

Corrosion of Molybdenum in Cooling Water

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Abstract

Cooling water from the PVD system can cause severe corrosion of molybdenum (Mo) sputtering targets. In the cooling water circuit there is often a direct contact of molybdenum with other components mainly consisting of copper and brass that can enhance the corrosive attack. The aim of this paper was to determine the corrosive effect of different water qualities on molybdenum at various temperatures and with various material combinations (Mo, Mo/Cu). In addition, the influence of different corrosion inhibitors was investigated.

Immersion tests were conducted in different water qualities. Cyclic polarization scans and Evans Diagrams were recorded to get a further understanding on the corrosion behavior of molybdenum and the buildup of galvanic elements in cooling water.

The material combination Mo-Cu in tap water with a temperature of 40°C results in the most severe corrosive attack. In deionized water a higher temperature yields to higher corrosion rates of molybdenum. The use of inhibitors can cause a strong decrease of the corrosion rates.

Keywords

Corrosion of molybdenum, Cooling water, Immersion tests, Cyclic polarization scans, Evans Diagrams, Inhibitors, Sputtering target

Introduction

Molybdenum is an important metal in the coating industry. Thin films of molybdenum (Mo) are used as electrical conductive layers in thin film transistors (TFT) and thin film solar cells. A PVD process, typically magnetron sputtering, is used to deposit thin films from planar or rotary sputtering targets. Investigations of molybdenum in different aqueous environments adjudge this material a corrosion resistance due to the formation of a passive layer on its surface [1]. Till today there are existing different opinions about the nature of the passive film [1]. The occurrence of MoO_2 , MoO_3 , Mo_2O_5 , $\text{Mo}(\text{OH})_3$, Mo_4O_{11} , Mo_8O_{28} and Mo_9O_{26} on the surface is possible [2].

When looking at cyclic polarization scans one can in contradiction not find a pronounced passive behavior of molybdenum [3]. This means that porous and highly permeable oxides are formed with molybdenum. The anodic dissolution of molybdenum proceeds to the oxidation state +6 [3].

Investigations of corrosion rates in humid atmospheres have shown that a corrosive attack occurs on molybdenum from up to 60% relative humidity [4]. The purpose of our studies is to explore the corrosion behaviour of pure molybdenum (chemical purity: 99.97%) and pure molybdenum in contact with copper in different water qualities and various temperatures. Also different corrosion inhibitors were tested to reduce the corrosive attack.

Experimental

In all investigations, cylindrical samples of pure molybdenum (99.97%) were investigated. To analyse the uniform corrosion on molybdenum, immersion tests were conducted in stirred tap water and deionized water (milliQ water) at temperatures of 20°C, 40°C and 80°C. The composition of the investigated waters is given in Table I. Pure molybdenum investigations were conducted with inert Teflon sample holders. The contact with copper like in service was carried out with copper sample holders. To achieve constant temperature, double walled glass vessels were used. Always four samples were tested simultaneously at different conditions and the material loss of the samples after 5h, 15h, 50h and 150h was gravimetrically determined. Furthermore the pH-value and the oxygen content of the water were determined after the removal of each sample. Electrolyte/surface ratio was 30 ml/cm².

Table I: Composition of investigated waters.

Parameter	Unit	Tap water	MilliQ water
pH-value	-	7.78	7.18
Electrical conductivity (25°C)	µS/cm	394	1.00
Oxygen content (O ₂)	mg/l	7.65	7.24
Acid capacity; K _{S, 4.3}	mmol/l	3.00	0.06
Alkalinity; K _{B, 8.2}	mmol/l	0.24	0.10
Chloride (Cl ⁻)	mg/l	5.87	< 0.4
Nitrate (NO ₃ ⁻)	mg/l	6.90	< 0.4
Phosphate (PO ₄ ²⁻)	mg/l	< 0.04	< 0.04
Sulfate (SO ₄ ²⁻)	mg/l	15.0	< 0.4
Aluminium (Al)	mg/l	0.011	< 0.01
Calcium (Ca ²⁺)	mg/l	58.0	< 0.5
Magnesium (Mg ²⁺)	mg/l	4.85	< 0.1
Silicium (Si)	mg/l	0.20	< 0.025

Cyclic polarization scans were conducted corresponding to ASTM G5-94 [5]. To record the cyclic polarization scans a Gamry-potentiostat „Reference 600™“ was used. The tests were also conducted at temperatures of 20°C, 40°C and 80°C in tap water and deionized water (milliQ water). A nonaggressive borate buffer was added to the waters to maintain sufficient electrical conductivity. Amount of buffer in solution was 30.92 g/l H₃BO₃ and 2.01 g/l Na₂B₄O₇. A platinum electrode acted as counter electrode and a calomel electrode as reference electrode. To achieve the desired temperature a thermostat was used. For all different conditions the open circuit potential was measured for one hour prior to polarization. The cyclic polarization scans were conducted with a scan rate of 200 mV/h and the reverse scans were started at a current density of 1 mA/cm². The corrosion current density was determined with Tafel-slope extrapolations. The resulted current densities were used to get the corrosion rates of molybdenum.

Evans diagrams for the material combination molybdenum with copper were recorded to get information of the buildup of galvanic elements. Untreated molybdenum samples and molybdenum samples after immersion tests were investigated to get further information about the developed oxide layers. Also the temperatures 20°C, 40°C and 80°C were investigated. The open circuit potentials of the two materials in the test vessel were recorded, whereas two calomel electrodes acted as reference electrodes. Afterwards, molybdenum and copper were short-circuited and the occurring potential and current was measured.

Immersion tests and cyclic polarization scans on molybdenum were also conducted in inhibited tap water at 40°C in contact with copper. Three inhibitors were investigated. The main active substances of the inhibitors are given in Table II.

Table II: Chemical composition of inhibitors and amounts of addition.

Inhibitor A [4.6 ml/l]	Inhibitor B [4 g/l]	Inhibitor C [0.08 g/l]
morpholine	high tension polymer	sodium-4(or 5)- methyl-1H-
sodium molybdate	phosphonates	benzotriazole
	benzotriazoles	sodium hydroxide
	organic acid	chlorotolyltriazole

Results

The results of immersion tests for molybdenum and molybdenum in contact with copper are shown in Fig. 1 and Fig. 2. It is visible that tap water is more aggressive than milliQ water. The increase of temperature from 20°C to 40°C causes an increase of material loss of molybdenum samples. Furthermore the pH-value of these waters decreased during the testing time from pH=7 to pH=5. A further increase of material loss with increasing temperature (80°C) could only be obtained for molybdenum without copper contact in milliQ water. All other investigations at 80°C have shown, that the material loss decreases referring to 40°C and no decrease of pH was measurable. The pH-value of pH=7 was constant during the testing time at 80°C. After the immersion test at 80°C it was visible that different surface layers from the normal black molybdenum oxide layer were built up. In milliQ water and in contact with copper a red layer was built on the molybdenum surface. In tap water a white layer was always built up on the molybdenum surface. The different layers were investigated by scanning electron

microscopy (SEM) and energy dispersive X-ray analysis (EDX). The results of the different layers are shown in Fig. 3 to Fig. 6.

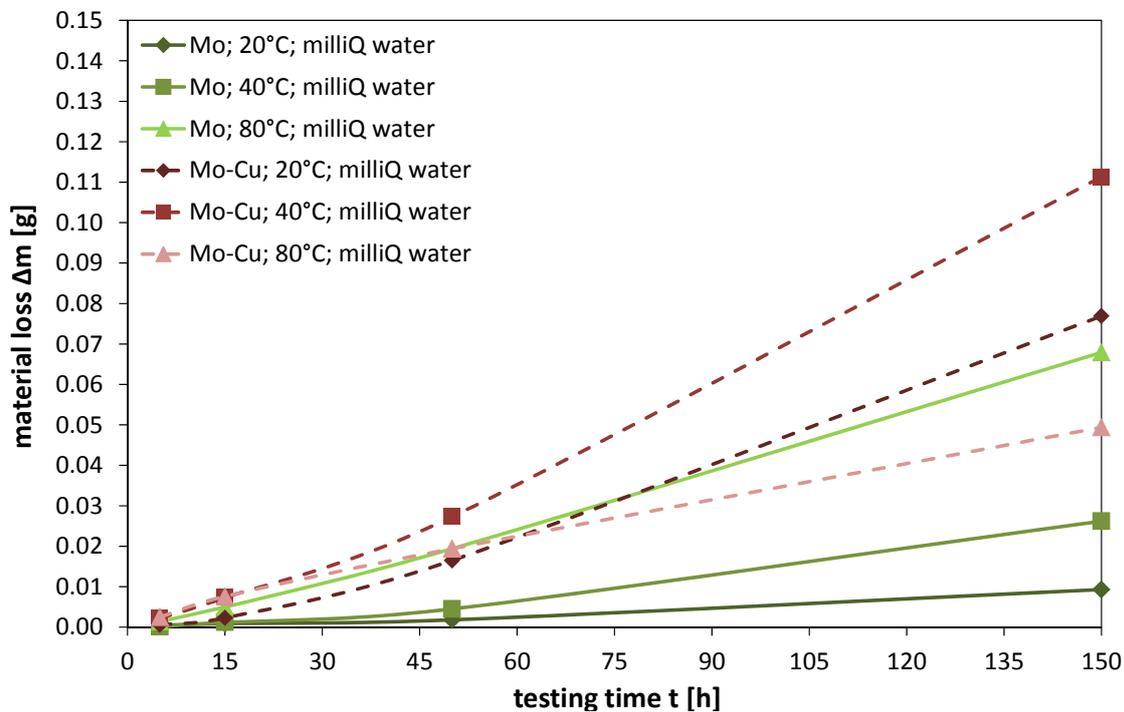


Figure 1: Material loss of molybdenum and molybdenum in contact with copper as function of the testing time in milliQ water at 20°C, 40°C and 80°C.

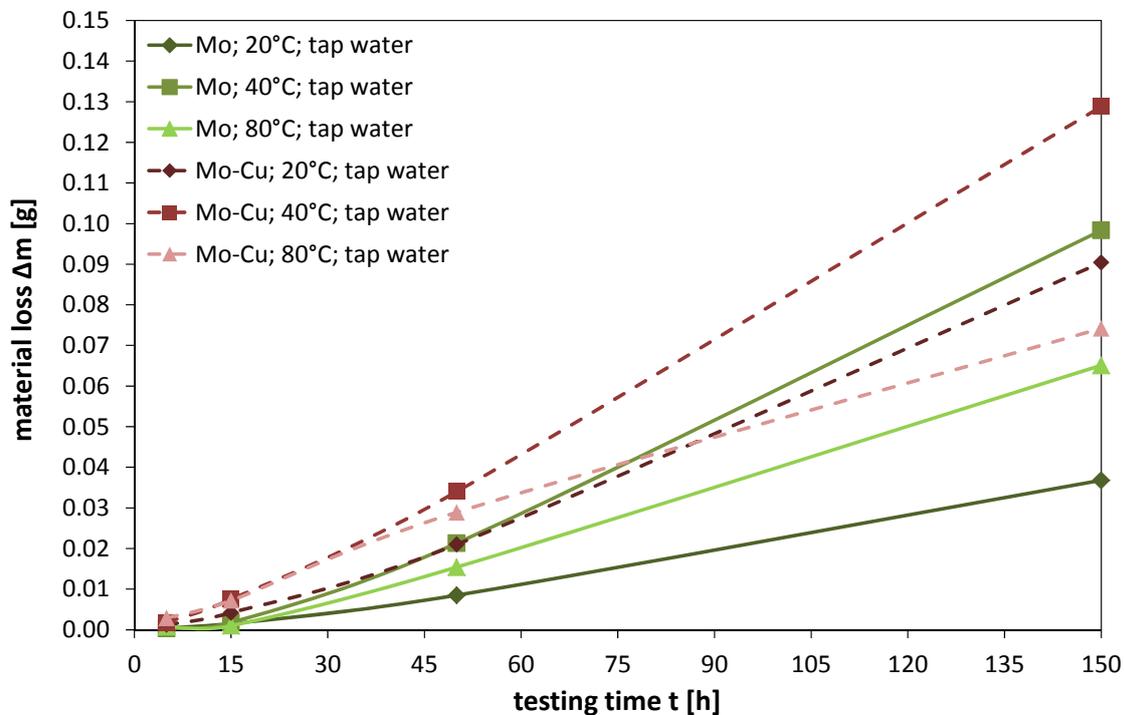


Figure 2: Material loss of molybdenum and molybdenum in contact with copper as function of the testing time in tap water at 20°C, 40°C and 80°C.

In Fig. 3, the black and porous mixed oxide/hydroxide surface layer on molybdenum is shown after a 150 h immersion test in milliQ water at 80°C. This surface is also representative for all molybdenum samples at 20°C and 40°C. There are two different surface areas occurring. The EDX analysis of the areas are pictured in Fig. 4. Area 1 is pure molybdenum and area 2 consists of a molybdenum oxide or molybdenum hydroxide. In Fig. 5 there is the white layer shown, which always occurs in tap water at 80°C on molybdenum after 150 h of immersion. A crystalline surface is visible and the EDX analysis shows a Ca-C-O-Mo-compound. The red surface layer on molybdenum in contact with copper, which only built up in milliQ water at 80°C is visible in Fig. 6. Copper from the sample holder has dissolved in the electrolyte and afterwards deposited on the molybdenum surface. The EDX analysis proves that the developed layer consists of a compound of Cu-Mo-O. These white and red layers are responsible for the decrease of the corrosion rates at 80°C.

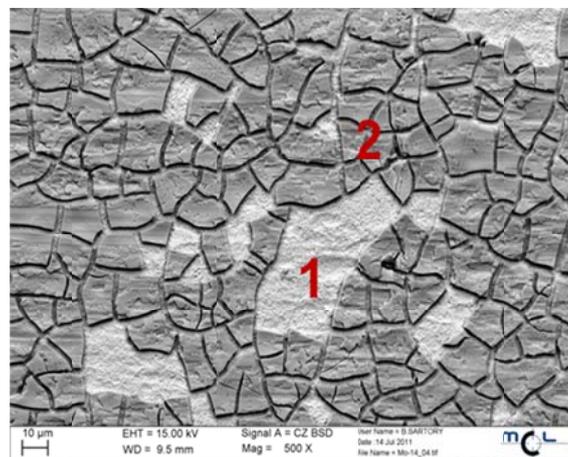


Figure 3: Surface of molybdenum after 150 h of immersion in milliQ water at 80°C.

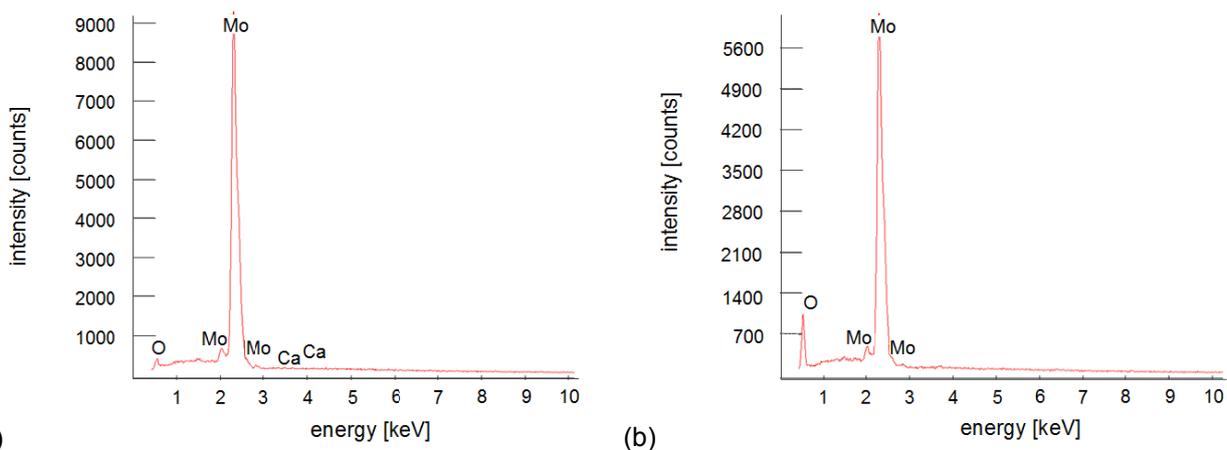


Figure 4: (a) EDX analysis of area 1 and (b) EDX analysis of area 2 of the molybdenum surface shown in Fig. 3 after 150 h of immersion in milliQ water at 80°C.

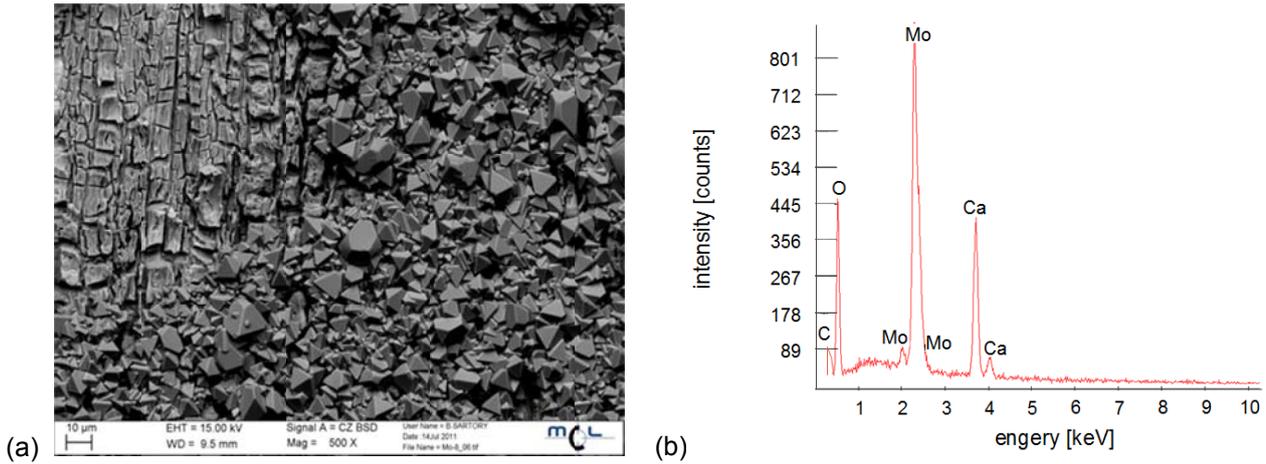


Figure 5: (a) Surface of molybdenum after 150 h of immersion in tap water at 80°C and (b) EDX analysis of the white crystalls.

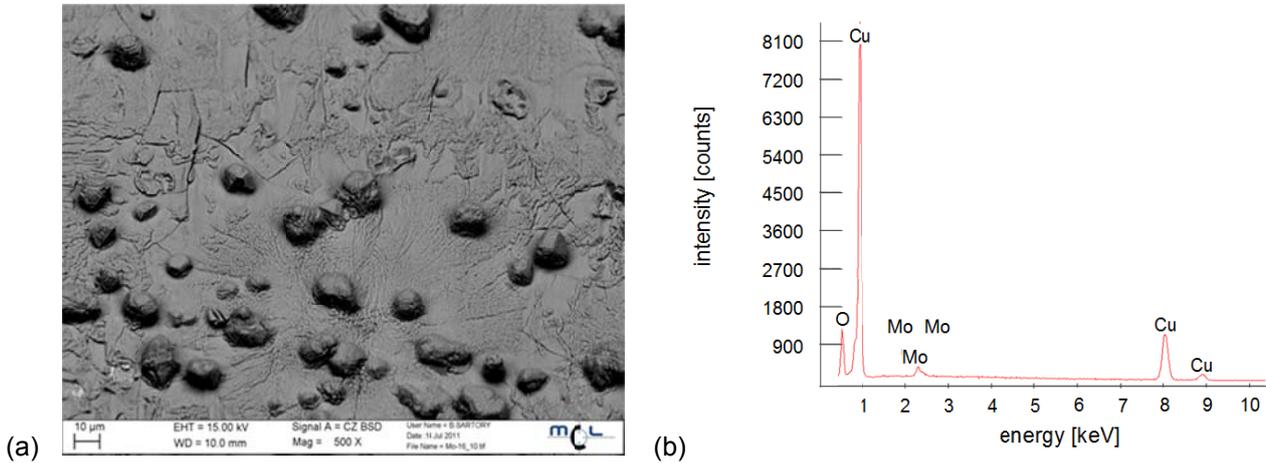


Figure 6: (a) Surface of molybdenum in contact with copper after 150 h of immersion in milliQ water at 80°C and (b) EDX analysis of the red layer.

The results of cyclic polarization scans of molybdenum in milliQ water and tap water with borate buffer at temperatures of 20°C, 40°C and 80°C are shown in Fig. 7 and Fig. 8. With increasing temperature the open circuit potentials are getting more active and the corrosion current densities increase. Higher temperatures cause a stronger corrosive attack. No hysteresis occurs between scan and reverse scan, which is a sign for uniform corrosion. The buildup of a calcium containing surface layer was not observed.

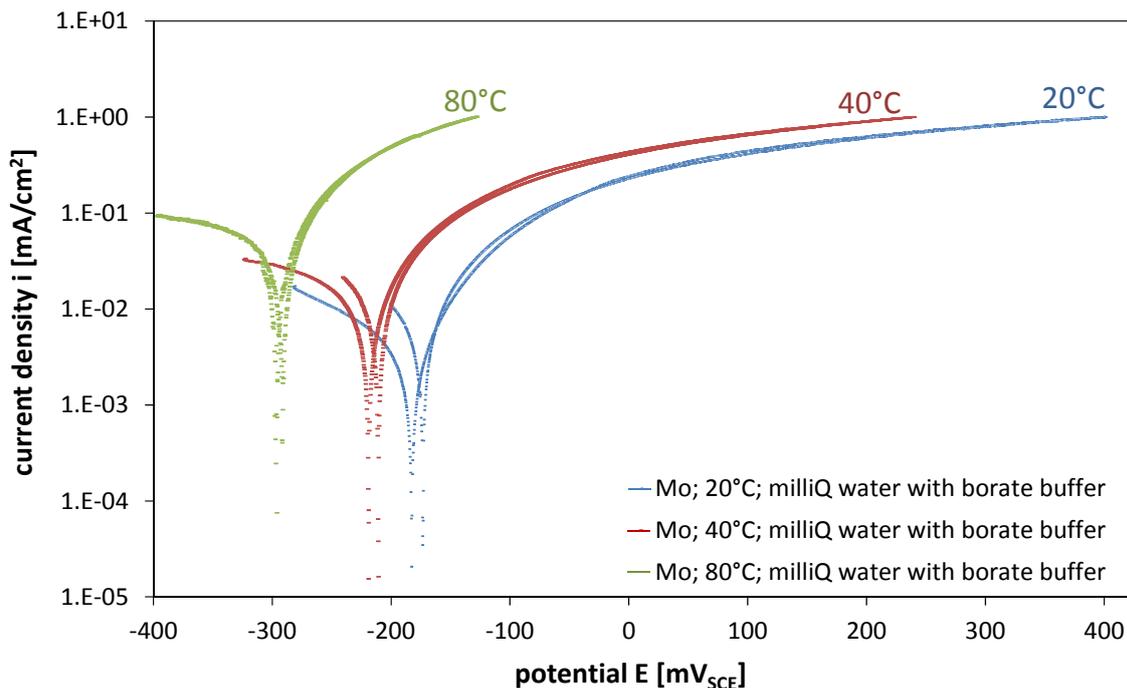


Figure 7: Cyclic polarization scan of molybdenum in milliQ water with borate buffer at 20°C, 40°C and 80°C; calomel reference electrode, platinum counter electrode, 200 mV/h scan rate.

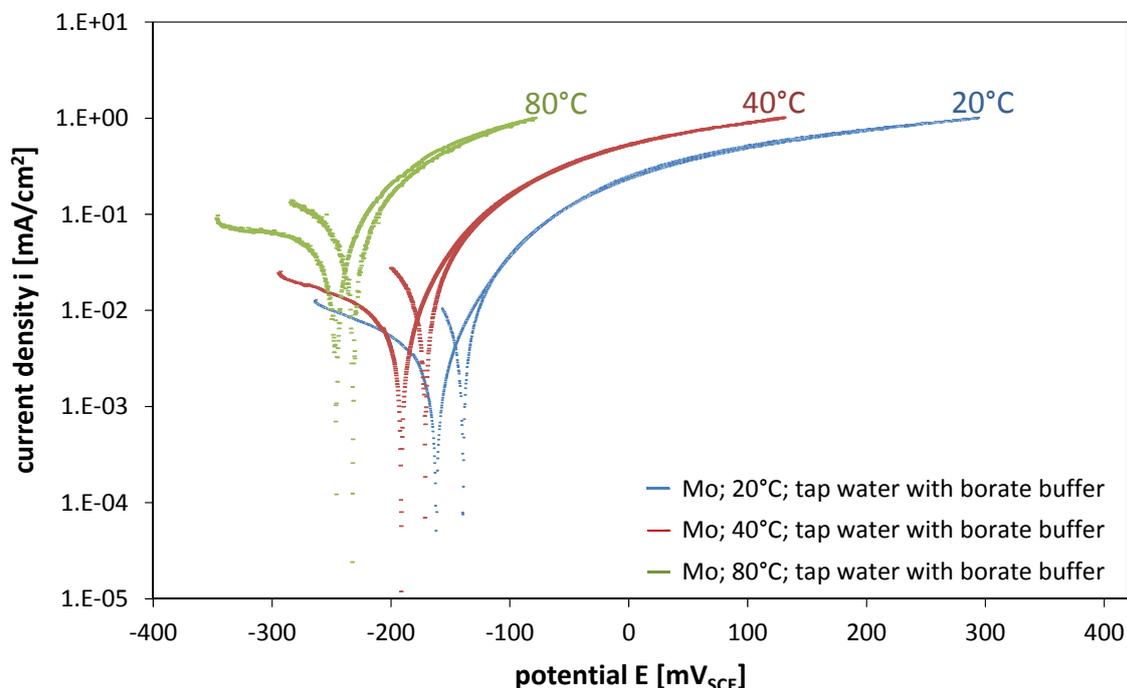


Figure 8: Cyclic polarization scan of molybdenum in tap water with borate buffer at 20°C, 40°C and 80°C; calomel reference electrode, platinum counter electrode, 200 mV/h scan rate.

The examinations of the different cyclic polarization scans are shown in Table III. No essential difference in the corrosion rates of molybdenum in milliQ water and tap water is obtained. The steady increase of corrosion rate with increasing temperature from 20°C to 80°C is a proof that the calcium rich layer that formed in long time immersion tests retards corrosion at 80°C.

Table III: Corrosion rates of molybdenum in milliQ water and tap water with borate buffer at 20°C, 40°C and 80°C; calomel reference electrode, platinum counter electrode, 200 mV/h scan rate.

Electrolyte	Temperature [°C]	Corrosion rate [mm/a]
milliQ water	20	0.022 ± 0.004
	40	0.050 ± 0.005
	80	0.260 ± 0.023
tap water	20	0.019 ± 0.004
	40	0.042 ± 0.010
	80	0.224 ± 0.028

Evans diagrams were recorded to get further insight of the buildup of galvanic elements between molybdenum and copper. In Fig. 9 there is shown the behavior of molybdenum in contact with copper as function of temperature (20°C, 40°C, 80°C) in tap water. Increasing temperature causes increasing galvanic currents and the open circuit potentials of molybdenum are getting more active. Again no special surface layers on molybdenum at 80°C were observed.

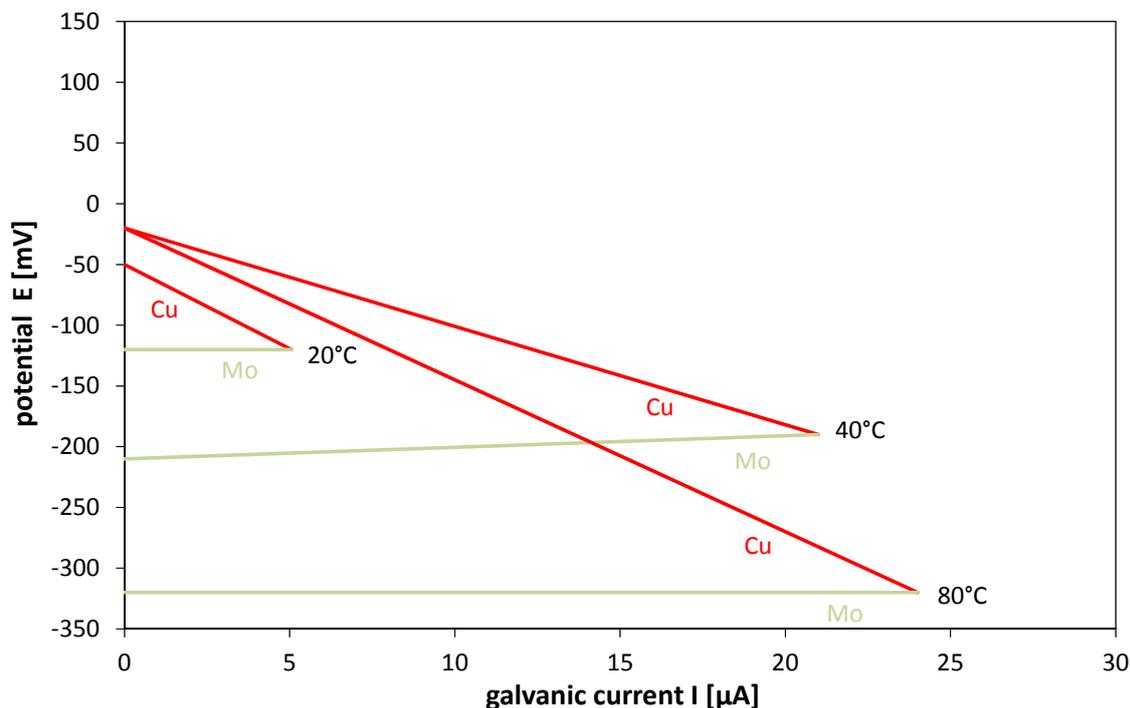


Figure 9: Evans diagram for the material combination not immersed molybdenum with copper in tap water at 20°C, 40°C and 80°C; calomel reference electrode.

Fig. 10 shows the comparison of two molybdenum samples in contact with copper at 40°C in tap water. One specimen has aged in tap water for 150 h at 40°C and contained a molybdenum oxide layer. These conditions were taken, because immersion tests have shown, that these are the most aggressive conditions for molybdenum. The immersed molybdenum sample shows lower galvanic currents. The

developed black molybdenum oxide on the surface, which was caused by the immersion test, decreases the corrosion rate of molybdenum.

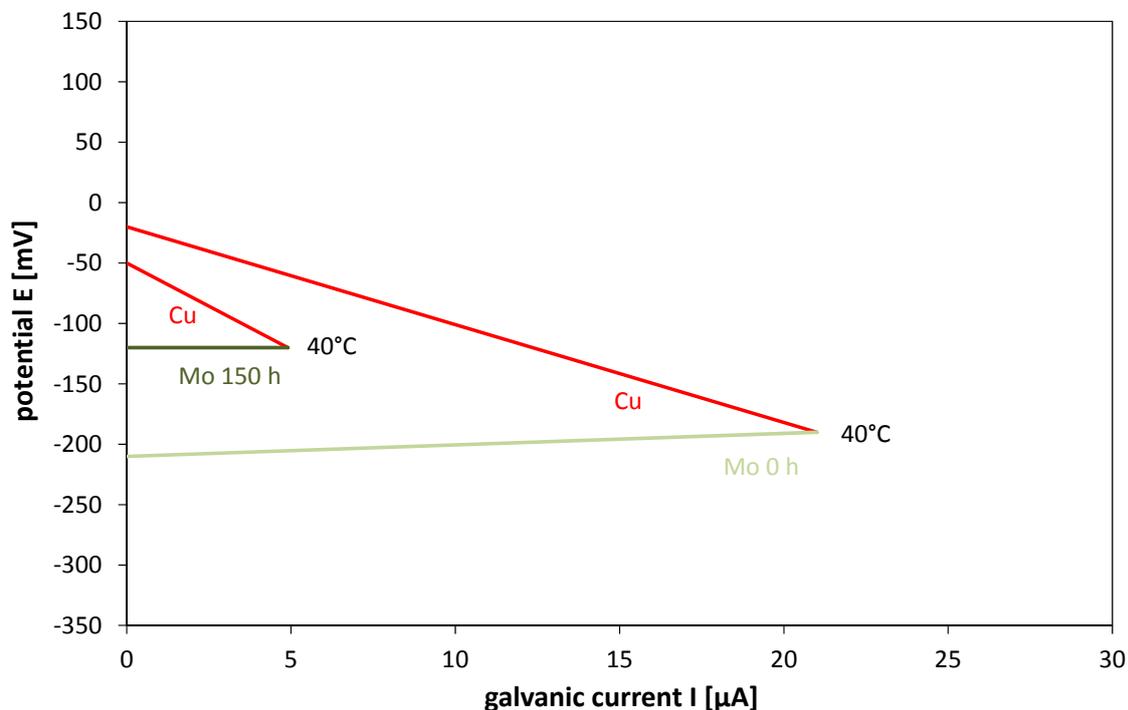


Figure 10: Evans diagram for the material combinations immersed molybdenum with copper and not immersed molybdenum with copper in tap water at 40°C; calomel reference electrode.

Investigations with inhibitors were also conducted. For this purpose immersion tests and cyclic polarization scans were done at 40°C in tap water. Three inhibitors A, B and C were added to tap water in specified concentrations. Results of immersion tests of molybdenum in contact with copper are shown in Fig. 11. It is visible that inhibitors B and C prohibit the material loss of molybdenum in contact with copper. Inhibitor A decreases the material loss, but does not prohibit it. The addition of the inhibitors has caused no decrease of the pH value during the testing time. The addition of inhibitors A and B to tap water has caused a constant pH-value of 8.7. Inhibitor C has caused a constant pH-value of 7. No typical black molybdenum oxide layers could be determined on the surfaces of the molybdenum samples after these immersion tests with inhibitors. The surfaces were metallic bright like before the tests.

Cyclic polarization scans with the different inhibitors were also recorded (Fig. 12). No borate buffer was added to the inhibited tap water. The four cyclic polarization scans deliver nearly the same open circuit potential but the scans have a different vertical position, which means different corrosion currents after the Tafel-slope extrapolations. The analyses have shown that inhibitors B and C decrease the corrosion rates of molybdenum less than 0.004 mm/a in tap water at 40°C.

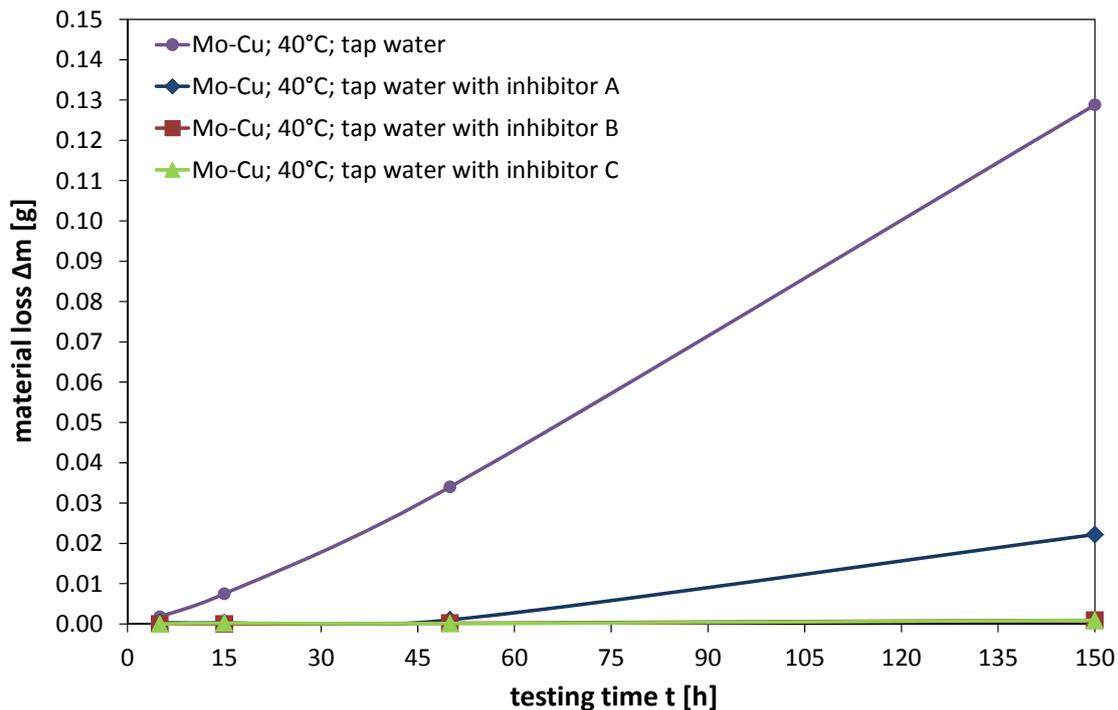


Figure 11: Material loss of molybdenum in contact with copper as function of the testing time in tap water and tap water with different inhibitors (A, B, C) at 40°C.

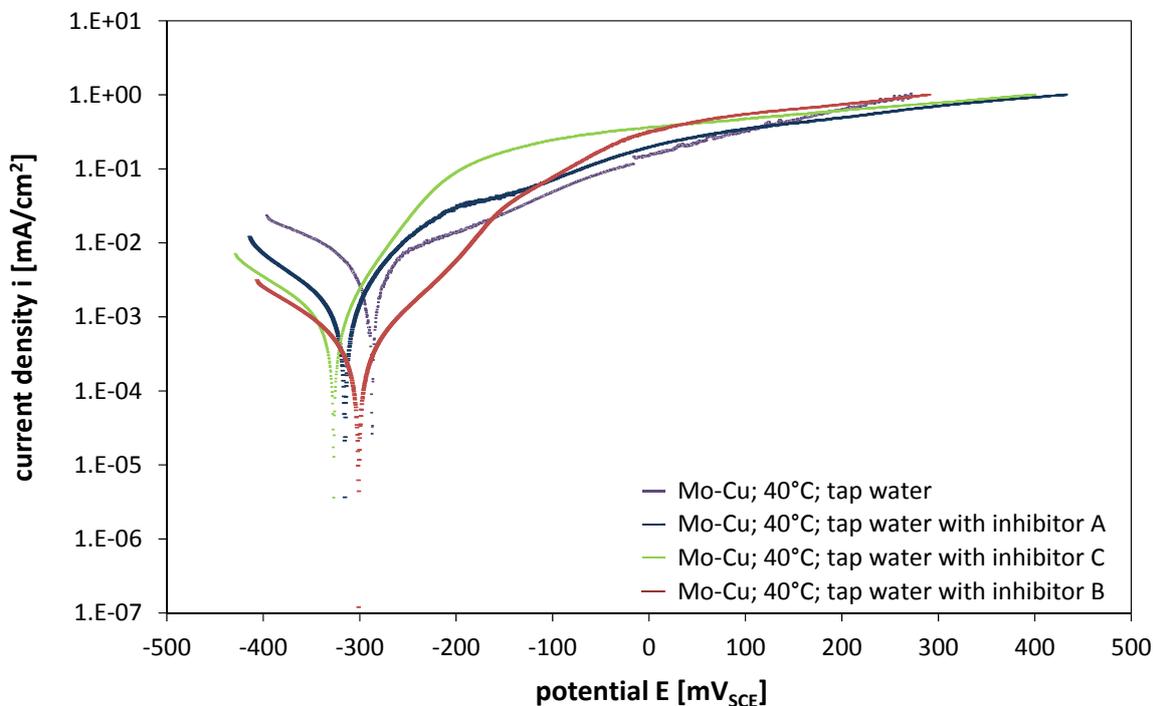
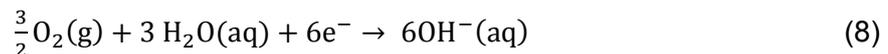
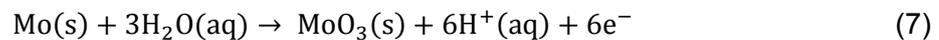
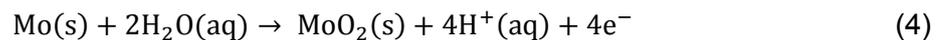
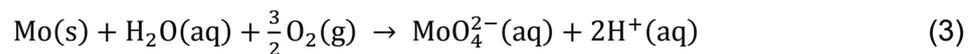
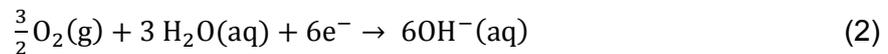
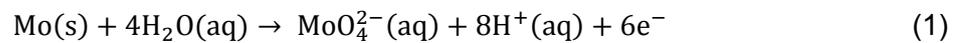


Figure 12: Cyclic polarization scans of molybdenum in tap water and inhibited tap water (A, B, C) at 40°C; calomel reference electrode, platinum counter electrode, 200 mV/h scan rate.

Discussion

All different investigations on molybdenum show an increasing corrosion rate with increasing temperature [6]. Immersion tests for molybdenum and molybdenum in contact with copper at 80°C in tap water and molybdenum in contact with copper in milliQ water carried out different results. The reason for this phenomenon is the building of surface layers, which decrease the corrosion rate. The most aggressive conditions in immersion tests for molybdenum are 40°C, tap water and the material combination with copper. Stronger attacks in tap water than in milliQ water are possible, because of the higher electrical conductivity and acid capacity of tap water. A pH decrease from 7 to 5, occurred during immersion tests in both media, happens according to the following reaction scheme.



The stability zones of molybdenum species are shown in the Pourbaix diagram of molybdenum in water [7]. In milliQ water a small amount of acid causes formation of stable oxides which decrease corrosive attack. The reason is lower acid capacity. The uptake of oxygen shall be faster in milliQ water than in tap water. Fig. 13 shows the oxygen concentrations in milliQ water, tap water and inhibited tap water as function of time during immersion tests. It shows the strongest decrease of the oxygen content in milliQ water and a rather constant content of oxygen in inhibited tap water. No pH decrease in inhibited water was obtained and the surfaces of the molybdenum samples were metallic bright. The inhibitors avoid the reaction of molybdenum with oxygen of the waters. The increase of the oxygen content in the end of the test is possible, because of the open oxygen circuit. Oxygen from air dissolves in the electrolytes. The material combination of molybdenum with copper causes a buildup of galvanic elements which increase the corrosion rate of molybdenum. Only material losses and not corrosion rates were discussed for this test, because the buildup of molybdenum oxides decreases the attack.

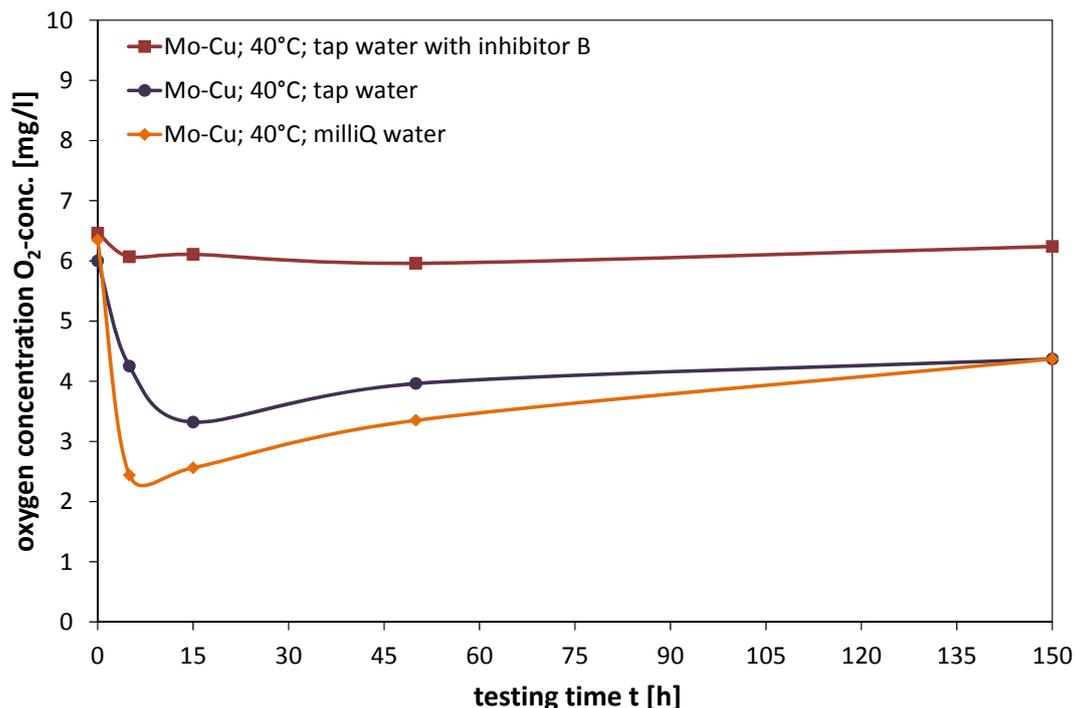


Figure 13: Oxygen concentrations as function of time during immersion tests in milliQ water, tap water and inhibited tap water for molybdenum in contact with copper at 40°C.

Electrochemical investigations show that the corrosion rate of molybdenum increases with increasing temperature. The buildup of white layers like in immersion tests at 80°C in tap water was not sustained. The reason for the absence is the short experimental time of the electrochemical tests. No essential differences of the molybdenum behavior in milliQ water and tap water were found. Cyclic polarization scans with inhibited waters have shown that the inhibitors decrease the corrosion rate of molybdenum to a minimum.

Conclusion

In waters molybdenum is corroded as molybdate and a steady decrease of pH is the result. When reaching pH=5 a layer of molybdenum oxide/hydroxide is formed which reduces corrosion rate. Therefore a lower acid capacity of water results in a lower corrosion rate due to faster pH decrease. An increase of temperature results in an increase of corrosion rate. Exceptions are the precipitation of a calcium rich layer in tap water at or above 80°C. The contact with copper enhances corrosion rate of molybdenum at all temperatures. At 80°C either a protective copper cementation layer (in milliQ water) or a calcium rich layer (in tap water) is formed that reduce the galvanic effect. Investigated inhibitors can fully protect molybdenum from further corrosion due to formation of adhesive organic layer on its surface.

Electrochemistry is due to its short term testing period a less applicable method for investigation of molybdenum corrosion since the protective layers cannot be formed. Instead immersion tests shall be used.

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