Corrosion-Resistance Characteristics of Sputtered Titanium-Hastelloy C[®] Glassy Alloy Coatings

G. M. Faldetta

August 1986

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ALLOY COATINGS

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ABSTRACT

The corrosion-resistance characteristics of sputtered titanium (Ti)-Hastelloy C[®] glassy alloy coatings were studied in 1 N HCl solution by potentiodynamic polarization methods. The sputtered Ti-Hastelloy C[®] glassy alloy coatings had excellent corrosion resistance, similar to that of sputtered and heat-treated tungsten stainless steel (W-304 SS) glassy alloys. More significantly, an optimum atom percent of Ti in the sputtered Ti-Hastelloy C[®] glassy alloy coatings for the desired corrosion-resistance characteristics was determined.

Hastelloy C[®] is a registered trademark of Cabot Corporation, Kokomo, Indiana.

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CORROSION-RESISTANCE CHARACTERISTICS OF
SPUTTERED TITANIUM-HASTELLOY C[®]
GLASSY ALLOY COATINGS

INTRODUCTION

The excellent corrosion resistance of amorphous iron-chromium-metalloid alloys obtained by rapid quenching from the liquid state have been reported.⁽¹⁾ These alloys reportedly had the best corrosion characteristics when they contained phosphorus as opposed to boron, silicon, or carbon. However when these materials were heat treated at or above their crystallization temperatures, phosphorus migrated to the newly-formed grain boundaries and caused severe intergranular corrosion.

In 1983, Wang and Merz⁽¹⁾ reported excellent corrosion-resistance characteristics of sputtered and heat-treated W-3D4 SS glassy alloys. They found the corrosion resistance of this material was equal to or better than the corrosion resistance of the quenched metal-metalloid amorphous alloys. They also found as the atom percent of W of the material was increased, the corrosion-resistance characteristics of the material improved proportionally.

The studies reported here show that sputtered Ti-Hastelloy C[®] glassy alloy coatings also have excellent corrosion-resistance characteristics based on electrochemical measurements of glassy alloy coatings containing varying atom percentages of Ti. The corrosion-resistance characteristics of the samples are compared to each other and to data reported by Wang and Merz for their sputtered and heat-treated W-304 SS glassy alloys. Furthermore, the optimum atom percent of Ti for the sputtered Ti-Hastelloy C[®] glassy alloy coatings with respect to the desired corrosion-resistance characteristics was determined.

EXPERIMENTAL

The corrosion specimen was a rectangular piece of glassy Ti-Hastelloy C[®] alloy coating that had been sputter-deposited onto a copper substrate. This rectangular specimen was 6.9 cm x 1.15 cm. It was cut from the center to the

edge of an eight-inch diameter deposit. The composition of the glassy alloy coating was varied so that Ti content was highest at the center and decreased towards the outer edge of the deposit. This composition gradient permitted study of the corrosion behavior as a function of alloy composition. This was done by measuring corrosion rates at various locations along the specimen and comparing the effect of Ti concentration on the corrosion resistance. Corrosion behavior for pure Ti and a wrought Hastelloy C[®] specimen was studied for comparison to that of the glassy alloy coating.

A metal rod was attached to hold the specimen in the test solution and to act as a current lead. The specimen surface was polished with 600 grit paper and cleaned with reagent grade methyl alcohol. The surface of the specimen was covered with transparent tape punched with seven circular holes to expose an area of 0.79 cm^2 for each hole. The tape was then smoothed down carefully to remove all the air bubbles to prevent leaking. A plastic sealer was painted on the copper and at the edges of the transparent tape to ensure that the copper was not exposed to solution and that the tape remained water tight. Only one of the holes was exposed to the solution for each test and the rest were covered with a paper circle covered with tape (see Figure 1). The test samples were labeled 54, 44, 38, 27, 18, 5, and 3; each number corresponds to the atom percent Ti of the sample.

The electrochemical cell used in corrosion measurements consisted of a one liter, five neck flask; 500 ml 1 N HCl solution; two graphite counter electrodes; a calomel reference electrode; and the specimen (as shown in Figure 2). The solution was sparged with argon before measurements to eliminate any effects from dissolved oxygen.

An EG&G PARC Model 350 Corrosion Measurement Console (see Figure 3) was used to measure galvanic corrosion, Tafel Plot, and potentiodynamic polarization.

The console was prepared to plot open-circuit voltage (vertical) versus time (horizontal) up to 10,000 sec. The potential initially becomes more positive or more negative rapidly, indicating surface passivation and oxidation is taking place. As the potential gradually stabilizes it yields an almost horizontal line from which the corrosion potential, E_{corr} , was obtained.

FIGURE 1. Sputtered Ti-Hastelloy C[®]
Glassy Alloy Specimen With
Rod Attached.

FIGURE 2. (a) EG&G Princeton Model K47 Cell Taken From Corrosion Cell System Manual; (b) Assembled Cell Used in Experiments.

FIGURE 3. Corrosion Measurement Console,
EG&G PARC, Model 350.

The corrosion potential can be used to determine the exchange current density, I_{corr} , from the Tafel Plot.

The Tafel plot is used to determine the exchange current density for determining the corrosion rate at open circuit potential. A varying potential is applied to the sample at a rate of 0.1 mV/sec and the current is recorded at user-specified intervals. The potentials applied are between 0.25 volts below E_{corr} and 0.25 volts above the E_{corr} of the sample. The console then plots this data, the voltage (vertical) versus current density (horizontal logarithmic), on a semilogarithmic paper. The curves show a cathodic region and an anodic region between the 0.25 volts below E_{corr} and the 0.25 volts above E_{corr} . The slopes of the cathodic curve and the anodic curve are then drawn if the length of the curve allows. Sometimes E_{corr} is

not centered between the curves and the cathodic or anodic curve is less than 0.25 units vertically. When this happens the slope is estimated and drawn in manually. Where these slope lines intersect the horizontal line, $y = E_{\text{corr}}$ is I_{corr} . The corrosion rate, C.R., can be calculated as follows:

$$\text{C.R. (mmpy)} = \frac{(0.13)(10^{-3})(I_{\text{corr}})(\text{E.W.})}{d}$$

where the corrosion rate, C.R., is in millimeters per year; I_{corr} is the current density of corrosion as determined from the graph; E.W. is the equivalent weight of the sample; and d is the density of the sample in g/cm^3 .⁽²⁾ The console will automatically calculate the corrosion rate when given the equivalent weight and density of the sample when the slopes of the cathodic and anodic curves (related to I_{corr}) are found by the console. If not, the corrosion rate must be calculated manually.

The densities for the glassy alloy deposit at various compositions were approximated from linear extrapolation between the density of Ti⁽³⁾ and the density of Hastelloy C^{®(3)} (Figure 4). The equivalent weights were also approximated from linear extrapolation of the equivalent weights of Ti and Hastelloy C[®] (Figure 5). The equivalent weight for Ti was calculated by dividing the atomic weight, 47.90 g/mole, by the number of equivalents/mole. Since the equivalents/mole of Ti can be either 3 and/or 4, both of these values were used in the calculation and the average taken. The equivalent weight for Hastelloy C[®] was calculated in the same way.

Table 1 shows the atom percent of Ti and respective densities, and equivalent weights of the samples for each sample.

The Potentiodynamic Polarization procedure was used for comparison of the corrosion and passivation characteristics of the glassy alloy coating at various compositions. A positive potential is applied to the sample at a rate, due to machine restrictions, of 1.001 mV/sec starting at a point near E_{corr} , and the current is recorded. The sample begins to corrode as can be seen by the increased current. As it corrodes there is normally an increase in corrosion rate until a passive oxide layer has started to build up. Once this happens, the current will remain relatively constant as the voltage is

*¹Taken from Metals Handbook, 8th Edition, Volume 1, "Properties and Selection," ASM.

*Taken from Lange's Handbook of Chemistry, p. 106.

FIGURE 4. Estimated Density for the Glassy Ti-Hastelloy C[®] Alloys.

* $\frac{\text{atom weight}}{n} = \frac{47.90}{3} \text{ averaged } \frac{47.90}{4}$

where n is number of equivalents

FIGURE 5. Estimated Equivalent Weight for the Glassy Ti-Hastelloy C[®] Alloys.

TABLE 1. Composition of the Glassy Ti-Hastelloy C[®] Alloys
Determined From the Elemental Analysis

<u>Sample</u>	<u>Ti, at.%</u>	<u>d (g/cm³)</u>	<u>E.W.</u>
54	53.85	6.51	18.92
44	44.00	6.95	20.40
38	38.07	7.25	21.29
27	27.01	7.75	22.95
18	18.39	8.05	24.25
5	4.50	8.75	26.34
3	3.14	8.80	26.55
0	0.00	8.94	27.02
100	99.99	4.50	11.98

increased further. This is due to chromium passivation in the glassy alloys and titanium passivation in the Ti sample. The console then plots the data as voltage (vertical) and current density (horizontal). The more constant the current remains, the closer the slope of the curve is to infinity--which indicates the sample has a high corrosion resistance.

RESULTS AND DISCUSSION

From the potential versus time plot (Figure 6) it can be seen that the values of E_{corr} for the samples of Ti-Hastelloy C[®] glassy alloys fall in the range from 0.15 to 0.24 volts. The curves for the sputtered glassy alloy coating samples and the curve for pure Ti all have basically the same shape. The curve for Sample 54, 53.85 at.% Ti, shows a sharp initial decrease in potential, but this is believed to be due to the copper substrate being accidentally exposed to solution during the experiment. Unfortunately, this potential versus time curve is the best data that could be acquired for Sample 54 because of the difficulty involved in testing the sample due to its position on the specimen. The curve for wrought Hastelloy C[®] is different from the others in the sense that it starts at a much lower potential of -0.08 volts, while the other curves begin at +0.06 volts. Also, the increase in potential to E_{corr} is more gradual than the slopes of the other samples.

FIGURE 6. Plot of E_{corr} Versus Time in 1 N HCl Solution

This indicates that the surface oxidation rate for wrought Hastelloy C[®] is slower than that for the glassy Ti-Hastelloy samples and Ti.

Samples 5 and 3 with 4.50 and 3.14 at.% Ti, respectively, behave much like the glassy alloy coating samples although they are crystalline with small grains.

The corrosion rates at open circuit potential, E_{corr} , for the pure Ti, wrought Hastelloy C[®], and the sputtered glassy alloy coating samples were calculated from the Tafel Plots (Figure 7). The values found were very small, near 0.001 mmpy (Table 2).

The passivation region for pure Ti was the largest, ranging from 0.6 up to approximately 4.0 volts (not shown on Figure 8). This passivation region is due to Ti passivation, whereas the sputtered glassy alloy coatings of Ti content less than 27 at.% (Samples 3, 5, 18, and 27) and the wrought Hastelloy C[®] all exhibited passivation in one relatively short region between 0.24 and 0.90 volts due to chromium (Cr) passivation. However, the sputtered Ti-Hastelloy C[®] glassy alloy coatings with 38, 44, and 54 at.% Ti exhibited two passivation regions. The first of these, from 0.24 to 0.90 volts, was attributed to Cr passivation.⁽¹⁾ From 0.95 to 1.10 volts, the voltage increased much more slowly as the current density continued to increase. In this region the Cr-passivation layer begins to break down. The region following this breakdown is the Ti-passivation region that ranges from 1.10 to 1.42 volts for 38 at.% Ti, and 1.10 to 1.35 volts for 44 and 54 at.% Ti.

All the samples had similar current densities of passivation, I_p , ranging from approximately 2×10^2 nA/cm² to 8×10^3 nA/cm² in the Cr-passivation region from 0.20 to 0.90 volts. Beyond this region only the pure Ti sample displayed a fairly constant current density as the potential increased. The potentials of the samples with less than 27 at.% Ti increased at a much slower rate causing the curve to become more horizontal as the slope approached zero, signaling the breakdown of the Cr-passivation layer. Samples 54, 44, and 38 with 54, 44, and 38 at.% Ti, respectively, also experienced the Cr-passivation layer breakdown, but for these samples the breakdown was apparently offset by the buildup of a Ti-passivation layer. Because of the Cr-passivation layer breakdown, the current density increased; therefore, the current density of the following Ti-passivation region was greater than that

FIGURE 7. Tafel Plots for the Glassy Titanium-Hastelloy C[®] Alloys in 1 N HCl Solution.

TABLE 2. Observed E_{corr} , I_{corr} and Calculated Corrosion Rate From Tafel Plots.

<u>Sample Number</u>	<u>Ti, at.%</u>	<u>E_{corr} (Volts)</u>	<u>I_{corr} (nA/cm²)</u>	<u>Corrosion Rate (mmpy)</u>
0	0.00	0.214	130.00	0.001
3	3.14	0.217	38.47	<0.001
5	4.50	0.202	97.24	0.001
18	18.39	0.193	72.75	0.001
27	27.01	0.179	78.00	0.001
38	38.07	0.195	47.87	0.001
44	44.00	0.148	11.52	0.001
54	53.85	0.161	10.79	0.001
100	99.99	0.240	620.00	0.001

FIGURE 8. Potentiodynamic Polarization Curves of Glassy Ti-Hastelloy C® Alloys in 1 N HCl Solution.

observed for pure Ti. Where the pure Ti sample had a current density of passivation, I_p , of 9×10^3 nA/cm², Samples 54, 44, and 38 had current densities of 3.5×10^4 , 4×10^4 , and 5×10^5 nA/cm², respectively.

The Ti-Hastelloy C[®] behaved similarly to the W-304L glassy coatings in that both glassy alloys exhibited two passivation regions, Cr passivation at low potentials and either Ti or W passivation at higher potentials.

In order to compare the corrosion-resistance characteristics in relation to the Ti and W concentrations in the glassy alloys, a curve was drawn of the atom percent of Ti versus the current density taken from the potentiodynamic polarization curves at a constant potential of 1.13 volts where Ti passivation begins (Figure 9); a similar curve was drawn for W (Figure 10). Comparing these curves it can be seen that the current densities decrease as the amount of Ti or W is increased, indicating an improvement in corrosion-resistance characteristics. The curve of current density gradually slopes downward until 27 at.% Ti is reached. As the atom percent of Ti was further increased, the curve sloped downward sharply until 44 at.% Ti was reached where the curve again became more horizontal, indicating a gradual decrease in current density. This showed that 44 at.% Ti was the optimum percentage of Ti for the occurrence of Ti passivation. An increase in the atom percent of Ti past this point did not further improve the corrosion-resistance characteristics of the material significantly. On the other hand, the graph of the atom percent of W versus current density is linear, which indicates that no optimum atom percent of W exists--at least between the values of 10 at.% W and 52 at.% W. For every increase in the atom percent of W there will be a proportional improvement in the material's corrosion-resistance characteristics.

CONCLUSIONS

1. Excellent corrosion-resistance characteristics were displayed by sputtered Ti-Hastelloy C[®] glassy alloy coatings; no pitting occurred, and the corrosion rates were very low--0.001 mmpy.
2. The corrosion resistance of sputtered Ti-Hastelloy C[®] glassy alloy coatings of less than 27 at.% Ti were characterized by a single long passivation region due to Cr passivation. The improved corrosion resistance of sputtered Ti-Hastelloy C[®] glassy alloy coatings of greater

FIGURE 9. Plot of the Current Density at 1.130V as a Function of Ti Composition in 1 N HCl Solution.

FIGURE 10. Plot of the Current Density As It Relates to the Atom Percent of W of the Glassy W-Stainless Steel Alloy in 1 N NaCl Solution at 1.130 V.

than 38 at.% Ti were characterized by two passivation regions, the first and longer one being from 0.24 to 0.90 volts due to Cr passivation, and the second being from approximately 1.10 to 1.42 volts (this varies according to the composition of the material) due to Ti passivation.

3. An optimum percentage of Ti, meaning the smallest amount of Ti that gives passive behavior similar to pure Ti-like passivity, for the sputtered Ti-Hastelloy C[®] glassy alloy coating was 44 at.% Ti. At this Ti concentration, the improvement in corrosion-resistance characteristics was maximized and was not improved greatly by adding more titanium.
4. Similarities were seen between the corrosion-resistance characteristics of sputtered Ti-Hastelloy C[®] glassy alloy coatings with sputtered and heat-treated W-304 SS glassy alloy. Both materials showed two regions of passivation. The corrosion-resistance characteristics improved with an increase in the atom percent of Ti or W, respectively. However, one difference was that an optimum Ti content was found. In contrast, the corrosion-resistance characteristics of W-SS 304 improved proportionately as W content was increased--at least between 10 at.% W and 52 at.% W. No limiting concentration value with respect to optimum performance was found for tungsten.

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