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Mössbauer Investigation of Segregation and Diffusion Mechanism of ^{119m}Sn in Poly- and Nanocrystalline Nb Grain Boundaries

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1. Introduction

Recently a method based on the emission Mössbauer spectroscopy of radioisotope nuclei inserted in grain boundaries worked out by Klotsman and Kaigorodov [1] was successfully employed in a number of studies of grain boundaries in transition and noble metals. In the present investigation this method is used to study the diffusion mechanism and grain boundary segregation in polycrystalline and nanocrystalline Nb.

2. Experiment and discussion

The average grain size of polycrystalline (PC) Nb was about 50 μm. Nanocrystalline (NC) Nb was obtained by high-pressure torsion (5 turns at a pressure of 4GPa), its mean grain size being about 100 nm. To manufacture Mössbauer sample-sources the ^{119m}Sn radionuclide was electrolytically deposited on one of the surfaces of the obtained PC or NC Nb. The radioisotope-covered samples were annealed for 7 h at 680K for PC Nb and at 574K for NC Nb for the atomic probe implantation into grain boundaries, the Mössbauer spectra being taken after that. Then further annealing for 2 h at higher temperatures was carried out (for up to 974K for PC and 806K for NC Nb) with subsequent measuring of the Mössbauer spectra.

At all investigated temperatures of the isochronal (2h) annealing there are two components in the ^{119m}Sn spectra of both polycrystalline and nanocrystalline Nb. One of them, component 1, is growing with the annealing temperature, while the other one, component 2, is decreasing. Component 1 is formed by the atomic probes localized in grain boundary cores, and component 2 corresponds to the atomic probes located in the near-boundary areas. The quadrupolar splitting of component 1 suggests that the surrounding of ^{119m}Sn atoms in high-angle grain boundaries of both PC and NC niobium is not symmetrical. It may be assumed that this quadrupolar splitting results from the distortions arising around the relatively big atoms of tin.

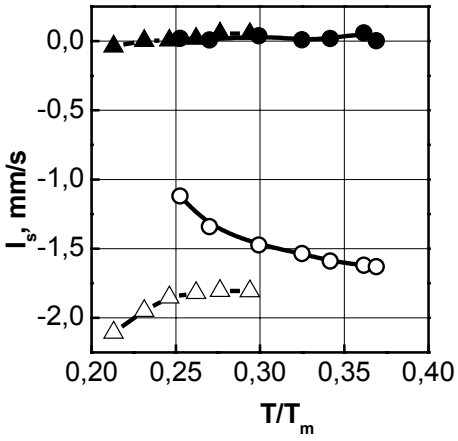

Fig. 1. I_s temperature dependences of components 1 (●,▲) and 2 (○,△) in ^{119m}Sn spectra of PC (●,○) and NC Nb (▲,△)

Fig. 1 demonstrates the annealing temperature dependences of the isomer shift (I_s). The isomer shift of component 1 is approximately the same for PC and NC Nb and does practically not change with temperature. This enables to conclude that the ^{119m}Sn atomic probes position in grain boundaries, and thus the structure and thermal stability of a grain boundary core itself, only slightly differ in PC and NC Nb and have a weak temperature dependence.

The isomer shift of component 1 is close to zero and is appreciably higher than that of the volume line measured on a Nb single crystal (-1.63 mm/s). This result demonstrates that the electron density of ^{119m}Sn nuclei in grain boundary cores of PC and NC Nb is substantially lower than in substitution positions of the Nb regular lattice. This suggests that Sn diffuses in grain boundary cores of polycrystalline and nanocrystalline Nb by a vacancy mechanism and can not diffuse along internodes.

Contrary to component 1, the isomer shifts of component 2 in poly- and nanocrystalline Nb noticeably differ and change with temperature. In case of the PC Nb the isomer shift of component 2 is appreciably higher than that of the volume source, and in case of NC Nb it is lower. This is most possibly due to the fact that in polycrystalline Nb its near-boundary zone is enriched with interstitial atoms, while in NC Nb there are many vacancies in this zone. With growth of temperature the isomer shift of component 2 of PC Nb decreases, and of NC Nb increases gradually approaching its value in a standard source.

Based on the analysis of temperature dependences of the area of spectrum lines using the modified Fisher's model [2] the segregation enthalpy (Q_s) and the ratio of the pumping zone extension (l) to the diffusion width of a grain boundary (d) were evaluated for polycrystalline niobium, the following values being obtained: $Q_s = 31 \pm 2$ kJ/mole, and $l/d = 30 \pm 6$. The evaluation of these parameters for nanocrystalline Nb gave unrealistic values. The latter is possibly due to the fact that it is impossible to distinguish a near-boundary pumping zone with high concentration of point defects in nanosized grains which are entirely saturated with vacancies.

3. Conclusion

It has been shown that Sn diffuses along grain boundaries of both poly- and nanocrystalline niobium by a vacancy mechanism. It has been found that Sn in Nb is an impurity which enriches grain boundaries. The segregation enthalpy of Sn in high-angle grain boundaries of polycrystalline Nb is determined to be 31 ± 2 kJ/mole. The ratio of the pumping zone extension to the diffusion width of a grain boundary in PC Nb has been evaluated as 30 ± 6. The Sn atomic probes position in grain boundary cores of both PC and NC Nb is approximately the same and practically does not change with temperature, while their position in near-boundary areas differs greatly and depends on temperature.

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References

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