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INFLUENCE OF GRAIN BOUNDARY SEGREGATION ON MECHANICAL PROPERTIES OF ACTIVATED SINTERED TUNGSTEN

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Résumé - Le tungstène fritte entre 1300 et 1500°C, en présence de petites quantités de Ni et Fe, a une faible résistance mécanique. La résistance à la flexion est d'environ 400 MPa et la rupture est toujours intergranulaire. La cohésion intergranulaire est contrôlée par la teneur et la distribution d'impuretés comme O, C, P et d'éléments d'addition comme Fe et Ni. Les mesures par S.E.A. montrent que la ségrégation de C augmente la cohésion des joints de grains dans le W, alors que la ségrégation de P la diminue.

Abstract - Tungsten sintered with small Ni and Fe additions at temperatures ranging between 1300 and 1500°C, shows low mechanical strength. The bend strength is about 400 MPa and the samples show always an intercrystalline fracture mode. The strength of the interfaces is controlled by the amount and distribution of impurities such as O, C, P and alloying elements such as Fe and Ni. AES measurements show, that segregation of carbon improves the cohesion of tungsten grain boundaries whereas P segregation decreased the cohesion.

INTRODUCTION

Small additions of VIIIA metals to refractory metals like W decrease the sintering temperatures below 1500°C. The mechanical strength of this so called activated sintered W is very poor /1,2/. All samples show an intercrystalline and therefore brittle fracture. It is well known that the segregation level at the grain boundary influences the cohesion. According to Seah /3,4/, the segregated atoms influence the force per area between the two parts of the solid when they are separated by a displacement normal to the fracture plane. Elements with a higher pair bonding energy compared to the matrix atoms increase the strength and vice versa. McMahon and Vitek /5/ proposed that segregated elements change the surface energy and therefore the work of fracture and the cohesion of the grain boundary. Additionally McMahon and Vitek also studied the influence of plastic work (e.g. crack blunting by dislocation emission) on the fracture energy and the relationship between the surface energy and the amount of plastic work. Small changes of the surface energy result in a pronounced change of the plastic work and also of the fracture energy. In binary alloys, only the interaction between the segregated elements and the host metal must be considered. In multicomponent systems such as activated sintered W, the interaction between the impurities and alloying elements among one another as well as with the host metal must be taken into account. Guttman /6/ proposed a model of the influence of alloying elements on the segregation behavior of impurities in ternary alloys. According to this model, alloying elements can increase the segregation of impurities (cosegregation) when the interaction coefficient between alloying element and impurity is stronger than the interaction coefficient between impurity and host metal. No model exists for the effect of the interaction between various segregated elements on the grain boundary cohesion.

In the present paper, our aim is to show the influence of heat treatment on the segregation level at grain boundaries in activated sintered W. Additionally, the

influence of the segregation level on the grain boundary cohesion as well as the effect of alloying elements on the segregation of impurities will be shown.

EXPERIMENTAL PROCEDURE

Commercially pure tungsten powder containing 47 ppm P, 31 ppm Si, 27 ppm As, 20 ppm C and 550 ppm Mo as the main impurities was used. The powder was doped with 0.05 wt.% Ni and 0.17 wt.% Fe. This composition corresponds to the solubility limit of Ni and Fe in W [7]. The mixed powder was cold isostatically pressed at 635 MPa. Five different sintering procedures were used (Table 1): The compacts were heated up at 3 K/min to 1470°C in flowing H₂ atmosphere and subsequently quenched or cooled at 3 K/min to 1000°C and quenched in H₂. Alternatively the compacts were preannealed in Ar which contained 3 vol.% CH₄ for 15 or 30 min at 1000°C and subsequently heated up at 3 K/min to 1470°C on H₂. These samples were cooled at 3 K/min to 1000°C in H₂ and quenched or were quenched and subsequently annealed at 700°C for 4 h in H₂.

The four point bend strength, the density and grain size were measured as well as the composition of the fracture surface using AES. For the AES measurements, fresh fracture surfaces were obtained by impacting the specimens in ultra high vacuum ($< 10^{-7}$ Pa) at room temperature in the fracture stage of a commercial Auger electron spectrometer (thin film analyzer, Phys. Electr. Ind.). Auger spectra of the fracture surfaces were taken about 1-2 min after fracture and therefore contamination (C,O) from the residual gas atmosphere was minimized. Quantification of the AES results is discussed in Ref. [10].

RESULTS

All specimens show a brittle intercrystalline failure (Fig. 1). The bend strength, theoretical density, grain size and the grain boundary composition are listed in Table 2. The density of the samples was > 98.3 % of the theoretical density.

Fig. 1 - Typical fracture surface of activated sintered W.

The bend strength decreases with decreasing cooling rate. Annealing at 700°C also decreases the strength of the sintered alloy. Similarly the grain size also varies with the cooling conditions. Quenched samples show a grain size of 28 μm whereas

Table 1 - Sintering procedure

Nr.	preannealing	cooling conditions
1	no	quenched
2	no	3 K/min to 1000°C and quenched
3	15 min	3 K/min to 1000°C and quenched
4	15 min	quenched and annealed at 700°C for 4 h
5	30 min	quenched and annealed at 700°C for 4 h

Table 2 - Bend strength, grain size and grain boundary compositions.

Sample	Bend Strength (Mpa)	Theoretical Density (%)	Grain Size (μm)	Grain Boundary Composition				
				Ni	Fe	O (at.%)	C	P
1	440	98,9	28	25	23	7	28	16
2	350	98,9	40	34	26	4	6	30
3	400	98,5	40	23	24	10	37	6
4	300	98,4	47	31	30	4	11	25
5	280	98,4	47	36	24	5	4	30

the grain size of slowly cooled or annealed samples is 40 μm and 47 μm . Similarly the grain boundary composition alters with the different cooling conditions. Slowly cooled or annealed samples show nearly the same grain boundary composition, whereas in quenched samples lower values of Ni, Fe and P but higher values of O and C are detected. The specimen preannealed in CH_4/Ar and after sintering cooled at 3 K/min (sample No. 3) shows a very high C content and a low P content at the grain boundary.

DISCUSSION

The bend strength of activated sintered W is dependent on the density /1/, grain size /1/, grain shape /2/ and grain boundary cohesion. For the study of the influence of the segregation level on the grain boundary cohesion, the influence of grain size and density on the bend strength must be considered. In recent works /1,7/ it was found that the strength of activated sintered W varies with the grain size d (in μm) and porosity ϵ as follows:

$$\text{Ref. /1/ } \sigma = 848 d^{-0.21} \exp[-4,49 \epsilon] \text{ (MPa)} \quad (1)$$

$$\text{Ref. /7/ } \sigma = 192 + 1266 d^{-1/2} \text{ (for sample with 98,9 \% density).} \quad (2)$$

According to a model of McLean /8/ the bend strength of W which shows inter-crystalline fracture depends on the grain size as follows /7/:

$$\sigma = 2,42 \cdot 10^3 d^{-1/2} \text{ (d in } \mu\text{m, MPa).} \quad (3)$$

The model of McLean does not take into account the influence of grain junctions on the fracture energy /9/. The deviation of the crack from its initial direction requires additional energy. Therefore the decrease of bend strength with increasing grain size is smaller than in eq. (3).

The measured bend strength extrapolated to 100 % theoretical density (with eq. (1)) as well as the calculated bend strength according to eqs. (1), (2) and (3) are listed in Table 3. The values of /1/ and /7/ show the same influence of grain size on the bend strength. Therefore, we conclude that it is the difference in grain boundary cohesion which causes the deviation of the bend strength of the different treated W samples from these values.

Table 3 - Influence of the grain size on the bend strength of W (assumption: 100 % intercrystalline fracture).

Grain Size (μm)	σ ($\rho = 100$ % T.D.) this work (MPa)	σ /1/ (MPa)	σ /8,7/ (MPa)	σ /7/ (MPa)
27	462	421	457	436
40	367	391	382	392
40	427	391	382	392
47	322	377	353	377
47	300	377	353	377

According to the model of Seah /3,4/ a grain boundary cohesion parameter $\Sigma\Delta FE(X_i^{gb})$ can be calculated. This parameter considers the fracture energy change (ΔFE) for each segregated element i as a function of a concentration in the boundary X_i^{gb} . Assuming a linear superposition of ΔFE of all elements at the boundary the following relation is obtained for the combined effect of the determined elements Ni, Fe, C, O, P /10/:

$$\Sigma\Delta FE(X_i^{gb}) = 1,1 X_C^{gb} - [1,8 X_{Fe}^{gb} + 1,6 X_{Ni}^{gb} + 2,4 X_O^{gb} + 3,4 X_P^{gb}] \text{ (J/m}^2\text{).} \quad (4)$$

Figure 2 shows the experimentally determined fracture strength (extrapolated to 10 μm with eq. (2)) versus the grain boundary cohesion parameter. With the X_i^{gb} values of Table 2, a good correlation is obtained, indicating that the observed behavior can at least semiquantitatively be interpreted by the model of Seah.

The evaluation of data necessary to quantify the model of McMahon /5/ is very difficult. In particular, the influence of segregated elements on the surface energy (γ) and therefore also on the plastic work γ_p of W is unknown. When inter-crystalline fracture occurs, γ_p is very low /9,11/. Therefore, the bend strength of activated sintered W is only dependent on γ . At room temperature, γ of W ranges between 4,4 and 6,3 J/m² /12/ and only small changes with segregation

Fig. 2 - Bend strength of activated sintered tungsten (extrapolated to a grain size of 10 μm) versus the grain boundary cohesion parameter $\Sigma \Delta F E (X_i^{gb})$.

occur /5/. Therefore, the bend strength of activated sintered W also varies only slightly with the segregation level and therefore with the cooling conditions. This is in agreement with the measurements (Table 2). The bend strength of samples with a high segregation level of C (37 at.% C) is only 19 % higher than the strength of samples which show a high P segregation level (30 at.% P).

From Table 2 it is evident that an inverse correlation between the C and P content at the grain boundary exists (Fig. 3). This figure also shows the correlation between the Ni, Fe and O concentration at the grain boundary and the segregation level of P. The concentrations of C as well as O decrease whereas those of Ni and Fe increase with increasing P content. According to Guttman /6/ cosegregation is possible when the interaction coefficient α between the alloying element and W as well as between the impurity and W is lower than the interaction coefficient between the alloying element and the impurity. The relative interaction coefficient $\alpha'_{MI} = \alpha_{MI} - \alpha_{WI} - \alpha_{WM}$ (I = impurity, M = alloying element) for the investigated systems are listed in Table 4. α'_{NiP} and α'_{FeP} are positive, whereas all other combination of segregated elements show a negative interaction coefficient. A positive value of α' expresses the fact that the balance between all the interactions between atoms results in a relative attraction between the solutes with respect to W. This is in agreement with the observed segregation behavior (Fig. 3). The contents of Ni and Fe at the grain boundary increase with increasing P content. Additionally, ternary W-M-I combinations with a negative α'_{MI} value also show a negative correlation in the segregation behavior. With increasing P content (and therefore increasing Ni and Fe content) at the grain boundary the C as well as the O level decrease (Fig. 3). It is interesting to note, that the O level is very low (4-10 at.%). The reason for this low O level is the very strong interaction between W and O (1203 kJ/mol), i.e., the formation of oxides in the bulk is preferred.

The amount of segregated P is governed by the segregation free energy of P, ΔG_P . In the six component system under study (W, Ni, Fe, O, C, P) the chemical interaction of all the elements leads to an alteration of the segregation free energy, ΔG_P^{chem} , which can be described by an expanded expression of Guttman's equation /15/:

Fig. 3 - Correlation between the P-content at the grain boundary and the segregation level of Ni, Fe, C and O.

Table 4 - Relative interaction coefficients of segregated elements in W.
($\alpha'_{MI} = \alpha_{MI} - \alpha_{WI} - \alpha_{WM}$; $\alpha = -\Delta H_{ij}/X_i X_j$; ΔH_{ij} from /13/ and /14/.)

Segregated Elements	α'_{MI} (kJ/mol)
Fe-P	+ 23
Fe-C	-151
Fe-O	-578
Fe-Ni	- 90
Ni-P	+ 80
Ni-C	-190
Ni-O	-783
P-O	-535
P-C	-227
C-O	-1173

$$\Delta G_p = \Delta G_p^0 + \Delta G_p^{\text{chem}} \quad (5a)$$

$$\text{where } \Delta G_p^{\text{chem}} = 2 \alpha_{WP} (X_p^b - X_p^{\text{gb}}) + \sum_i \alpha'_{ip} (X_i^{\text{gb}} - X_i^b) \quad (5b)$$

with $i = \text{Fe, Ni, O, C, X}_i^b$ and X_i^{gb} are the bulk and grain boundary molar fractions of element i , respectively.

With eq. (5) the value of ΔG_p in the W alloy cannot be calculated because ΔG_p^0 is unknown. With the data listed in Table 2 it is possible to make an estimation of the influence of the additional segregated elements on ΔG_p and therefore on X_p^b . To simplify eq. 5b, X_p^b was neglected because $X_p^b \ll X_i^{\text{gb}}$. Values of ΔG_p^{chem} of the five investigated samples are listed in Table 5 ($\alpha_{WP} = 151 \text{ kJ/mol /14/}$). Although the description of the six component system by a sum of the differences of binary interaction terms in eq. (5b) is a rather simplified approximation, a good correlation between the observed P content at the grain boundary and ΔG_p^{chem} is obtained (Fig. 4). High negative values of ΔG_p^{chem} reduce ΔG_p and therefore the segregation level of P is low.

Fig. 4 - Measured segregation level of P versus ΔG_p^{chem} calculated with eq. (5b).

Table 5 - ΔG_p^{chem} of the investigated samples.

Sample	ΔG_p^{chem} (kJ/mol)
1	- 124
2	- 92
3	- 131
4	- 90
5	- 92

CONCLUSIONS

The observations described above can be summarized as follows:

- The cooling conditions influence the segregation level at the grain boundary.
- C improves the grain boundary strength whereas P and, less effectively, O, Ni and Fe decrease the cohesion. This is in agreement with the model predictions of Seah /3,4/.
- The segregation of Ni, Fe and P is enhanced by each other.
- With increasing Ni, Fe and P content at the grain boundary, the C and O content decrease.
- The latter results are in agreement with the multicomponent segregation theory of Guttman /6/.

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