PROCEEDINGS OF THE IV INTERNATIONAL CONFERENCE/HIGH TEMPERATURE CAPILLARITY

JOURNAL OF MATERIALS SCIENCE **40** (2005) 2465 – 2470

Corrosion behaviour of steels and refractory metals in flowing Lead-Bismuth Eutectic at low oxygen activity

G. BENAMATI, A. GESSI*
ENEA C.R. Brasimone, 40032 (BO), Italy
E-mail: gianluca.benamati@brasimone.enea.it

G. SCADDOZZO
Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy

The corrosion behaviours of AISI 316L and T91 steels, and several refractory metals as W, Mo and Ta, were investigated in flowing lead-bismuth eutectic (LBE) at 400°C. The tests were performed in the LECOR (Lead Corrosion) loop, at low oxygen activity in LBE. The results obtained show that all materials exhibited a weight loss after exposure to the flowing LBE, except for the case of tantalum, which exhibits a weight gain. The resistance to corrosion offered by refractory metals has been found higher in comparison to the case of both steels. Moreover, the austenitic steel behaved more resistance to corrosion induced by LBE than the martensitic steel, under the test condition adopted.

1. Introduction

The lead-bismuth eutectic (LBE) is foreseen as spallation target and coolant in ADS system, due to its favourable physical, chemical, thermodynamic and neutron properties. The compatibility of materials with the liquid metal became one of the important issues in ADS when them are in contact with LBE. In this frame, studies on the behaviour of several selected materials exposed to flowing LBE under definite oxygen concentration have been carried out at Brasimone ENEA centre.

The aim of the experimental activities performed with the LECOR loop was to describe corrosion mechanism and to estimate corrosion rates of AISI 316L austenitic steel, T91 martensitic steel, W, Mo and Ta exposed to flowing Pb-Bi with low oxygen activity.

The martensitic T91 steel is a readily available industrial material (stabilized with vanadium and niobium additions), which was qualified as steam generator material for non-nuclear and nuclear power plants. The modified 9Cr-1Mo steel T91 has higher strength, low thermal stress and lower ductile-brittle transition temperature (DBTT) shift after irradiation. Another material of interest is the austenitic steel AISI 316L, that have a superior weldability. The refractory metals are considered as reference materials too, in the hot window target concept.

This paper is focused on the corrosion properties of these materials after exposure in flowing LBE with low oxygen concentration. Corrosion tests were performed in the LECOR loop under continuous controlling of the oxygen concentration in LBE.

2. Experimental

The corrosion tests were performed in the LECOR loop. As shown in Fig. 1, the plant has a "figure-of-eight" configuration, typical for a corrosion loop, with a high temperature section running from the economiser (EX) to the test sections (TS) and a low temperature section including the delivery and return pipes between the S2 tank and the economiser, including the by-pass line. The S2 vessel contains a mechanical pump, with submerged impeller, sized to provide the loop with a maximum liquid metal flow-rate of 4 m^3/h.

The three test sections TS1/2/3, containing the specimens to be investigated are placed downstream of the electrical heater (H). In the steady state, the thermal power provided by the heater is equal to the power extracted by the forced air heat exchanger (C). This configuration enables a continuous transport of corrosion products from the hot region, where the test sections are located, to the cold region where they are partially released, simulating the actual behaviour of coolant fluid in a thermal production plant. The structural materials of the loop are as follows: the cold part is fabricated in austenitic steel, while the hot region is in ferritic steel representing a good compromise between the requirements of acceptable ductility and corrosion resistance in a liquid metal environment.

---

*Author to whom all correspondence should be addressed.

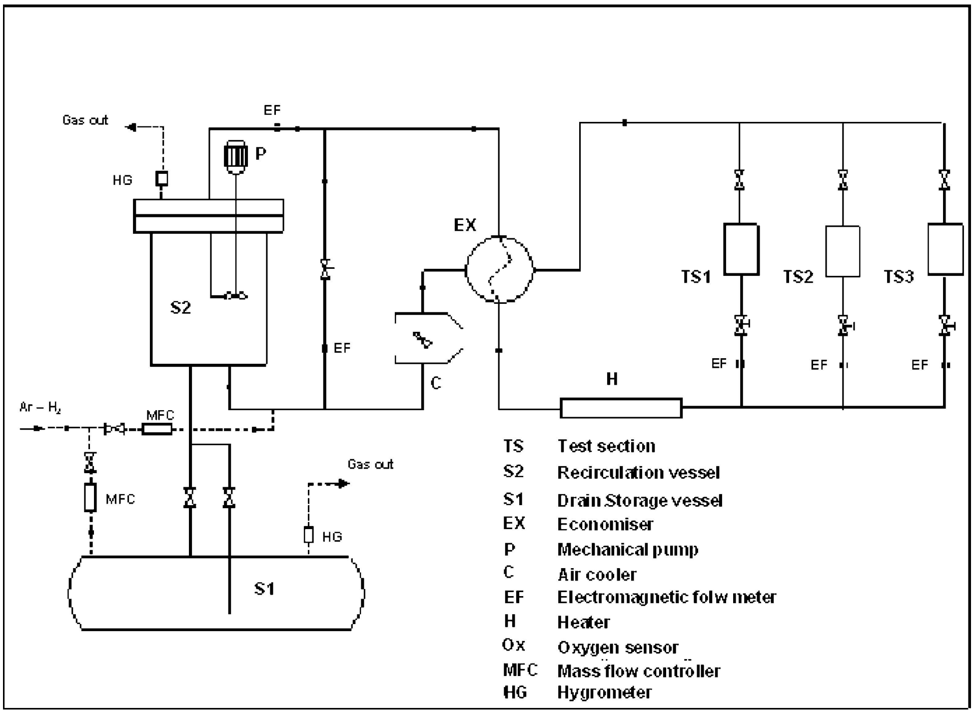


Figure 1 The LECOR loop.

During normal plant operations the total liquid metal flow-rate available to the test sections is adjusted through the by-pass line, while the liquid metal flow-rate in each test section is automatically controlled by electro-pneumatic regulation valves using feedback signals from electromagnetic flow-meters (EF).

Two kinds of stainless steel were investigated in this wotk, one is austenitic steel AISI 316L, the other is martensitic steel T91.The chemical compositions of the materials, which were given by the supplier, are summarized in Table I.

The as-received steels were machined to cylindrical specimens with 10 mm diameter and 50 mm length. Before placing the specimens into the test sections of the loops, they were degreased and weighed. The dimensions of each specimen were measured. There was no additional heat treatment to the specimens after machining. The specimens were fitted together in the test section by fixing their ends with pins. The test section temperatures of both loops were 400°C, and the cold branch temperatures of the loops were 300°C. The oxygen concentration in LBE were maintained in the range of 10^{-8}–10^{-10} wt% and monitored with electrochemical probe. The total duration of the tests was 4500 h. Some specimens were removed for analysis after 1500 h of exposure time.

After corrosion tests, one specimens of each material was immersed in a fresh solution ($CH_3COOH:H_2O_2:C_2H_5OH = 1:1:1$) at room temperature to remove the adherent LBE. Specimens were then cleaned and dried for visual examination and weight measurement. Specimens without cleaning were cut and polished for cross section examination by optical microscopy (OM) and scanning electron microscopy (SEM). Energy dispersion X-ray spectroscopy (EDX) was used to analyse the chemical composition of the adherent corrosion products and bulk materials.

TABLE I The chemical compositions of the stainless steels (wt.%, balance Fe)

Element	Cr	Ni	Mo	Mn	V	Nb	Si	C
AISI 316L	17.3	12.1	2.31	1.8	–	–	0.35	0.02
T91	8.26	0.13	0.95	0.38	0.20	0.075	0.43	0.105

3. Results

3.1. Steels

Fig. 2 shows the weight changes over time for all steel coupons that were tested in the LECOR loop. Both austenitic stainless steel AISI 316L and martensitic steel T91 exhibited weight loss after they were exposed in LBE with low oxygen concentration. With increasing test time, the weight loss of specimens increased significantly. The value of weight loss for T91 after 4500 h was 0.184 mg/mm^2, while the value for AISI 316L was 0.155 mg/mm^2.

Optical microscopy analysis on the cross section of both steels showed that they suffered a very limited attack after 1500 h of exposure. With increasing exposure time, the specimens were corroded evidently (see Fig. 3).

In order to reveal the microstructure of the corroded layer, the specimens were etched with a solution of oxalic acid. Fig. 4 is the SEM micrograph of an AISI 316L specimen after exposed in flowing LBE. As shown in this figure, a corroded layer was detected already after 1500 h. The EDX point analysis performed on this layer, but on a not etched part, revealed that the depletion of Ni and Cr had occurred in this layer (see Fig. 4b). This means that the austenitic steel AISI

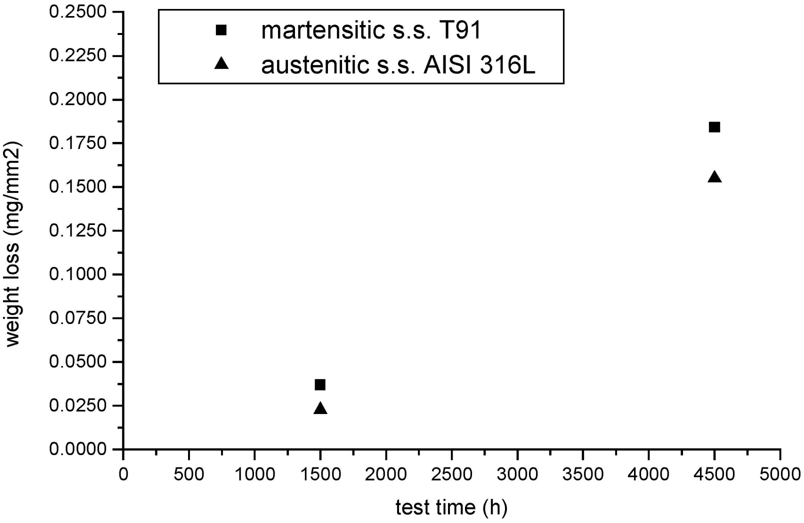


Figure 2 Specific weight change of steels after exposure in LECOR loop.

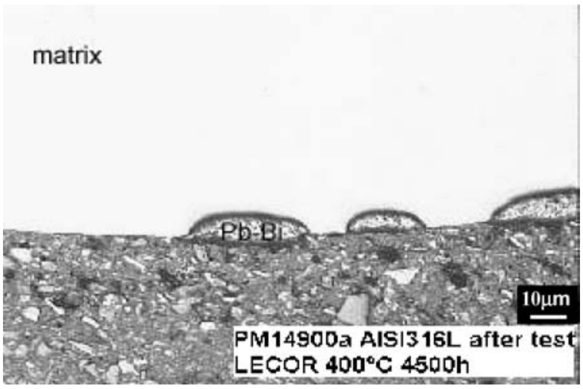


Figure 3 Optical micrograph of austenitic steel exposed in LECOR loop after 4500 h ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400°\mathrm{C}$).

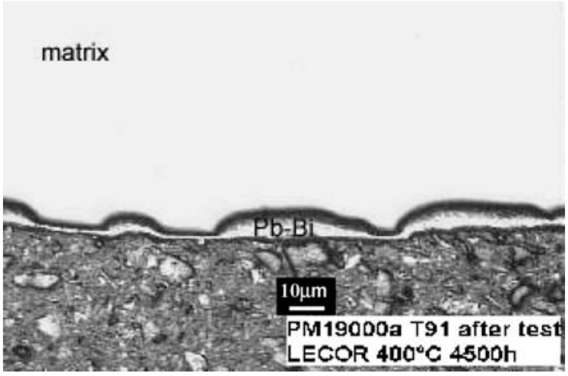


Figure 5 Optical micrograph of T91 exposed in LECOR loop after 4500 h ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400°\mathrm{C}$).

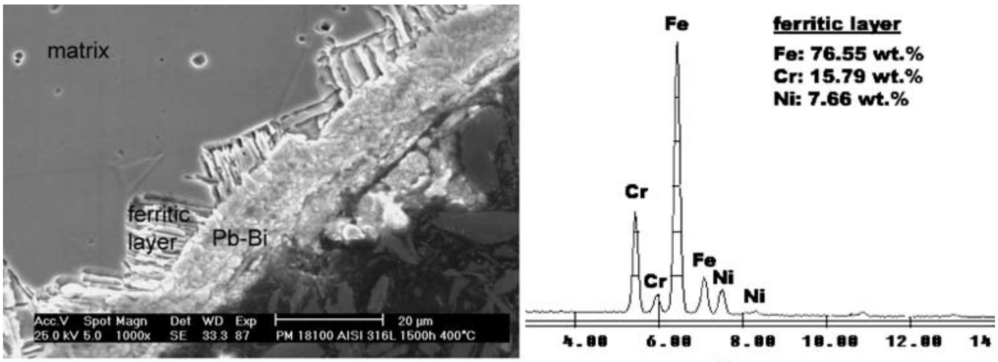
316L was corroded by dissolution of the alloying elements to the liquid metal and formed a ferritic layer. This is consistent with the result of weight loss of the specimens.

Concerning the martensitic steel T91, an uniform attack on the surface of the specimen after 4500 h of exposure (see Fig. 5) was detected. The SEM results showed the liquid metal penetrated into the matrix of steel (see Fig. 6).

The corrosion rates of steels have been estimated with the measurement of weight variation (Δm) assuming a linear evolution of the weight loss. After 4500 h of exposure, the calculated corrosion rate of austenitic steel AISI 316L is: $V_{\mathrm{corrosion}} = 6.8\ \mathrm{mg} \cdot \mathrm{dm}^{-2} \cdot \mathrm{d}^{-1}$; while the corrosion rate of martensitic steel T91 is: $V_{\mathrm{corrosion}} = 10.2\ \mathrm{mg} \cdot \mathrm{dm}^{-2} \cdot \mathrm{d}^{-1}$.

3.2. Refractory metals

Visual examination of all refractory specimens (Mo, W and Ta) did not show evident attacks by LBE. The weight change measurements on the



(a) (b)

Figure 4 SEM cross-section (a) and EDX spectrum (KeV versus relative counts) of austenitic steel in LECOR loop ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400°\mathrm{C}$, $t = 1500$ h).

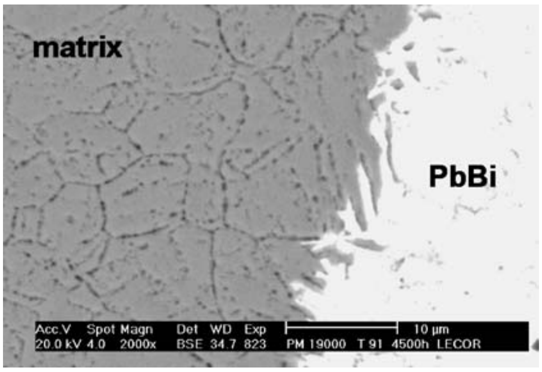


Figure 6 SEM cross-section of T91 after exposure in LECOR loop ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400°\text{C}$, $t = 4500$ h).

specimens corroded at different time were reported in Table II.

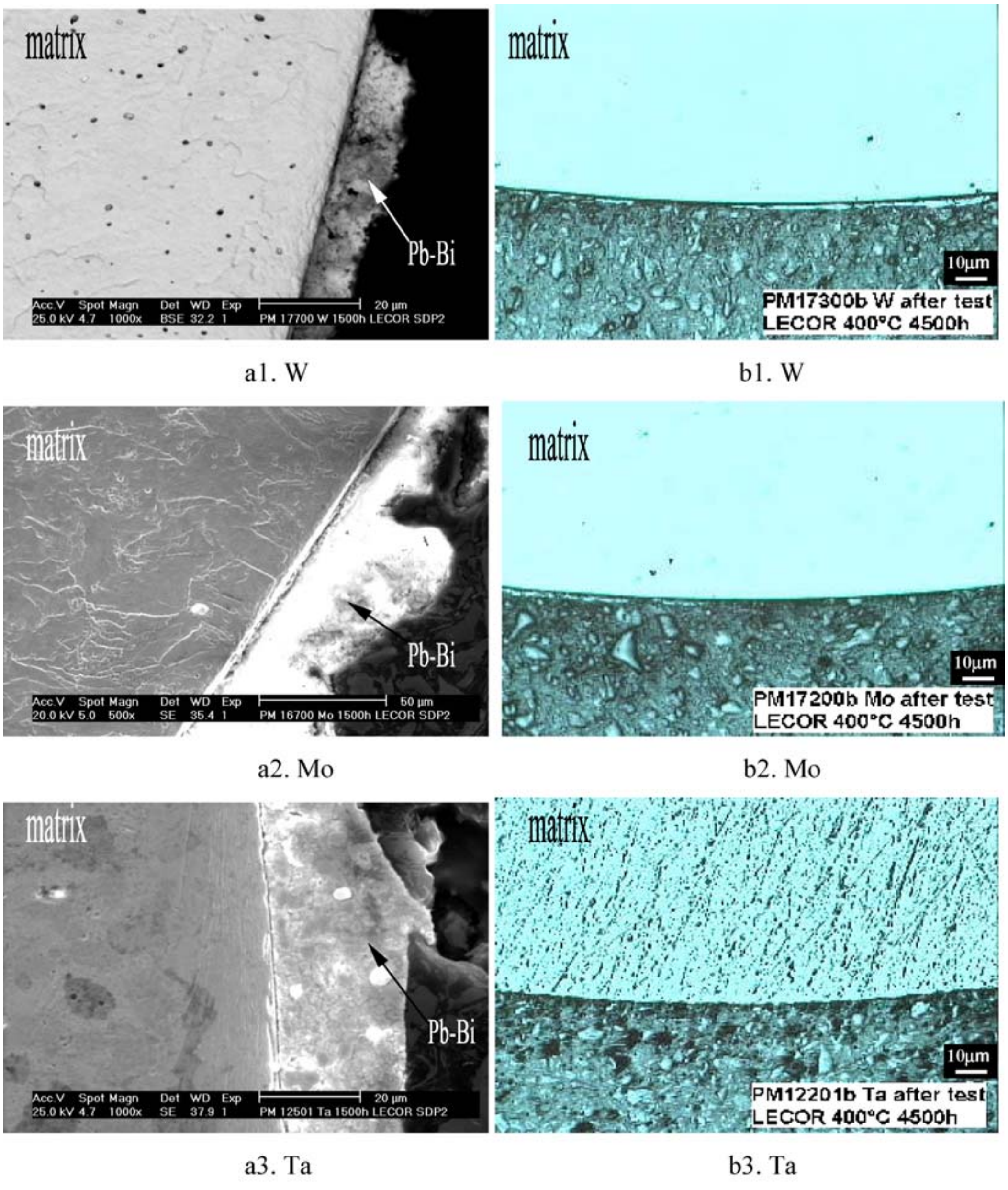
In Fig. 7 the OM-micrographs of the corroded refractory metals are reported and it is evident that these metals still exhibit a smooth surface, even after 4500 h of exposition. For pure W and Mo, the weight loss could be associated with the uniform dissolution, and this can be explained by the low solubility of W and Mo in LBE at 673 K.

Ta exhibited a different behaviour in comparison to the previous materials, showing a weight gain.

4. Discussion

4.1. Steels

At the fixed low oxygen concentration ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%) both steels exhibited the dissolution of alloying elements, and a weight loss was measured. For austenitic steel AISI 316L, Ni depletion has been detected, with the formation of a ferrite layer in the corrosion area. This seems due to the high solubility of Ni in LBE (the solubility of Ni in LBE at 400°C is about 16000 wppm [2]). For martensitic steel T91 a uniform



a1. W b1. W

a2. Mo b2. Mo

a3. Ta b3. Ta

a. 1500h SEM b. 4500h (b3 is 3000h) OM

Figure 7 Metallurgical micrographs of refractory metals (LECOR, $T = 673$ K).

TABLE II Weight variation of refractory metals exposed in LECOR

Metal	W		Mo		Ta	
Test time (h)	1500	4500	1500	4500	1500	3000
Weight loss (mg/mm^2)	1.36×10^{-3}	1.54×10^{-3}	1.08×10^{-3}	4.5×10^{-3}	$0.80 \times 10^{-3*}$	$-1.37 \times 10^{-3*}$

*Minus sign means weight gain.

attack by LBE was observed, and the liquid metal penetration appears on the interface between steel and liquid metal. However, no preferential dissolution of alloying elements was detected in the attack area. Comparing the corrosion rates of AISI 316L and T91, the corrosion rate found for the martensitic steel is higher than that for austenitic steel. As previously referred, the optical analysis on the corroded specimen showed a very limited attack after 1500 h for both steels. The corrosion became well clear for T 91 after 4500 h while for the austenitic steel at the same time is possible to distinguish some not attacked regions on the specimens surface (see Fig. 2). For T 91 the corrosion proceeds uniformly on the whole surface of the specimens, as shown in Fig. 5. This behaviour could be explained assuming that a thin layer of natural oxides is present on the specimens when they are inserted in the test section, and it works as barrier against the liquid metal attack. Before that the corrosion can take place, this layer has to be destroyed. Under the test condition adopted in the LECOR loop, the natural oxides film on the martensitic steel is more easily removed by the LBE than the ones on the austenitic steel. This could be the reason for the higher corrosion rate obtained for the martensitic steel and could also explain the increase in the corrosion rate observed with increasing the time of exposure.

4.2. Refractory metals

Also in the case of refractory metals W and Mo, the corrosion mechanism is governed by dissolution. However, the low solubility of pure elements in the LBE under the test conditions results in a very good resistance to the liquid metal. Then, the weight loss of refractory metals is two orders of magnitude smaller than that of steels. Concerning Ta, the weight gain found on the specimens can be explained by the formation of a very thin oxide layer on the surface, even if it has not been detectable with the analytical techniques used. This assumption can be reported considering the free energy of formation of the oxides. As shown in Fig. 8, the oxygen potential needed to form Ta oxide is much lower than for the other refractory metals and for Fe; the experimental conditions could be consistent to this assumption. Indeed, estimating the thickness of the oxide film as an ideal cylindrical shell uniformly growth around the specimen, the result of less than 1 micron is obtained. This value is close to the sensitivity limit of the performed microanalysis, that could be the reason because of the film has not been detected. Then, concerning the morphology of the Ta oxide, more detailed analysis will be necessary to clarify the nature as well as the dimension of this oxide.

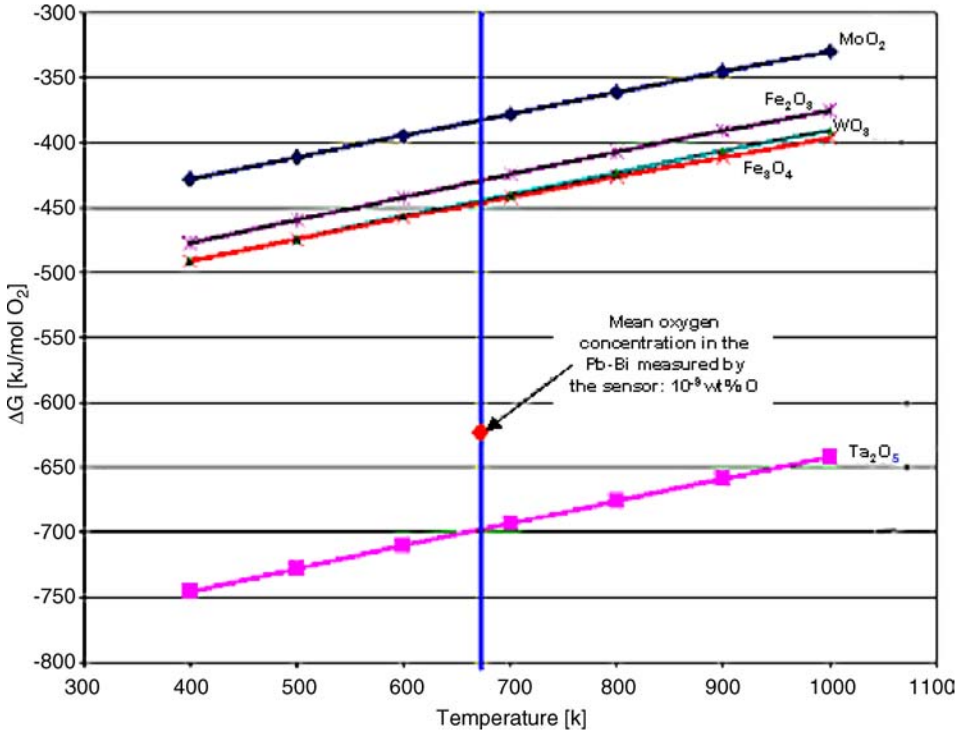


Figure 8 Comparison of the oxidation potential of W, Mo, Ta and Fe with the mean oxidation potential in the LECOR loop.

5. Conclusion

The main conclusions are summarized as follows:

Under the experimental conditions both austenitic and martensitic steels exhibited weight loss, and the corrosion was due to the dissolution of alloying elements.

The austenitic steel AISI 316L was affected by preferential dissolution of Ni and Cr in the LBE, and the growth of a ferritic layer on the surface has been detected. Under the same condition the martensitic steel T91 was affected by uniform corrosion, and no preferential dissolution has been noted.

The higher corrosion rate found for the martensitic steel in comparison to the austenitic steel, could be explained by the presence of a thin natural oxide layer on the surface of the specimens. Under the test conditions adopted this layer is more resistant to the LBE attack in the case of the austenitic steel, so the corrosion proceeds slowly in the case of AISI 316L.

All the refractory materials tested exhibited a weight loss after 1500 h and 4500 h exposure in LECOR except Ta. The weight loss of refractory metals is by two orders of magnitude smaller than that of steels.

The assumption of the growth of a thin oxide layer on the Ta specimens could explain the weight gain found, and is consistent with the experimental condition adopted.

Acknowledgement

This work has been supports by the EU project TECLA. The authors are grateful to Mr. L. Rapezzi and his collaborators for operating the LECOR loop, to Mr. S.Storai for performing the tensile tests. Especially to Dr. F. Concetta for her important comments on this work. The authors would also like to tanks the ASP (Associazione per lo Sviluppo Scientifico e Tecnologico del Piemonte) and the CRT Foundation for their special contribution.

References

1. C. FAZIO, I. RICAPITO, G. SCADDOZZO and G. BENAMATI, *J. Nucl. Mater.* **318** (2003) 325.
2. M. AZZATI, A. GESSI and G. BENAMATI, ENEA Report, HS-A-R-014, Jan. 2003.
3. I. R. BEATTIE and T.R.GILSON, *J. Chem. Soc. A* (1970) 980.
4. C. FAZIO, G. BENAMATI, C. MARTINI and G. PALOMBARINI, *J. Nucl. Mater.* **296** (2001) 243.
5. G. MULLER, A. HEINZEL, J. KONYS, G. SCHUNACHER, A. WEISENBURGER, F. ZIMMERMANN, V. ENGELKO, A. RUSANOV and V. MARKOV, *J. Nucl. Mater.* **301** (2002) 40.

Received 31 March
and accepted 20 October 2004