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Formation of Corrosion Resistant Amorphous Ti-B Alloys[†]

Masaaki Naka* and Tetsuya Okada**

Abstract

Corrosion resistant amorphous Ti-B films were prepared on various substrates by RF sputtering. The alloying of B at a content of 8 at% or more stabilizes the amorphous structure. The corrosion properties of the Ti alloys were evaluated by measuring the polarization curves in 1N HCl. Although the addition of B to crystalline bulky Ti shifts the corrosion potentials of Ti to the less noble values of -0.5 V(SCE) or less, that of B to amorphous sputtered Ti moves the corrosion potentials to the noble side of +0.3 V(SCE). The current densities of amorphous Ti-B alloys at 0.1V(SCE) of the passive state are lower than that of the crystalline bulky alloys.

KEY WORDS: (Amorphous Alloys) (Sputtering) (Titanium) (Boron) (Corrosion Resistance)

1. Introduction

The application of materials in new engineering fields needs alloys of greater corrosion resistance. New corrosion resistant alloys have been developed by two methods, namely the alloying of large amounts of corrosion resistant elements such as chromium, and the purifying of corrosion resistant alloys. We have now a third method to improve the corrosion resistance of alloys. Amorphization from the crystalline structure of alloys gives them high corrosion resistance since amorphous alloys have no defects such as precipitates and crystalline boundaries which are initiation points for corrosion¹⁾.

Naka et al.²⁻⁴⁾ reported that amorphous stainless iron, cobalt and nickel alloys showed high corrosion resistance. Titanium is also another candidate material for corrosion resistant alloys. Amorphous titanium alloys containing P as a glass forming element which were produced from the liquid state exhibited high corrosion resistance⁵⁾.

Amorphous alloys were so far prepared by rapidly quenching molten alloys on a rotating copper wheel to obtain high cooling rates. The high cooling rate prevents the nucleation of crystals from liquids. Vapor quenching also provides an easy process for making amorphous alloys and coating them on various substrates⁶⁾.

This paper tries to improve the corrosion resistance of titanium by amorphizing using the alloying element of B as a glass forming element in the sputtering process, and examines the corrosion properties of amorphous Ti-B alloys.

2. Experimental Procedure

The RF magnetron sputtering technique was used to prepare amorphous alloys in low pressure argon gas of 6.65 MPa.

Targets used were 100 mm in diameter and 5 mm thick and were composed of Ti and B. The substrates of aluminum were water cooled.

The main sputtering conditions were a sputtering power and time of 600 W and 14.4 ks, respectively. The film thickness of the alloys prepared was 20 μm . The structure of sputtered films was investigated by x-ray diffractometry.

The corrosion behavior of the films was evaluated by measuring polarization curves in 1N HCl with a potential sweep rate of $2.5 \times 10^{-3} \text{ Vs}^{-1}$ in 1N HCl.

3. Results and Discussion

Figs. 1 and 2 show the x-ray diffraction patterns of sputtered Ti-B alloys. The structures of alloys of No. 1 (0 at% B) and No. 2 (2.9 at% B) are hcp crystalline phase. The Ti-B alloys containing B content from 8 at% to 51 at% B which show only a few diffuse diffraction peaks are amorphous.

By adding B content of 51 at% or more the Ti-B alloys become crystalline phases composed of Ti_3B_4 and TiB_2 . The glass forming range of Ti-B is presented in the Ti-B phase diagram in **Fig. 3**. The addition of B to Ti produces Ti-B alloys with a wide range of B contents. It is known that alloys showing a deep suppression of liquidus temperature in eutectic reactions become easily

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amorphous. The melting points of Ti-B alloys definitely are suppressed by adding B. This may imply that the amorphous structures of Ti-B alloys are also stabilized by mixing B to Ti. The amorphous Ti base alloys containing P were prepared by a liquid quenching technique. Although the liquid quenching process restricts the composition range of amorphous alloys and the size of the alloys in ribbon type tape, the vapor quenching process

provides the wide composition range of amorphous alloys and also the coated films on various substrates. The corrosion behavior of sputtered Ti-B alloys were investigated by measuring polarization curves of the alloys in aerated 1N HCl. Fig. 4 shows the polarization curves of sputtered crystalline Ti-B alloys containing B content of 0 to 2.91at% in 1N HCl. Though the crystalline pure Ti is passivated at potentials between 0 and +0.5 V(SCE), it actively dissolves at potentials of +0.5 V(SCE) or more. The sputtered Ti-B alloys with 2.91at% B and 5.18at% B are also passivated, but they shows less noble corrosion potential than 0 V(SCE). The polarization curves of amorphous Ti-B alloys containing B content of 12.67 at% B to 16.20 at% B are shown in Fig. 4. The corrosion potentials of Ti-B alloys are shifted from -0.3 V(SCE) of 5.18 at% B to +0.4 V(SCE) with increasing B content. The amount of boron

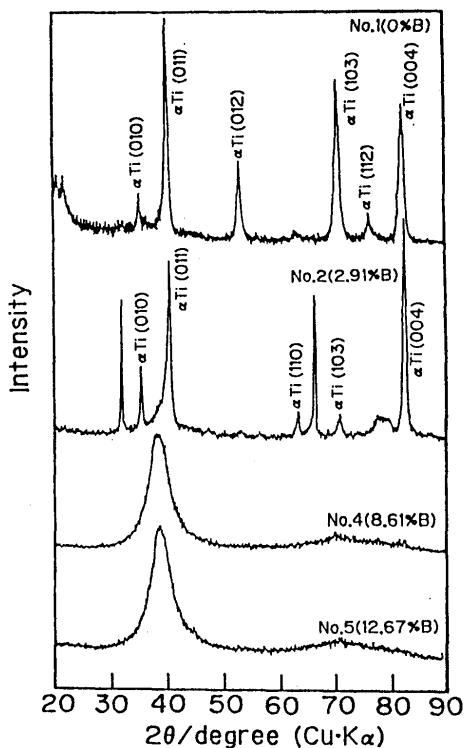


Fig. 1 X-ray diffraction patterns of sputtered Ti-B alloys.

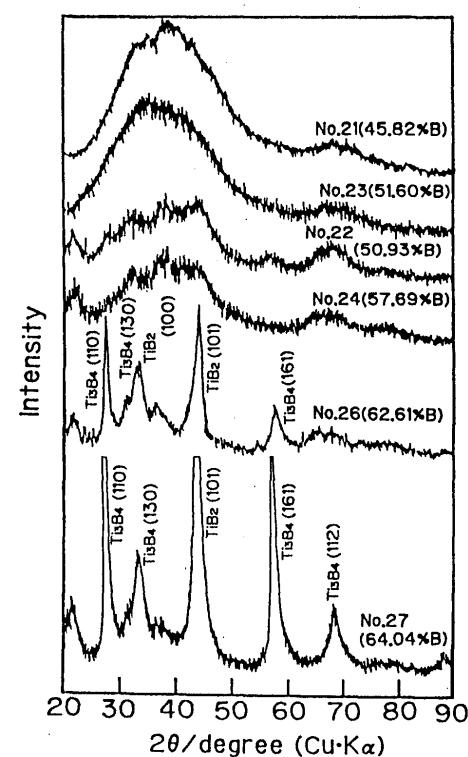


Fig. 2 X-ray diffraction pattern of sputtered Ti-B alloys.

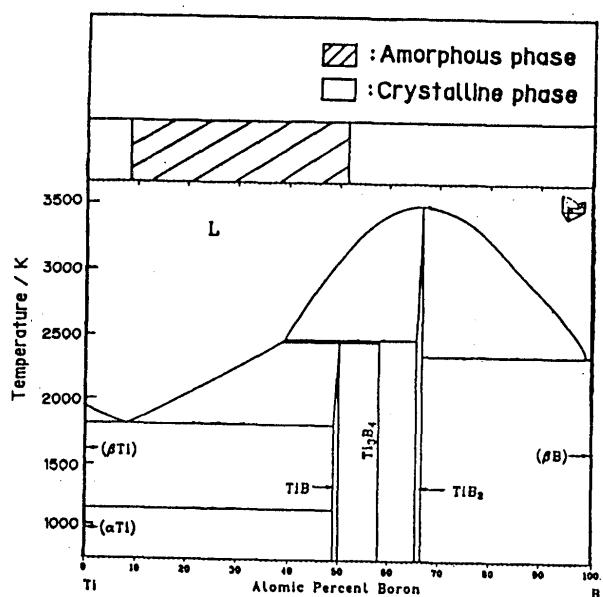


Fig. 3 Glass forming range of Ti-B alloys.

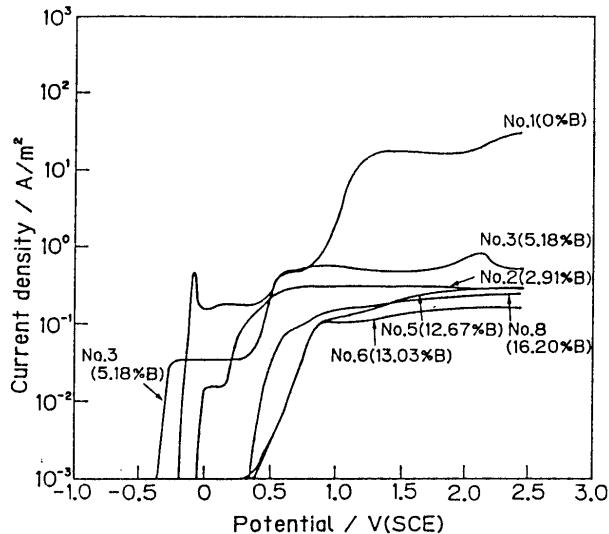


Fig. 4 Polarization curves of sputtered crystalline and amorphous Ti-B alloys in 1N HCl.

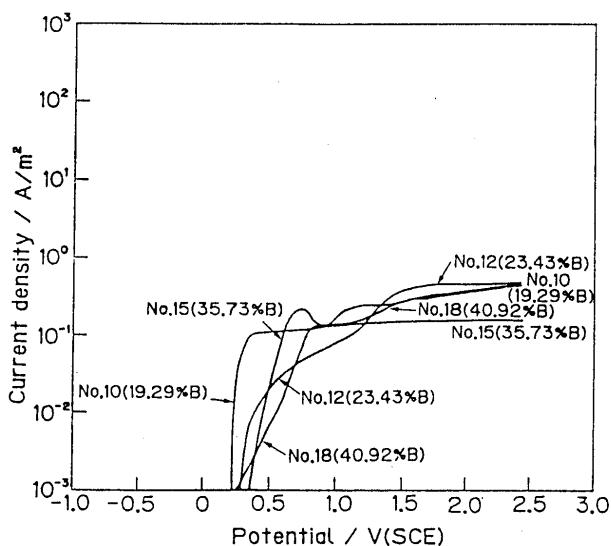


Fig. 5 Polarization curves of Ti-B amorphous alloys in 1N HCl.

hydroxide on the alloy surface at the natural immersion state in 1N HCl may increase with increasing B content in Ti-B amorphous alloys. Amorphous Ti-B amorphous alloys are spontaneously passivated in 1N HCl. The current densities at the passive state of +0.5 V(SCE) or more for Ti-B amorphous alloys are definitely lower than that of sputtered pure Ti. This means that the amorphization of Ti-B alloys improves the corrosion resistance of Ti, particularly in more positive potentials.

Fig. 5 shows the polarization curves of Ti-B amorphous alloys containing B content of 19.29 at% B to 40.92 at% B. All amorphous alloys are spontaneously passivated by immersion in 1N HCl. The corrosion potentials of the Ti-B amorphous alloys are around +0.3 V(SCE).

The current densities in the passive state for the Ti-B amorphous alloys are the same value of about 10^{-1} A/m². After passivation the surface properties are the same in Ti-B amorphous alloys. Compared with crystalline pure Ti, the surface of the Ti-B amorphous alloys are very homogeneous and corrosion resistant. The amorphous Ti-B alloys have no defects such as precipitates and crystalline boundaries which operate as corrosion initiation sites.

Fig. 6 shows the polarization curves of amorphous Ti-B alloys with 45.8 at% B and 51.6 at% B and crystalline Ti-B alloys with 50.9 at% B and 64.0 at% B in 1N HCl. The amorphous Ti-B alloys containing high B content which are spontaneously passivated show lower current densities in the passive state. On the other hand, the crystalline Ti-B alloys containing high B content which

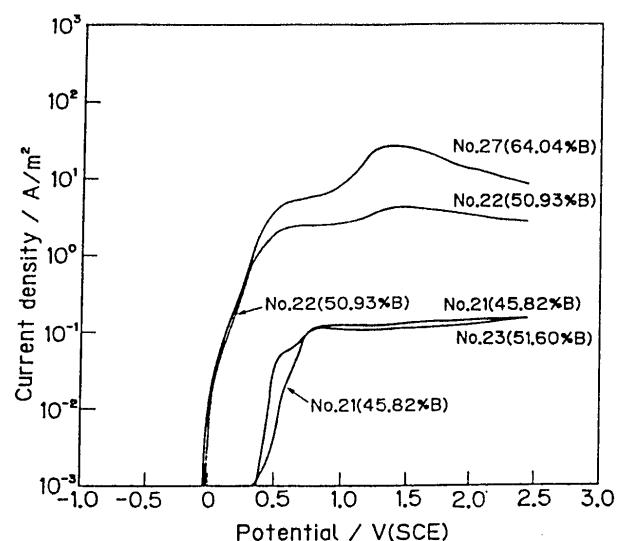


Fig. 6 Anodic polarization curves of Ti-B amorphous alloys in 1N HCl.

are not passivated, actively dissolve with increasing potential.

The sputtered Ti-B alloys become crystalline by the addition of large amounts of boron of 51 at% or more, since the alloys have crystalline borides of Ti_3B_4 and TiB_2 . The crystalline defects such as crystalline boundaries in the borides work as corrosion sites.

In order to make clear the role of amorphization of Ti-B alloys in corrosion behavior, the corrosion potentials of Ti-B sputtered alloys are plotted against B content in the alloys as shown in Fig. 7. The corrosion potentials of sputtered crystalline Ti-B alloys with small amounts of B content including pure Ti are around -0.3 V(SCE), and the potentials of crystalline Ti-B alloys with large amounts of B content are around 0 V(SCE). On the other hand, the Ti-B amorphous alloys containing B content from 12.67 at% to 51.6 at% show higher corrosion potentials of +0.3 to +0.4 V(SCE). The amorphization of structure causes a shift of corrosion potentials of Ti-B alloys from 0 V(SCE) to nobler side of +0.3 V(SCE) or more. The corrosion potentials of the bulky crystalline Ti-B alloys including pure crystalline Ti are also included in Fig. 7. The corrosion potential of pure Ti does not change by sputtering, but the corrosion potentials of bulky crystalline Ti-B alloys are less noble, compared with sputtered crystalline Ti-B alloys.

The crystalline bulky Ti-B alloys including TiB_2 are corrosive in 1N HCl, since the corrosion potentials of the alloys are around -0.5 V(SCE). The passive current

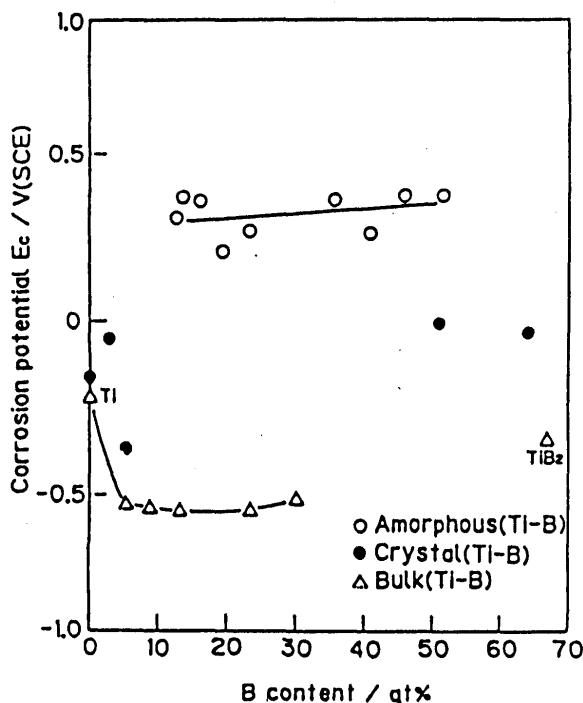


Fig. 7 Compositional dependence of corrosion potential for Ti-B amorphous alloys, Ti-B crystalline alloys and Ti-B bulky alloys.

densities of sputtered Ti-B alloys at +0.1 V(SCE) are plotted in Fig. 8. The values of crystalline Ti-B bulky alloys are included in the figure. The passive current density of sputtered pure Ti is higher than that of crystalline Ti. This occurs because the micro crystalline film has the micro-defects as corrosion initiation sites. The passive current densities of sputtered crystalline Ti-B alloys show a minimum around a B content of 10 at%, and increase sharply with increasing B content. On the other hand, the passive current densities of amorphous Ti-B with B content from 15 at% to 51 at% is about 10^{-1} A/m², and one or two order of magnitude lower than that of the crystalline Ti-B alloys. Though the current densities of crystalline Ti-B bulky alloys are lower than those of crystalline Ti-B sputtered alloys, the values of the bulky alloys are larger than those of the amorphous alloys.

Amorphous Ti-B alloys are chemically homogeneous, and have no crystalline defects such as precipitates and grain boundaries which will operate as corrosion sites in corrosive solutions. This is attributable to that the amorphous Ti-B alloys show more noble corrosion potentials and lower passive current densities than those of crystalline sputtered or bulky Ti-B alloys.

These results indicate that the amorphization of Ti-B alloys definitely improve the corrosion resistance of the alloys.

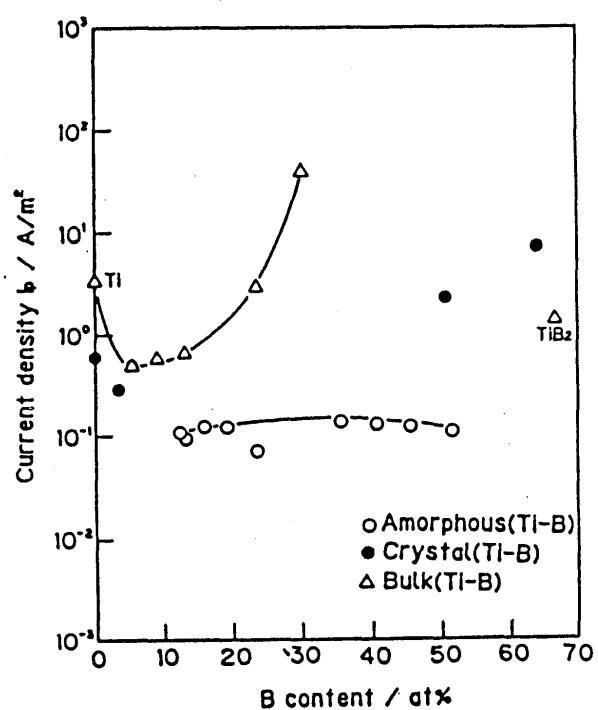


Fig. 8 Compositional dependence of passive current densities for Ti-B amorphous alloys, Ti-B crystalline alloys and Ti-B bulky alloys.

4. Conclusions

The Ti-B binary alloys were prepared by argon sputtering. The structure and corrosion properties were investigated by x-ray diffraction and polarization methods.

Ti-B amorphous alloys containing B content of 8 at% B to 52 at% B were amorphous. Amorphization of Ti-B alloys shifts the corrosion potentials from -0.5 V(SCE) of crystalline bulky Ti-B alloys to +0.3 V(SCE), and reduces the passive current densities of 10^0 - 10^2 A/m² at +1.0 V(SCE) for crystalline bulky Ti-B alloys to 10^{-1} A/m² for Ti-B amorphous alloys.

The amorphous Ti-B alloys exhibit high corrosion resistance. The amorphization of the alloys definitely improves the corrosion resistance. The amorphization makes the alloys chemically homogeneous, and the amorphous alloys have no crystalline defects such as

precipitates and crystalline boundaries. These factors clearly improve the Ti-B alloys.

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