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Formation enthalpies of vacancy–oxygen complexes and single vacancies in the core of grain boundaries in polycrystalline Cr, Ta, and W

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Abstract

Atomic probes (APs) $^{57}Co(^{57}Fe)$ are localized in the grain boundary (GB) core and adjacent regions of the lattice in polycrystalline metals by means of GB diffusion. Spectra of nuclear gamma resonance (NGR) of radiation of APs $^{57}Co(^{57}Fe)$ were used for analysis of the nearest neighborhood of APs. Vacancies, which are formed in the GB core of polycrystalline metals during annealing in a technical vacuum over the temperature range (0.2–0.4)T_{melt}, are captured by traps (oxygen atoms) and form stable complexes with oxygen (complexes-VacO). For the first time, formation enthalpies $Q_{\mathrm{cmpl,1}}$ of complexes-VacO and formation enthalpies $Q_{\mathrm{Vac,1}}$ of single vacancies in the GB core in Cr, Ta, and W polycrystals have been determined from Arrhenius dependencies of the contribution $\delta_{\mathrm{Vac,1}}$.

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1. Introduction

Grain boundaries (GBs) in polycrystals are studied systematically, in particular by a method [1–3] that uses: (a) atomic probes (APs) providing spectral information about the states occupied by the APs, and (b) GB diffusion of APs ensuring localization of the APs in the GB core and adjacent lattice regions (ALRs). The spectroscopy of nuclear gamma resonance (NGR) of radiation of $^{57}Co(^{57}Fe)$ in Refs. [1–3] is used for the investigation of states populated by these APs.

Isomer shifts (IS) δ_1 and δ_2 of the two components 1 and 2 in the spectra of NGR radiation of the APs $^{57}Co(^{57}Fe)$, which are localized in the GB core and ALRs of polycrystals, respectively, depend on the temperature T of annealing in a technical oil-free vacuum of about 10^{-6}–10^{-5} Torr. IS δ_2 are much smaller than the IS δ_{vol} characterizing volumes of pure metals (Fig. 1). The difference $\Delta\delta=\delta_2-\delta_{\mathrm{vol}}<0$ is caused by doping of the polycrystals with oxygen during their annealing in a vacuum. The volume V of a metal increases upon oxygen doping because the relaxation volume of the oxygen impurity in the metals $v_o>0$ [4,5]. The increase of the metal volume V is accompanied by the decrease in the density of conduction s-electrons, by the drop of the density of s-electrons on the APs nucleus, and decrease of IS δ (Fig. 1) in the emission spectra of NGR of $^{57}Co(^{57}Fe)$ radiation [4,6].

As the annealing temperature increases, vacancies are formed in the GB core. The vacancies are captured by traps (oxygen atoms) and are fixed in vacancy–oxygen complexes (complexes-VacO). Therefore, vacancies can be preserved at the place of their formation without the need for rapid cooling of the polycrystals to room temperature, at which the NGR spectra are recorded. Vacancies in the volume [8–10] and in the GB core [11,12] of the metals

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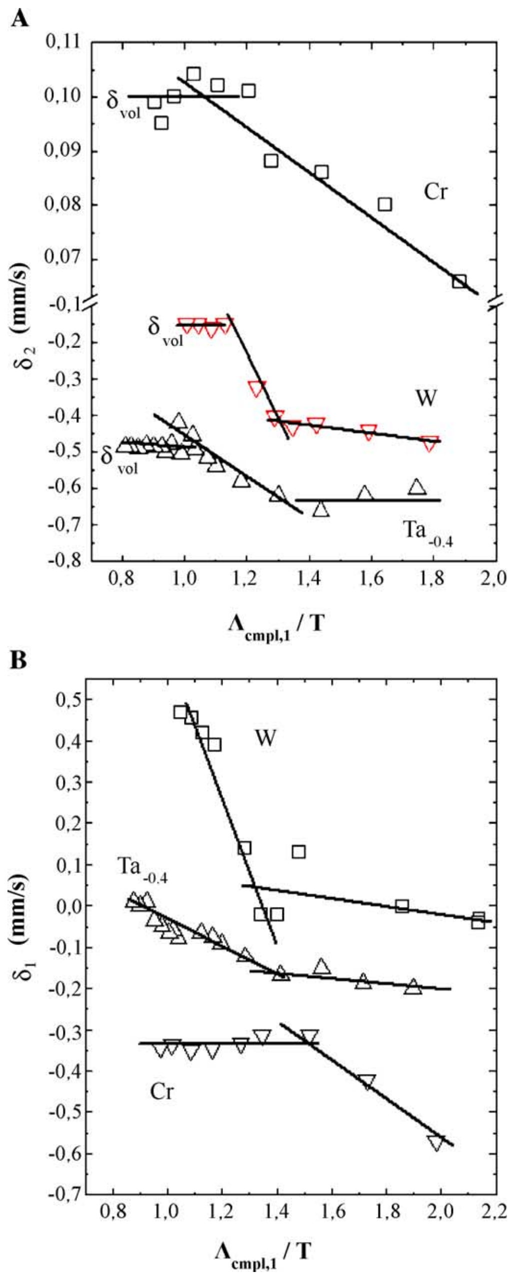

Fig. 1. Dependencies (A) δ_1 (1/T) and (B) δ_2 (1/T) of IS of components 1 and 2 in the emission spectra NGR of radiation of ^{57}Co(^{57}Fe), which were localized in the GB core (state 1) and ALRs (state 2) in Cr, Ta, and W polycrystals. The lines are only guides for the eyes.

have a negative relaxation volume: $v_{\text{Vac}}<0$. Therefore, the increase of the vacancy's concentration is accompanied by the decrease of metal interatomic spacings and by the increase of the density of valence s-electrons on the APs nucleus and of the quantities δ_2 and δ_1 (Fig. 1) [6,7].

In the present study, the Arrhenius dependencies of the contributions $\delta_{\text{cmpl},1}$ to IS δ_1 were used for the measurement of formation enthalpies $Q_{\text{cmpl},1}$ of complexes-VacO in the GB core in polycrystalline Cr, Ta, and W. Formation enthalpies $Q_{\text{Vac},1}$ of single vacancies were determined using the linear dependence $\{Q(\Lambda)\}_{\text{cmpl},1}$ and the calculated minimum formation enthalpy of free vacancies in the core of a special large-angle GB in Mo [13].

2. Theoretical background

The change of the IS δ of the component in the NGR spectrum depending on the concentration of point defects C in a metal can be written as:

$$\mathrm{d}\delta/\mathrm{d}C = (\partial\delta/\partial\ln V)(\mathrm{dln}V/\mathrm{d}C). \tag{1}$$

The rate $(\partial\delta/\partial\ln V)$ of variation of δ with V is constant [15] in each metal:

$$(\partial\delta/\partial\ln V)\equiv\Delta\delta_{\text{vol}}/|\Delta\ln V| = -\chi. \tag{2}$$

The coefficient $(\mathrm{dln}V/\mathrm{d}C)\equiv v$ in Eq. (1) denotes the relaxation volume of a point defect, which is determined from X-ray diffraction data [4]. In solid solutions with a set of point defects, it is defined as the sum of relaxation volumes v_{i} of all the point defects [14]:

$$(\mathrm{dln}V/\mathrm{d}C) = \sum(v)_{\text{i}}. \tag{3}$$

The IS δ_1 of component 1 in the NGR spectra includes the following contribution:

$$\delta_1 = \left(\delta_{\text{intr}} - |\delta_{\text{o}}| + \delta_{\text{cmpl}}\right)_1, \tag{4}$$

where δ_{intr}, $\delta_{\text{o},1}$, and $\delta_{\text{cmpl},1}$ are the contributions from APs localized on the pure GB core or GB cores containing only free oxygen atoms or only complexes-VacO, respectively. The contribution $\delta_{\text{cmpl},1}$ is proportional to the concentration $C_{\text{cmpl},1}$ of complexes-VacO, each comprising one oxygen atom and one vacancy [7]. The concentration $\mathrm{C}_{\text{cmpl},1}$ is given by the relationship [9,16]:

$$C_{\text{cmpl},1} = \{C_{\text{O}}C_0\exp(-Q_{\text{Vac}}X)\exp(E_{\text{VacO}}X)\}_1. \tag{5}$$

Here $\mathrm{Co}_{,1}$ is the concentration of free oxygen atoms, C_0 is a preexponential factor, Q_{Vac} is the vacancy formation enthalpy, E_{VacO} is the enthalpy of the interaction between one vacancy and an oxygen atom in the complexes-VacO, $X=1/RT$, and R is the gas constant. The formation enthalpy $Q_{\text{cmpl},1}$ of complexes-VacO is found from the expression:

$$Q_{\text{cmpl},1} = -\partial\ln\delta_{\text{cmpl},1}/\partial x = -\partial\ln C_{\text{cmpl},1}/\partial x$$
$$= (Q - E_{\text{VacO}})_1. \tag{6}$$

3. Results and discussion

Each measurement of the emission spectrum of NGR of radiation of ^{57}Co(^{57}Fe) was made at room temperature of the test polycrystalline samples (source) and the resonance absorber after each annealing step of an isochronal series.