Microstructure and Mechanical Properties of Si and Y Doped Tantalum

M. Bischof[a], S. Mayer[a], H. Leitner[a], H. Clemens[a], K. Pranzas[b], P. Staron[b], G. Dehm[c], W. Knabl[d], A. Voiticek[d], E. Geiger[d]

[a] Department of Physical Metallurgy and Materials Testing, Montanuniversität, Austria
[b] Institute for Materials Research, GKSS Research Centre, Geesthacht, Germany
[c] Max-Planck-Institut für Metallforschung, Stuttgart, Germany
[d] PLANSEE AG, Reutte, Austria

Summary

Tantalum has a wide range of applications due to its high melting point, its corrosion resistance and its mechanical and electrical properties. One of these applications are fine wires which are needed for Ta-capacitors. During fabrication of such components the wires are exposed to high temperatures up to 1800°C and thus grain growth combined with embrittlement becomes a major problem. In general, doping with elements which form nanometer to submicron sized oxide or silicide particles is an appropriate way to prevent uncontrolled grain growth. In the present work the effects of doping with varying combinations of Si and Y on microstructure and mechanical properties of cold-worked and annealed Ta wire have been investigated. For these purposes methods including small-angle neutron scattering and transmission electron microscopy as well as classical metallography have been applied. Samples doped with Si show a higher hardness and strength than those doped with Y or made from pure Ta powder. The particle size distributions of doped Ta-samples change significantly with increasing annealing temperature and time as coarsening and dissolution of the prevailing particles take place. Therefore, particles do not play a significant role on grain growth kinetics at temperatures as high as 1800°C. However, this loss in retarding forces is partially compensated for by an increased solution drag originating from elements in solid solution.

Keywords

Tantalum, Doping, Recrystallisation, Grain growth, Mechanical properties

1. Introduction

High demands on modern materials can sometimes only be met by refractory metals which feature high melting points and good corrosion resistance. Tantalum is one example of these metals, having a melting point of 2996°C. Its very good corrosion resistance comes from a chemically stable oxide layer that covers the blank metal immediately when exposed to an oxygen containing atmosphere. This oxide layer makes Ta a widely used metal for applications in chemical and medical industries, but it is also responsible that tantalum became a preferred material for electronic components like capacitors. For the latter application, thickness and quality of the oxide layers are increased by anodic oxidation, leading to a well isolating dielectric layer with extraordinarily good adhesion properties [1].

However, commercially pure Ta has some drawbacks, too. For example, it exhibits only medium strength and its high affinity to oxygen leads to the formation of grain boundary oxides which cause embrittlement. A large grain size, as obtained after a high-temperature treatment, intensifies this effect.

One part that is needed to build a Ta-capacitor is a fine Ta connecting wire with a diameter of 200 µm and less. During the sintering process, which connects the wire to the capacitor's main body, it gets exposed to a temperature of 1800°C for at least 30 minutes. Moreover, the ambient material contains significant amounts of oxygen, which may quickly diffuse into the wire at these temperatures. However, after this high temperature treatment the wire has to show sufficient strength and ductility in order not to break during further handling. As mentioned above, commercially pure Ta does not meet these demands. Therefore, additional hardening and grain growth retarding effects must be utilised. As another requirement, namely a minimal loss in electrical conductivity, has to be fulfilled as well common hardening effects like substitutional or interstitial alloying may not be used intensively. Thus, strengthening by precipitates or dispersoides of a second phase seems to be a very promising approach. However, these particles must be selected very carefully as to provide an appropriate recrystallisation behaviour of the material, which is another demanding factor. Recrystallisation must not be inhibited when the material is annealed at 1400 °C in

order to allow a softening between consecutive forming steps. After this annealing treatment a fine, fully recrystallised microstructure is aspired.

The experimental approach as chosen for our investigations was threefold: Dispersoides of stable Y_20_3 should allow recrystallisation, but prevent rapid grain growth at high temperatures, while Si, which has a considerable solubility in Ta at elevated temperatures, but almost none at room temperature, should form extremely fine precipitates of Ta_3Si or Ta_2Si when the wire is cooled after its high-temperature treatment. Moreover, the affinitiy of Si for O is even higher than that of Ta, thus preventing the formation of embrittling Ta_2O_5 or similar oxides. At elevated temperatures Si and O form volatile SiO, thereby reducing the content of gettered oxygen within the wire [2]. Y was chosen as dispersoide forming element due to its extremely low solubility in solid Ta even at elevated temperatures, thus making diffusion-controlled coarsening of Y_2O_3 dispersoides at high temperatures very unlikely. Similar approaches have been reported in previous papers [2, 3]. The present work concentrates on prevailing phase reactions as well as the resulting microstructural and mechanical properties over a wide range of different annealing conditions.

2. Experimental Details

To investigate the influence of each dopant separately, four model alloys were produced via a powdermetallurgical (PM) route on industrial scale as described in [3]. One alloy was doped with Si and YN, one with YN and two with different amounts of Si. YN was used as it transforms into the more stable oxide Y_2O_3 as soon as it gets into contact with oxygen. For comparison one alloy was produced as an ingot. Ingots produced via electron beam melting have much lower impurity contents. The specimens were prepared either from 200 µm Ta wires or from 6 x 6 mm² rods, whatever shape was more appropriate for the experiments to be carried out. The rods represent an intermediate processing step of the wire production which is performed by several consecutive swaging, rolling, drawing, and annealing steps. The chemical compositions of all samples are listed in Table 1. For the sake of simplicity the samples are named with respect to their dopants.

The Y-contents have been determined semi-quantitatively using inductive-coupled plasma mass spectroscopy. The error of this method should be less than 10 ppm. Si was analysed quantitatively using photometry, for which the errors are in the range of +/- 10 %. For wire samples Si 400 and Si 800 the Si-contents were determined in the cold-worked condition and after annealing at 1800°C, 1900°C and 2000°C in order to

	Nominal comp. [ppm]		Chemical analysis [ppm]					
Sample	**Si**	**YN**	**Si**	**Y***	**O***	**H***	**N**	**C**
Si-YN (rod)	400	100	208	15/24	125	2/1	<5	<5
Si 400 (sint.)	400	-	251	n.a.	61	4	<5	7
Si 400 (rod)	400	-	175	<5	50/55	8	5	<5
Si 400 (wire)	400	-	193	<5	97	10	<5	30
Si 800 (sint.)	800	-	421	n.a.	38	5	<5	<5
Si 800 (rod)	800	-	482	n.a.	56	3/9	<5	<5
Si 800 (wire)	800	-	350	n.a.	194	14	16	37
YN (sint.)	-	100	n.a.	26	53	3	5	<5
YN (rod)	-	100	<20	16	64/71	5	<5	<5
YN (wire)	-	100	<20	22	132	12	8	28
pure (ingot)	-	-	<20	n.a.	21	3	<5	8

Table 1: Nominal compositions and results of chemical analysis for all samples and their prematerials (sintered powder or molten ingot). * For some samples two independent analyses of the indicated elements were made. Both values are listed in the table.

determine the volatility of Si. The amount of C was determined by combustion analysis while for the determination of N, H and O the carrier gas hot extraction method was used. It should be denoted that the amount of O obtained for wire specimens might be overestimated due to their large specific surface area which is prone to adsorption of O.

Table 2 gives an overview of all samples which have been investigated and their annealing treatments. All heat treatments have been performed in a vacuum furnace (< 10^{-6} mbar). The heating rates were approximately 200 $Kmin^{-1}$, while the cooling rates were much lower. The cooling time from 1300°C to 1000°C was in the range of 3 minutes and 50 minutes when cooled from 2000°C to 1000°C. Annealing treatments between 1300°C and 2000°C in steps of 100°C were carried out in order to determine the starting temperature of recrystallisation. The heating elements were switched off as soon as the target temperature was reached, meaning that no holding time was allowed. Heat treatments with holding times of 1, 10 and 30 hours were conducted at 1800°C exclusively. These heat treatments should reveal the grain growth kinetics of the

	holding time / h							
T / °C	Si-YN (rod)	Si 400 (wire)	Si 400 (rod)	Si 800 (wire)	Si 800 (rod)	YN (wire)	YN (rod)	pure (wire)
850	0.5	-	-	-	0.5	-	-	-
1250	2	-	2	-	2	-	2	-
1300	-	0	-	0	-	0	-	-
1350	2	-	2	-	2	-	2	-
1400	-	0	-	0	-	0	-	-
1450	2	-	2	-	2	-	2	-
1500	-	0	-	0	-	0	-	-
1600	-	0	-	0	-	0	-	-
1700	-	0	-	0	-	0	-	-
1800	-	0,1,10,30	-	0,1,10,30	-	0,1,10,30	-	0.5
1900	-	0	-	0	-	0	-	-
2000	-	0	-	0	-	0	-	-

Table 2: Investigated samples and their corresponding annealing treatments

differently doped samples. Microhardness measurements (HV 0.05) were performed to determine the macroscopic hardness. The given values are mean values of at least 15 individual measurements. The grain size was determined by light-optical microscopy (LOM) using the line intercept methode. The specified values are mean values of at least 200 grains. Furthermore, tensile tests (following the standard EN 10002, part 1) were carried out on wire samples to acquire tensile strength and fracture elongation. The elongation was obtained by measuring the cross-head displacement. Two measurements per annealing condition were carried out. The fracture surfaces were analyzed in a scanning electron microscope (SEM) in order to determine the fracture mechanisms.

Specimens for small-angle neutron scattering (SANS) and double crystal diffraction (DCD) experiments were either cold-worked or annealed for 2 hours at 1250°C, 1350°C or 1450°C for to determine the changes of the particle size distributions accompanied by annealing treatments. SANS and DCD measurements were carried out at the Geesthacht Neutron Facility (GeNF) in Geesthacht, Germany. The

specimens were 6x6 mm^2 rods from which pieces of about 2 mm thickness were cut off. The scattered neutrons were detected by a position-sensitive detector with a resolution of 256 x 256 pixels. The range of the scattering vector q (0.025 - 2.5 nm^{-1}) was covered by 4 different distances between detector and sample (1 m, 3 m, 9 m, and 21 m). Appropriate apertures and collimators were used. The measurements were performed using neutrons with a wavelength of 0.58 nm. The measured intensity was corrected for sample transmission, background and detector efficiency. The scattering data were averaged over the azimuthal scattering angle and absolute cross-sections were calculated by comparison with the incoherent scattering of vanadium. For detailed information on the SANS technique the reader is referred to [4]. The DCD is working at a wavelength of 0.44 nm and was used to extend the q-range for two orders of magnitude in order to observe scattering from larger particles [5]. Details concerning DCD data analysis can be found in [6]. Size distributions were determined from the scattering curves by means of a fitting software which is provided by GeNF and performs an indirect transformation as it was described by Glatter [7]. A calculated scattering curve is thereby fitted to a measured scattering curve by means of a least-square procedure. Between 8 and 10 log-normal distributions were used to find the specific optimum for each curve between small error values and little fitting deviation. In the case of DCD only one log-normal distribution was used as the use of more distributions could have led to an over-interpretation of the scattering curve causing large errors in the size distribution. A scattering contrast of 5.44×10^9 cm^{-2} was assumed for all samples.

Specimens for transmission electron microscopy (TEM) were annealed at 830°C for 30 minutes in order to reduce the dislocation density of the cold-worked material. They were prepared from 6x6 mm^2 rods by dimple grinding and subsequent ion milling. The TEM, a JEOL 2000FX, was operated at 200 kV. It is equipped with an EDS detector and a digital camera unit. All TEM measurements were carried out at the Max-Planck-Institut für Metallforschung in Stuttgart, Germany.

3. Results

3.1. Mechanical Tests

The tensile tests conducted on wire specimens show the dependence of strength and ductility on the specific annealing condition [8]. Cold-worked samples exhibit very high tensile strength accompanied by a very low fracture elongation (Figure 1). However, heating to 1300°C, even without any holding time, reduces the tensile strength and improves the ductility of all tested wires significantly (Figure 2). Error bars given in Figures 1 and 2 show the range between minimum and maximum value of each measurement. The strength of the Si-doped wires decreases with increasing annealing temperature to reach a local minimum at 1500°C (Figure 2a). YN-doped wires generally have lower strength and the difference is most pronounced at 1300°C. In contrast to Si-doped samples recrystallisation has fully completed at this temperature. In particular, both Si-doped wires reach a local maximum in strength at annealing temperatures around 1800°C (Figure 2a). Annealing treatments above this temperature lead to a reduced strength. Longer annealing times at 1800°C reduce both tensile strength and fracture elongation of the samples, whereby this effect is obviously retarded for the Si 800 samples (Figure 1).

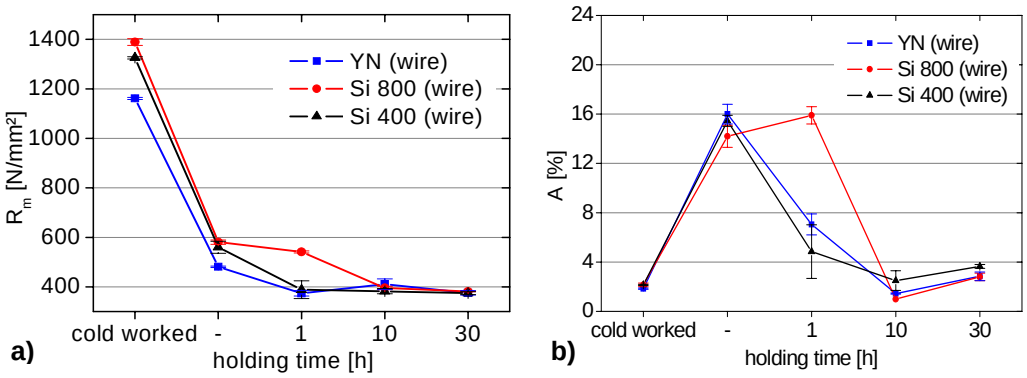

Figure 1: Results from tensile tests performed after cold working or annealing at 1800°C for different times: a) Tensile strength; b) Fracture elongation

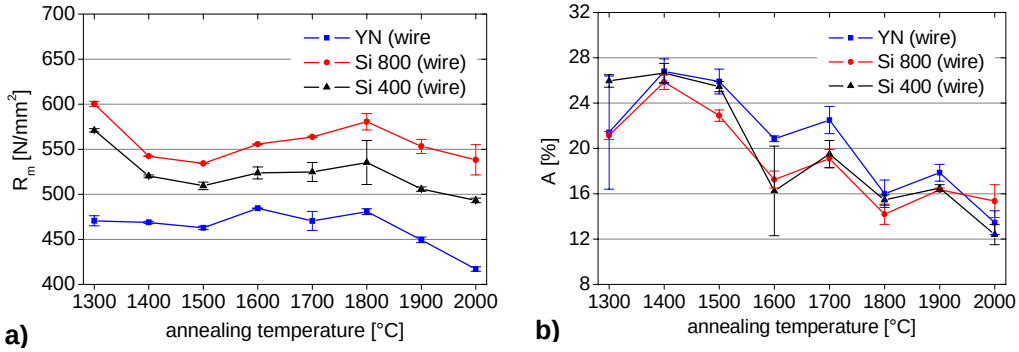

Figure 2: Results from tensile tests performed after heating up to a specific temperature followed by immediate cooling: a) Tensile strength; b) Fracture elongation

The results of microhardness measurements show the same tendency as the corresponding tensile strength data, however, local minima at 1500°C and maxima at 1800°C are even more pronounced (Figure 3a). One surprising fact is that the YN-doped wire has a maximum at 1800°C, while the Si 400 wire has not, what in fact is the only significant contradiction to the tensile test data. After annealing at 1800°C for 30 minutes the wire samples made of pure ingot material show lower strength than the doped PM variants (Figure 3b). However, scattering is relatively large and the difference is not pronounced. The error bars as shown in Figure 3 represent the standard deviation of 15 independent measurements.

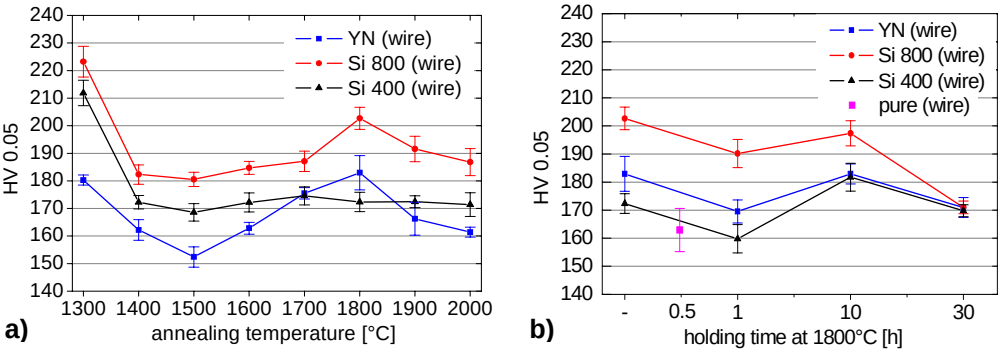

Figure 3: Microhardness (HV 0.05) of the tested wire samples. a) Samples heated up to the target temperature followed by immediate cooling. b) Samples annealed at 1800°C for different times.

3.2. Microstructural investigations

The grain growth kinetics are similar for the samples doped with Y and different amounts of Si. As can be seen from Figure 4a, there is virtually no grain growth up to a temperature of 1500°C. At 1500°C recrystallisation has finished for all samples as evidenced from metallographic examinations. Heating up to temperatures between 1500°C and 2000°C leads to considerable grain growth for all different types of wires. When exposed to 1800°C for 1 hour, the grain size of all wires increases rapidly, but

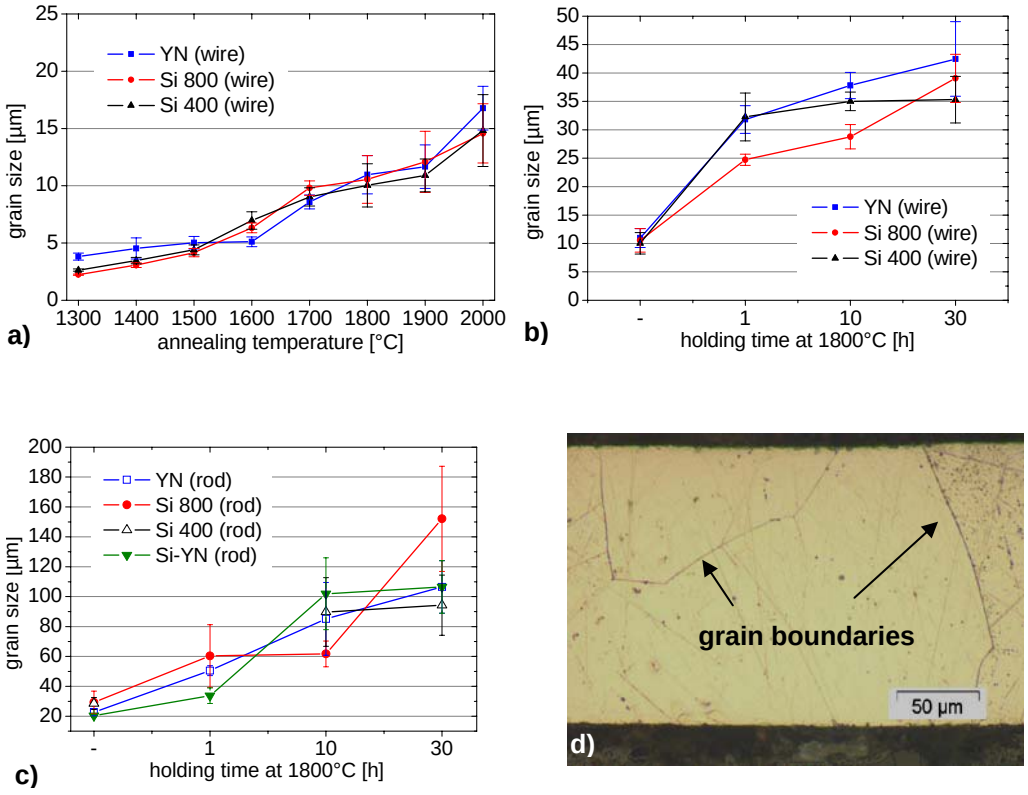

Figure 4: Average grain size of annealed samples. a) Wire samples heated up to target temperature indicated (no holding time). b) Wire samples annealed at 1800°C for different times. c) Samples prepared from 6x6 mm² rods and annealed at 1800°C for different times. The results derived from the Si-YN variant are included. d) Large grains in a wire made from pure Ta ingot and annealed at 1800°C for 30 minutes,LOM

for longer holding times up to 30 hours there is little additional grain growth (Figure 4b). The reason for that is the small wire diameter of only 200 µm. When the grain size reaches the magnitude of the wire diameter an equilibrium condition is reached leaving not enough driving force for further significant grain growth. Contrarily, grain growth kinetics measured on 6x6 mm² rods of the same materials show that growth does not stop at values of about 40 µm which obviously is a threshold for doped wire samples (Figure 4c). Differences between different doped alloy variants can hardly be discerned due to a large scattering of the measured values, especially for large grain sizes. However, for smaller grain sizes, scattering is smaller and up to annealing times of 10 hours at 1800°C the specimens with the most stable microstructure are the ones doped with 800 ppm Si (Figure 4b,c). It is a surprising fact that after an annealing time of 30 hours the same specimens show a relatively large grain size. The grain size of the wires made from Ta ingot could not be determined as it obviously exceeds the wire diameter. The investigated wire specimens contained only a few grain boundaries (Figure 4d). It is obvious that for pure ingot Ta which exhibits only small amounts of interstitial elements (Table 1) the retarding forces are smaller than for doped PM Ta. Thus, an equilibrium condition which prevents the grains from further growing is reached much later.

3.3. SANS and TEM investigations

Figure 5a shows the evolution of the particle size distribution of the material containing both Si and Y with increasing annealing temperatures. Evidently, a large portion of small particles dissolves after annealing at 1250°C for 2 h. The volume fraction in the size interval between 2 and 20 nm decreases from 1.6% to 0.1%. However, the volume fraction of larger particles in the size range of 50 - 200 nm remains almost constant (~1.8%). After annealing at 1350°C for 2 hours the volume fraction of small particles is similarly small, but in contrast to annealing at 1250°C also larger particles disappear. The volume fraction in the range between 50 and 200 nm is only 0.7% in this case. After annealing for 2 hours at 1450°C the size distribution is similar to the one obtained after annealing at 1350°C. From the DCD measurements, which cover a wider particle range, it is apparent that only little changes occur during annealing. The fraction of large particles in the interval of 200 nm to 10 µm is 0.6% in the cold-worked condition. During annealing for 2 hours it becomes slightly larger. It reaches a maximum at 1% after annealing at 1350°C and decreases slightly to 0.8% after annealing at 1450°C. The peak of the DCD-based distribution shifts from 300 nm to about 600 nm, indicating that the dissolution of small particles is accompanied by a coarsening of large particles. A scattering contrast of 5.44×10^{9} cm^{-2} was used for all samples which is valid for Ta_2Si in

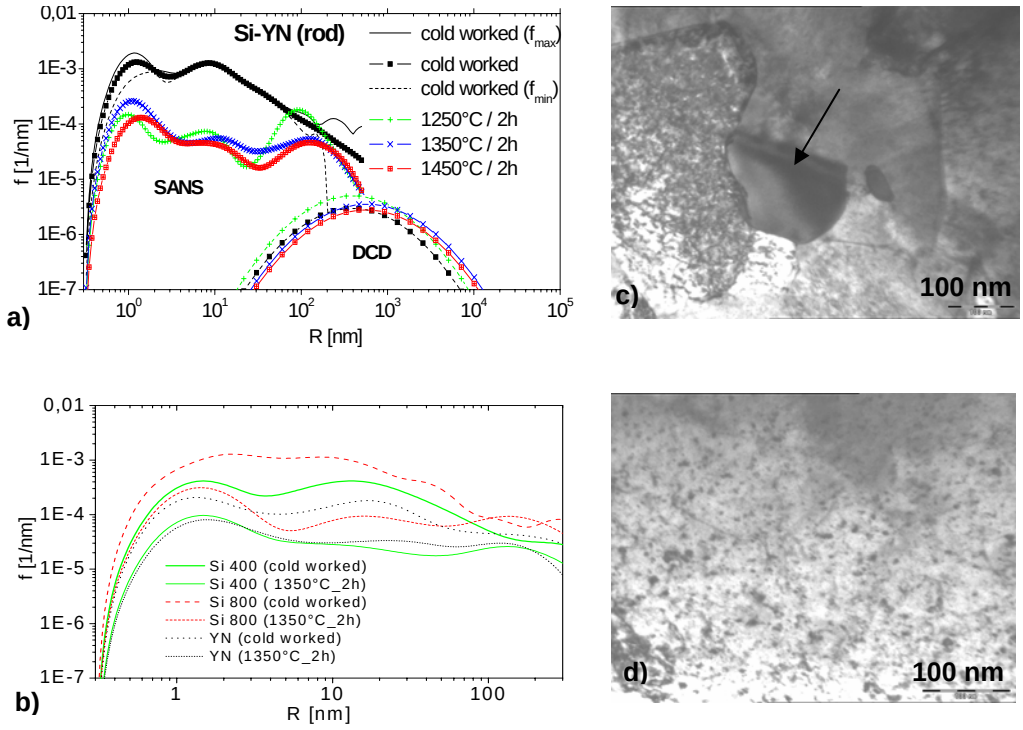

Figure 5: a) Particle size distributions of the Si-YN variant. (Samples prepared from 6x6 mm² material.) b) Particle size distributions in samples Si 400, Si 800 and YN. c) TEM micrograph of a large Ta_2Si precipitate (arrow) in the matrix (Si-YN sample, annealed for 30 minutes at 830°C). d) TEM micrograph of fine particles in the matrix (Si 800 sample, annealed for 30 minutes at 830°C).

a pure Ta matrix. This assumption was taken because in Si-containing materials larger Ta_2Si particles (> 100 nm in diameter, see Figure 5c) were analysed by TEM using electron diffraction. Small particles were also found in TEM (Figure 5d), however, their chemical composition is unknown. It should be noted that other particles than Ta_2Si (e.g. oxides) will have other scattering contrasts. Thus, the reported particle volume fractions should not be understood as absolute values than a preliminary base for discussion.

Figure 5b shows the particle size distributions of the differently doped variants (YN, Si 800 and Si 400) in the cold-worked condition as well as after annealing at 1350°C for 2 hours. For both conditions the largest particle fractions were obtained for Si 800,

followed by Si 400 and the variant doped with YN. The large difference between cold-worked and annealed samples is similar to the difference determined for Si-YN material.

It should be noted that no Y-containing particles could be detected in any of the samples analysed by TEM. In a previous investigation [3] only very coarse Y_2O_3-dispersoides (> 1µm) were found by means of SEM.

4. Discussion

From the obtained results it is evident that complex phase reactions accompanied by microstructural changes take place when doped Ta specimens are exposed to temperatures higher than 1300°C. However, considering the chemical compositions given in Table 1, it seems difficult to combine the apparent phase reactions, the mechanical and the microstructural properties with the initial doping conditions of the different variants. One reason for that is a relatively high and varying O content. Another reason is seen in the large deviation of the analysed content of dopants from the nominal doping condition. The O content in all variants increases during processing and reaches a maximum value for wire samples. Consequently, for the interpretation of the results O must be taken into consideration. Other interstitial elements seem to play a minor role only.

According to [9, 10], the equilibrium O_2 partial pressure over a solid solution of O in Ta is very low. For temperatures up to about 1900°C it is lower than the obtained O_2 partial pressure in the vacuum furnace, thus favoring absorption of O. For temperatures higher than 1900°C the equilibrium O_2 partial pressure exceeds the value obtained in the furnace and as a consequence, degassing of O occurs. Furthermore, at temperatures above 1500°C all Ta-oxides and silicides are expected to dissolve, leading to a homogenous solid solution. After the subsequent cooling sequence, fine TaO_x suboxides cause precipitation hardening and O which remains in solid solution causes a strong solid solution hardening effect at room temperature [10]. These theoretical findings agree well with the results derived from microhardness measurements. The increase in hardness between 1500°C and 1800°C is most pronounced for the YN variant which contains no Si. Therefore, it can be concluded that Si reduces the hardening effect caused by O. The hardness peak which is asserted for the Si 800 variant after heating up to 1800°C results from the re-precipitation of fine silicides from solid solution. The Si content of the Si 400 variant seems too low to facilitate the formation of silicides which contribute to hardening. The

decreasing hardness observed for all samples annealed above 1800°C is caused by O degassing as well as a lower Hall-Petch effect due to an increasing grain size.

Samples doped with Si exhibit a higher recrystallisation temperature than samples doped with Y which is most likely an effect of fine tantalum silicide and oxide particles. The presence of these fine precipitates was clearly proven by SANS and TEM investigations. The particle volume fractions obtained by SANS are much higher for the Si-doped variants than for the Y-doped one. Another fact that can clearly be seen from SANS is the dissolution of fine particles during annealing (Figures 5a,b).

The grain growth behaviour of all PM alloy variants is similar. This also applies for pure PM Ta as reported in [3], where “unintentional doping” with O causes large dragging forces against grain growth. Significant differences appear only for samples annealed at 1800 °C for 1 hour and 10 hours. Here the samples doped with 800 ppm Si exhibit a smaller grain size than the others. After these annealing treatments there is still a sufficient amount of Si left which causes an additional solute drag to grain growth. However, this behaviour changes completely after an annealing time of 30 hours (Figure 4c). Here, Si 800 shows the largest grains. So far, the reason for this behaviour can not be explained. It is the subject of ongoing research and will be presented in a forthcoming paper. As can be seen from Table 3, the volatilisation of Si seems to play a mayor role since it is evident that after an annealing treatment at 1800°C for 30 hours no Si is left.

After an annealing treatment of 1 hour at 1800°C the ductility of the Si 800 wire outperforms that of the other variants. This can partially be explained by its smaller grain size. However, after 10 hours at the same temperature there is no detectable difference in ductility, although the average grain size of the Si 800 wire is still smaller. Referring to Table 3, during the first hour of annealing at 1800°C a large amount of Si seems to be exhausted to prevent the formation of embrittling oxide phases, whereby this amount is much larger for variant Si 800 than for variant Si 400. For longer

	1800°C *	1900°C *	2000°C *	1800°C/1h	1800°C/10h	1800°C/30h
Si 800 (wire)	355	334	359	167	87	< 20
Si 400 (wire)	190	172	178	138	34	< 20

Table 3: Si contents of annealed wire samples in ppm. (* no holding time at annealing temperature)

annealing times than 1 hour at 1800°C, the Si content of both Si-doped wires is similarly small and obviously in both cases insufficient to suppress embrittling.

5. Conclusions

Doping of PM Ta with Si assures an adequate recrystallisation behaviour and moderate grain growth at elevated temperatures as long as the loss of Si by volatilisation can be suppressed. At high temperatures particles play only a minor role for the grain growth behaviour and retardation forces are mainly caused by elements in solid solution. In this context the O content of the material is believed to be of similar importance as the Si content. However, “unintentional doping” with O does not guarantee reproducible properties of the wire as it depends on the purity of the used raw materials which might fluctuate within its specification limits. At 1800°C and annealing times shorter than 1 hour, doping with a sufficient amount of Si greatly improves the ductility of the wires. Doping with 800 ppm Si is recommended to assure the demanded grain size stability and ductility required for wire used for the production of Ta-capacitors. The effect of doping with Y could not be approved which is most likely a result of an insufficient dispersion of the Y_2O_3 particles.

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6. References

[1] J. Gill, Basic Tantalum Capacitor Technology (Technical Information), AVX Ltd., Paignton, England

[2] P. Kumar, C.E. Mosheim, Refractory Metals and Hard Materials 12, 1993, 35-40

[3] M. Bischof, H. Leitner, H. Clemens, P. Staron, G. Dehm, A. Voiticek, W. Knabl, Z. Metallkunde 95, 2004 (7), 573-578

[4] G. Kostorz in: Treatise on Materials Science and Technology (ed. G. Kostorz, H. Herman), 1979 Vol.15: Neutron scattering, 227-289

[5] D. Bellmann, P. Staron, P. Becker, Physica B 276-278, 2000, 124-125

[6] P. Staron, D. Bellmann, J. Appl. Cryst. 35,2002, 75-81

[7] O. Glatter, J. Appl. Cryst. 13,1980, 7-11

[8] S. Mayer, Diploma Thesis (Montanuniversität Leoben), 2005

[9] Hyun Seon Hong, Kyung Sub Lee, J. Alloys and Compounds 360, 2003, 198-204

[10] G. Hörz, Acta. Met. 27, 1979, 1893-1906