CORROSION BEHAVIOUR OF GLASSY MATERIALS – A CRITICAL REVIEW

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ABSTRACT

Glassy materials are metastable systems. They exhibit a tendency to crystalline forming thermodynamically stable phases. The degree of corrosion is hindered by passivation. Corrosion and passivation of aluminium, magnesium, zirconium, nickel, iron and chromium based alloys are reviewed. Common alloying elements to these alloys and their mode of action are discussed.

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INTRODUCTION

Fundamental investigations on a variety of disordered systems now constitute a significant portion of the activity of many physical and chemical laboratories. Disordered phases of condensed matter including materials are far more abundant and of no less technological value than the idealized single crystals /1- 4/. Glassy materials, also termed 'amorphous alloys', have gained technological importance despite several drawbacks such as small dimensions, some physical irregularities and even some chemical in-homogeneities. Reproducible results were obtained from electrochemical and surface analytical techniques /5-11/.

CHARACTERISTICS OF GLASSY MATERIALS

A crystal is an assembly of innumerable identical atoms or molecules uniformly packed in regular rows and planes to fill all the space available. The physical situation at some point 'r' in space is exactly reproduced at any other point and is given by

$$\vec{r} + \vec{l} = \vec{r} + l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3 \,, \qquad (1)$$

where a_1, a_2, a_3 are three basis vectors and l_1, l_2, l_3 are integers. A diffraction pattern of a single crystal represents an assembly of reflections ordered around a central reflection. They can be classified as the reciprocal lattice points. A diffraction pattern of a polycrystal represents an assembly of concentric circles; they are cross sections of the Ewald sphere with sphere representing reciprocal lattice points of a set of the randomly oriented microcrystals the constituents of the system. Diffraction pattern glass is a broadened halo, i.e. a diffuse disc around a central reflection.

To characterize disordered systems the radial distributions function, RDF, is used. For one component system this function g(R) is defined by setting the formula

$$\zeta_0 \; g(R)\, 4\pi\, R^2\, dR \qquad (2)$$

to give the average number of atoms in a sphere of radius R and thickness dR. The centre of the sphere is located at the centre of any atom, and L0 is the density at the material under study. The RDF is related to the structural factor S (k):

$$S(k) = 1+\zeta_0 \int_0^\infty [4\pi R2\,(g(R)-1)\sin(KR)/KR]\,KR \qquad (3)$$

which experimentally can be determined from x-ray diffraction or from the neutron diffraction. For the wavelength, λ, the intensity of the beam scattered elastically by an angle 2Φ is proportional to $S(4\pi \sin\Phi/\lambda)$. Equation (3) implies that $[g(R)-1]$ is a Fourier transform of $[S(K)-1]$ determined in the roentgenographic or neutrongraphic diffraction experiments.

In order to construct RDF for a multicomponent system the g(R) should be replaced by a set of analogous functions gab(R) where 'a' denotes the component 'a' atom located at the centre of a spherical layer of the radius R and the thickness d(R) in which the component "b" atoms are counted. In a single experiment one measures the weighed sum of these functions.

PROPERTIES

Dahlborg /12/ suggests that the short range ordering decide about the mechanical, chemical and other properties of a given glass. Contemporary understanding of the metallic properties of crystals is based on periodicity, Brillouin zones, Bloch states and selection rules resulting from the point group symmetry. But glassy materials are disordered yet metallic. Some iron base alloys exhibit soft magnetic properties which together with their high magnetic permeability make them attractive materials for tape recording heads and magnetic shielding. Low core losses of some glasses have resulted in their applications as electric transformer cores. Those with high electric resistivity can be used as standard electric resistors.

Figure 1 shows the current density (dissolution rate) Vs electrode potential for Ni-Zr glassy alloys in H_2SO_4+Na_2SO_4 aqueous solution. The corresponding results for crystalline Ni are also given for a comparison. The effect of Zr on extending passivity region and reducing current density within the passive region is obvious.

PREPARATION

The first successful experimental cooling of a liquid metal by a rapid quenching ~ 106 K/sec to obtain glass was done in 1960 /13/, and consisted of a splat cooling method to get a small specimen of Au75 Si25 glassy alloy. The most common method is continuous casting where glassy ribbons are produced directly from the melt at a rate of 30 m/sec. Many metal / metalloid glasses have been obtained so far by rapid cooling. To stabilize amorphous structure effectively the total amount of metalloids (Si, C, B and/or p) in such glasses has to be at 20-25 %. The first metal glass, Mg-Zn, was obtained by Calka *et al.* /14/. Other methods used for production of glassy materials are not necessarily connected with a rapid over-cooling. These are sputter deposition, vapor deposition, mechanical alloying, galvanic deposition (plating) and ion implantation.

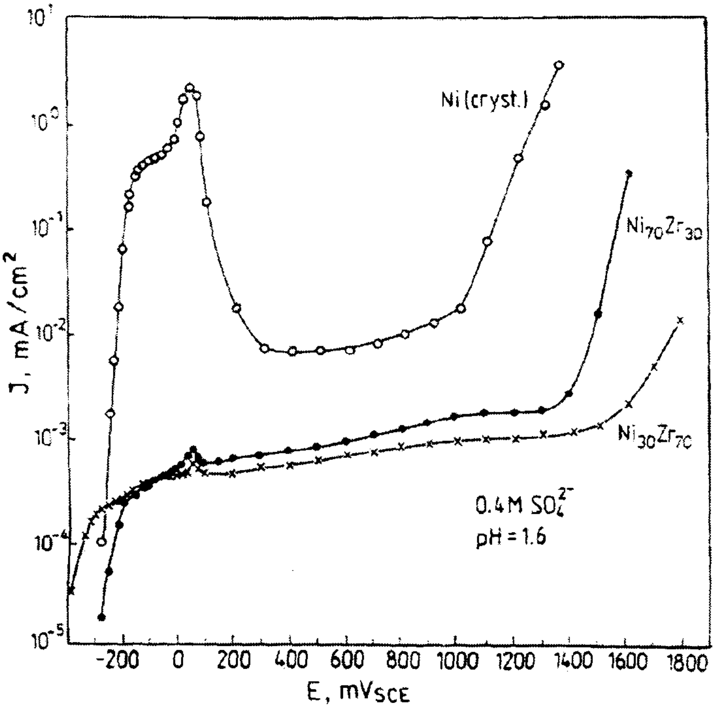

Fig. 1: Current density (dissolution rate) Vs electrode potential for Ni-Zr glassy alloys in H_2SO_4+Na_2SO_4 aqueous solution. The corresponding results for crystalline Ni are also given for a comparison. The effect of Zr on extending passivity region and reducing current density within the passive region is obvious.

Rapidly solidified aluminium alloys are candidate materials for applications in marine and aerospace industries. Al-Ti based alloys are particularly attractive because of their high strength to weight ratio /15/. The various aluminium alloys studied have included 2518 and 2024 alloys, 7090 alloys, Al-Fe Al-Li, Al-Mg, Al-Cu, Al-Er, Al-Fe-Mo, Al-Mg-Zn and Al-Zn-Mg-Cu alloys /16-23/.

Al-Ti based alloys when prepared by a rapid solidification technique exhibited higher general corrosion and localized corrosion resistance than ingot metallurgy, with Al 7075-773 alloy /24/ in 3.5 wt% NaCl solution. The sputter deposited method is used to prepare amorphous Al-Ti, Al-Zr, Al-Nb, Al-Ta, Al-Mo and Al-W alloys; in 1M HCl they suffered pitting, but their pitting potentials were 350-1850 mv higher than the pitting potential of aluminium /25/ on anodic polarization, Al-Mo alloys dissolved and molybdate was found in solution. Colorization on the surface of Al-W was seen due to the presence of tungsten cation in the passive film. In borate buffer containing chloride solutions /26/ the passive film on Al-Mo amorphous alloys consisted of oxidized Al and the presence of oxygen. Above the pitting potential an isotropic localized dissolution took place. The localized current density within the growing pits was 10 times higher than that flowing from the remaining passive surface. Al-Mn amorphous /27/ coating was obtained by electro deposition. The deposit was fcc aluminium when the Mn content <17% and amorphous between 25-45% Mn. The deposit was four times more corrosion resistant than aluminium. In neutral borate-boric acid containing chlorides, Al-Ti alloy (31-60 at wt %) prepared from sputtering exhibited pitting resistance compared to aluminium-Ti crystalline alloys. Modification of the alloy ratios in the Al-Mn (x)-MT /8, 2/ system [where x=4.4-9.3% at] amorphous alloys improved the corrosion resistance in acid medium /28/. A fully amorphous phase is observed near 9% W. When W ion implantation into Al was done /29/, passivation was found to be enhanced by amorphisation. Rapidly quenched $Al_{87}Fe_{10}Nb_3$ and $Al_{87}Fe_8Nb_5$ alloys were found to be pitting resistant compared to crystalline alloys in 1M NaCl and 0.1M HCl solutions. In borate buffer solution Al-Mo and Al-W amorphous alloys were found to consist of less oxide /30/. Mo and W acted as "dissolution moderators", restraining the substrate dissolution process. The presence of Mo and W enhanced the pitting resistance. Amorphous Al-Mn (Fe or Ni) alloys in decreased 1N HNO3 /31/ proved to be more corrosion resistant than iron.

CORROSION AND PASSIVATION OF MAGNESIUM ALLOYS

Crystallized Mg_2Ni and Mg_2Ni_2 amorphous alloys synthesized by mechanical alloying in KOH solutions were studied. Protective film of $Mg(OH)_2$ could not sufficiently protect corrosion by nickel substitution /32/. Amorphous and nanocrystalline magnesium based Mg-Ni alloys were produced by melt spinning, exhibiting higher corrosion resistance compared to partially and fully crystalline $Mg_{87}Ni$ 12% alloys. But the difference in corrosion rate was not significant due to the fine microstructure of nano crystalline alloy /33/. The dissolution rates were studied of melt-spun ribbons of seven fully amorphous Mg based alloys (Mg-Ni-Pd) containing up to 15 % Nd and 20 % Ni in 3% NaCl containing saturated Ca $(OH)_2$ solution. The dissolution rates decreased with time due to $Mg(OH)_2$ formation. Microcrystalline alloy with Ni or Nd was compared /34/ for corrosion resistance.

CORROSION AND PASSIVATION OF ZIRCONIUM ALLOYS

Glassy Cu60, Zr40 and Cu56, Zr42 P2 melt spun alloys showed lower corrosion rates in H_2SO_4 solutions /35/. [[The zirconium surface film and P as n-type dopant.]] Corrosion behaviour of amorphous Zn67 Ni33 alloy was compared with crystalline alloy in 1M HCl, 1N H_2SO_4 and 1N HNO_3 solutions. Corrosion rates of amorphous alloy were higher. An enrichment of nickel by approximately 'c' factor of 2 at the oxide film alloy interface as well as larger oxygen uptake occurred in the crystalline specimens as compared to amorphous alloy. Surface oxide film /36/ formed in all media consisted of ZrO_2 and $Zn(OH)_4$. Amorphous Fe 84 Nb7 B9, Fe 84 Zr 7 B9, Fe 83 Zr 3.5 B9 Cu 1 alloys exhibited decreased corrosion resistance compared to crystalline alloys /37/. Nb addition offered greater corrosion resistance compared to Zr addition. Amorphous Zn65 Al 7.5 Ni10 Cu 17.5 alloy in phosphate-citric acid buffer in the absence and presence of chloride was studied. An increase of chloride ion concentration increased the pitting susceptibility /38/. Phosphate ions adsorbed on ZrO surface raised the susceptibility to pitting and hardly adsorbed on aluminium oxide surface. The pitting resistance decreased with decrease of pH due to the shift of OCP /39/. However, pitting did not occur spontaneously. Figure 1 presents the polarization curves for nickel and nickel zirconium alloys.

CORROSION AND PASSIVATION OF NICKEL-METALLOID ALLOYS

Glassy Ni–P alloys were studied in 0.2 N H_2SO_4 and 0.2 N HCl solutions. Glassy alloys passivated at potentials up to several hundred mV anodic to Eo, whereas Ni dissolved in the active state at comparable anodic over potentials. At higher anodic over potentials, Ni-P underwent transpassive dissolution but Ni passivated. The behavior of Ni-P in 0.2N HCl was virtually identical to that in H_2SO_4. The alloy resisted pitting corrosion in chloride solutions /40/.

For Ni-Ti-P alloys with Ti<10% and for Ni-Cr-P alloys with Cr <3% in 1M HCl solutions /41/, very fine pitting bordering on general corrosion was seen. On 32 Fe-36 Ni-14Cr-12P-6B alloys the presence of Cl^- ions was essential for film breakdown. Electrochemical noise amplitude measured on the glassy alloys was much less than that observed on the crystallized sample as well as on a crystalline iron-Cr alloy, indicating that the amorphous alloy had a higher resistance to breakdown as well as a rapid repassivating ability /42/. Hydrogen embrittlement was seen on 83.3 Ni-16.7 P alloy from 0.1M NaOH solutions. The low energy sites for H_2 started filling up first, thus increasing the chemical potential for further trapping of H_2 /43/. Rapidly quenched amorphous Ni-19P alloy was studied in 1M HCl solutions. Structural relation by quenching and heterogeneities decided the corrosion rate. They offered less corrosion compared to nickel. Table 1 presents the effect of crystallization on the anodic dissolution of glassy materials.

Table 1

Effect of crystallization on the rate of anodic dissolution of glassy materials

Glassy phase	Crystalline phase	Change of anodic current density
Co75B25	Co3B	Strong decrease
Ni66B34	Ni2B	Strong decrease
Cu60Zr40	Cu10Zr7	None

Source: P.C. Pearson, P.V. Nagarkar and R.M. Latanision in R.E. White, J.O.M. Bockris and B.E. Conway (Eds) *Modern Aspects of Electrochemistry* Vol. 21 Plenum Press, NY, 1990, 121.

J.C. Turn and R.M. Latanision, *Corrosion*, **39**, 1883,271

Table 2

Parameters derived from E-log polarization curves in 5% NaCl solutions

System	Ecorr mv Vs SCE	Anodic tafel slope mv/decade	Cathodic tafel slope mv/decade	Corrosion current density, microA/cm^2
Mild steel	- 640	35	30	9.4
Pure nickel	- 495	73	63	5.3
Ni-0.6% B deposit	- 260	37	37	0.4
Pure iron	- 594	57	52	11.5
Fe+0.6%B Alloy deposit	- 410	32	37	50

Source: Visalakshi Ravindran and V.S. Muralidharan "Corrosion resistance of boron alloy electrodeposits" paper presented at the international congress on emerging corrosion control strategies for the millennium, ***Glucorr*** 2002, India

CORROSION AND PASSIVATION OF AMORPHOUS NICKEL ALLOY ELECTRODEPOSITS

Corrosion resistance behaviour of electrodeposited transition metal boron alloy has been studied in 5% sodium chloride solutions. Figure 2 presents the potentio-dynamic polarization curves for nickel and nickel-boron alloy deposits and Figure 3 shows the potentio-dynamic polarization curves for iron and iron-boron alloy deposits. When compared to mild steel, nickel alloy offered the least corrosion and iron alloy the highest (Table 2). Nickel boron alloy electrodeposits offered higher hardness, which increased with % boron in the alloy (Table 3).

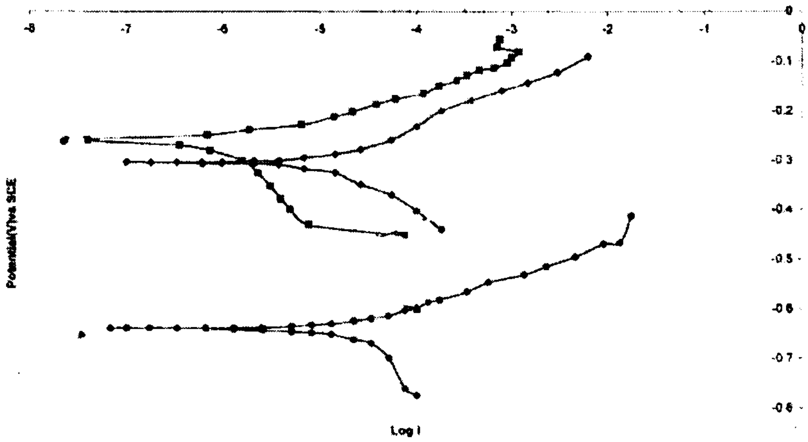

Fig. 2: E-Log I curves obtained for different materials in 5% NaCl solutions. pure nickel; b) mild steel; c) nickel + 5% Boron

Table 3

Hardness values of various electrodeposits

Electro deposit	Hardness values(Hv)
Nickel	100
Nickel+0.4% B	100
Nickel+0.5% B	120
Nickel+0.6% B	178

Source : Visalakshi Ravindran and V.S. Muralidharan "Corrosion resistance of boron alloy electrodeposits" paper presented at the international congress on emerging corrosion control strategies for the millennium ***Glucorr*** 2002, India

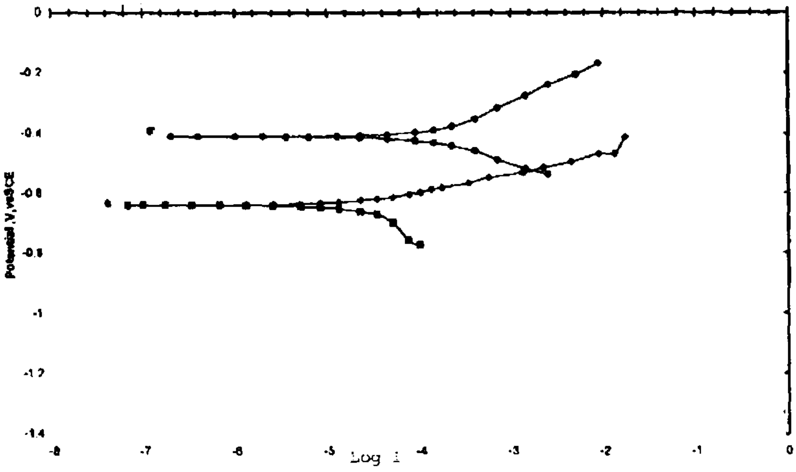

Fig. 3: E-Log I curves obtained for different materials in 5% NaCl solutions. a) pure iron; b) iron + 0.5% Boron

Ni-P alloys can be deposited both by electroless and electro plating /44/. Co deposition process of solid particles with electroless Ni-P is also known /45-49/. Due to various shorting of electroless processes, the electrode position is preferred. Corrosion resistance of electrodeposited NiP alloys was investigated by immersion in 5% acetic acid by the salt spray and by polarization measurements in 0.1 M H_2SO_4 and 32% NaOH solutions /50-57/. Corrosion resistance increased with P content. The corrosion potentials of high P alloys were higher (nobler) and the corrosion currents were lower than those of lower P counter parts. The dissolution rate of Ni at its Ecorr was an order of magnitude faster than that of NiP. Good pitting resistance was found for amorphous nickel alloys in a potential range at which crystalline nickel or low –P deposits were pitted. Corrosion sets in at grain boundaries, dislocations and inclusions in crystalline materials. The absence of such sites in amorphous structures makes for improved corrosion resistance. A protective phosphate layer on the deposit surface was also shown by the polarization measurements and XPS analysis /58, 59/. The corrosion resistance of electroplated layers was somewhat lower compared with their electroless counterparts while the salt spray tests conducted showed similar behavior. The reason for the corrosion was mostly due to porosity of the deposits. Passivation of nanocrystalline (nc) and amorphous Ni-P alloys in 0.1 M H_2SO_4 solution was studied /60/. An enrichment of elemental P compared to nickel was seen at the surface suggesting that nickel dissolved preferentially. The high volume fraction of grain boundaries and triple junctions on the nc specimens resulted in enchained dissociation adsorption of O_2 and OH^- ions. Because of the defective nc surfaces dissolution and oxidation of surface P atoms from hypophosphite to soluble phosphates anions. At higher anodic potentials thick porous films were seen. Electroless Ni-Mo-P alloy deposit offered less corrosion in acidic neutral and alkaline solutions compared to nickel /61/.

Electrodeposited amorphous Ni-W, Ni-W-P alloys deposits /62/ exhibited higher corrosion resistance. In 1M HCl solutions, the corrosion rate of 304 S.S was 10 times that of Ni-W-P alloys, 40 times that of Ni-W alloy. Electrodeposited amorphous Ni-W and Ni-W-P alloys offered enhanced corrosion resistance in HNO_3, HCl, H_2SO_4 and in 5% NaCl solutions. The corrosion behavior depended on substrates also /63/.

CORROSION AND PASSIVATION OF IRON METALLOID ALLOYS

Glassy alloy families Fe–B and Fe–Ni–B alloys were studied in pH ranging from 4 to 8.4. The influence of substitution of B by Si and the presence of Cl^- and SO4 2^- ions in solution were studied /64/. Five Fe-P alloys with P content (0.002 to 0.12 %) in H_2SO_4 and HCl solutions (pH=0) were studied /65/. PH 3 generated during corrosion process acted as a stimulator at low P concentrations or as an inhibitor of corrosion at high P concentrations. Pure polycrystalline iron and of rapidly quenched Fe80 B 20 alloy were studied in chloride and sulphate media /66/. In chloride solutions the boron alloy exhibited characteristics differing from those of iron. Rapidly quenched Fe80 P20 and Fe80 P13 C7 alloys in sulphate media exhibited faster kinetics for the hydrogen evolution and dissolution of iron hindered. Vitrovac 10049 (Fe40 Ni40 B20), Met glass 2826 MB (Fe 40 Ni38 Mo4B18) and Vitrovac 4040 (Fe39 Ni39 Mo4Si6B12) commercial metallic glasses in 1N Na_2SO_4 of varying pH and 0.5 N H_2SO_4 were studied /67/. In alkaline and neutral sulphate solutions Mo and Si had a subtle effect in reducing i_{corr}. Mo imparted passivation in neutral sulphate and failed to passivate the glass in H_2SO_4 solutions. No perceptible change in i_{corr} was found with the addition of Mo to the glass in H_2SO_4 solution. While Si increased the corrosion rate of the glass, it also promoted passivation in H_2SO_4. In the presence of Cl^- ions, the Si containing glass was susceptible to pitting. Devitrification of Vitrovac

4040 led to active dissolution irrespective of the crystalline products present while the nature of the crystalline phases formed during the devitrification decided corrosion rate. Two magnetic metallic glasses, Fe40Ni40B20 and Fe39 Ni39 Mo2 (SiB) 20, were studied in H_2SO_4 and NaCl solutions /68/. In 0.1 M H_2SO_4 solutions, Fe30Ni30Mo2(SiB)20 corroded two times faster than the other alloy while in 3.5% NaCl solutions corrosion rates were the same. There was passivation in H_2SO_4 solution while in NaCl solutions no passivation was seen. Several iron based alloys (80Fe-20P, 80Fe-20B) were studied for passive film formation /69/. Electronic properties of surface oxides were found to be a better criterion for correlation. The pitting potential of the recrystallised alloys was 0.1 V higher than the pitting potential of the recrystallised alloy /70/. Glassy Fe Ni xB (x =14, 16, 22 and 24 at %) with Fe Ni/ Fe ratio of 0.6 ions was susceptible to crevice corrosion in 1.0 M H_2SO_4 solution. Increasing the nickel content to 60% in 20 Fe- 60 Ni -20 B alloy did not affect more the pitting resistance of these amorphous alloys than their chemical composition. 80 Fe -20 B amorphous alloy pitted in a chloride containing borate solution [[!!and that he stop erevicing!!]] Co- Fe –B- Si, Ni- Si -B, Fe-B- Si and Ni-Cu–Si-B alloys underwent crevice corrosion in H_2SO_4 solutions (loc.cit). The influence of metalloid content and thermal treatment on micro structural evolution and corrosion resistance of Fe-Cu-Nb-Si-B amorphous alloys was studied with different Si/B ratios /71/. The crystalline alloy was dependent on the Si/B content. In 0.1 M H_2SO_4 corrosion resistance increased with Si content due to nano-crystallization. The effect of metalloid content and partial crystallization on corrosion resistance of Fe-M-B alloys was studied (loc.cit). Greater corrosion resistance was seen when Nb was present. The electrodeposited Fe- P, Ni -Fe29- P18 and Ni- Fe0.7–P18.7 amorphous alloys were not passivated in 0.1 N H_2SO_4(72). The ratios between the basic components of Ni, Fe and P alloys in the surface film were different from those in the bulk. In the case of Ni-Fe-P alloys the surface film was enriched with Fe, which was very pronounced in the alloys with low Fe content. In Fe-P alloys, Fe was depleted in the film. This was due to the different degree of oxidation on the surface where iron oxides of the types. Fe_2O_3 and Fe_3O_4 were seen. It was presumed that in alloys. Fe-P and Ni- Fe 29-P18 after anodic treatment in 0.1 M H_2SO4 a relatively thick diffusion barrier was formed which consisted mainly of iron oxides and P compounds and displayed good ionic conductivity, offering higher dissolution rates.

CORROSION AND PASSIVATION OF CHROMIUM-METALLOID ALLOYS

Additions of molybdenum and W to amorphous Fe-SCr-13P-7C and Fe-15Cr-13P-7C alloys decreased the active dissolution current in 6M HCl solutions /73/. Mo and W prevented the dissolution of chromium from the air formed films during passivation on anodic polarisation. W addition was more effective than Mo addition. When an excess amount of Mo and W was added the passivity was lost and at extreme anodic potentials the passive films were devoid of chromium. The passivation of amorphous alloys Fe 70 Cr 10 X13 C7 (X=P, B) was studied. The enrichment of P underneath the passive film, reducing to a great extent the ionic conductivity of the interface and to the incorporation of Cr OOH and phosphates in the passive film, were seen by XPS analysis. The corrosion properties of amorphous Fe-Cr alloys were strongly depend on the metalloid composition of the alloy /75/. Addition of P improved the passivation and stable passive film. The coverage of the surface by a porous precurser layer of Fe-phosphate led to a self passivation even in deaerated acidic solutions containing oxidizing species. The incorporation of oxidised P as phosphate in the outer part of the Cr_2O_3 film rendered this to be cation selective in nature, thus preventing the penetration of aggressive chlorides. The passive film of the P containing alloys is therefore highly resistant against pit initiation. The high localised corrosion resistance was further due to high repassivation stability on the alloy. On local damage to the passive film, the formation of the Fe-phosphate precursor layer took place, rapidly leading to a fast repassivation.

The active current density of amorphous /76/ Fe-8Cr-7W-13P-7C alloy was almost 3 orders of magnitude lower than that of Fe-8Cr-13P-7C alloy. The Cr-W ions were concentrated in the surface film on a W containing alloy in the active region. The chromium enrichment in the passive film became more significant with increasing W content. Passivation of low W alloys seems to occur by the formation of the passive film with the least enrichment of Cr ions necessary for passivation. Passivation of W containing alloys took place through transformation of the air formed film to the passive film as a result of preferential dissolution of a small amount of Fe without the dissolution of chromium anions.

Amorphous chromium deposit was prepared by electrodeposition /77/. In 1M HCl and 1M H_2SO_4 solutions XPS studies revealed that the passive film formed was similar to that of conventional chromium and consisted mainly of

Cr OOH. Using copper mold casting cylindrical amorphous alloys with low contents of three corrosion resistant elements, Cr, Ta, and Mo, were prepared. Ni-5Cr-5Ta 3Mo-16P-4B alloy in 6 and 12M HCl solutions behaved similarly to melt spun amorphous alloy /78/. TEM observation revealed the presence of nano-crystalline precipitates. All other copper mould cast Ni-16P-4B alloys with Cr, Ta, and Mo were composed of crystalline precipitates. Chromium phosphorous alloy electrodeposits exhibited inclusions of Cr (PO3) along with Cr3P (Table 4).

Table 4

Phases and compounds indentified from XRD

Solution Cr-P ratio	Compound	Phases
1:1	$Cr(PO)_3$	(202)
	CrP	(111)
	Cr_3P	(112)
	CrP	(103)
	P	(121)
	CrP	(413)
1:1.5	$Cr_{12}P_7$	(210)
	$Cr_{12}P_7$	(300)
	$Cr(PO)_3$	(410)
	Cr_2P	(400)
	Cr_2P	(311)
	Cr_3P	(323)
1:2	$Cr_{12}P_7$	(300)
	Cr_2P_7	(301)
	$Cr(PO)_3$	(410)
	Cr_2P_7	(400)
	Cr_2P_7	(311)
	Cr_3P	(323)

Source: C.L.Aravinda, S.M. Mayanna and V.S. Muralidharan, unpublished data

Amorphous metallic films of $Mo_{49}Cr_{33}$ B_{18} deposited on to glass and quartz substrates by magnetron sputtering technique exhibited corrosion current density 3 orders of magnitude less than the corrosion current density of 304 St St in 1N H_2 SO_4 solution /79/. Amorphous Fe- Ni x -Mo4-B13 alloy prepared by the 'melt spinning' technique enhanced the corrosion resistance in 1N NaOH solutions. The molybdenum content (4-8.5%) in the amorphous Fe-Ni20-Mox-B13 is increased the corrosion resistance only in alkaline solution /80/. The passivation of phosphorous implanted Fe-6Cr and Fe-18Cr alloys in 0.1N H_2SO_4 with and without the addition of chloride ions /81/. The implantation process causes a change in microstructure from crystalline to amorphous as the total P increases. 20 atomic % P increased the passivation rate and decreased the total charge passed during the film growth in the absence of Cl^- ions. When 500 rpm Cl^- was added, the P-implanted Fe-18Cr alloy passivated while Fe-6Cr alloy pitted. The corrosion and passivation of type 304 SS and of the amorphous alloys Fe-10Cr-13B-7C and -13P-7B were studied in deaerated 0.5N ethanolic HCl /82/. The alloy with 13% P appeared to show two separate regions of film were formed than at more noble potentials. Studies carried out on the corrosion of amorphous and crystallized stainless steel revealed that amorphous s.s. did not corrode (Table 5).

Table 5

Corrosion rates of amorphous alloys and crystalline Stainless Steels in 6% $FeCl_3$ Solutions

	Corrosion Rate (mm/year)	
Specimen	40°C	60°C
Crystalline Stainless Steels		
18Cr-8Ni	17.86	120.0
	17.64	120.0
17Cr-14Ni-2.5Mo	-	27.47
	-	31.01
Amorphous Alloys	-	0.0000
$FeCr_8P_{13}C_7$	-	0.0000
$FeCr_{10}P_{13}C_7$	0.0000	0.0000
	0.0000	0.0000
$FeCr_{10}Ni_5P_{13}C_7$	0.0000	0.0000
	0.0000	0.0000

Source: M. Naka, K. Hashimoto and T. Masumoto, *Corrosion* 32 (1976) 146

Amorphous Fe-xCr-P-C alloys required /83/ a minimum of 8% Cr to prevent pitting in a 1M NaCl solution. Such Cr additions also resulted in a negligible weight loss at the OCP and in the transpassive region chromium was sent to dissolve as Cr^{6+} without pitting. For Cr content < 8% these alloys exhibited pitting in the transpassive potential region. Only amorphous Fe-Cr-P-C alloy resisted pitting in 3% NaCl solution /84/ in contrast to some crystalline alloys such as Fe-10Cr, which pitted on amorphous Fe-10Cr-13P-7C, and Fe-10Ni-10Cr-13P-7C alloy pitting was seen at 1.75v /85/. Additions of 15% Cr to glassy Fe-40Ni-xCr-16P-4B did not alter the resistance to pitting but resulted in a change in the nature of the transpassive reaction from O_2 evolution on Fe-Ni-P-B to Cr dissolution on Fe-Ni-Cr-P-B /86/. The pitting resistance of glassy Fe-Ni-xCr-P-B (X=2-15%) was studied in acidified 1M NaCl as a function of pH. All alloys passivated; however in the transpassive region beyond 1.0 V (SCE) numerous pits were noticed (~30μm). In a few cases a shallow pit (<10μm in depth) was observed at potentials below the O_2 evolution potential. Studies on glassy Fe-xCr-13B-7C and Fe-xCr-13B-7Si in 3% NaCl showed that the alloys with 2 and 5% Cr pitted at potential slightly above the OCP, but increasing the concentration to 8% Cr raised the pitting potential to ~ 1.0V /87/. Glassy 32Fe-36Ni-14Cr-6B pitted in chloride solutions. The noise amplitude measured on the glassy alloy was much less than that observed on the crystalline Fe-Cr alloy /88/ indicating that the amorphous alloy had a higher resistance to breakdown as well as a rapid repassivating alloy. Addition of 8% Cr prevents pitting compared to only 4% Mo in glassy Fe-Mo-P-C. Molybdenum was seen to promote the formation of FeOOH layer /89/. I N 5M HCl solution pitting was not seen above x >7% in Fe-xMo-25Cr-20B alloy /90/. The implantation of Cr did not alter the OCP but increased the critical pitting potential by 0.6V.The passive c.d. on the Cr implanted alloy was slightly less than that on the Ta implanted alloy /91/.

Amorphous Fe-10Cr-13P-7C and Fe-10Cr-10Ni-13P-7C did not crevice /92/ indicating that chemical composition was an important factor in determining crevice susceptibility. On cold rolling glassy Fe-30Ni-16Cr-2V-15P-6B exhibited a higher passive current density as well as crevice corrosion; however on holding the potential in the transpassive region for an hour the current decreased to the value of the unrolled specimen, showing that the crevices formed during rolling were repassivated and on subsequent scans the sample showed no effect on cold rolling /93/. For glassy Fe-7Cr-20Ni-14P-7C alloy in 2.5M H_2SO_4, even small concentrations of Cl^- ions reduced the fracture stress at the OCP to half the value in air /94/. In neutral NaCl solutions and in acid solutions containing low amounts of Cl^- ions, no embrittlement was seen. The susceptibility to cracking, the ratio of the fracture stress σ in solution to the fracture stress in air, was very low at cathodic potentials. With the addition of Cl^- ions, no embrittlement was seen.

The addition of Cl^-decreased the fracture stress ratio in the potential region between 0.5 to 1.0V. In the potential range below the hydrogen equilibrium potential, hydrogen embrittlement was responsible for the fracture of the alloys. In the passive region the fracture stress decreased with increasing potential and Cl^{--} ions were thought to be responsible for and involved in the embrittlement. At transpassive potentials film dissolution occurred and the fracture stress was similar to that in air. Glassy Fe-13P-7C and Fe-10Cr-13P-7C alloys underwent hydrogen embrittlement during tensile testing combined with hydrogen charging /95/. Hydrogen embrittlement was increased by the addition of hydrogen recombination poisons such as As, S and Sb to the solution as in the case of crystalline alloy /96/. Glassy 32Fe-36Ni-14Cr-12P-6B alloy in boiling $MgCl_2$ underwent SCC. Localised corrosion induced hydrogen entry and subsequent embrittlements of the alloy were seen /97/. Fe-5Cr-12Mo-x and Fe-10Cr-x (x =1C, 20B or 13P-7C) alloys were tested for hydrogen embrittlement in 1M HCl, 0.5M NaCl, and 0.5M H_2SO4 solutions (98). The time to failure in a bending test was shortest for the carbon-containing alloys. The P containing alloys were less susceptible to HE due to their low corrosion rates and a quicker passivating ability, especially when Cr was present in the alloy. For the case of boron containing samples, the passivating ability was considerably reduced and the general corrosion rate was high enough to prevent the formation of a crack by selective local dissolution. Table 6 summarizes the pitting behavior of glassy materials.

Table 6

Pitting of glassy metal alloys

Alloy	Solution	Pitting
Fe-Cr-13P-7C	1M HCl	No
Cr>7%	3% NaCl	No
Fe-Cr-13P-7C and	6% $FeCl_3$	No
Fe-Ni-Cr-P-C	0.01-1M HCl	No
	1M NaCl	No
	1M H_2SO_4	No
Fe-M-13P-7C	2M H_2SO_4	Yes
Fe-10Cr-10Ni-13P-7C	2M H_2SO_4	Yes
Fe-M-13P-7C		No
M= Cr>4%	1M HCl	No
M= Mo>4%	1M HCl	No
M= W>6%	1M HCl	No
Fe-Co-13P-7C	3M NaCl	No
Fe-2(Ti,Nb,V,W or		No
Mo)-3Cr-13P-7C	1M HCl	No
Fe-20Cr-13P-7C	1M HCl	No
Fe-C(Cr-P-Mo)	1M HCl	No
Fe-Cr-Mo+C or B		
or (P+C) or (B+Si)	6M HCl	No
Fe-12Mo-18C	1M HCl	No
Fe-16Mo-18C	1M HCl	No
Fe-B-C+Cr>8%	3% NaCl	No
Fe-B-Si+Cr>8%	3% NaCl	No
Fe-40Ni-20B		
Fe-39-Ni-10B-xSi	Borate buffer, pH=8.4	Yes
x<12%		
x>12%		Yes

Fe-25Cr-xMo-20B	6M HCl	No
x>5%		No
Fe-25Cr-10Zr	1M HCl	Yes
Fe-Cr film	1M NaCl	Yes
Cr-25B	1M HCl	No
Ti-25B	1M HCl	No
Ni-P+Cr,W,Mo	0.5M H_2SO_4	No
Ni-Cr-15P-5B	0.3M H_3PO_4	No
Cr>7%	1M HCl	Yes
Ni-Cr-15P-5B	1M HCl	No
Cr=5,7,9%	1M NaCl	No
Co-13P-7B and other elements	10% $FeCl_3$	No
Co-Cr-20B and other elements	1M HCl	No
Fe-40Ni-14P-7B	1M HCl	No
Fe-35Ni-15Cr-14P-7B	1M H_2SO_4	No
Fe-40Ni-15Cr-16P-4B	0.1M NaCl	No
Fe-19Ni-18Cr-11W	1M NaCl	No
After		
1 h at 773K	1M NaCl	No
1 h at 873K	pH=7	Yes
Fe-5Ni-9Cr-54W after		
DSC thermal scan to 1098K		
xCr-B, x>60%		No
Amorphous	HCl, pH=0.4	No
Microcrystalline		Yes

Source: M.D. Archer, C.C. Corke and B.H. Harji, *Electrochemical Acta*, 32,1987,13

CONCLUSIONS

Glassy materials are metastable systems. They exhibit a tendency to crystallize, forming thermodynamically stable phases. One would expect the glass to dissolve at a faster rate than that for a crystal since the activation energy barrier is expected to be lower for a metastable glass than for a crystal. However, for the majority of glassy alloys, crystallisation introduces not only structural changes (long range ordering, dislocations, grain boundaries, etc,..) but also produces chemical variations which result from the formation of a heterogeneous mixture of thermodynamically stable crystalline phases. Therefore the structural and chemical effects usually cannot be separated. Only for a few simple glasses, devitrification resulted in the formation of one single crystalline phase, which then dissolved at a lower or at a similar rate as compared with that for the amorphous phase.

The degree of reducing reactivity of an alloy by passivation depends on composition and homogeneity of the alloy and what follows, on composition of both passivating film itself and the film/ substrate interphase. Two mechanisms of reduction of the reactivity of homogeneous alloys by passivation can be distinguished by

1. "passivity promoter" mechanism: The alloying element easily becomes oxidised and enriched within the film, thus improving its protective ability and stability.
2. "Metal dissolution moderator / blocker" mechanism: The alloying element is not reactive and tends to remain unoxidised at the film / metal interphase during the passivation process. It moderates the metal dissolution, thereby increasing the energy barrier of the anodic process of oxidation of metal atoms.

For amorphous nickel alloys, Cr and P additions helped to improve passivity while W and P helped for nickel electrodeposits. For chromium alloy, additions of P improved passivation and made them less susceptible to SCC.

In passivating type protection electronic properties of surface oxides decide passivating ability rather than chemical properties.

Additions of W and Mo acted as dissolution moderators for aluminium alloys. They also reduced the dissolution rates for iron alloys.

Therefore the glassy materials (GM) are particularly suitable to drastically reduce the resistivity / corrosion by passivation via optimising composition without any simultaneous change of homogeneity of the alloy.

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