DOE/ARC-02-011

Corrosion of Titanium Matrix Composites

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Abstract

The corrosion behavior of unalloyed Ti and titanium matrix composites containing up to 20 vol% of TiC or TiB_2 was determined in deaerated 2 wt% HCl at 50, 70, and 90°C. Corrosion rates were calculated from corrosion currents determined by extrapolation of the tafel slopes. All curves exhibited active-passive behavior but no transpassive region. Corrosion rates for Ti + TiC composites were similar to those for unalloyed Ti except at 90°C where the composites were slightly higher. Corrosion rates for Ti + TiB_2 composites were generally higher than those for unalloyed Ti and increased with higher concentrations of TiB_2. XRD and SEM-EDS analyses showed that the TiC reinforcement did not react with the Ti matrix during fabrication while the TiB_2 reacted to form a TiB phase.

Keywords: titanium, composite, particulate, titanium carbide, titanium diboride

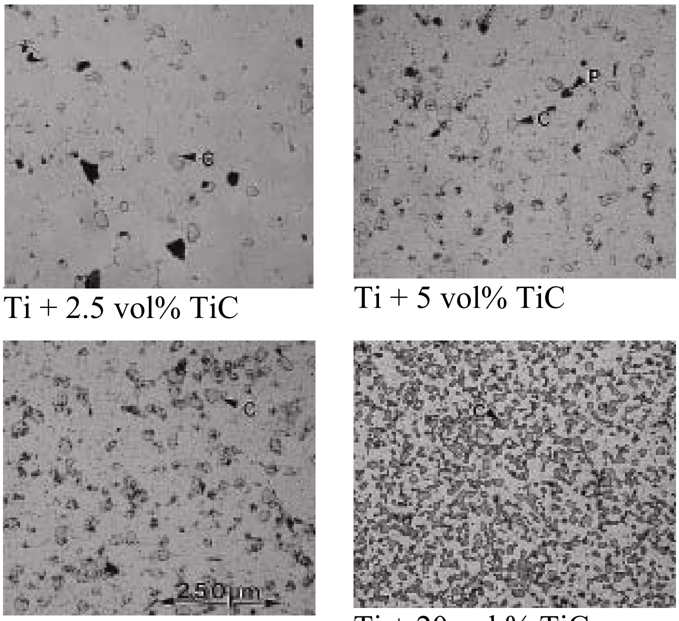
Introduction

Titanium and its alloys have low density and high strength, stiffness, and creep and corrosion resistance. Titanium-based composites have current applications in non-aerospace applications such as industrial, automotive, and consumer [1-5]. Some areas of use for titanium based alloys and composites are steam turbine blades, coal transport systems, automotive springs, valve spring retainers and valves, and consumer eyeglass frames, cooking ware, and bicycles. Particulate-reinforced titanium matrix composites are being considered for wear resistant (gears, bearings, shafts), erosion and corrosion resistant (tubing), and creep resistant (engine) applications [5].

The purpose of this paper is to determine the effect of different particulate reinforcements (TiC and TiB_2) at several concentrations affect the corrosion behavior of titanium matrix composites. The wear behavior of those composites has been published elsewhere [6] and shown to correlate well with particulate concentration and microhardness. That is, as the particulate concentration increases, the microhardness increases and the wear rates decrease. Ti + TiB_2 composites had lower wear rates than Ti + TiC composites in similar environments. While the wear properties have been well characterized, however, little is known about their corrosion properties. Research presented here will report the effect of a reducing acid (deaerated 2 wt% HCl) at several temperatures on the corrosion of all constituents of the composite.

Experimental

Titanium powder was dry blended with 0, 2.5, 5, 10, and 20 volume percent (vol%) TiC or TiB_2. All powders were commercially available and were –325 mesh (-44 :m in size). Blending of the powders was accomplished in glass jars using a turbula type mill. Rectangular, green composite powder billets (approximately 19 mm X 19 mm X 254 mm)



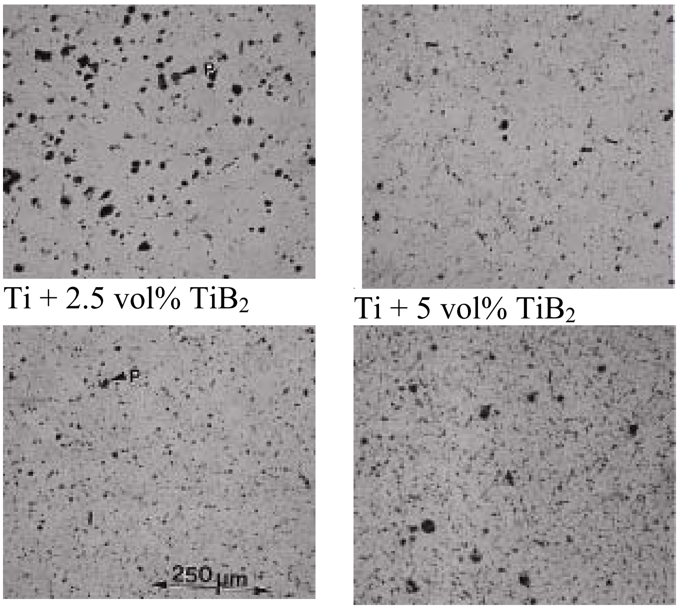
Ti + 2.5 vol% TiC

Ti + 5 vol% TiC

Ti + 10 vol% TiC

Ti + 20 vol % TiC

Fig. 1: Low magnification (100X) optical micrographs of the microstructure of sintered Ti-TiCcomposites. C = TiC, P = pore.



Ti + 2.5 vol% TiB_2

Ti + 5 vol% TiB_2

Ti + 10 vol% TiB_2

Ti + 20 vol % TiB_2

Fig. 2: Low magnification (100X) optical micrographs of the microstructure of Ti-TiB_2 composites. P = pore.

were produced by cold isostatic pressing (CIPing). Roughly 275 g of mixed powder was placed in polyurethane mold bags and CIPed at 275 MPa pressure. The green composite billets were consolidated by sintering in vacuum (X 10^{-4} Torr) at 1400^{o}C. The heating rate was 10^{o}C/min and after 2 h at the sintering temperature, the specimens were furnace cooled.

The densities of the composites were measured by the Archimedes (water immersion) method. These densities were compared to the theoretical density, calculated using the volumetric rule of mixtures (ROM), in order to determine the residual porosity (100-theortical ROM density) present after sintering. Theoretical densities for the sintered Ti and composites was calculated using the following densities: Ti = 4.55 g/cm^3, TiC = 4.93 g/cm^3, and TiB_2 = 4.5 g/cm^3. Calculations were made assuming no significant reaction between the reinforcement and the matrix (which was not correct for the Ti-TiB_2 composites. The microstructures were evaluated by optical and scanning electron microscopy (SEM) in both secondary and backscattered imaging modes. The phases present after sintering were determined by X-ray diffraction (XRD) and SEM using energy dispersive spectroscopy (EDS). Vickers' microhardness was obtained on the composites. For composites that contained porosity, the Vickers' indentations were made away from pores in pore-dense regions.

Corrosion experiments were conducted in deaerated 2 wt% HCl at 50, 70, and 90^{o}C. This test environment was chosen to provide a mildly corrosive environment in which the Ti was susceptible to attack. The solution was deaerated in order to maintain reducing conditions that favor dissolution of the passive film on Ti.

Table 1: Density and hardness of pressed and sintered Ti and Ti-matrix composites

Composite	Density		Hardness
	g/cm^3	% theoretical	Vickers
Ti	4.45	99.1	297
Ti + 2.5 vol% TiC	4.02	89.1	245
Ti + 5 vol% TiC	4.26	94.2	296
Ti + 10 vol% TiC	4.26	93.8	304
Ti + 20 vol% TiC	4.40	96.0	354
Ti + 2.5 vol% TiB_2	4.00	88.8	265
Ti + 5 vol% TiB_2	4.20	93.3	234
Ti + 10 vol% TiB_2	4.32	96.0	413
Ti + 20 vol% TiB_2	4.44	98.8	610

Small pieces of the composites were mounted in epoxy and then exposed in a modified flat cell. Deaerated and heated solution was continuously pumped from a 2 L reservoir through the flat cell and returned. The solution being pumped into the flat cell was directed at the exposed area of the sample in order to promote stirring of the solution near the working electrode and eliminate diffusion-controlled conditions.

The corrosion behavior of the composites was determined using the potentiodynamic polarization technique. Polarization scans were initiated at 300 mV more negative than the measured open circuit corrosion potential and stopped at approximately 2 V versus the saturated calomel electrode (S.C.E.). Corrosion currents were determined by the intersection of the extrapolated Tafel regions at the corrosion potential.

Results and Discussion

Microstructure

The microstructures of the sintered Ti + TiC and Ti + TiB_2 are shown in Fig. 1 and Fig. 2, respectively. These photomicrographs show the presence of matrix, reinforcement phase, and porosity. The measured and theoretical densities and hardness of the composites are given in Table 1. The Ti + TiC composites consisted of discrete or individual TiC particles within the Ti matrix, Fig. 1 [6]. XRD and SEM-EDS analyses confirmed that there was no reaction between the TiC and the Ti matrix, Fig. 1. The Ti + TiB_2 composites consisted of boride needles or platelets in the Ti matrix [6]. XRD analyses showed however that in addition to Ti and TiB_2, these composites contained the reaction product TiB. Even though there was a reaction between Ti and TiB_2 particles on sintering, the measured porosity (based on the theoretical densities) correlated well with microstructural observations because TiB has a theoretical density of 4.5 g/cm^3 [6].

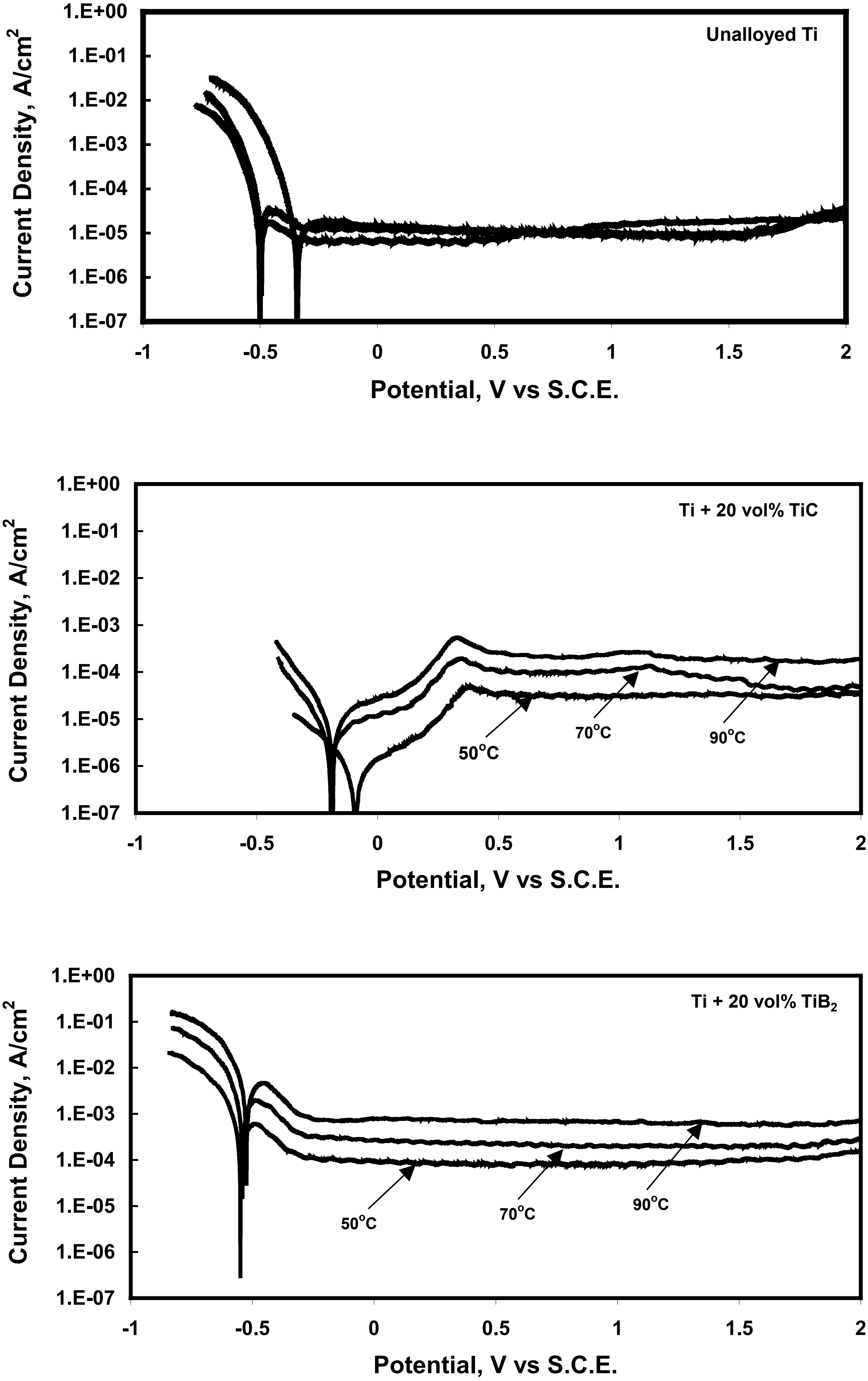


Fig. 3: Potentiodynamic polarization curves as a function of temperature for unalloyed Ti, and Ti + TiC and Ti + TiB_2 composites.

Corrosion Behavior

Potentiodynamic polarization curves were determined for all of the composites at all three temperatures. An example of those for unalloyed Ti, Ti + 20 vol% TiC, and Ti + 20 vol% TiB_2 are shown in Fig. 3. All of the curves show active-passive behavior and no transpassive region. The unalloyed Ti shows very little effect of temperature except for a positive shift in the corrosion potential at 90°C.

Polarization curves for the Ti + TiC composites show increased currents due to higher temperatures and higher particulate concentrations. All curves also show what appears to be a secondary passivation reaction at approximately 0.4 V vs S.C.E. A comparison of these curves to those for unalloyed Ti suggests that the secondary passivation peak may be related to another phase. Since analyses of the composites showed the presence of no other phases except the Ti matrix and the TiC reinforcement, it is most likely due to the corrosion and passivation of TiC. An examination of the polarization curves in Fig. 4 for four Ti + TiC composites tested at 90°C helps support the interpretation that the secondary passivation peak is related to TiC. The maximum current density of this peak increases with reinforcement concentration.

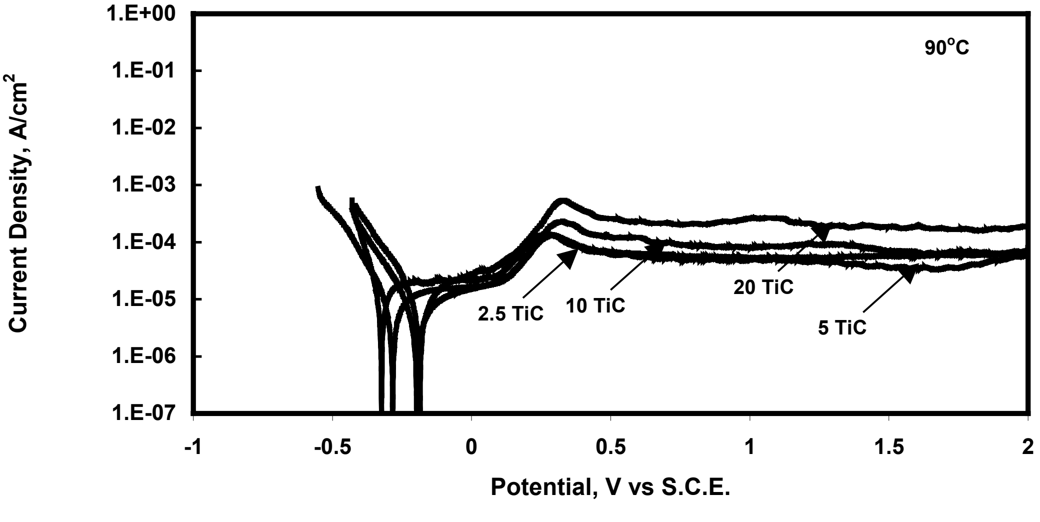


Fig. 4: Effect of composite composition on the potentiodynamic polarization behavior of Ti + TiC composites.

Polarization curves for the Ti + TiB_2 composites also show increased currents for higher temperatures and higher particulate concentrations. The curves for the Ti + TiB_2 composites are, however, very similar to those for unalloyed Ti. The addition of the TiB_2 increased the primary passivation and the passive currents but did not appreciably affect the corrosion potential. This is in contrast to the Ti + TiC composites and suggests that the Ti + TiB_2 composites corrode more rapidly than but in a manner similar to unalloyed Ti. Earlier research [7] on the corrosion of pressed and sintered TiB_2 showed that it did not passivate in deaerated HCl, that the corrosion potential was similar to the –0.5 V vs S.C.E. shown in Fig. 3 for unalloyed Ti and for the Ti + TiB_2 composites, and that current densities in the "passive" region were approximately 1 X 10^{-2} A/cm^2. This helps explain the similarities and the differences between the polarization cures for unalloyed Ti and those for the Ti + TiB_2

composites. It also suggests that the corrosion behavior of the reaction phase, TiB, is similar to both Ti and TiB_2.

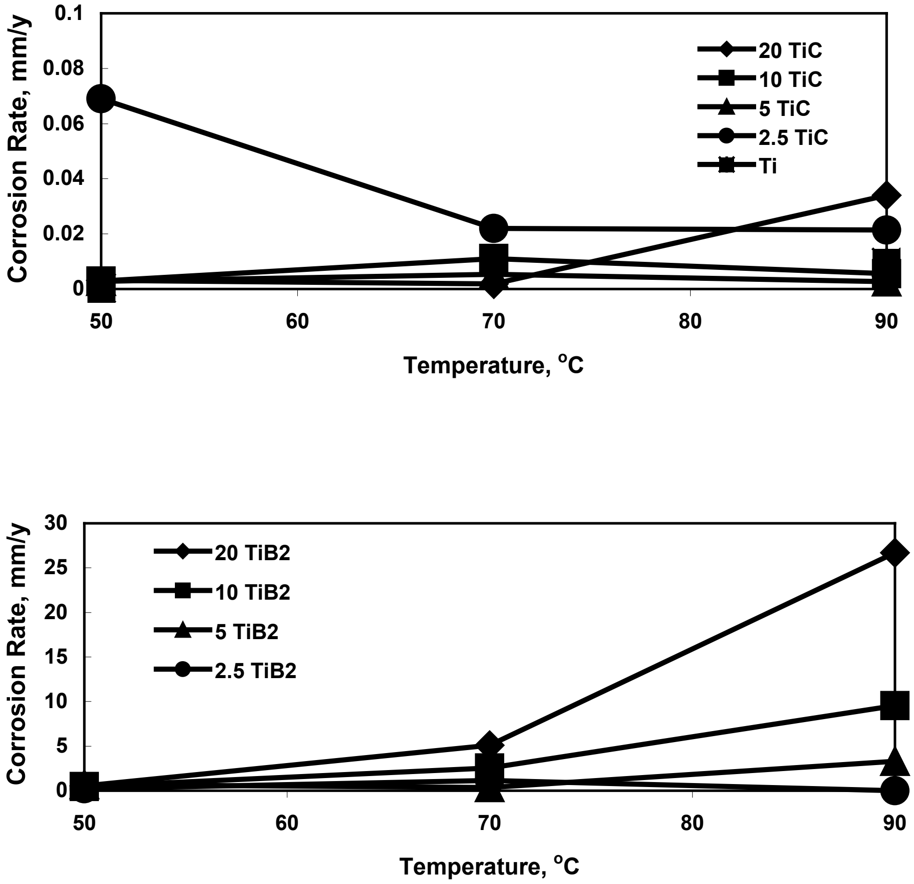
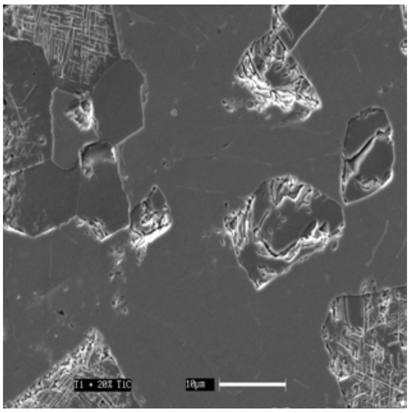


Fig. 5: Effect of particulate concentration and solution temperature on the corrosion rate of Ti + TiC and Ti + TiB_2 composites.

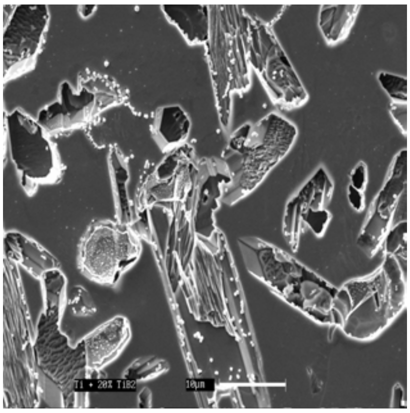
Corrosion rates were calculated from corrosion currents measured from all of the polarization curves. These corrosion rates are plotted as a function of particulate concentration and solution temperature in Fig. 5. TiC has only a minor effect on the corrosion rate of unalloyed Ti. Corrosion rates of three of the four composites at all temperatures are essentially the same. The Ti + 2.5 vol% TiC composite has a corrosion rate-temperature behavior that does not fit the pattern of the other composites. A reason for this as indicated in Table 1, is that the density of this composite is significantly lower than that of the other TiC-containing composites. This indicates a higher degree of porosity. Another factor that may be correlated is that Ti-matrix composites with lower amounts of reinforcement tend to have larger grain sizes than those with larger amounts of reinforcement [6].

Fig. 5 also shows that the corrosion rates of Ti + TiB_2 composites increase with both increasing solution temperature and with increasing amount of reinforcement. TiB_2 and the reaction product TiB have a much greater effect on the corrosion rate of the composite than TiC. Corrosion rates for most of the TiB_2 composites are 1 to 3 orders of magnitude greater than those for the TiC composites tested under identical conditions.

Optical micrographs of the corroded surfaces of composites containing 20 vol% reinforcement are shown in Fig. 6. In both cases there does not appear to be any significant attack of the unaltered Ti matrix areas. There is minor corrosion visible on the surfaces of the TiC reinforcement in the Ti + 20 vol% TiC composite. For the Ti + TiB_2 composite, it is evident that the TiB_2 reinforcement and the TiB-altered matrix surrounding it were heavily corroded.



Ti + 20 vol% TiC



Ti + 20 vol% TiB_2

Fig. 6: Effect of corrosion on the microstructure of composites.

Conclusions

- Ti + TiC composites are significantly more resistant to corrosion in a reducing mineral acid solution than Ti + TiB_2 composites
- Corrosion of the reinforcement occurred to varying degrees in both type of composites.
- The TiC reinforcement produced a secondary passivation peak in the potentiodynamic polarization curve of the Ti + TiC composites.

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