J Mater Sci (2010) 45:2133–2139
DOI 10.1007/s10853-009-4048-9

HTC2009

The effect of an interfacial tantalum oxide layer on interactions in the Ta/Sn system

M. Gelbstein · N. Froumine · N. Frage

Received: 25 May 2009 / Accepted: 17 November 2009 / Published online: 15 December 2009

Abstract Liquid Sn is a corrosive agent for tantalum at high temperatures. Oxidation of tantalum is often used to form a surface protective oxide layer in order to improve its chemical resistance in the liquid metal. In this study the stability of tantalum oxide layer, obtained by thermal oxidation and plasma anodization of tantalum, in contact with liquid Sn was examined in the 700–1000 °C temperature range. It was established that the stability of the oxide layer is controlled by its dissolution into the substrate, which takes place along with the formation of non-stable Ta sub-oxides. It was found that the thermal oxide layer may provide sufficient protection against tantalum corrosion by liquid Sn up to 700 °C, whereas the protective layer obtained by the plasma anodization gives an adequate corrosion resistance up to 1000 °C.

Introduction

Tantalum is a widely used metal for structural applications in severe environments owing to its outstanding properties such as high melting point, high strength, low thermal expansion, and high ductility. It is often used as liquid metal container, tubes in industrial heat exchanger (liquid metals heat carriers), wall material for fusion reactors and tool material in casting processes. In these applications tantalum is subjected to chemical attack, which may affect the microstructure, composition, and surface morphology of tantalum and may result in contamination of the contacting liquid metal.

The results of several studies on the interactions between tantalum and liquid alkaline metals are reported in literature [1–3] and are related to the application of alkaline metals as coolant in variety of power generating systems. However, only a few studies were conducted on the behavior of tantalum in contact with other liquid metals, such as Bi, Pb, Al, Cs, and Sn. Preliminary results on the degradation of tantalum in these molten metals were reported mostly in the early 1960s [4–6]. It was pointed out that molten Sn is a very corrosive agent for tantalum at high temperatures [7]. In order to improve the resistance of tantalum to chemical attack in contact with liquid Sn, a thin adhesive and protective coating, which will act as a diffusion barrier, has to be formed. Our preliminary examination of several oxides stability with liquid Sn indicates that tantalum oxide exhibits high chemical resistance. Non-wetting conditions were observed in the Sn/Ta_2O_5 system at 1000 °C ($\theta = 145°$) and no evidence of interfacial interactions was detected. Along with the fact that tantalum oxide coating is easily fabricated and is adhesive to metallic tantalum, surface oxidation was chosen as a method to form a diffusion barrier layer.

Even though the chemical stability of the bulk Ta oxide is adequate, the stability of Ta oxide coatings in contact with liquid Sn may be significantly affected by the protective layer dissolution in the substrate due to high oxygen solubility in tantalum. The thermal stability of the oxide layer strongly depends on its chemistry, microstructure, morphology, thickness, and adhesion, which may be altered by applying various methods of oxidation. In the present study two approaches for tantalum oxidation were applied, namely thermal oxidation and plasma anodization.

M. Gelbstein · N. Froumine · N. Frage
Department of Material Engineering, Ben-Gurion University,
P.O. Box 653, Beer-Sheva 84105, Israel

M. Gelbstein (✉)
NRCN, P.O. Box 9001, Beer-Sheva 84190, Israel
e-mail: micam@bgu.ac.il

The protective properties of tantalum oxide layers, which obtained by different methods were investigated in the 700–1000 °C temperature range. The sessile drop method was applied in order to track the changes in surface chemistry and to evaluate the efficiency of tantalum oxide as a diffusion barrier.

Experimental

Commercial Ta (99.95% purity) obtained in a melting process followed by cold-rolling and thermal annealing was used. The average mean diameter of the grains measured using Image Pro software analysis was 225 ± 5 μm.

The substrates were polished down to 1 μm diamond past and were cleaned ultrasonically in ethanol. The oxidation of tantalum was obtained using two methods: (i) thermal oxidation in air at 500 °C for 5 h and (ii) plasma anodization by a inductively coupled radio-frequency (13.56 MHz) technique using an $Ar:O_2 = 80:20$ mixture under positive bias voltage (0.1VDC) and current (24 mA/cm^2). The oxidized substrates were characterized using XRD analysis and SEM examination using BSE detector. The thermal stability of the oxide layers in the 700–1000 °C temperature range in vacuum was examined by XRD.

Sessile drop wetting experiments were performed on oxidized and non-oxidized tantalum substrates and on a bulk Ta_2O_5 oxide substrate in the 700–1000 °C temperature range. The experiments were conducted in a resistance furnace with tungsten heating elements under vacuum of 1.0×10^{-6} Torr. After wetting experiments the samples were cross-sectioned and the interface was studied using SEM (BSE) and EDS analysis.

Results

Sn/Ta compatibility

The wetting behavior of liquid Sn on tantalum substrate was found to be almost independent on the temperature and invariable contact angle (of about 63°) was measured in the 800–1000 °C temperature range.

SEM examination of the interface between Sn drop and tantalum substrate obtained after wetting in the 700–1000 °C temperature range is shown in Fig. 1. The interface was found to be extremely corroded at all temperatures and large tantalum grains were detected in the Sn drop. No continues layer of Sn–Ta intermetallic phase was observed at the corroded interface.

Thermal oxidation of Ta in air: thermal stability of the oxide layer and its interaction with liquid Sn

A dense and uniform oxide layer of about 1 μm thick was formed on the tantalum surface after thermal oxidation of tantalum in air (Fig. 2).

X-ray pattern of the thermally oxidized substrate at 500 °C for 5 h (Fig. 3) shows the presence of bcc-Ta and the thermodynamically stable oxide Ta_2O_5. Additional sets of peaks, with a relatively low intensity, corresponding to tantalum sub-oxides were also detected (Ta_4O peaks at $2\theta = 37.6°$, 39.3° 50.8°, and 65.9° and Ta_2O peaks at $2\theta = 18.7°$ and 32.5°). The XRD patterns of the oxidized substrates after vacuum annealing at various temperatures between 700 and 1000 °C are presented in Fig. 3. After annealing in vacuum at 700 °C for 30 min only the set of peaks corresponding to the stable Ta_2O_5 oxide is presented.

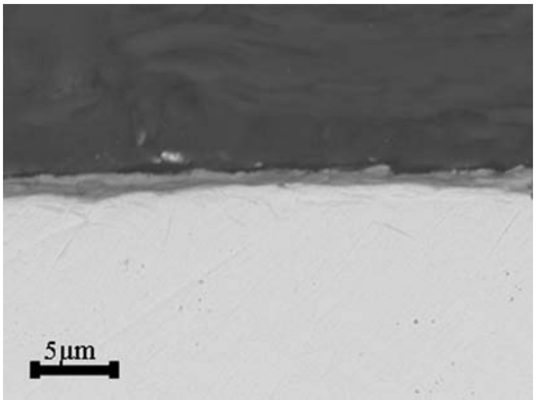


Fig. 2 Cross-section SEM image of thermally oxidized tantalum

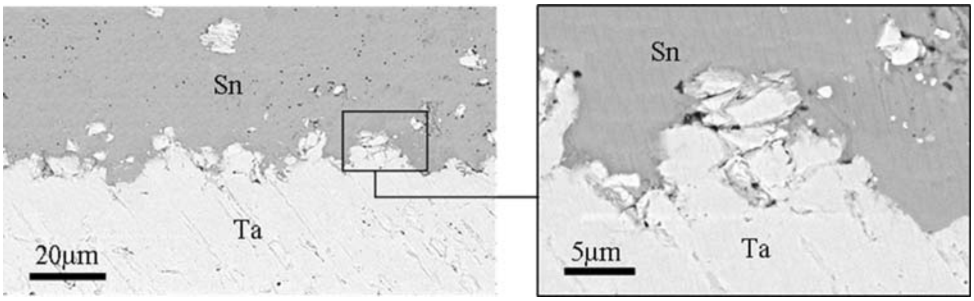


Fig. 1 SEM images of the Sn/Ta (225 μm grain size) interface obtained in the 700–1000 °C temperature range

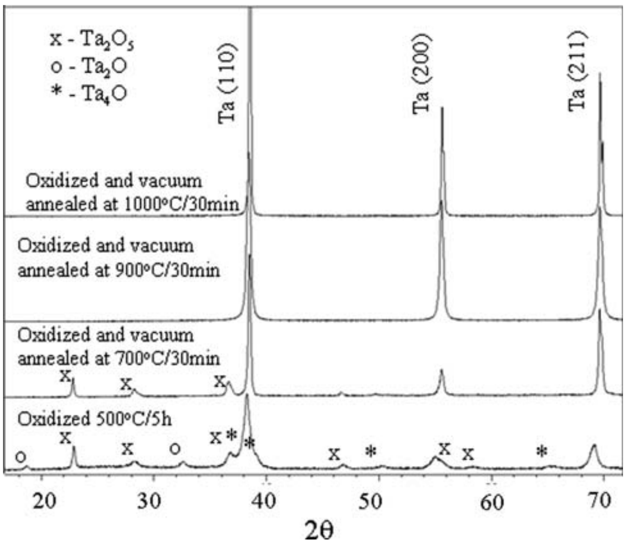


Fig. 3 XRD patterns of oxidized tantalum surface at 500 °C for 5 h and subsequent vacuum annealing at 700, 900, and 1000 °C for 30 min

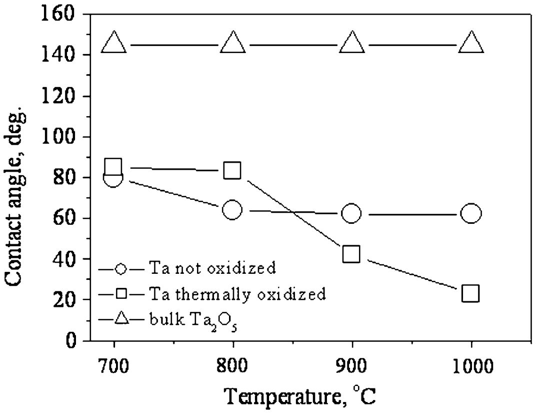


Fig. 4 Temperature dependence of the final contact angle of liquid Sn measured after 60 min on a non-oxidized tantalum, a thermally oxidized tantalum and a bulk Ta_2O_5 substrates

After heat treatment at 900 °C this set of peaks disappears, while narrowing the Ta peaks is clearly observed. After annealing at 1000 °C already both $K_{\alpha1}$ and $K_{\alpha2}$ tantalum peaks were resolved.

The interaction of the thermally oxidized tantalum with liquid Sn was examined. Figure 4 shows the final contact angles of liquid Sn drops measured on a non-treated tantalum, a thermally oxidized tantalum, and a Ta_2O_5 substrates after 60 min of contact at various temperatures. The contact angle in the Sn/Ta_2O_5 system is about 145° and no changes with temperature were observed. The Sn drops were detached from the oxide substrate during cooling and no evidence of the interaction at the interface was found. The contact angle on a non-treated tantalum substrate slightly decreases between 700–800 °C and remains constant (of about 63°) in the 800–1000 °C temperature range. The contact angle for the substrate after thermal oxidizing decreases with temperature and riches of about 20° at 1000 °C.

SEM images of the cross-sectioned samples after wetting experiments on the thermally oxidized substrate at various temperatures are shown in Fig. 5. The presence of an interaction layer composed of Sn–Ta–O oxide particles was observed at the interface at 700 °C. This layer is of the same thickness measured for the original Ta-oxide layer formed during the thermal oxidation (Fig. 2). The tantalum surface beneath the layer appears flat and not corroded.

With increasing temperature the amount of Sn–Ta–O oxide particles decreases and at 1000 °C no evidence of the ternary oxide was found. The tantalum interface cease to be flat above 900 °C and small tantalum particles detach from the substrate surface. However, the level of corrosion and the degree of surface roughness obtained during Sn interaction with the thermally oxidized substrate at 900 and 1000 °C are less than those obtained during the wetting of the non-oxidized tantalum substrate.

Plasma anodization of Ta in oxygen plasma: thermal stability of the oxide layer and its interaction with liquid Sn

Unlike the thermally oxidized tantalum the XRD pattern of the plasma anodized substrate (Fig. 6) shows the presence of a well-developed crystalline Ta_2O_5 oxide layer. After vacuum annealing at 1000 °C for 1 h, only a partial dissolution of the oxide layer took place resulting in the appearance of the bcc-Ta peaks.

SEM image of the oxide layer formed after plasma anodization of tantalum is given in Fig. 7.

The oxide layer was also found to be uniform and dense, however, relatively thicker (~7 μm) compared to the oxide layer formed during thermal oxidation of tantalum.

The time dependence of the contact angle of a liquid Sn drop on a plasma anodized tantalum substrate in the 700–1000 °C temperature range is shown in Fig. 8. The value of the contact angle after 1 h of contact at 700 °C is equal to that measured for theTa_2O_5 substrate. After cooling from 700 °C the drop was detached from the plasma anodized tantalum substrate and no reaction products were detected on the base of the Sn drop and on the tantalum substrate. With increasing temperature the rapid spreading of the Sn drop on the plasma anodized tantalum takes place. At 800 °C an apparent contact angle of about 80° was obtained after 55 min of contact, while the same value of contact angle at 1000 °C was obtained already after 1 min of contact. This value of contact angle is very close to that measured for the thermally oxidized tantalum,

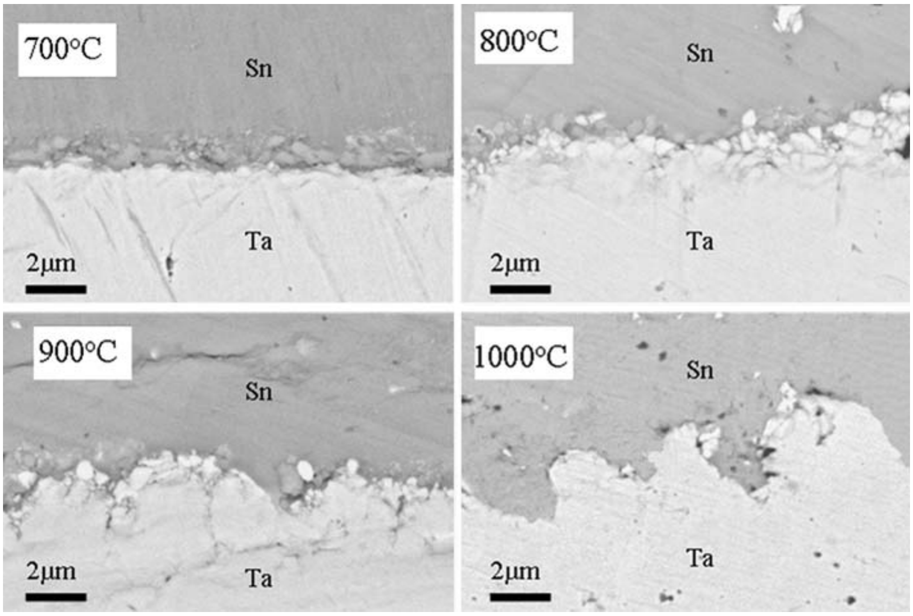


Fig. 5 Cross-sections of the liquid Sn/Thermal oxide/Ta interface at the designated temperatures

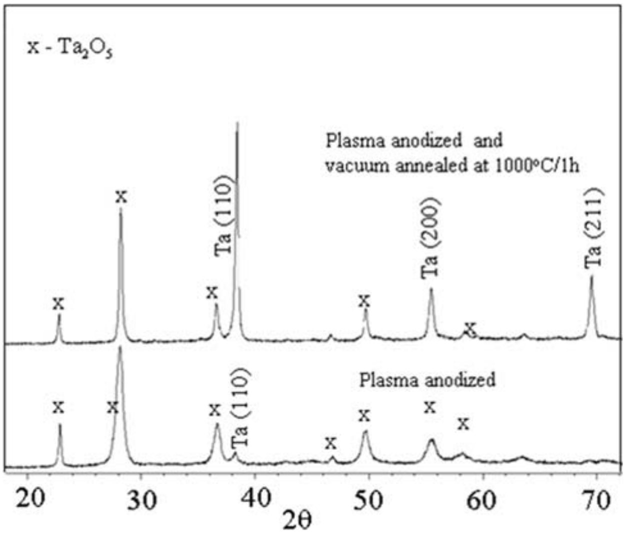


Fig. 6 XRD patterns of tantalum after plasma anodization and vacuum anneal at 1000 °C for 1 h

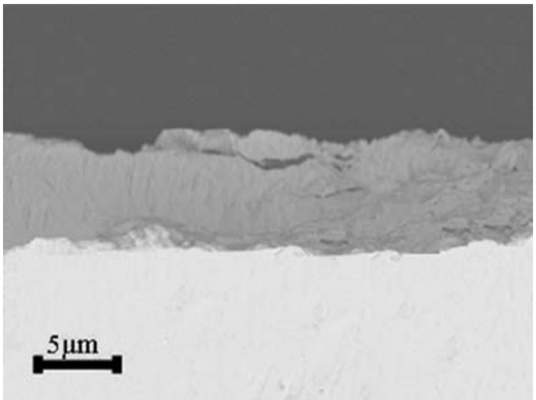


Fig. 7 Cross-section SEM image of plasma anodized tantalum

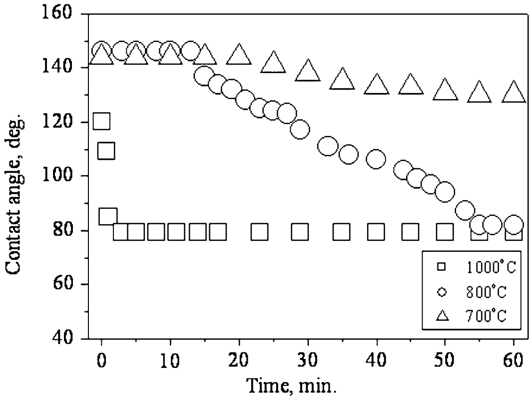


Fig. 8 Spreading kinetics of liquid Sn drop on plasma anodized tantalum substrate at various temperatures

where a thin layer of Sn–Ta–O oxide was detected at the interface.

The presence of homogenously distributed ternary Ta–Sn–O oxide particles was also detected throughout the plasma oxide layer after the wetting experiments in the 800–1000 °C temperature range (Fig. 9).

Discussion

It seems that the degradation of tantalum in contact with liquid Sn occurs via dissolution of tantalum grain boundaries in molten Sn resulting in the detachment of tantalum grains and sub-grains from the substrate surface. According to the Sn–Ta binary phase diagram (Fig. 10) [8], the solubility of tantalum in liquid Sn is ranging between 1.8 and 2.3 at.% Ta in the 700–1000 °C temperature range and the formation of the intermetallic phase is expected. Actually, the

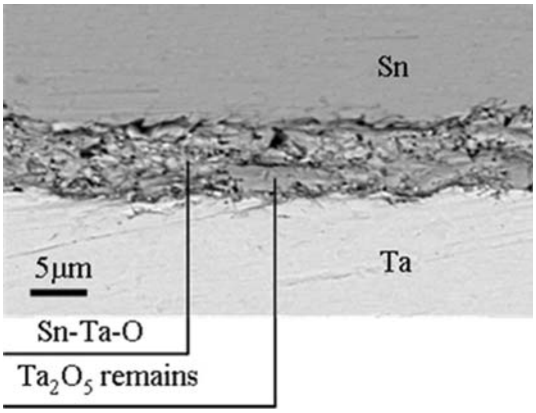


Fig. 9 Cross-sections of the liquid Sn/Plasma oxide/Ta interface at 1000 °C

intermetallic phase was not detected at the interface (Fig 1). We suggest that the detached Ta grains break the continuous intermetallic layer and drag its fragments into the melt volume. Moreover, the corroded and rough interface may act as a wedge and inhibits the spreading of liquid Sn, thus the measured value of the contact angle dose not truly reflect the wetting behavior in the liquid Sn/Ta system. To confirm this assumption, an additional set of wetting experiments was conduced on a sintered tantalum substrate characterized by smaller grain size (35 μm) and lower values of final contact angle between 25° and 18° were measured in the 900–1000 °C, respectively. SEM image of the cross-section at the liquid Sn/Ta (35 μm grain size) interface (Fig. 11) shows that the interface is also corroded, however, only submicron size tantalum particles were detached from the tantalum surface and were detected in the liquid Sn drop. The level of the substrate surface roughness in this case is much lower and thus may explain the low values of the final contact angles measured on Ta of smaller grain size.

To prevent the corrosion of tantalum by liquid Sn, an oxidation of the tantalum surface was preformed. It is well known that the oxidation of tantalum occurs through the oxygen dissolution in Ta up to its solubility limit followed by the formation of tantalum sub-oxides and finally the

Fig. 10 The Sn–Ta binary phase diagram [8]

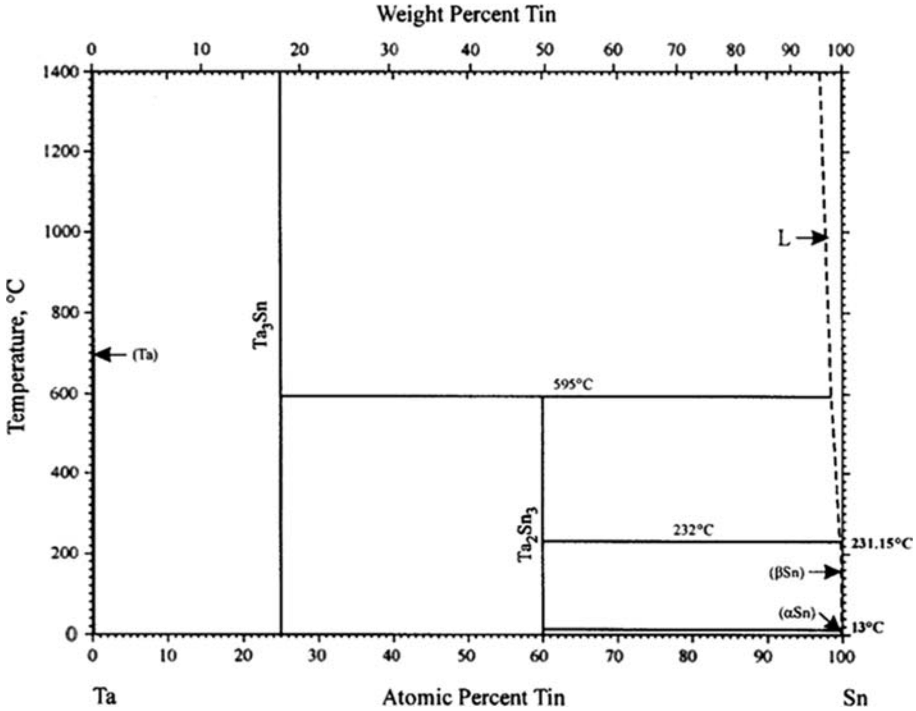
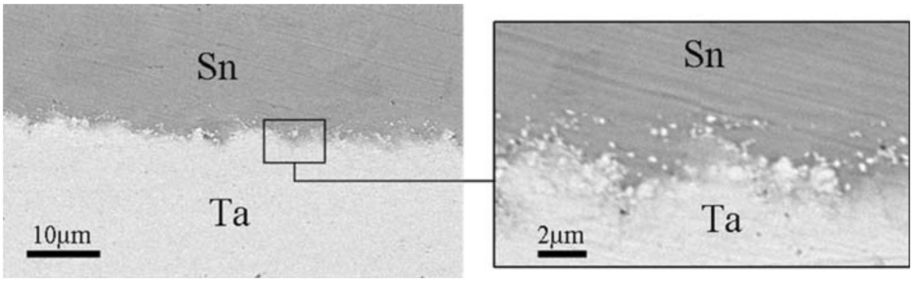


Fig. 11 Representative SEM image of the Sn/Ta (35 μm grain size) interface obtained in the 900–1000 °C temperature range



formation of the stable Ta_2O_5 phase [9], according to the sequence:

$$Ta_{(s)} + O_{2(g)} \rightarrow [\text{Ta-O}]_{\text{solid solution}} \rightarrow Ta_6O \rightarrow Ta_4O \rightarrow Ta_2O \rightarrow Ta_2O_5 \quad (1)$$

As mentioned above, the presence of Ta_2O and Ta_4O sub-oxides were detected after thermal oxidation at 500 °C (Fig. 3), whereas, during plasma anodizing of tantalum surface under the described conditions the final stage of the oxidation was achieved and only the stable oxide phase was detected (Fig. 6).

The efficiency of the protective tantalum oxide layer formed on tantalum surface is related to its thermal stability, namely dissolution within the Ta substrate, under vacuum at high temperature and to its chemical stability in contact with liquid Sn. According to the experimental results for the thermally oxidized tantalum (Fig. 3), the dissolution of Ta sub-oxides (Ta_2O and Ta_4O) takes place already at 700 °C, while the dissolution of the stable Ta_2O_5 oxide occurs at higher temperatures (900–1000 °C). The enhanced oxide layer dissolution with increasing temperature is attributed to the increase in oxygen solubility in tantalum from 1.7 to 2.7 at.% O, between 700 and 1000 °C.

The same feature was observed during the thermal annealing of the plasma anodized tantalum. However, in this case, only partial dissolution of Ta_2O_5 was observed after annealing for 1 h at 1000 °C due to the relatively thick oxide layer (Fig. 7) obtained by plasma anodizing method.

The chemical interaction between molten Sn and tantalum oxide may be considered along with a thermodynamic analysis of the ternary Sn–Ta–O system. This system was investigated by Bieger et al. [10] and the isothermal section of the ternary phase diagram at 950 °C was constructed (Fig. 12). According to this isothermal section the ternary pyrochlore type compound (PC) with a stoichiometric range from $Sn_{1.9}Ta_{1.76}O_{6..54}$ (PC1) to $Sn_{1.423}Ta_{1..997}O_{6.419}$ (PC2) is expected. Unfortunately, the Sn-rich corner of this isothermal section is not detailed.

The schematic view of the Sn-rich corner is presented in Fig. 13. In this figure, points *a*, *b*, and *c* correspond to three-phase equilibrium between liquid Sn–Ta–O solution and two oxide phases (SnO_2 and PC1) and to three-phase equilibrium between liquid Sn–Ta–O solution and two oxide phases (PC2 and Ta_2O_5), respectively. The area bellow the *a–b–c–d* curve corresponds to the single phase (liquid Sn–Ta–O) region. Points *b′* and *c′* correspond to the Ta contents in liquid solutions, which are in equilibrium with two oxide phases. The values of the Ta concentrations at these points may be calculated using the thermodynamic data presented in [10].

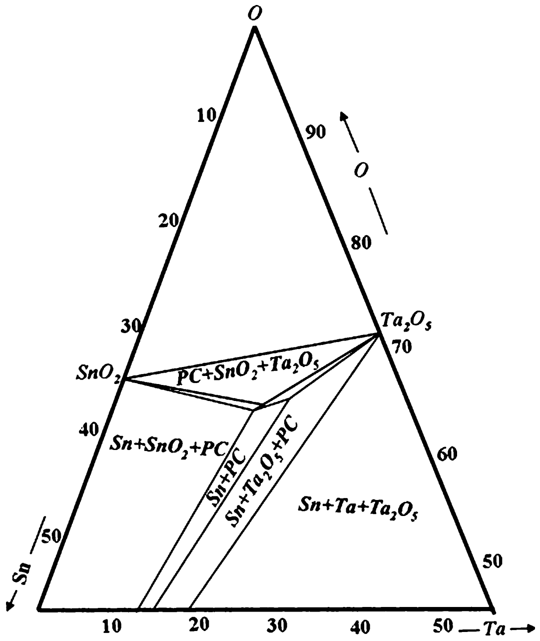


Fig. 12 Isothermal cross-section of the ternary Sn–Ta–O system at 950 °C [10]

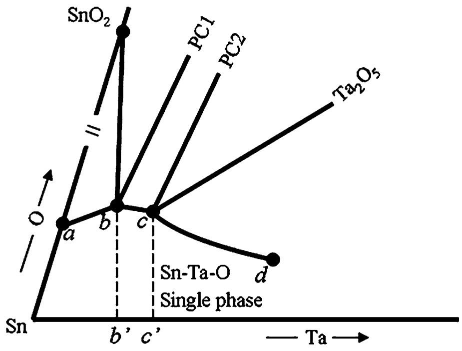


Fig. 13 Schematic illustration of the Sn-rich corner in the Sn–Ta–O system

According to Fig. 12 the formation of ternary oxide is expected when liquid solution is in equilibrium with either Ta_2O_5 or SnO_2. It seems that the latter equilibrium is not feasible, since the presence of SnO_2 may be only attributed to oxygen transport from the experimental environment. In this case, the formation of the ternary oxide should also be detected in the Sn/Ta system, however, in the absence of Ta oxide no evidence of the ternary oxide was found. Thus, the only equilibrium between the Sn–Ta–O solution, PC2 and Ta_2O_5 has to be considered:

$$1.423[\text{Sn}] + 1.283Ta_2O_{5(s)} \rightarrow Sn_{1.423}Ta_{1.997}O_{6.419(s)} + 0.569[\text{Ta}] \quad (2)$$

The square brackets denote that the elements are in the liquid solution.

The standard Gibbs energy for the reaction (2) was calculated using standard formation Gibbs energies for the ternary (PC2) [10] and for the Ta_2O_5 [11]. The calculated value of ΔG^0 (2) at 1223 K is equal to 210.5 kJ/mole. The equilibrium constant K for reaction 2, $K = \frac{a_{Ta}^{0.569}}{a_{Sn}^{1.423}}$ (oxides phase are considered as pure compounds) is equals to 10^{-9} and corresponds to the value of Ta activity equals to 1.58×10^{-16}(activity of Sn was taken equal to 1). This very low value indicates that Ta_2O_5 is extremely stable in contact with liquid Sn. This fact is in a good agreement with the results for the Sn/Ta_2O_5 system, where no evidence of reaction was detected.

The question is: what is a reason for the formation of the ternary Sn–O–Ta compound, which was detected within the protective layer?

We suggest that this feature may be related to the dissolution of Ta oxide layer in the metal substrate, which takes place through the reversed sequence of the oxidation process (Eq. 1) and involves the formation of unstable Ta sub-oxides. These chemically active sub-oxides are significantly less thermodynamically stable than Ta_2O_5 and may react with molten Sn.

In the case of the thermally oxidized tantalum, the oxide layer formed is composed of both the stable phase and the sub-oxides. At 700 °C, the formation of the ternary Sn–Ta–O compound may be attributed to the interactions between molten Sn and the sub-oxide presented in this layer. At higher temperatures the rate of dissolution is enhanced and the relatively thin thermal oxide layer is completely dissolved, thus the formation of the ternary oxide was not detected between 900 and 1000 °C. In the case of the plasma-anodized tantalum a thicker layer composed only of the stable Ta_2O_5 phase was formed and thus at 700 °C no evidence of the reaction products was detected in contact with the liquid Sn. With increasing temperature the rate of Ta_2O_5 oxide dissolution increases, accompanied with the formation of Ta sub-oxide, and the oxide layer ceases to be continuous. Subsequently, liquid Sn may penetrate the oxide layer and react with the sub-oxides to form the ternary compound Sn–Ta–O.

It has to be noted that according to Fig. 9, the ternary compound acts as a diffusion barrier in the same extent as stable Ta_2O_5 oxide.

Thus, it may be concluded that thermal oxidation provides the sufficient protection against liquid Sn attack up to 700 °C, while the oxide layer formed by plasma oxidation may be used as protective layer up to 1000 °C.

Conclusions

In this work the degradation behavior of tantalum in liquid Sn was demonstrated in the 700–1000 °C temperature range. According to the experimental observations and the thermodynamic analysis, Ta_2O_5 was considered as a potential material for a diffusion barrier in contact with liquid Sn.

The diffusion barrier layer was formed by thermal oxidation of tantalum in air and by plasma anodization of tantalum in oxygen plasma and its stability was investigated. The durability of tantalum oxide layer was attributed to its dissolution in the Ta substrate at high temperature under vacuum and to the interfacial chemical interactions with liquid Sn. The formation of the ternary Sn–Ta–O oxide was detected between the liquid Sn and the oxide layer at the Sn/Ta-oxide/Ta interface. It was suggested that this may be attributed to the formation of less thermodynamically stable tantalum sub-oxides during the dissolution of the stable Ta_2O_5 into the solid tantalum substrate.

It was established that the efficiency of the thermal oxide layer as a diffusion barrier in contact with liquid Sn is limited up to 700 °C, while plasma anodization of tantalum provides sufficient protection up to 1000 °C.

Acknowledgement The authors wish to thank Dr. Avi Raveh from NRCN for his expert assistance in producing the plasma anodized tantalum samples.

References

1. Klueh RL (1972) Metall Trans 3:2145
2. DiStefano JR (1989) J Mater Eng 11:215
3. Hickam CW (1967) NASA Technical Note TN-D4213
4. Reed EL (1954) J Am Ceram Soc 37:1946
5. Eremenko VN, Natanzon YV, Dybkov VI (1976) J Less Common Metals 50:29
6. Winslow PM (1965) Corrosion 21:341
7. Lance JR, Kemeny GA (1963) ASM Trans Quart 56:204
8. Okamoto H (2003) J Phase Equilib 24:484
9. Kofstad P, Krudtaa J (1963) J Less Common metals 5:477
10. Bieger W, Krabbes G, Ritschel M, Wiezner U (1999) Eur J Solid State Inorg Chem 28:999
11. Rao YK (1985) Stoichiometry and thermodynamics of metallurgical processes. Cambridge University Press, London