

Mössbauer Investigation of Sn Diffusion and Segregation in Grain Boundaries of Polycrystalline Nb

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The parameters of nuclear γ resonance (Mössbauer) spectra on ^{119m}Sn nuclei inserted into grain boundaries of polycrystalline Nb have been determined at the annealing temperatures of 680 to 994 K [0.25-0.36 melting temperature (T_m)]. Two components are observed in the nuclear emission γ resonance spectra at all of the annealing temperatures considered. One of them (component 1) is suggested to result from the ^{119m}Sn atomic probes localized in grain boundary cores, while the other one (component 2) corresponds to that located in the near-boundary areas. Diffusion annealing temperature dependences of both components parameters have been analyzed. The coefficients and enthalpy of Sn grain-boundary segregation are determined based on this analysis, as well as the ratio of the diffusion pumping zone extension to the grain boundary width and the enthalpy of the atomic probes “pumping” from grain boundaries into the bulk.

1. Introduction

Grain-boundary diffusion determines many properties of structural materials. On the other hand, the grain boundary diffusion parameters are sensitive to the structure and composition of grain boundaries. That is why great attention has been paid to the determination of grain-boundary diffusion characteristics. The results obtained in the area of grain-boundary diffusion by the early 1990s are presented by [1995Kau], and the further achievements in this area are analyzed in the overviews by [1997Mis], [1999Mis], and [2003Her].

Most of the grain boundary diffusion measurements were made by the use of radiotracers and serial sectioning technology. These techniques give the dependence of mean concentration on depth in a layer parallel to the specimen surface, which is referred to as the *concentration profile* or *penetration profile*. This function bears the information on grain-boundary diffusion parameters. The concentration profile measurements on polycrystals in diffusion kinetic regimes B and C enable the determination of sdD_b (where s is the segregation factor, d is the diffusion width of a grain boundary, and D_b is the grain-boundary diffusivity) and D_b , based on which it is possible to calculate the value of sd . In its turn, if d is supposed to be known (and it is usually assumed that $d \approx 0.5$ nm), then s may be evaluated as well.

An investigative technique based on the use of Mössbauer emission spectroscopy with radioisotope nuclei inserted into grain boundaries has been worked out by [1990Klo] and [1994Kai]. The Mössbauer atomic probes

that are capable of giving spectra information are introduced into a substance under investigation with annealing conditions that ensure their primary localization in grain-boundary cores. The registered resonance γ radiation gives information on the properties of those states in which the atomic probes appear to locate. The potentialities of this technique and the diffusion measurements using radiotracers supplement each other to a certain degree. In particular, the former allows the easier determination of segregation factors without any assumptions about grain-boundary diffusion width.

This method was recently successfully applied to the study of the structure and physical properties of high-angle grain boundaries in a number of transition and noble metals (e.g., 1990Kai, 1994Kai, 1998Kai1, 1998Kai2, and 1998Kai3). In these publications, grain boundaries were investigated using the ^{57}Co Mössbauer nuclei. The ^{119m}Sn nuclei have not yet been practically used to study internal interfaces, although in some cases it is of great importance to use those very nuclei. The application of the emission Mössbauer spectroscopy on ^{119m}Sn nuclei is of special interest for the investigation of local structure, diffusion, and physical properties of grain boundaries and adjacent areas in polycrystalline niobium (Nb), because the manufacture of superconducting Nb_3Sn -based bronze-processed composites is based on Sn penetration from the Cu-Sn matrix into Nb filaments [2003Pop].

The main goal of the current study is to investigate grain boundaries in polycrystalline Nb by nuclear emission γ resonance (NGR) spectroscopy on ^{119m}Sn nuclei.

2. Experimental Procedure

The research was carried out on a high-purity polycrystalline Nb. The secondary ion mass spectrometry (SIMS) analysis conducted with the CAMECA IMS-3f ion analyzer (France) has shown the total concentration of substitution impurities to be about 5 atomic parts per million (at. ppm). The concentration of interstitial impurities ap-

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peared to be substantially higher, namely, ~ 350 at. ppm O and ~ 100 at. ppm C. There was no texture in the specimens investigated, and the average grain size was about $50 \mu\text{m}$.

To obtain a Mössbauer source, the $^{119\text{m}}\text{Sn}$ radionuclide (~ 80 MBq) was electrically deposited on the surface of a polycrystalline Nb sample with an area of about 1 cm^2 . To insert the $^{119\text{m}}\text{Sn}$ atomic probes into grain boundaries, this sample was then annealed at 680 K , for 7 h . After the annealing, the residual undiffused $^{119\text{m}}\text{Sn}$ radionuclide was removed from the sample surface by a selective etchant (HCl).

The main rapid diffusion paths in Nb polycrystals of recrystallization origin are common high-angle grain boundaries. Rapid diffusion is also possible along dislocations and special boundaries. Diffusion coefficients along the latter defects of crystal structure are appreciably lower than that along the high-angle grain boundaries [1994Kau], and, respectively, they control a narrower diffusion zone. To exclude the effects of dislocations and special boundaries on the Mössbauer grain-boundary spectra, a layer of about $1 \mu\text{m}$ thickness was removed from the sample surface by chemical polishing.

Along with the grain-boundary Mössbauer source, a bulk (standard) Mössbauer source was manufactured with the same techniques, with about 20 MBq of $^{119\text{m}}\text{Sn}$ deposited on the surface of a single crystal of high-purity Nb. The latter was annealed at 1273 K for 4 h . The emission Mössbauer spectrum of the reference source is a singlet with an isomer shift of -1.63 mm/s and a width of 0.91 mm/s .

The NGR spectra were measured on a Mössbauer spectrometer operating in a constant rate regimen. After the measurement of the NGR spectrum of polycrystalline Nb that was annealed at the lowest temperature, the latter was annealed at higher temperatures with intervals of 20 to 80 K and the same duration of 2 h with subsequent measuring of NGR spectra. All of the measured isomer shifts are presented relatively to BaSnO_3 . The emission NGR spectra expansion in constituents was accomplished with the specialized Univem MS program (Rostor State University, Russia) for the Mössbauer spectra treatment.

3. Results and Discussion

The characteristic emission NGR $^{119\text{m}}\text{Sn}$ spectra in polycrystalline Nb after annealing at different temperatures are shown in Fig. 1. It can be seen that at all of the annealing temperatures there are two components in these spectra, the origin of which have been definitely established by [1990Klo] and [1994Kai]. Component 1, which was more intensive at lower temperatures, corresponds to the atomic probes localized in the grain-boundary cores. The quadrupolar splitting of this line (~ 0.44 - 0.48 mm/s) testifies that the $^{119\text{m}}\text{Sn}$ atomic probe positions in high-angle boundaries of polycrystalline Nb possess nonsymmetrical ion surroundings. This quadrupolar splitting is assumed to result from the distortions forming around relatively large Sn atoms. This assumption is supported by the fact that there is no quadrupolar splitting of component 1 when ^{57}Co atomic probes are used [1994Kai, 1998Kai1, 1998Kai2, 1998Kai3].

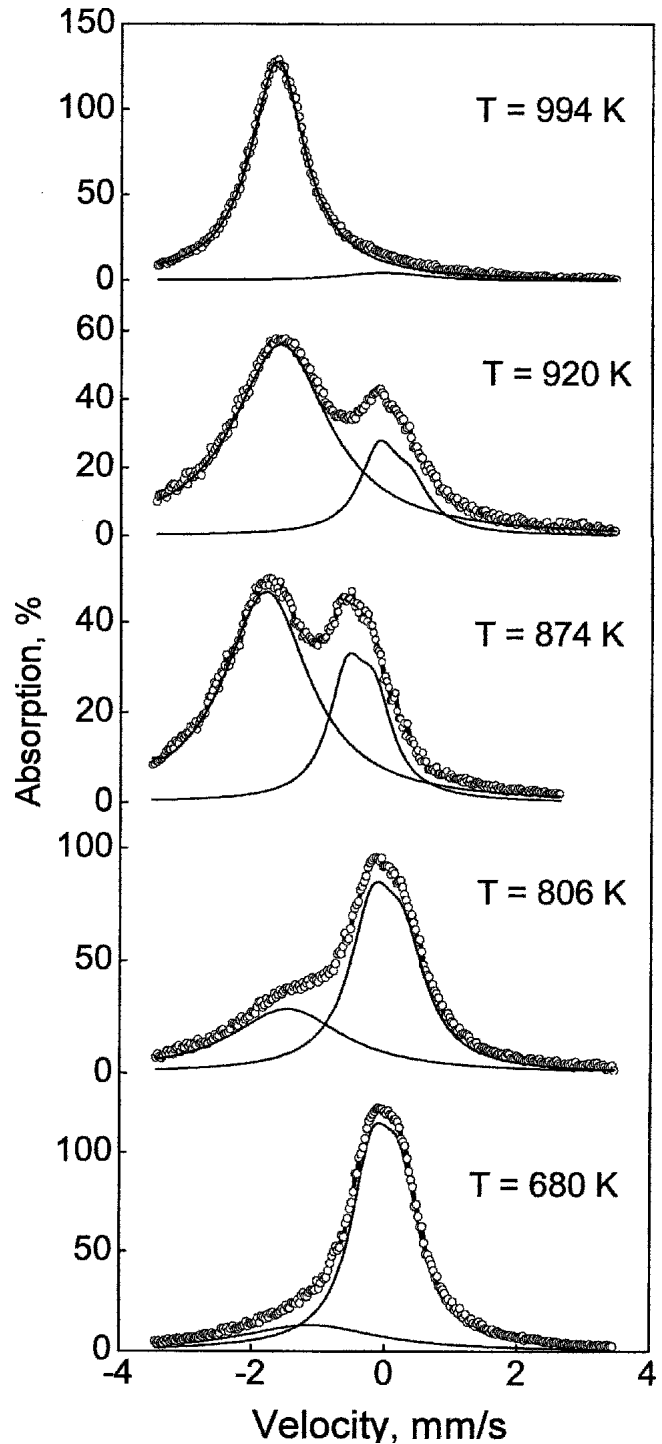


Fig. 1 The expansion of NGR $^{119\text{m}}\text{Sn}$ spectra in polycrystalline Nb. The experimental spectrum is shown by markers, and the spectrum components are shown by solid lines. The annealing temperatures are indicated on the figure.

The second line (component 2) is the result of the $^{119\text{m}}\text{Sn}$ atomic probes localized in near boundary areas. It may be considered as a single but noticeably broadened line, its width being 2.59 mm/s after the annealing at 680 K . Evaluations using the data of [1965Ask] on the volume diffusion

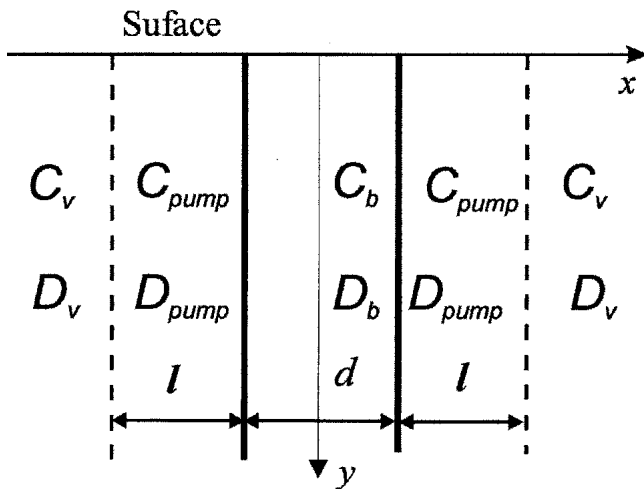


Fig. 2 Scheme of the modified Fisher model

of Sn in Nb show that the diffusion kinetic regimen C is realized at 680 to 806 K. The calculation for annealing at 806 K for 2 h gives a value of ~0.01 nm for the Sn volume diffusion effective depth.

At the same time, the presence of component 2 in the grain-boundary spectrum testifies to an appreciable penetration of the ^{119m}Sn atomic probes in the bulk of the polycrystalline Nb.

Analogous results were obtained at the Mössbauer investigation of grain boundaries of a number of polycrystalline metals employing ⁵⁷Co nuclei [1994Kai, 1998Kai1, 1998Kai2, 1998Kai3]. This observation was one of the reasons for the modification of the classic model of Fisher [1951Fis]. Thus, in [1996Kur] a hypothesis was suggested that between grain-boundary cores and crystallite volume there existed a so-called *pumping zone* of *l* width with a high concentration of point defects, in which the diffusion coefficient *D_{pump}* satisfies the inequality:

$$D_v \ll D_{pump} \ll D_b \tag{Eq 1}$$

where *D_v* is the diffusion coefficient in the volume of crystallites.

The modified model of Fisher is schematically shown in Fig. 2, where the designations *C_b*, *C_{pump}*, and *C_v* are concentrations in grain-boundary cores, the pumping zone, and crystallite volume, respectively. This model does not contradict the experimental results obtained using concentration profile measurements in polycrystals, because it predicts the penetration profiles, which virtually coincide with those based on the model of Fisher [1951Fis] (in case the pumping zone extension does not change in the process of the diffusion experiment). At the same time, it allows the explanation of the results of the Mössbauer investigations of grain-boundary diffusion.

The authors further discuss the experimental results on the basis of this model with its mathematical description presented in [1996Kur]. According to this model, there are three temperature intervals of primary intercrystalline dif-

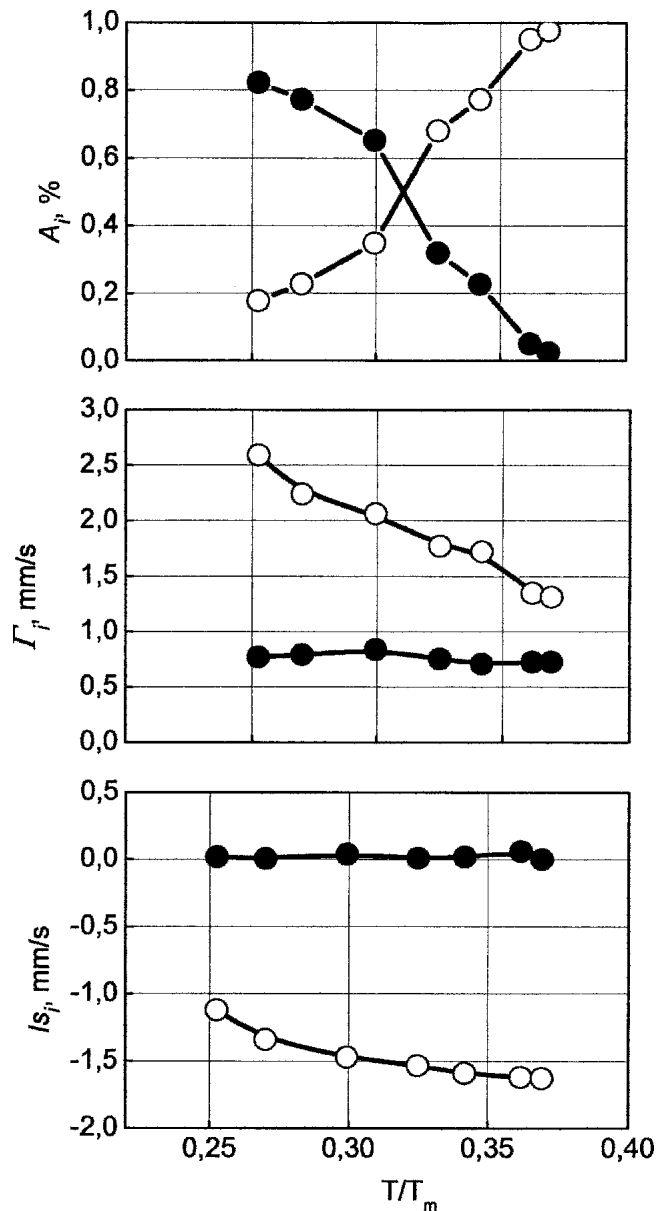


Fig. 3 Dependences of NGR ^{119m}Sn spectra parameters on the annealing temperatures. ●, component 1; ○, component 2

fusion: (1) *D_{pump}t* << *l*² (the stage at which the pumping region is being filled with the atomic probes, which is commonly not possible to observe experimentally); (2) *D_{pump}t* ≅ *l*², but *D_vt* << *l*² (the stage at which the pumping region is filled with the atomic probes); and (3) *D_vt* > *l*² (the stage at which the pumping front crosses the boundary between the pumping zone and the bulk of a crystallite).

Figure 3 demonstrates the emission NGR ^{119m}Sn spectra parameters in polycrystalline Nb (where *A_i* are the relative areas, *Is_i* are isomer shifts, and *Γ_i* are the widths of the components) on the temperature of isochronal annealing. There are two regions in the dependences of relative areas. At low temperatures (up to about 0.3 × *T_m*), the *A_i* dependence on the annealing temperature is relatively weak. From

previous studies, it may be concluded that this temperature interval corresponds to the stage of saturation of the pumping zone with the diffusing impurity. At this stage, the $^{119\text{m}}\text{Sn}$ atomic probes concentration in a pumping zone reaches its equilibrium state, and the volume diffusion rate is still too low for Sn atoms to transfer from the pumping zone into the volume of crystallites.

In that case, the diffusing impurity concentration in C_b and C_{pump} are related as:

$$C_{\text{pump}} = \frac{C_b}{s} \quad (\text{Eq 2})$$

The segregation factor is expressed through the segregation enthalpy (Q_s):

$$s = \exp\left(\frac{Q_s}{RT}\right) \quad (\text{Eq 3})$$

At the saturation stage, the occupancies of states q_i are related to the grain-boundary width d , the pumping zone width l , and the segregation factor s by:

$$\frac{q_1}{q_2} = \frac{s}{2(l/d)} \quad (\text{Eq 4})$$

From the temperature dependence of q_1/q_2 , it is possible to determine the segregation enthalpy of the diffusing impurity:

$$Q_s = R \frac{\partial \ln\left(\frac{q_1}{q_2}\right)}{\partial\left(\frac{1}{T}\right)} \quad (\text{Eq 5})$$

At this stage, the relative occupancies of states are proportional to the relative areas of the spectra lines, because the probabilities of the Mössbauer effect for states 1 and 2 at low annealing temperatures are approximately equal [1998Kai1, 1998Kai2]. This enables the determination of Q_s based on the temperature dependence of A_1/A_2 in the low-temperature interval of 680 to 806 K. Using the resultant value $Q_s = 31 \pm 2$ kJ/mol, the values of s were calculated for different temperatures, and then the ratio of the pumping zone extension to the diffusion grain-boundary width was determined to be $l/d = 30 \pm 6$.

At higher temperatures (i.e., above $0.3 \times T_m$), the relative area temperature dependences become steeper, indicating the stage of the crystallite volume occupation with the diffusing impurity.

Based on the temperature dependences of the occupancies of states at this stage, the activation enthalpy of the process controlling the Sn pumping to the grain volume was determined to be ~ 300 kJ/mol, which is close to the activation enthalpy of Sn volume diffusion in Nb (330 kJ/mol) [1965Ask]. This makes it possible to conclude that it is the volume diffusion that controls the pumping of atoms from a boundary into the volume. Besides, this suggests that the

pumping zone does not decompose at the highest annealing temperatures that were investigated, 994 K ($0.36 T_m$), at which point the grain-boundary component of the spectrum practically entirely vanishes.

The isomer shift of component 1 is close to 0 and is substantially higher than that of the volume line measured on the Nb single crystal (-1.63 mm/s). This result shows that the electron density in state 1 (i.e., in the grain-boundary cores) for the polycrystalline Nb is appreciably lower than that in substitution positions of the Nb regular crystal lattice. Thus, after diffusion annealing in the $^{119\text{m}}\text{Sn}$ atomic probes locate the grain-boundary cores for positions with reduced atomic density, and these are the substitution positions in a high-angle boundary structure. Sn is an impurity with a large radius, its atomic volume being 23% higher than that of Nb [1991Phy], and that is why Sn is not able to diffuse into a grain-boundary core along its inter-nodes but only along vacancy-like positions of the same type with minimal energy barriers.

High-angle grain boundaries of polycrystalline Nb that were obtained by the rolling and annealing of highly pure Nb single crystals were investigated in [1988Kai] by employing the ^{57}Co (^{57}Fe) Mössbauer nuclei. Also found were two components in the emission Mössbauer spectrum of polycrystalline Nb, one of them formed by ^{57}Co (^{57}Fe) atomic probes located in grain-boundary cores (component 1), and the other by ^{57}Co (^{57}Fe) atomic probes situated in the Nb regular crystal lattice near boundaries (component 2). The isomer shift of component 1 was found to be higher than that of component 2. For the emission NGR spectroscopy on ^{57}Co (^{57}Fe) nuclei, this result indicates the higher density of s-electrons of the ^{57}Co (^{57}Fe) nuclei located in grain-boundary cores compared with the electron density of those atomic probes that are in the regular lattice node positions near boundaries. Based on that observation, the conclusion about the interstitial character of cobalt diffusion in high-angle grain boundaries of polycrystalline Nb was made in [1988Kai].

When the atomic volume of a diffusing impurity is larger than the atomic volume of a matrix (the case of Sn in Nb) or is commensurable with the latter (the case of Co in Cr) [1998Kai2], the vacancy diffusion mechanism is realized in high-angle boundaries. In both the ^{57}Co -Cr and $^{119\text{m}}\text{Sn}$ -Nb systems, the Mössbauer impurity diffusion along high-angle polycrystal grain boundaries also occurs by the vacancy mechanism.

The isomer shift and the line width of component 1 change negligibly with annealing temperature, indicating that the Sn atomic probe surroundings in polycrystalline Nb grain boundaries change only slightly with temperature.

Contrary to component 1, the component 2 parameters appreciably change with the annealing temperature. At the lowest investigated annealing temperature of Nb polycrystals (680 K), the isomer shift of the volume line is equal to -1.12 mm/s, which is substantially higher than that of the volume (standard) source (-1.63 mm/s). The higher isomer shift value is due to the lower electron density on the $^{119\text{m}}\text{Sn}$ nucleus. The analogous effect, that is, the lower electron density on nuclei in the pumping zone compared with that in the volume at low annealing temperatures ($T/T_m < 0.3$), was

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observed in other metals investigated using the ^{57}Co atomic probes [1994Kai, 1998Kai1, 1998Kai2, 1998Kai3]. The most probable cause of the isomer shift increase in the near-boundary pumping zone is segregation of the interstitial impurities in this zone. The interstitial impurities in metals are known to result not only in a shift of spectral lines, but also in a broadening of them [1969 Sau, 2002Klo]. The number of interstitial atoms located close to the $^{119\text{m}}\text{Sn}$ probe (in the first and second coordinate spheres) may be different, which results in some distribution of isomer shifts and line widths. As a result, the experimental width of component 2 in polycrystalline Nb annealed at 680 K is appreciably higher (2.59 mm/s) than the volume source line width (0.91 mm/s).

With the growth of the annealing temperature, the isomer shift decreases, approaching to its value in the standard source. This is apparently explained by an increase in the concentration of nonequilibrium vacancies and vacancy-impurity complexes in the pumping zone. It was shown in [2003Klo] that vacancies and their complexes with interstitial impurities decrease the lattice periodicity, contrary to the effect of individual interstitial impurities. As a result, the electron density on the $^{119\text{m}}\text{Sn}$ nuclei grows, and, correspondingly, the component 2 isomer shift decreases with temperature growth. The growth in the concentration of vacancies and their interstitial impurity complexes with the increase of the annealing temperature results in a decrease of the concentration of individual interstitial impurities and a weakening of their influence on the component 2 width in NGR spectra of polycrystalline Nb. As a result, the width of the volume line decreases with the increase in the annealing temperature. The second possible reason for the decrease of the electron density on $^{119\text{m}}\text{Sn}$ nuclei and the volume line width with growth of the diffusion annealing temperature may be the withdrawal of interstitial impurities from the pumping zone.

4. Conclusions

The study of high-angle grain boundaries in polycrystalline Nb with the use of $^{119\text{m}}\text{Sn}$ Mössbauer nuclei inserted by a kinetic regimen of C type has shown that the $^{119\text{m}}\text{Sn}$ atomic probes occupy two types of sites in the grain-boundary diffusion zone, namely, in grain-boundary cores and in near-boundary areas of the regular lattice. The atomic $^{119\text{m}}\text{Sn}$ probes are located in grain-boundary cores in positions with reduced atomic density, which indicates the presence of a vacancy-type mechanism of Sn diffusion along the polycrystalline Nb high-angle boundaries. This results from the fact that the $^{119\text{m}}\text{Sn}$ probe in Nb is a large-radius impurity, and it cannot diffuse along the internodes.

According to the character of the temperature dependences of both component areas (occupancy of states), it has been shown that Sn in Nb enriches grain boundaries. The mean activation enthalpy of Sn segregation on high-angle grain boundaries of polycrystalline Nb is determined to be 31 ± 2 kJ/mol. The ratio of the extension of a high-concentration point defect zone, l , to the diffusion width of a grain boundary, d , is shown to be $l/d = 30 \pm 6$.

In the investigated temperature interval, the parameters of a grain-boundary line (component 1) in the emission NGR spectra (isomer shift, line width, and quadrupole splitting) only slightly depend on the annealing temperature. This means that at these temperatures there are no appreciable changes in the composition and structure of grain-boundary cores of polycrystalline Nb. At the same time, the parameters of the volume line (component 2) substantially change in the temperature interval considered. These peculiarities are apparently connected with differences in the atomic structure of grain-boundary cores and near-boundary areas.

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