CORROSION RESISTANCE OF TWO MAGNETIC METALLIC GLASSES IN ACIDIC AND NEUTRAL AQUEOUS SOLUTIONS

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The corrosion resistance of two magnetic metallic glasses, viz. $Fe_{40}Ni_{40}B_{20}$ and $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ was evaluated in H_2SO_4 and NaCl solutions by weight loss measurement and electrochemical techniques. In exposures upto six days the corrosion rate of $Fe_{40}Ni_{40}B_{20}$ was about 5 mpy while $Fe_{30}Ni_{39}Mo_2(SiB)_{20}$ corroded about two time faster in 0.1 M H_2SO_4 solution. In 3.5% NaCl both alloys corroded at about the same rate, nearly 2 mpy. In potentiostatic polarization measurements the Mo bearing alloy passivated in the potential range +0.45 V to +1.45 V with respect to saturated calomel electrode in H_2SO_4 solutions of concentration 0.001 M to 0.1 M, but both alloys failed to passivate in NaCl solutions.

Metallic galsses produced by rapid quenching from the melt are of current interest because of their excellent magnetic properties, high strength and extreme pliability [1]. Several iron, nickel and cobalt base amorphous alloys have been developed with superior magnetic properties and some of them are being commercially used in transformers and other electrical machinery. While it is well known [2,3] that chromium bearing metallic glasses have excellent corrosion resistance in aqueous media, the environmental stability of magnetic metallic glasses is yet uncertain. In the present investigation the corrosion resistances of two commercially available magnetic metalic glasses $Fe_{40}Ni_{40}B_{20}$ and $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ in H_2SO_4 & NaCl media were determined using weight loss measurement and electrochemical tests.

EXPERIMENTAL

Commercial metallic glass ribbons of the nominal composition $Fe_{40}Ni_{40}B_{20}$ (15 mm width x 0.25 mm thickness) and $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ (15 mm width x 0.035 mm thickness) provided by M/s Vacuumschmelze GmbH, Hanau, were used for the present study. Their amorphous nature was initially confirmed by X-ray diffraction method. In the potentiostatic polarization method, one end of the specimen was soldered to a copper wire. The soldered junction and edge of the specimen were covered with a lacqure so as to provide an exposed area of 3 Cm^2. For immersion tests rectangular specimens of 6.0 cm^2 area were used. No surface treatment was given to the specimen and they were used in the as received condition after washing with acetone and distilled water.

Total immersion tests were performed in 0.01M H_2SO_4 and 3.5% NaCl in corning glass flasks of 150 ml for exposure times upto 144 hours. The specimens were removed at different intervals, washed with distilled water and dried to measure the weight loss.

Potentiostatic polarization studies were carried out using a Wenking Potentioscan (Model POS73) in 0.1, 0.01 and 0.001 M H_2SO_4 and 3.5, 1.0, 0.1, 0.01 and 0.001 % NaCl solutions. All the potentials were measured against a saturated calomel electrode (SCE) and the Luggin capillary tip was facing the shiny side of the specimen. Intially the Open Circuit Potential (OCP) was recorded after a constant value is reached and then starting from OCP the specimen was cathodically polarized at 50 mV intervals upto -300 mV. The polarization current were noted after stabilizing the specimen for about one minute at each potential. The specimen was then kept at OCP condition till a steady OCP was again obtained. After, this the anodic polarization was carried out in 25 to 50 mV intervals. The corrosion current densities for both alloys were calculated by extrapolating the anodic and cathodic tafel slopes.

All the solution were prepared by using double

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distilled water and reagent chemicals. The polarization studies and immersion tests were carried out at 28°C.

RESULTS AND DISCUSSION

Weight Loss Data

Corrosion rates estimated from the immersion tests are plotted against exposure time in Fig. 1. In 0.1 M H_2SO_4, for exposure upto 144 hours, the corrosion rate of $Fe_{40}Ni_{40}B_{20}$ is about two times lower than that of $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ whereas in 3.5% NaCl both the alloys showed almost the same corrosion rate of about 2 mpy (Mils Penetration per year). It is clear from the above observation that molybdenum does not help in improving the corrosion resistance of $Fe_{40}Ni_{40}B_{20}$ alloy and the presence of silicon probably leads to the higher corrosion rates in 0.1M H_2SO_4. It has been reported [4] that the corrosion rate of Fe-Cr-B amorphous alloys in 0.1 M H_2SO_4 increases when B is replaced partially by Si. Under open circuit conditions, iron goes into solution as Fe^{2+} and Fe^{3+}, Ni as Ni^{2+} and boron and silicon form borate and silicate respectively [5,6]. Both these latter compounds are unstable in acidic media and are incapable of forming a protective film. In NaCl, a greenish yellow salt film is formed on the surface of these alloys which gives some protection thereby reducing the corrosion rate.

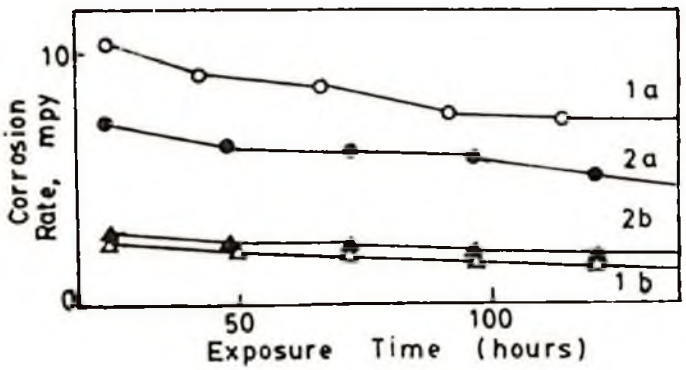
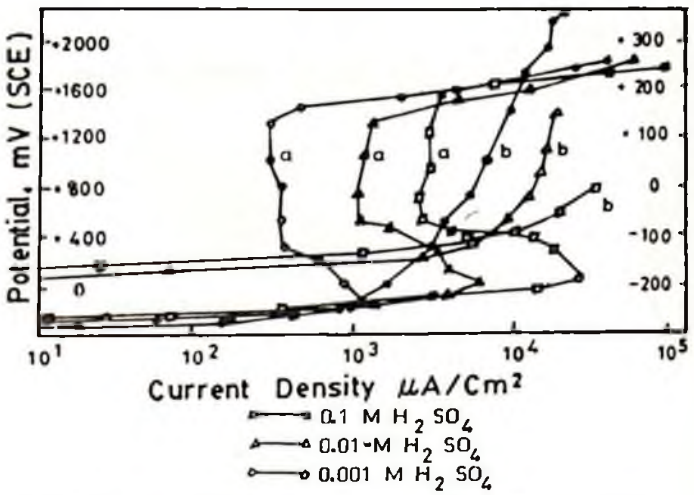


Fig.1 Plot of corrosion rate against exposure time (1) $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ (4040) and (2) $Fe_{40}NH_{40}b_{20}$ (0040) alloys
a) 0.1M H_2SO_4 ; b) 3.5% NaCl solution.

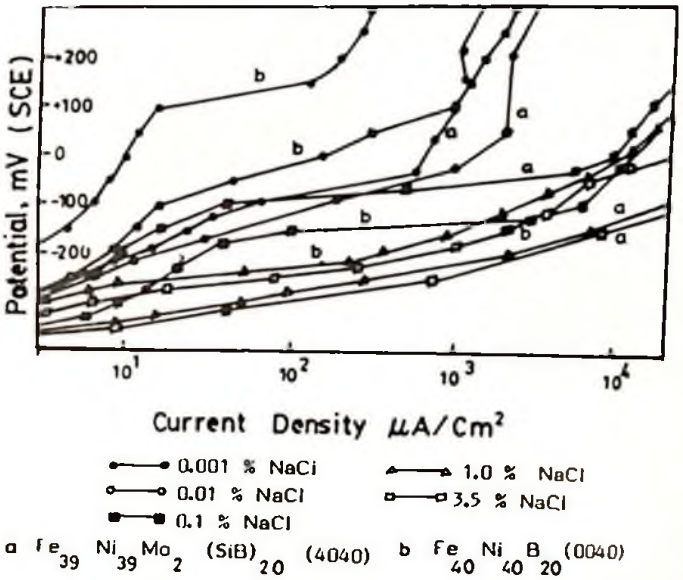
Anodic Polarization Behaviour

Polarization curves for the two alloys in various concentrations of sulphuric acid solution are shown in Figs 2 and 3 Corrosion



a $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ (4040) b $Fe_{40}Ni_{40}B_{20}$ (0040)

Fig. 2 Anodic Polarization curve for the alloy in sulphuric acid solutions of various concentrations.



a $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$ (4040) b $Fe_{40}Ni_{40}B_{20}$ (0040)

Fig. 3 Anodic polarization curve for the alloy in sodium chloride solutions of various concentrations.

parameters calculated from these curves are given in Table 1. It is evident from Fig.2 that the Mo bearing alloy shows a passive region (0.4 V to 1.45 V) in all the concentrations of sulphuric acid solution. Table 1 shows that the critical current density ($I_{crit.}$) and the passive current density (I_{poss}) increase with the concentration of the corrodent. No passivity is observed in the $Fe_{40}Ni_{40}B_{20}$ alloy.

XPS [5] analysis has shown that the passive films on Fe-Ni amorpnous alloys consist essen-

TABLE 1

CORROSION PARAMETERS FROM POLARIZATION CURVES IN SULPHURIC ACID

Various parameters	Acid Concentration (Molar)	Vitrovac 0040 $Fe_{40}Ni_{40}B_{20}$	Vitrovac 4040 $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$
E_{corr} mV (SCE)	0.001	- 290	- 320
	0.01	- 230	- 285
	0.1	- 185	- 255
I_{corr} $\mu A/cm^2$	0.001	6.0	11.0
	0.01	9.0	16.0
	0.1	22.0	46.0
I_{pass} mA/cm^2	0.001	No passivation	0.325
	0.01	"	1.20
	0.1	"	2.5
I_{crit} mA/cm^2	0.001	No passivation	1.1
	0.01	"	6.0
	0.1	"	32.0
Passivation range mV/(SCE)	0.001	No passivation	+400 to +1600
	0.01	"	+400 to +1550
	0.1	"	+400 to +1500

tially of ferrous and ferric ions and very little of Ni ions. Alloying with Mo facilitates the passivation of iron alloys by the formation of protective iron oxide film even in 1 N HCl [7]. In general, even if the potential is set in the passive region an initial increase of dissolved metal in the vicinity of the electrode surface is necessary for the passive film formation. The passive film formation is helped by molybdenum by forming a protective diffusion barrier on the surface of the electrode [7,8]. But Mo does not play any role in the active dissolution and is not able to lower its corrosion rate at open circuit potentials.

The role of Si in the corrosion behaviour of metallic glasses is not known unambiguously. Neka et al [4] reported that Si accelerates the corrosion of metallic glasses in 0.01 M H_2SO_4, which agrees with the present results. Partial replacement of B by Si in Fe-Ni-B alloys resulted [9,10] in improved passivation characteristics and better resistance to pitting. Si additions lower the current densities in both active and passive regions and enlarge the passivation range [10]. The passive films formed on Si containing metallic glasses were enriched in Si. XPS analysis [9,11] have shown a preponderence of SiO_2^- like products in the passive film.

TABLE 2

CORROSION PARAMETERS FROM POLARIZATION CURVES IN SODIUM CHLORIDE

Various parameters	NaCl (percentage	Vitrovac 0040 $Fe_{40}Ni_{40}B_{20}$	Vitrovac 4040 $Fe_{39}Ni_{39}Mo_2(SiB)_{20}$
E_{corr} mV (SCE)	3.5	- 385	- 380
	1.0	- 375	- 370
	0.1	- 365	- 355
	0.01	- 345	- 325
	0.001	- 335	- 310
I_{corr} $\mu A/cm^2$	3.5	7.8	7.5
	1.0	6.5	6.0
	0.1	3.8	3.5
	0.01	2.6	2.2
	0.001	1.8	1.65

It has been reported earlier [7,12] that Mo helps in the passivation of Fe-Ni glasses in the presence of metalloide like P, Si and B by the synergistic interaction among polyanions of these elements. The enchanced dissolution of the Si-containing 4040 glass under open circuit conditions enables the accumulations of anion species near the alloy/sollution interface faster than that in the case of 0040 and an active-passive transition occurs in the acidic media.

In the NaCl solutions (Fig. 3) both the alloys were unable to passivate and continuously dissolved at all potentials. Table 2 gives the corrosion parameters calculated from the polarization curves of Fig. 3 for both alloys the corrosion current density decreased with the de-crease in the concentration of NaCl solution. Passive film formation is not possible in this environment and even the salt film which is formed in the open circuit condition is not able to show any passivity at higher anodic potentials.

CONCLUSIONS

The present study indicates that the addition

of 2% M_o to Fe-Ni-B-Si glasses induces electrochemical passivity in sulphuric acid solution but not in sodium chloride solutions. Under open circuit potential condition in sulphuric acid solution, the Mo bearing alloy corrodes 2 times faster than that without Mo, whereas the dissolution rate is almost the same in sodium chloride solution for both the alloys.

This paper is another example of the use of potentiostatic polarization measurements in the evaluation of the corrosion behaviour of metallic glasses. In a previous paper [3] it was shown that good corrosion resistance, passivity & resistance to localized corrosion in Fe, Ni and Co base metallic glasses require the presence of Cr in the alloy. The Ni-Co base alloy studied earlier had Cr, and Mo and it exhibited extremely high corrosion resistance and good resistance to localized corrosion. The two magnetic metallic glasses studied here do not contain Cr and thus are much inferior in their corrosion resistance.

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