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<u>Résumé</u> : L'autodiffusion du ¹⁸⁵W et l'hétérodiffusion du ⁵⁷Co aux joints de grains du tungstène fritté ont été mesurées sur une large gamme de température. La diffusion intergranulaire du ¹⁸⁵W dans du tungstène dopé en Ni a également été examinée dans l'optique du frittage activé. Dans les trois cas une discontinuité inhabituelle sur le diagramme d'Arrhénius a été observée à environ 1370K. Son amplitude est différente pour l'autodiffusion et l'hétérodiffusion. Les résultats sont discutés conformément au modèle de transition de phase intergranulaire de Militzer et Wieting.

<u>Abstract</u> Grain boundary self- and ⁵⁷Co impurity diffusion were measured in sintered tungsten on a large temperature interval. Additionally the diffusion of ¹⁸⁵W was investigated in Ni-doped tungsten grain boundaries in the context of the activated sintering process. In all three cases an unusual discontinuity was observed in the Arrhenius plot occurring around 1370 K with quite different magnitudes for self and impurity diffusion. The results were discussed in terms of the grain boundary phase transition model of Militzer and Wieting.

INTRODUCTION

Sintering is a metallurgical process of growing importance. It requires the transport of atoms to and across the contact points between particles in a powder compact. Thus surface-, grain boundary- and volume diffusion are in principle involved in such a process. The sinterability of W, Mo, Nb or Ta powder can be considerably improved by small additions of Ni, Co, Fe or Pd./1/ The sintering rate increases drastically and thus the sintering temperature can be enormously reduced, e.g. to the range of about 1500 K for W. This enhancement of the sintering process is called "activated sintering". Only a few atomic layers of additive are typically required to have this large effect on the sintering kinetics. It is obvious that the additive must provide some type of diffusion enhancement, however, it is not quite clear which type of diffusion mechanism is really responsible for the activated sintering process. A very high diffusivity of the base metal in the additive layer or the occurrence of short-circuit diffusion paths due to the presence of this layer have been discussed./2-4/

The research on activated sintering systems has provided some criteria in selecting such systems/5/: i) the solubility of the additive in the base metal should be low. This correlates with segregation of the additive atoms in the particle-particle interfaces; ii) the diffusivity of base metal atoms in the additive layer or the coexisting equilibrium activator phase should be much larger than self diffusion in the base metal itself at the sintering temperature. In general this correlates with a low liquidus temperature of the additive as compared to that of the base metal, which in fact means a much higher vacancy concentration in the activator phase than in the base metal at a given sintering temperature.

Solutes of low solubility and of small atomic radii with respect to that of the solvent are frequently found to be fast diffusers and diffuse by a dissociative mechanism. This means that such solutes are partially dissolved as interstitials in the solvent and migrate in an interstitial mode. Recently we found that fast diffusing impurities in the bulk are also extreme fast diffusers in the grain boundary, partly due to the strong segregation and partly due to an interstitial type diffusion behaviour/6/. Since the additivesFe, Co, Ni are candidates for fast diffusers in refractory metals it seemed attractive to combine the process of activated sintering with the idea of fast grain boundary diffusion and to study grain boundary diffusion in the temperature range of the activated sintering. The systems W-Co; and W-Ni were chosen from the C1-570

view points of experimental feasibility and technical importance. In the following results of still ongoing experiments are reported:

- i. volume and grain boundary diffusion of 57 Co in W
- ii. grain boundary self-diffusion in W
- iii. grain boundary tracer diffusion of ¹⁸⁵W in Ni-doped tungsten grain boundaries

The same sintered tungsten material and the radiotracer technique were used for all experiments which for the first time lead to directly comparable results of grain boundary diffusion in an activated sintering system.

EXPERIMENTAL PROCEDURE AND DETERMINATION OF GRAIN BOUNDARY DIFFUSION

The mathematical solution of the grain boundary diffusion problem when applying the sectioning technique to a tracer diffusion profile was developed by Whipple/7/ and Suzuoka/8/ and can for example be described in the following, very appropriate form/9/

$$P = s\delta D_{gb} = 1.3 \cdot D_v^{0.5} t^{-0.5} \left(-\frac{\partial \ln \bar{c}}{\partial y^{6/5}} \right)^{-1.667}$$
(1)

 \bar{c} is the mean tracer concentration in a section of the diffusion profile at depth y parallel to the sample surface, after a diffusion time t. D_v and D_{gb} represent the diffusion coefficients of the material fluxes from the grain boundary into the adjacent bulk and inside the grain boundary, respectively. Usually D_v is identified with the true volume diffusion coefficient. δ is the grain boundary width and s is the segregation factor. In the case of self diffusion s = 1. In that part of the diffusion profile where grain boundary diffusion dominates equation(1) requires a linear decrease of $\ln \bar{c}$ versus $y^{6/5}$. The experiments were performed on sintered tungsten material, supplied by Metallwerke Plansee. The nominal purity was 99.98%, C(15), Fe(20), Mo(40) and P(20) being the major impurities(in wt.ppm). The samples, 10mm diameter and 1-2mm in thickness, were polished optically flat and were preannealed at about 2400 K for ca. 3 h in a tungsten container by electron heating in vacuum (~ 10^{-6} Pa) for recrystallization, increasing thereby the mean grain diameter d from about 5 to 150 μ m. The obtained regular grain structure was very suitable for grain boundary diffusion experiments in the conditions of Harrison type B kinetics/10/ for which the annealing time was to be limited to $2(D_v t)^{1/2} < 0.2d$. The carrier free radiotracer ⁵⁷Co was evaporated in vacuum from a tungsten strip on the sample surface while the ¹⁸⁵W tracer was droped in the form of H₂O₂-solution on the sample and was dried .

For preparing the Ni-doped tungsten grain boundaries a thick layer of inactive Ni was evaporated on the samples and was allowed to diffuse into the grain boundaries for t=10 h at about T=1473 K. Afterwards the remaining Ni material was removed from the surface by polishing Below 1673 K the samples were diffusion annealed in quartz tubes under purified argon while at higher temperatures an electron heat treatment was performed in the same way as for the recrystallization procedure. After the diffusion anneal the samples were reduced in diameter by grinding to eliminate radial diffusion effects. The diffusion profile was obtained by sectioning thin layers ($\leq 1 \mu$ m) parallel to the sample surface on a specially designed grinding machine. Weighing the sample on a microbalance after each sectioning allowed to calculate the thickness of the slices.

The γ -decays of ⁵⁷Co were counted precisely with a well-type NaI(Tl)- or intrinsic Ge-detector. Since ¹⁸⁵W is a β -emitter only, a methane flow counter was used to measure the tungsten self diffusion profiles.

RESULTS

In order to calculate the grain boundary diffusion parameter P from the measured slope of the grain boundary diffusion profile the volume diffusion coefficient D_v is needed according to eqn.(1). Volume self diffusion in tungsten was precisely measured over the very large temperature range of $\Delta T = 1700$ K /11/. These data, which allow a reliable extrapolation to the lower temperature range of the present investigation, were used to calculate D_v^W .⁵⁷Co volume diffusion was measured in tungsten single crystals of high purity in the context of the present investigation in the temperature range of 1365 K to 2324 K. The presently available data, which are not yet complete and which will be described elsewhere in more detail, showed a downward curvature in the Arrhenius plot, qualitatively similar to the results of the fast diffuser Fe in α -Zr/12/. Approximating the values above and below T = 1600 K, by an Arrhenius relation yields

$$D_{v}^{Co}(T) = 1.3 \cdot 10^{-10} \exp\left(-\frac{210k Jmol^{-1}}{RT}\right) m^{2} s^{-1} \quad \text{for } T > 1600 \ K$$
(2)

$$D_{v}^{Co}(T) = 4.3 \cdot 10^{-4} \exp\left(-\frac{418k J mol^{-1}}{RT}\right) m^{2} s^{-1} \quad \text{for } T < 1600 \ K \tag{3}$$

At T = 0.4 T_m the ratio between Co impurity and W self diffusion adopts the large value of $D_v^{\nu}/D_v^W =$ 6.6.10⁵ which is comparable to the corresponding results for Co diffusion in Nb/13/: $D_v^{Co}/D_v^{Nb} = 1.2.10^5$ and for which a dominating interstitial diffusion via a dissociative mechanism has explicitly been demonstrated recently/14/. Taking additionally into account the equivalent size conditions when dissolving Co in W and Nbrespectively, and the very small frequency factor of about $10^{-10}m^2s^{-1}$ (eqn.(2)), an interstitialtype mechanism can be assumed as well for volume diffusion of Co in W. The temperature range below T=0.43 T_m, in which the downward curvature was observed for Co in W, has not yet been investigated for Co in Nb. The curvature can be tentatively explained by the formation of less mobile Co-Co or Co-impurity dimers. Some typical penetrations profiles for ¹⁸⁵W grain boundary diffusion in W are presented in figure 1. Profiles of ⁵⁷Co diffusion in W have already been shown/15/. In many cases the grain boundary diffusiondominated linear part in the plots of $\ln \bar{c}$ versus $y^{6/5}$ is extended over two to three orders of magnitude in decrease of tracer concentration. The Co diffusivity was measured in the temperature interval between 890 K and 1873 K corresponding to 0.24 to 0.51 Tm; tungsten self diffusion experiments range from 987 to 2173 K,i.e. 0.27 to 0.59 Tm. The Arrhenius plots of the calculated P values are shown in figures 2 and 3 respectively. The experiments of ¹⁸⁵W grain boundary diffusion in Ni-doped tungsten boundaries are less, complete and cover the temperature range between 1081 and 1573 K only. The results are plotted in figure 4. At this point we emphasize again that the results are directly comparable with each other, because they were obtained on the same material using the same experimental tracer technique. The three Arrhenius plots comprise several interesting features which need discussion and explanation. Parts of the results for Co in W showing already the unusual shape in the Arrhenius plot (fig.2) have been published recently $\frac{15}{15}$ and it was explained that artefacts have to be excluded to cause these results.

DISCUSSION

The most striking feature of the present results certainly is i) the discontinuity in the Arrhenius line which occurs for all three curves in a more or less broad temperature interval at ii) about the same mean temperature of 1370 K. iii) the magnitude of this discontinuity, however, quite different. It is of the order of two to three decades for P^{Co} and less than one for P^W . It is quite large again in Ni-doped tungsten grain boundaries. The unusual drastic decrease in P with decreasing temperature seems iv) to split the Arrhenius line into a high and a low temperature branch. Also the absolute magnitudes of P are quite different in the three cases. Table 1 summarizes for comparison some results at two characteristic temperatures in the high and the low temperature region.

Table 1. Results of volume D_v and grain boundary diffusion P for tungsten and cobalt in tungsten and in nickel-doped tungsten boundaries $\left(P_{(Ni)}^{W}\right)$ at two temperatures. $\left(D_v/(m^2s^{-1}) \text{ and } P/(m^3s^{-1})\right)$

T/K	$D^{C\circ}_v$	D_v^{W}	P^{Co}	P^{W}	$P_{(Ni)}$
1600	$1 \cdot 10^{-17}$	$2.8 \cdot 10^{-23}$	$5.9 \cdot 10^{-21}$	$4.5 \cdot 10^{-25}$	$2.2 \cdot 10^{-22}$
1100	$6.1 \cdot 10^{-24}$	$4.3 \cdot 10^{-31}$	$1.9 \cdot 10^{-25}$	$7.1 \cdot 10^{-31}$	$2.2 \cdot 10^{-29}$
T/K	$D_v^{C\circ}/D_v^W$	$P^{C_{\circ}}/P^{W}$	$\overline{P_{(Ni)}^W}/P^W$	$P^{C\circ}/D_v^{C\circ}$	P^{W}/D_{v}^{W}
1600	$3.6 \cdot 10^5$	$1.3 \cdot 10^{4}$	489	$5.9 \cdot 10^{-4}$	$1.6\cdot 10^{-2}$
1100	$1.4 \cdot 10^7$	$2.7 \cdot 10^5$	31	$3.1 \cdot 10^{-2}$	1.7

The interpretation of the findings i) to iv) is a difficult task which cannot be done unambiguously, because the grain boundary composition in the sintered tungsten material is somewhat complex. An AES analysis



Fig.1 Grain boundary diffusion of ¹⁸⁵W in W



T/(K) 1400 1200 2400 1800 1000 10¹⁷ ⁵⁷Co in W , 10¹⁹ $P = s \cdot \delta \cdot D_{GB} \left(m^3 s^{-1} \right)$ 10²³ 10²⁵ 10²⁷ 10 'n 5 ģ i, 6 Ż 8 1/T/(10-4K-1)

Fig.2 Arrhenius plot of grain boundary diffusion of $^{57}\mathrm{Co}$ in W



Fig.3 Arrhenius plot of grain boundary diffusion of $^{185}\mathrm{W}$ in W

Fig.4 Arrhenius plot of grain boundary diffusion of $^{185}\mathrm{W}$ in Ni-doped W

of intergranular surfaces of in vacuum fractured tungsten samples, which were identical to those in the present investigation, revealed carbon and phosphorus as principal impurities, segregated in almost equal concentrations in the grain boundaries. It is well known that on one side P and Ni (and thus Co) exhibit cosegregation in W boundaries with a positive interaction coefficient of segregation $\alpha' \simeq 80 \text{ kJ/mol}$ while on the other hand site competition occurs between C and Ni(and thus Co) with $\alpha' \simeq -190 \text{ kJ/mol}/16/$. In the following the main results will be briefly commented.

Figures 2 and 3 and the results in table 1 demonstrate that Co as a fast diffuser in the bulk also diffuses very fast in the boundary. Similar observations were recently made in grain boundary diffusion of Co in α -Zr/6/ and Ag in Pb/17/ which are two typical fast diffuser systems. In the temperature range of the present investigation $P^{Co} \simeq (10^4 \text{ to } 10^5) \cdot P^W$. This large difference results from the segregation factor s of Co in W times the difference between $D_{gb}^{C_0}$ and D_{gb}^W (eqn.(1)). The approximation/18/: $s \simeq (1 \text{ to } 10)/X_0$, taking into account the solubility X_0 of Co in tungsten ($X_0^{C_0} \simeq 0.009$ at 1962 K and 0.007 at 973 K/19/), yields a maximum segregation factor of $s \simeq 10^2$ to 10^3 . The remaining difference of about 100 between P^{C_0} and P^W therefore is a real difference in $D_{gb}^{C_0}$ and D_{gb}^W , which is difficult to explain by a vacancy mechanism in the boundary. Contrary to grain boundary self diffusion which proceeds by vacancy jump process, it is attractive to assume a faster, interstitial-like process to understand large values of D_{ab}^{Co} . This situation is much more extreme in the case of Co in α -Zr/6/. The surprising discontinuity in the Arrhenius plots occurs for impurity as well as self diffusion very remarkably at about the same temperature. From this it is clear that the origin of this behaviour has to result from properties of the sintered tungsten material. Guttmann's segregation model/20/, which includes interactions between segregating atoms in the frame of a regular solution, has been recently applied by Militzer and Wieting/21/ to develop a model for explaining interfacial phase transitions due to self-interaction or mutual interaction if one or different species, respectively, segregate in the boundary. The phase transition results in the occurrence of a miscibility gap of the segregants in the boundary below a critical temperature which depends on the interaction energy and the segregant concentration in the bulk.

In the present experiment we assume carbon to be the dominant segregant in tungsten boundaries, neglecting for simplicity somewhat arbitrarily the influence of phosphorus. If due to the interaction of the Catoms in the boundaries a transition of the grain boundary phase occurs we expect in the boundaries at low temperatures a comparatively high C-concentration, which decreases discontinuously at a certain higher temperature. The transition temperature should be more or less the same in all our experiments, because all samples were equally prepared. This is in fact indicated in figures 2 to 4.

Case of grain boundary self-diffusion

Figure 3 shows at about 1370 K a discontinuous increase of P^W by a factor of 5 to 10. This gives very strong evidence that the step in the Arrhenius line stems from the grain boundary properties of the material itself. The temperature corresponds to $0.37T_m$ which is too low to assume a structural phase transition in the boundary/22,23/. If the grain boundaries, however, are released from segregated, C-atoms tungsten atoms may now be able to occupy to a larger extent high energy grain boundary sites, resulting in the observed increase in P, the magnitude of which is reasonable for such an effect.

Case of ⁵⁷Co grain boundary diffusion

As mentioned above the interaction energy between C and Ni and thus certainly also for Co is repulsive. Therefore the possibility for cosegregation is comparatively small as long as the carbon concentration is high in the boundary, i.e. below the phase transition temperature, which results in lower values of P^{Co} , figure 2. Above around 1370 K the segregation of Co and thus P^{Co} increases drastically as experimentally observed. Also D_{gb}^{Co} itself may increases due to a larger probability for interstitial jumps in the carbon released boundary. Since many grain boundaries are involved with slightly different properties the step in P^{Co} is extended over a larger temperature interval.

Case of ¹⁸⁵W diffusion in Ni-doped boundaries

This is the case of "activated sintering". Figure 4 shows a drastic increase of W self-diffusion of about two decades around 1370 K due to the presence of Ni in the boundary. As compared to P^W from figure 3, $P_{(N_1)}^W$ is enhanced by a factor of 490 at 1600 K and 31 at 1100 K. A similar large high temperature enhancement of P^W was already reported in the literature/4/. The question arises why $P_{(N_1)}^W$ is promoted

with respect to P^W . Different from the case of Co-impurity diffusion, there is no segregation factor of tungsten involved in the observed values of $P_{(Ni)}^W$. Thus the enhancement must result from a change in D_{gb}^W . If we assume that in analogy to Co now Ni is partly interstitially dissolved in the boundary and partly diffuses interstitially, the formation of W-Ni dumbbells may be assumed. Rotational and dissociative jump processes of such a dumbbell thus enlarge the mobility of tungsten atoms considerably. The probability of dumbbell formation increases with the Ni-content in the boundary, which is comparatively low due to site competetion with C at low temperatures and increases appreciably after the assumed phase transition in the boundary, explaining in this way the enhancement of $P_{(Ni)}^W$ around 1370 K. This explanation has to be regarded as a suggestion only. It relates the process of activated sintering to tungsten grain boundary diffusion which is enhanced by the formation of rapidly mobile tungsten-activator atom pairs in the grain boundary. Some of the assumptions, however, can be experimentally checked by grain boundary diffusion experiments in high purity tungsten material.

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