refractory bcc metals may have a natural place between the divacancy-dominated high-temperature self-diffusion in Al, for example, and the interstitial-dominated diffusion in Si, at the covalent extreme.

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