Corrosion behaviour of amorphous $Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$ alloys investigated by potentiodynamic polarization method

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Abstract. Potentiodynamic polarization studies were carried out on virgin specimens of amorphous alloys $Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$ in 0·5 M HNO_3, 0·5 M H_2SO_4 and 0·5 M NaOH aqueous media at room temperature. The value of the corrosion current density (I_{corr}) was maximum for $Ti_{48}Cu_{52}$ alloy in all the three aqueous media as compared to the remaining two alloys. The value of I_{corr} for the alloy $Ti_{48}Cu_{52}$ was maximum ($I_{corr} = 2·6 \times 10^{-5}$ A/cm^2) in 0·5 M H_2SO_4 and minimum ($I_{corr} = 3·5 \times 10^{-6}$ A/cm^2) in 0·5 M NaOH aqueous solutions. In contrast, the alloy $Ti_{60}Ni_{40}$ exhibited the least corrosion current density in 0·5 M HNO_3 ($I_{corr} = 4·0 \times 10^{-7}$ A/cm^2) and in 0·5 M NaOH ($I_{corr} = 5·5 \times 10^{-7}$ A/cm^2) aqueous media as compared to those for Ti–Cu alloys, while its value in 0·5 M H_2SO_4 was comparable to that for $Ti_{50}Cu_{50}$. It is suggested that the alloy $Ti_{60}Ni_{40}$ is more corrosion resistant than the alloys $Ti_{48}Cu_{52}$ and $Ti_{50}Cu_{50}$ in all the three aqueous media.

Keywords. Amorphous alloys; polarization; potentiodynamic; corrosion.

1. Introduction

Metallic glasses constitute good model systems for studying properties of a disordered system and are generally formed by cooling the alloy melt at rates of 10^5–10^6 K/s using conventional melt-spinning techniques in the form of thin amorphous ribbons (Klement *et al* 1960). These materials possess attractive properties such as high fracture strength, soft magnetic behaviour, high electrical resistivity that make them superior to their crystalline counterparts. Investigations have revealed that these unusual properties of glassy alloys are a consequence of their amorphous structure. The study of thermo-chemical behaviour (oxidation/corrosion) of amorphous alloys is very important for understanding their environmental degradation and for determining their suitability for possible applications. In contrast to several investigations reported on corrosion studies on Zr-based amorphous alloys (e.g. Dey *et al* 1989; Asami *et al* 1993 and references therein), only few investigations on Ti-based amorphous alloys are available in the literature (Naka *et al* 1978; Walmsley *et al* 1984; Jorge *et al* 1988; Tan and He 1988; Cervinaka 1993; Nakamura and Nagumo 1993; Akiyama *et al* 1994; Murthy *et al* 1995; Dutta *et al* 2001). In a corrosion study on Ti–Cu alloys the corrosion behaviour of the equiatomic amorphous $Ti_{50}Cu_{50}$ and $Zr_{50}Cu_{50}$ and their crystalline counterparts in various aqueous media was investigated at room temperature and it was found that the corrosion resistance of amorphous form of the alloy was superior to that of its crystalline counterpart (Naka *et al* 1978). Jorge *et al* (1988) studied the electrochemical behaviour of the glassy alloys, $Cu_{66}Ti_{34}$ and $Cu_{63}Zr_{33}$, in 1 M H_2SO_4 and found that during cathodic polarization alloy $Cu_{66}Ti_{34}$ undergoes depassivation–dissolution of titanium which is slower and more homogenous than the crystalline alloy corrosion. In a recent investigation, Dutta *et al* (2001) studied the effects of microcrystalline phases and quenched in defects on the corrosion of rapidly solidified $Ti_{47}Cu_{53}$ and $Ti_{50}Cu_{50}$ alloys in acidic chloride environments. A comparative study on corrosion investigations by polarization method on several compositionally different Ti-based amorphous alloys in non-chloride containing solutions is missing in the literature. This has motivated us to carry out the present study with an aim to investigate the corrosion behaviour of amorphous $Ti_{60}Ni_{40}$, $Ti_{50}Cu_{50}$ and $Ti_{48}Cu_{52}$ in several aqueous media: 0·5 M HNO_3, 0·5 M H_2SO_4 and 0·5 M NaOH under identical experimental conditions. The investigations were carried out using the potentiodynamic polarization method and the values of the corrosion current density (I_{corr}) and open-circuit potential (OCP) of these amorphous alloys were determined in various aqueous media.

2. Experimental

Specimens of suitable size (about 2–5 cm long) were cut from melt-spun amorphous ribbons of Ti–Cu and Ti–Ni alloys having nominal compositions (in at %) of $Ti_{48}Cu_{52}$ (1·1 cm × 0·3 cm × 25 μm), $Ti_{50}Cu_{50}$ (1·1 cm × 0·4 cm × 25 μm) and $Ti_{60}Ni_{40}$ (1·1 cm × 1 cm × 30 μm). Amorphous nature of these specimens was checked by X-ray diffrac-

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tion (XRD). Crystallization kinetics of these alloys have earlier been reported in the literature (Jain *et al* 2001, 2003). The alloys $Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$ exhibited on-set crystallization temperature (T_x) of 718 K, 720 K and 761 K, respectively, at a heating rate of 20 K/min in a differential scanning calorimetry (DSC) experiment. Each specimen was cleaned with acetone and ethanol and dried in air prior to inserting it in the corrosion cell for electrochemical studies. The specimen was joined with a wire using silver paint so as to maintain good electrical contact during corrosion testing. The region of the sample which was painted with silver paint was covered with epoxy resin in order to prevent any reaction of the silver paint with the solution during the electrochemical studies. Potentiodynamic polarization studies were carried out using potentiostat Echo chemie (Model auto Lab. 30) in solutions of 0·5 M H_2SO_4, 0·5 M HNO_3 and 0·5 M NaOH at room temperature (25°C). First conditioning of the working electrode was done by applying – 1 V for 120 s in order to clean the surface of the specimen, i.e. to remove any oil or grease which may stick on the surface of the specimen and then wait for $1·8 \times 10^3$ s to stabilize the open circuit potential (E_{open}). In the second conditioning stage, the scanning was done for both cathodic and anodic regions by applying end potentials using a computer interfaced with the potentiostat. The end potentials were taken between – 1 V to + 1·75 V for scanning and the scanning rate was 1 mV/s. The counter electrode was platinum (Pt) and the potential was referenced to a standard saturated calomel electrode. As it was difficult to define linear Tafel regions in the anodic arm of the observed polarization plots, the value of corrosion current density was obtained using the method of Stern and Roth (Stern and Roth 1957; Jones 1996) for non-linear anodic regions in the polarization plots. In this method the anodic polarization data in the potential region near the free corrosion potential (E_{corr} or OCP) are derived from cathodic polarization data using the equation

$$i_a = i_c - i_{app,c},$$

where $i_{app,c}$ is applied cathodic current density and i_c and i_a are the cathodic and anodic current densities, respectively. The values of i_c are obtained by selecting a linear region in the cathodic arm of the polarization plots and the intersection of the lines representing i_a and i_c yielded the value of the corrosion current density, i_{corr} and the open circuit potential (E_{corr}) (Stern and Roth 1957; Jones 1996).

3. Results and discussion

The potentiodynamic polarization plots representing both the cathodic and anodic regions for amorphous $Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$ alloys in various aqueous media are shown in figures 1, 2 and 3, respectively. It is observed from the anodic polarization plots obtained in 0·5 M H_2SO_4 aqueous solution (figures 1a–c) that all the three alloys,

$Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$, show active-, passive- and transpassive behaviour and the passivity regions for amorphous $Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$ alloys lie in the potential range 0·041 V to 0·458 V, – 0·032 V to 0·337 V and 0·170 V to 0·470 V, respectively. On the other hand, passivity trends close to the open circuit potential (OCP) are observed for all the alloys in 0·5 M HNO_3 (figures 2a–c). This behaviour could be understood due to the oxidizing nature of this medium, which facilitates the passive layer formation in the alloy rather easily close to the OCP. Further, short clear passivity regions are also observed in 0·5 M NaOH as can be seen from figures 3a–c for all the alloys.
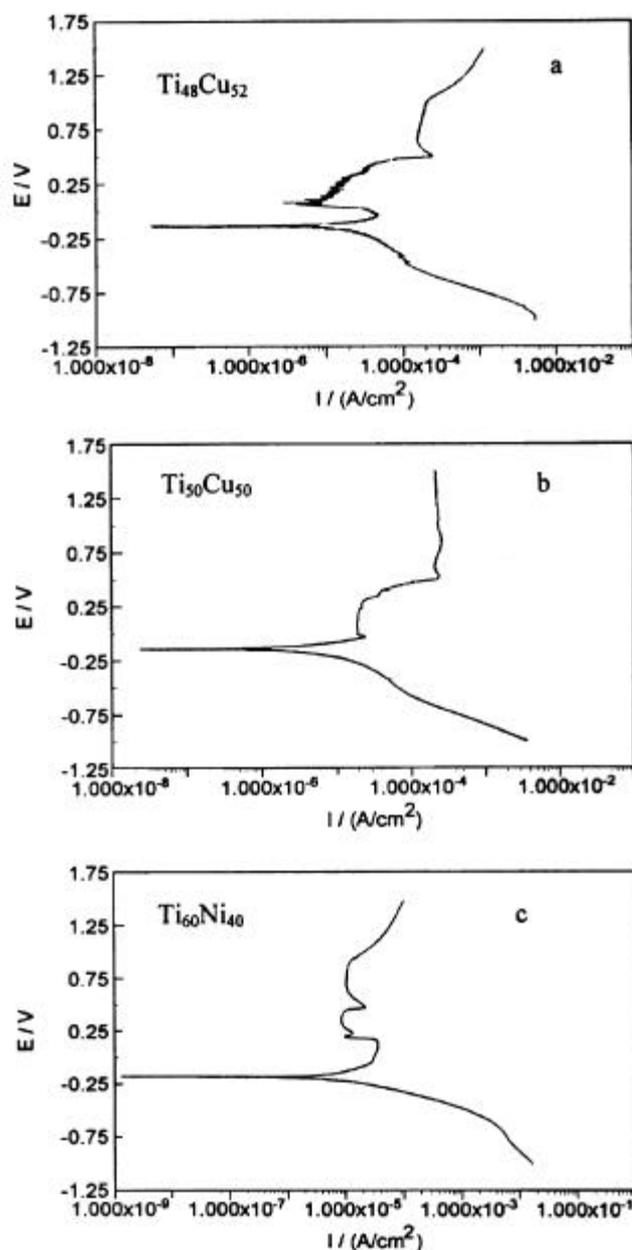

Figure 1. Potentiodynamic polarization plots in 0·5 M H_2SO_4 for amorphous **a**. $Ti_{48}Cu_{52}$, **b**. $Ti_{50}Cu_{50}$ and **c**. $Ti_{60}Ni_{40}$.

The values of the corrosion current density (I_{corr}) and the open circuit potential (OCP or E_{corr}) obtained from these plots are mentioned in table 1. It is observed from table 1 that the value of I_{corr} for Ti₄₈Cu₅₂ is maximum in all the aqueous media as compared to the other two binary alloys, Ti₅₀Cu₅₀ and Ti₆₀Ni₄₀, while the alloy, Ti₆₀Ni₄₀, displays the lowest value of I_{corr} in all media except in 0·5 M H₂SO₄ (I_{corr} value of Ti₅₀Cu₅₀ and Ti₆₀Ni₄₀ in 0·5 M H₂SO₄ are comparable). It is further observed from table 1 that OCP values for all the three alloys in 0·5 M HNO₃ are positive or lie towards noble side and shift to active side (negative) in 0·5 M H₂SO₄ and 0·5 M NaOH aqueous media indicating that the alloys are less prone to corrosion in 0·5 M HNO₃ as compared to the other two i.e. 0·5 M

H₂SO₄ and 0·5 M NaOH. It is further seen from table 1 that the I_{corr} values in 0·5 M HNO₃ for all the alloys are lowest as compared to those in the other two media. The observed values of I_{corr} thus suggest that Ti₄₈Cu₅₂ is the least corrosion resistant and the binary alloy, Ti₆₀Ni₄₀, is the most corrosion resistant. This behaviour may be attributed to the differences in the alloy constituents and their compositions, which result in different oxide films on the surfaces of these alloys during room temperature oxidation. It has been shown by X-ray photoelectron spectroscopy (XPS) studies that the oxide film on as-quenched amorphous Ti₅₀Cu₅₀ and Ti₆₀Ni₄₀ at room temperature consisted of TiO₂ on the surface while Cu and Ni were detected only near the oxide–alloy interface (Hawang *et al* 1985;
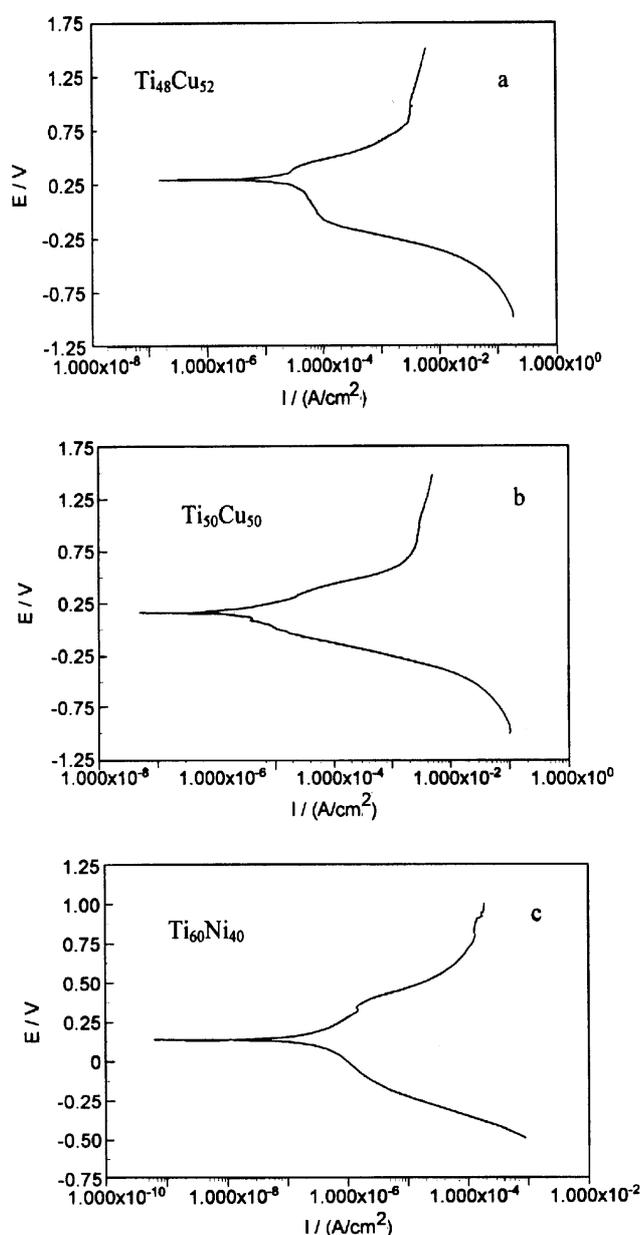

Figure 2. Potentiodynamic polarization plots in 0·5 M HNO₃ for amorphous **a.** Ti₄₈Cu₅₂, **b.** Ti₅₀Cu₅₀ and **c.** Ti₆₀Ni₄₀.
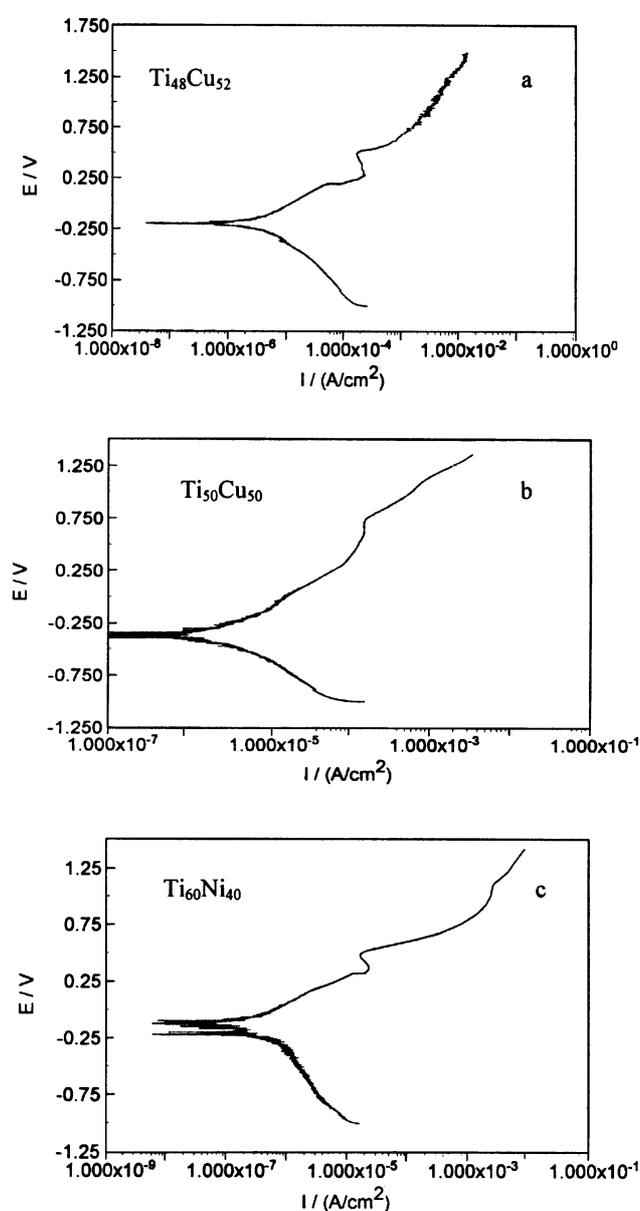
Figure 3. Potentiodynamic polarization plots in 0·5 M NaOH for amorphous **a.** Ti₄₈Cu₅₂, **b.** Ti₅₀Cu₅₀ and **c.** Ti₆₀Ni₄₀.

Table 1. Electrochemical response of the virgin specimens of binary amorphous alloys, $Ti_{48}Cu_{52}$, $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$, in three different aqueous media.

Alloy	0·5 M H_2SO_4		0·5 M HNO_3		0·5 M NaOH	
	E_{corr} (V)	I_{corr} (A/cm^2)	E_{corr} (V)	I_{corr} (A/cm^2)	E_{corr} (V)	I_{corr} (A/cm^2)
$Ti_{48}Cu_{52}$	− 0·136	2.60×10^{-5}	0·295	5.5×10^{-6}	− 0·193	3.5×10^{-6}
$Ti_{50}Cu_{50}$	− 0·136	8.0×10^{-6}	0·159	2.0×10^{-6}	− 0·375	3.25×10^{-6}
$Ti_{60}Ni_{40}$	− 0·181	8.5×10^{-6}	0·136	4.0×10^{-7}	− 0·125	5.5×10^{-7}

Srivastava *et al* 1994). During anodic polarization studies also the surface oxide film has been shown to consist of ZrO_2 in case of Zr-rich Zr–Ni amorphous alloys (Dey *et al* 1989) and TiO_2 in case of Ti-rich Ti–Cu amorphous alloys (Schennach *et al* 2001). On the other hand it has been reported that the oxide film on Cu-rich $Cu_{66}Ti_{34}$ amorphous alloy consisted of oxides of both Cu and Ti (Jorge *et al* 1988). In view of the observed depletion of Cu or Ni in the oxide films on these Ti-rich alloys at room temperature, the characteristics of the oxide film (TiO_2) on the surface will primarily be governed by the amount of Ti in these alloys. Therefore, the role of Cu or Ni in oxide film formation at room temperature may be important for alloys which are Cu- or Ni-rich. It is thus likely that during anodic polarization of these alloys a passive film of TiO_2 with better protective quality is formed on Ti-rich amorphous alloy, $Ti_{60}Ni_{40}$, as compared to other two binary alloys, $Ti_{50}Cu_{50}$ and $Ti_{48}Cu_{52}$, containing lesser amounts of Ti. This is also supported by our electro-chemical investigations which show that the corrosion current density calculated by potentiodynamic polarization method was found to be minimum for the alloy, $Ti_{60}Ni_{40}$ and maximum for the alloy, $Ti_{48}Cu_{52}$, in all the aqueous media (cf table 1). It is further noted from the investigations reported by Naka *et al* (1978) that the corrosion resistance of amorphous $Zr_{50}Cu_{50}$ alloy is better than the alloy, $Ti_{50}Cu_{50}$, in 1 N HNO_3, 1 N H_2SO_4 and 1 N NaOH aqueous solutions and the amorphous $Ti_{50}Cu_{50}$ exhibited the highest corrosion rate in 1 N H_2SO_4 followed by those in 1 N HNO_3 and 1 N NaOH. The trends for the corrosion current density of amorphous $Ti_{50}Cu_{50}$, $Ti_{48}Cu_{52}$ and $Ti_{60}Ni_{40}$ alloys in our study are in agreement with the trend of corrosion rate data obtained by Naka *et al* (1978) for $Ti_{50}Cu_{50}$ in these media.

4. Conclusions

(I) The corrosion current density (I_{corr}) for the binary amorphous alloy, $Ti_{48}Cu_{52}$, was found to be maximum followed by that for the $Ti_{50}Cu_{50}$ and $Ti_{60}Ni_{40}$ in 0·5 M H_2SO_4, 0·5 M HNO_3 and 0·5 M NaOH aqueous solutions. The low corrosion current density of $Ti_{60}Ni_{40}$ is attributed to the presence of higher atomic percentage of Ti.

(II) It is suggested that amorphous $Ti_{60}Ni_{40}$ is more resistant to corrosion than $Ti_{50}Cu_{50}$ and $Ti_{48}Cu_{52}$ in 0·5 M H_2SO_4, 0·5 M HNO_3 and 0·5 M NaOH aqueous solutions.

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