CORROSION BEHAVIOUR IN NEUTRAL ENVIRONMENT OF SOME TERNARY TITANIUM ALLOY

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The purpose of this paper is to determine the effect of the alloying elements on the passive film formation on the Ti-Mo-Ni alloy, in concentrated chloride solutions, at high temperatures. The alloying of titanium with molybdenum and nickel has the following effects on the passivity behaviour of ternary Ti-0.5Mo-1Ni alloy: the shifting in noble direction of the alloy corrosion potential due to the couple galvanic effect of the molybdenum and nickel; the enlargement of the alloy passive potential range, as result of the molybdenum and nickel participation with its insoluble compounds at the consolidation of the alloy passive film; the decrease of the alloy passive current densities because of the same consolidation effect of the passive layer; both the titanium and Ti-0.5Mo-1Ni alloy do not present pitting corrosion; the decrease of the alloy corrosion rates in concentrated chloride solutions, in comparison with base metal.

Introduction

The increase of the corrosion resistance of titanium (specially in very aggressive solutions at high temperatures) by the alloying is the main method suggested by the researchers and industrial producers.

Molybdenum is added as alloying element to titanium both for the improvement of the mechanical properties and for the increase of the corrosion resistance [1,2]. The unusual electrochemical behaviour of molybdenum is due to the fact that the molybdenum has a large immunity potential range as the titanium dissolves in its active potential range [3]. So, alloying titanium with molybdenum will appear important changes of the alloy anodic polarization curve: the shifting in the noble direction of the corrosion potential, the enlargement of the passive potential range, the decrease of the critical passivation and passive current densities, etc.

The alloying of titanium with nickel in low concentration [4÷6] has a beneficial effect on the decrease of the corrosion rate in acid solutions.

So, The Institute for Non-Ferrous and Rare Metals, Romania obtained in experimental charges, the new ternary Ti-Mo-Ni alloy, which is studied in this paper.

The purpose of this research is to determine the effect of the alloying elements on the Ti-0.5Mo-1Ni alloy corrosion behaviour in concentrated chloride solutions (30% KCl, 25% NH_4Cl, 50% $MgCl_2.6H_2O$, 40%$LiCl.H_2O$, 20%$CuCl_2.2H_2O$, 20% $NiCl_2.6H_2O$, artificial sea water) at high temperatures.

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Experimental

The titanium and Ti-Mo-Ni alloy were obtained by vacuum melting. The composition of the alloy is: 1.04%Ni, 0.53%Mo, 0.11%O, 0.0065%N, 0.055%Cl,< 0.002%Mg, < 0.05%Al, < 0.005%Mn, < 0.005%P, < 0.005%Zn, < 0.01%Cr, < 0.05%Si, < 0.025%Sn, rest Ti. The alloy has α + β bi-phase structure.

The corrosion behaviour of this alloy was studied in comparison with titanium: 0.0095%Fe, 0.05%O, 0.0045%N, 0.035%Cl, < 0.0025%Mg, < 0.05%Al, < 0.005%Mn, < 0.005%P, < 0.005%Sn, < 0.01%Cr, < 0.05%Si, < 0.02%Sn, rest Ti.

The cylindrical electrodes were abraded with emery paper, fixed in a Stern-Makrides mount system, rinsed with tap and distilled water, degreased in boiling benzene and dried.

The experiments were performed in concentrated chloride solutions (at the limiting solubility) of: 30% KCl, 25% NH_4Cl, 50% $MgCl_2.6H_2O$, 40%$LiCl.H_2O$, 20%$CuCl_2.2H_2O$, 20% $NiCl_2.6H_2O$, artificial sea water. The solution temperature was kept at 23,50 and 75 ^{0}C.

The potentiostatic and potentiodynamic electrochemical polarization measurements were carried out in order to determine: the corrosion potential E_{corr}, the passive potential range ΔE_p, the transpassive potential E_T and the dissolution current density in the passive range, i.e., passive current density i_p. The linear polarization method was used to obtain the corrosion current density $i_{corr} = k(di/dE)_{Ecorr}$ from Stern formula considering k=26 mV. The potentiostatic polarization measurements started from –0.8V to +4.0V (vs. SCE) using a rate of 50mV at every 2min.; the potentiodynamic cyclic polarization was performed starting from –0.8V to +2.0V using a scan rate of 2mV/sec.; the linear polarization were applied for ± 10mV around the corrosion potential. The electrochemical set-up consisted of a potentiostat (PAR 173 type), a XY recorder (Endim 62002 type) and a universal impulse generator (AT type).

The electrochemical polarization glass cell was provided with a central room for the electrode assembly, two equidistant platinum counter electrodes, a Luggin probe connected with a saturated calomel reference electrode (SCE).

Results and Discussion

The polarization curves of titanium and Ti-0.5Mo-1Ni alloy in concentrated chloride solutions are given in Fig. 1. These curves show the following characteristics.

– The titanium and Ti-0.5Mo-1Ni alloy anodic polarization curves exhibit no active dissolution range, namely, from the corrosion potential the titanium and its alloy directly pass to passive state. So, it results that the titanium influence to spontaneously form the protective, compact TiO_2 oxide [7÷10] is very important on the electrochemical behaviour of the Ti-0.5Mo-1Ni alloy which is self passivated by the TiO_2 oxide.

– The shifting in nobler direction (Table 1) of the alloy corrosion potential (E_{corr}), due to the couple galvanic effect of the molybdenum and nickel; in 30% KCl, 40%$LiCl.H_2O$,

and 20%CuCl$_2$.2H$_2$O solutions this effect does not appear, probably, because of the secondary reactions of the alloying elements with these solutions [11÷13].

– The enlargement of the alloy passive potential range (ΔE_p – Table 1) as result of the beneficial molybdenum and nickel effect, which participates with their insoluble compounds [3] at the consolidation of the alloy passive film.

– Alloy passive current densities (Table 1) are almost equally or lower than of the base metal because of the same consolidation effect of the passive layer by the insoluble molybdenum and nickel compounds [14] (MoCl$_3$.xH$_2$O, MoOCl.4H$_2$O, MoOCl$_4$, Ni(OH)$_2$, Ni$_3$O$_4$).

– Both the titanium and Ti-0.5Mo-1Ni alloy do not present pitting corrosion in these very concentrated chloride solutions in which the stainless steels and another alloys do not resist; this pitting corrosion resistance is due to the very good stability of the passive layer.

Table 1. Electrochemical characteristics of Ti and Ti-0.5Mo-1Ni alloy

Corrosion media	Metal, alloy	Corrosion potential E_{corr} (mV)	Passivity potential range ΔE_p (mV)	Transpasivity potential E_T (mV)	Passivity current density i_p (μA/cm^2)
30%KCl	Ti	-250	800	+1200	2
	Ti-0.5Mo-1Ni	-350	1200	+1100	1.35
25%NH$_4$Cl	Ti	-350	1400	+1200	0.8
	Ti-0.5Mo-1Ni	-150	1600	+1300	2.7
50%MgCl$_2$.6H$_2$O	Ti	-300	1300	+1200	2
	Ti-0.5Mo-1Ni	-150	1400	+1300	2
40%LiCl.H$_2$O	Ti	-250	1500	+1300	3
	Ti-0.5Mo-1Ni	-300	2500	+2700	9
20%CuCl$_2$.2H$_2$O	Ti	+500	500	+1500	2
	Ti-0.5Mo-1Ni	+450	600	+1400	3.1
20%NiCl$_2$.6H$_2$O	Ti	-50	500	+800	2.4
	Ti-0.5Mo-1Ni	-50	950	+1100	3.1
Artificial sea water	Ti	-500	700	+900	2.4
	Ti-0.5Mo-1Ni	-350	1000	+900	2

The corrosion rates of titanium and Ti-0.5Mo-1Ni alloy were obtained by liner polarization. From Table 2 can be seen that the alloy has lower corrosion rates than the titanium. The alloy has very good resistance in all tested solutions.

Table 2 The corrosion rates (mm/yr) of titanium and Ti-0.5Mo-1Ni alloy

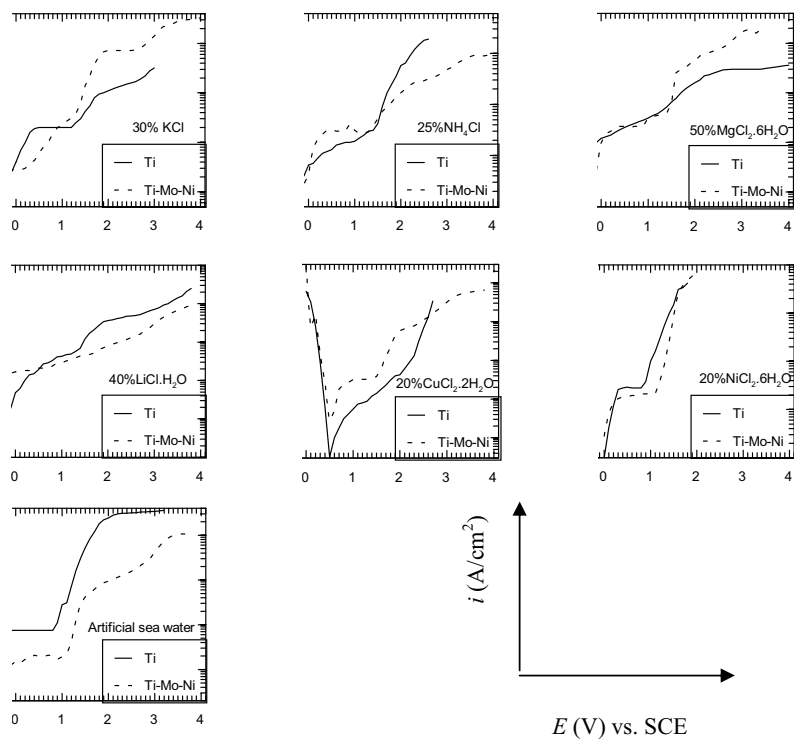| Corrosion media	Corrosion rate (mm/yr)	
	Ti	Ti-0.5Mo-1Ni
30%KCl	$1.2 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$
25%NH$_4$Cl	$5.1 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$
50%MgCl$_2$.6H$_2$O	$2.0 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$
40%LiCl.H$_2$O	$1.7 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$
20%CuCl$_2$.2H$_2$O	$3.5 \cdot 10^{-3}$	$5.4 \cdot 10^{-3}$
20%NiCl$_2$.6H$_2$O	$3.8 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$
Artificial sea water	$4.4 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$

Fig. 1: *Potentiostatic polarization curves for* Ti *and* Ti-0.5Mo-1Ni *alloy in concentrated chlorides at* 75^{0}C.

Conclusions

The alloying of titanium with molybdenum and nickel produces the following effects on the passivity behaviour of the ternary Ti-0.5Mo-1Ni alloy:

8. the shifting in noble direction of the alloy corrosion potential due to the couple galvanic effect of the molybdenum and nickel;

9. the enlargement of the alloy passive potential range, as result of the molybdenum and nickel participation with their insoluble compounds at the consolidation of the alloy passive film;

10. the decrease of the alloy passive current densities because of the same consolidation effect of the passive layer;

11. both titanium and Ti-0.5Mo-1Ni alloy do not present pitting corrosion.

12. the decrease of the alloy corrosion rates in concentrated chloride solutions, in comparison with base metal (titanium).

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