Polarization and Galvanic Studies Of Cobalt-Titania Cermets in Corrosive Environments

By E. P. Rajiv and S.K. Seshadri

Cobalt and cobalt-titania composite coatings were prepared by electrodeposition and sediment-electrocodeposition methods respectively. These coatings were investigated for their corrosion behavior potentiokinetically, both in 3.5-percent sodium chloride solution and 1 N sulfuric acid. The solutions used were not de-aerated. The study showed that as the wt. percent content of titania in the cobalt matrix increases, the corrosion resistance, as well as the passivation, improves in both solutions. To determine the severity of corrosion these coatings cause when coupled with most commonly used structural steels, a zero-resistance ammeter was used to calculate the actual rates of corrosion of steel in such galvanic cells. The composites were found to cause less corrosion of medium carbon steel than cobalt when coupled galvanically in 3.5-percent sodium chloride solution.

Corrosion resistance in a specific environment is an important property to be considered, in addition to mechanical, physical and tribological properties, in determining the usefulness and application range of composites. Composites have an *a priori* advantage over metals in mechanical and tribological applications, and have been widely used in engineering applications, from bearing seats and pistons to aerospace fuselages and engines.[1,2] In industry, where composites are most often used as an anti-wear material, corrosive environments sometimes play an insidious role, impairing wear resistance, (e.g., erosion corrosion and fretting corrosion).

Composites are, in general, either dispersion and particulate- strengthened or fiber-strengthened. These dispersoids or fiber reinforcements do not always ameliorate the corrosion resistance of a matrix metal in a specific environment. There are certain cases where they lead to catastrophic failure of materials. Green and Ahamed[3] have discussed such deterioration in nickel and copper composites reinforced by tungsten and tantalum filaments in a variety of environments, such as nitric acid, hydrofluoric acid, sodium and ammonium hydroxides, and oxalic acid, as a result of the selective attack of the environment on the composites. Mica-dispersion-strengthened aluminum alloys showed the same detrimental effect in sodium chloride solution.[4] In other cases, the dispersoids, such as PTFE, did not significantly improve the corrosion resistance of a matrix metal like nickel.[5] However, there is a range of composites, such as alumina, silicon nitride, etc., which, when dispersed in nickel,[6,7] show a definite improvement in corrosion resistance, compared to the matrix metal alone.

Cobalt and cobalt-composite coatings are well known for their very good anti-wear and frictional properties. The present study is an attempt to understand the corrosion behavior of electrodeposited cobalt and sediment-electro-codeposited cobalt-titania composites in 3.5-percent sodium chloride solution and 1 N sulfuric acid. Because bimetallic contact is likely in engineering applications, the influence of such a contact, namely that of medium carbon steel with cobalt and cobalt-titania composite coatings, has also been studied.

Experimental Procedure

Cobalt and cobalt-titania composite coatings used for corrosion studies were produced by electrodeposition and sediment electro-codeposition methods, respective y, from a sulfate electrolytic bath.[8] The bath contained 400 g/L of cobalt sulfate $(COSO_4 \bullet 7H_20)$, 30 g/L of boric acid (H_3B0_3) and 0.15 g/L of the surfactant, sodium dodecyl sulfate. The pH and temperature of the solution were 2.5 and 30 "C, respectively; cathode current density was 400 A/m'. The anode used was of wax-impregnated graphite and the specimens to be coated formed the cathode. These specimens were circular discs of mild steel, 30 mm dia. x 5 mm thick.

Before deposition, the substrate steel discs were polished with very fine grade emery papers (0-4), degreased and washed with distilled water and acetone. The specimens were coated, keeping them in a horizontal position in the electrolytic slurry of titania particulate (about one µm in size). The suspension and sedimentation periods of titania particulate were regulated by a solid-state timer-controlled magnetic stirrer. Composites of different composition were deposited from baths of different titania concentrations (1,5, 10,20 and 30 g/L). Analysis of the dispersoid content in the composites (in wt. percent) was done gravimetrically after dissolving the composites in a warm 50-percent nitric acid solution.

Passivation and polarization studies of the composite coatings were done in 1 N sulfuric acid and 3.5-percent sodium chloride solution, respectively. The scan rate used for passivation studies was two mV/see, and for polarization studies, five mV/sec. These studies were carried out by using a scanning potentiostat.[a] Potentials were measured with reference to **a** saturated calomel electrode.

The medium carbon steel specimens used for bimetallic corrosion studies were 5-mm-thick circular discs of 35-mm diameter and chemical composition as shown in Table 1. These steel specimens were degreased, washed with distilled water and acetone. About one cm^{2}0f each specimen was exposed to the sodium chloride solution. A zero-resistance ammeter technique[9,10] was used to investigate the different galvanic corrosion cells established by combining the medium carbon steel with either cobalt-metal or cobalt-titania composites of varying composition. The galvanic current density was continuously

Table 1
Composition of Medium Carbon Steel Specimens

C	Mn	P	S	Si	Cu	Ni	Cr	Mo
				Percent				
0.69	0.58	0.01	0.029	0.18	<0.02	<0.03	<0.05	<0.01

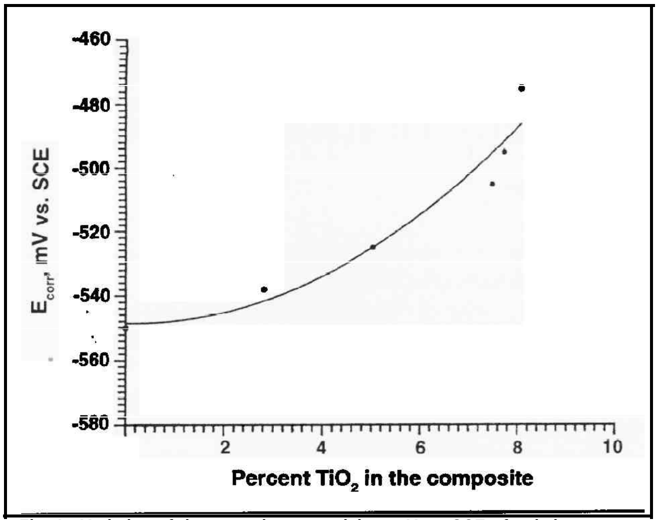

Fig. 1—Variation of the corrosion potential E_{corr} mV vs. SCE of cobalt composites in 3.5% sodium chloride solution with titania content in a cobalt matrix.

monitored. The current-time trace was then graphically integrated to get coulombs, from which the average galvanic current was obtained. The corrosion rates in mm/yr were then calculated using the relation,

$$\text{corrosion rate} = 3.2706\ Mi/zd,$$

where M is molecular mass in g/mol., z is the number of electrons involved in the corrosion reaction, i is the current density in mA/cm^2, and d is the density of the metal in g/cm^3.

Results

The variation of corrosion potential E_{corr} of the cobalt-titania composites with percent titania content is shown in Fig. 1. The composites became more noble as the content of titania in the cobalt-matrix increased.

The polarization curves of medium carbon steel, cobalt and cobalt-titania composites in 3.5-percent sodium chloride solution are shown in Figs. 2,3 and 4. The i_{corr} values and the rates of corrosion in mm/yr are given in Table 2. It appears that as the titania content in the cobalt-composite increases, i_{corr} and, therefore, corrosion rate decreases continuously. Figure 5 depicts the effect of increasing titania content in the cobalt-matrix on the passivation behavior of cobalt in 1 N sulfuric acid. The critical passivation current densities and passivation potential ranges for each type of coating are listed in Table 3. This indicates how the increased titania in the cobalt matrix helps in reducing critical passivation current density and in increasing the passivation potential range of cobalt. The critical passivation current density is reduced from 0.26 A/cm^2 to 0.057 A/cm^2 and the passivation potential range is enlarged from 0.8-1.3 V to 0.00 V-1.3 V when titania content in cobalt matrix is increased from 0.00 to 8.09 weight percent.

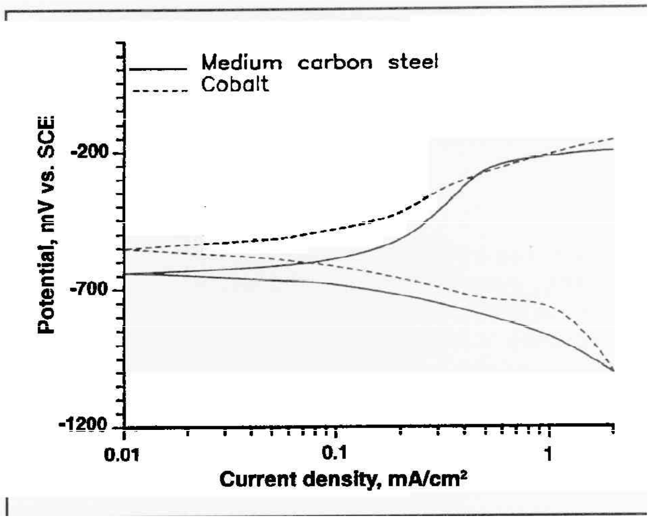

Fig. 2—Polarization behavior of medium carbon steel and cobalt in 3.5 % sodium chloride solution.

Figure 6 shows the variation of galvanic current density, i_g with time for different medium carbon steel/cobalt or cobalt-titania composite coating galvanic cells. In all cases, the galvanic current density at first increases with time, then gradually decreases and finally remains stable. The average galvanic current densities for the different cells are given in the Table 4. From the plots, as well as from the table, we can conclude that the average galvanic current density is highest (91 .25 µA) for the cell having cobalt coating as one of the electrodes. The galvanic current density decreases as the titania content in the cobalt composite increases.

Discussion

The two predominant and mutually independent factors which influence the corrosion of a metal matrix composite are the specific corrosion rates of the dispersoid and the metal forming the composite in a given environment, and the galvanic effect

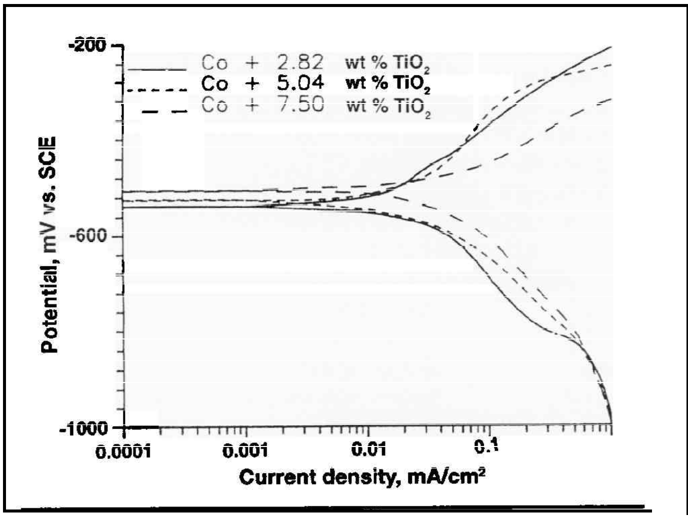

Fig. 3—Effect of titania content (2.82, 5.04 and 7.5 wt percent) in the cobalt matrix on polarization behavior of cobalt in 3.5 % sodium chloride solution.

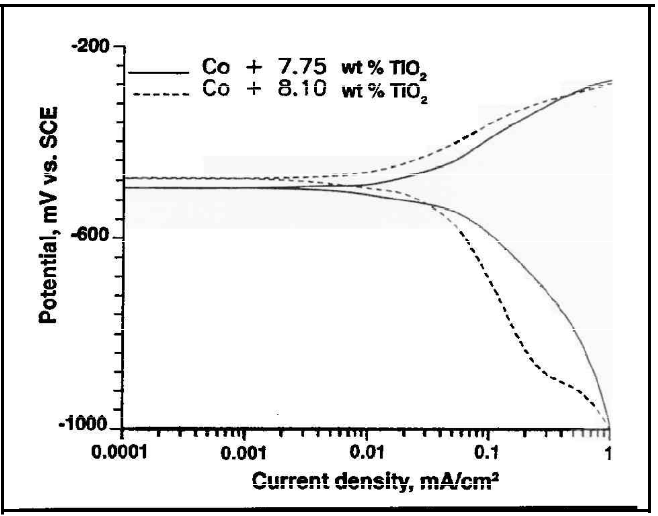

Fig. 4-Effect of titania content (7.76 and 8.09 wt percent) in the cobalt matrix on polarization behavior of cobs/t in 3.5 % sodium chloride solution.

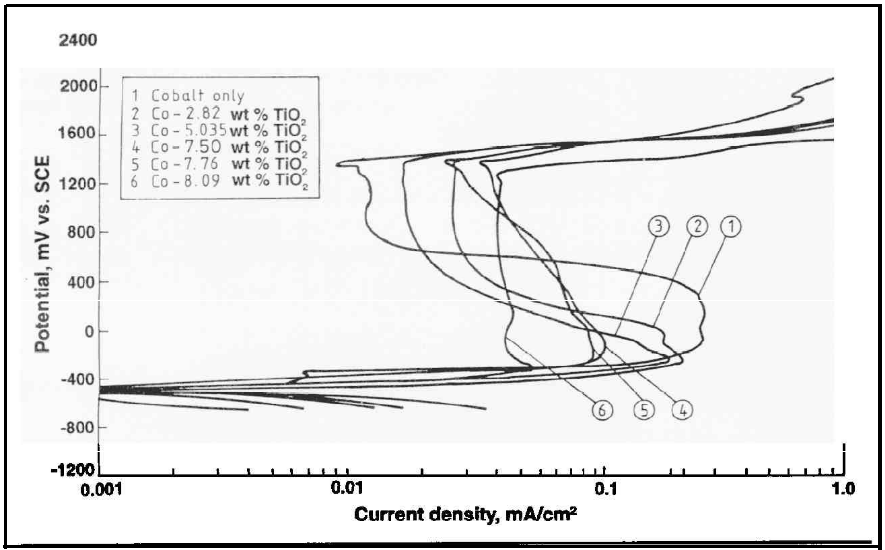

Fig. 5-Effect of increasing wt percent titania content in the cobalt matrix on the passivation behavior o cobalt in 1N sulfuric acid.

between them.[11] In a metal-fiber-reinforced metal matrix composite, the role of the above factors is quite understandable. For non- metallic-fiber-reinforced, or particulate- or dispersion-strengthened composites, the second factor is dependent upon the electrical conductivity of the fiber or the particulate. If the fiber or the particulate is conductive, such as boron or graphite, etc., the contribution from the galvanic effect will be greater. If it is non-conductive, however, the galvanic effect will be zero and, because of its less likely selective dissolution, there will be an overall improvement in corrosion resistance.

The observed corrosion behavior of cobalt and cobalt-titania composites may be explained in the light of the above facts. Because the dielectric constant of titania is 96 at 10^{-6} Hz at 25 °C, and its electrical resistivity is greater than 8 x 103 ohm-cm, and it is known to have excellent corrosion resistance in sea water and chloride solutions,[12] the rate of corrosion decreases as titania content in the cobalt matrix increases. Similarly, in passivation, the increased titania content facilitates reduction of the exposed area, thus decreasing the apparent critical current density for passivation and increasing the passivation potential range.

The trend in galvanic corrosion also supports this theory. The increased titania content in the cobalt matrix makes the matrix increasingly cathodic compared to the medium carbon steel which acts as the anode in the galvanic cell. The real cathodic area on the composite decreases, however, as the titania content in the cobalt coating increases, although the apparent area remains the same. Decreasing the cathode area decreases its cathodic current for oxygen reduction on the cathode, which is directly proportional to the real exposed area of the composite coating. Now, because the galvanic current of a cell is equal to the cathodic current," (i.e., $I_g = I_c$) the galvanic current will decrease as titania content in the cobalt coating increases. In neutral nonde-aerated 3.5-percent NaCI solution, the cathodic reaction is diffusion-controlled oxygen reduction. The limiting cathodic current density for oxygen reduction is different for both anode and cathode, as

Table 2
Corrosion Current Densities*

Wt. % of titania in cobalt-matrix	i_{corr} µA.cm^{-2}	r_{corr} mm.y^{-1}
0.00	35.0	0.38
2.82	24.0	0.26
5.04	19.0	0.21
7.50	15.0	0.16
7.76	12.0	0.13
8.09	09.2	0.10
MS	52.0	0.56

*i_{corr} and rates of corrosion r_{corr} of cobalt and its composites in 3.5% sodium chloride solution.

Table 4
Galvanic Current Densities*

Wt. % of titania in cobalt-matrix	i_g µA.cm^{-2}	r_g m.m.y^{-1}
0.00	91.25	1.06
2.82	75.83	0.88
5.04	52.50	0.61
7.50	32.90	0.38
7.76	22.50	0.26
8.09	09.16	0.10

*i_g and corrosion rates of r_g of meduim carbon steel (MS) in various MS/ cobalt-titania composites galvanic cells in 3.5% sodium chloride solution.

Table 3
Critical Passivation Current Densities*

Wt. %. of titania in cobalt-matrix	i_{crit} A.cm^{-2}	Pass. pot. range, V
0.00	0.26	+0.8 - +1.3
2.82	0.23	+0.4 - +1.3
5.04	0.18	+0.2 - +1.3
7.50	0.11	+0.0 - +1.3
7.76	0.10	+0.0 - +1.3
8.09	0.06	+0.0 - +1.3

*i_{crit} and passivation potential ranges of cobalt and its composites.

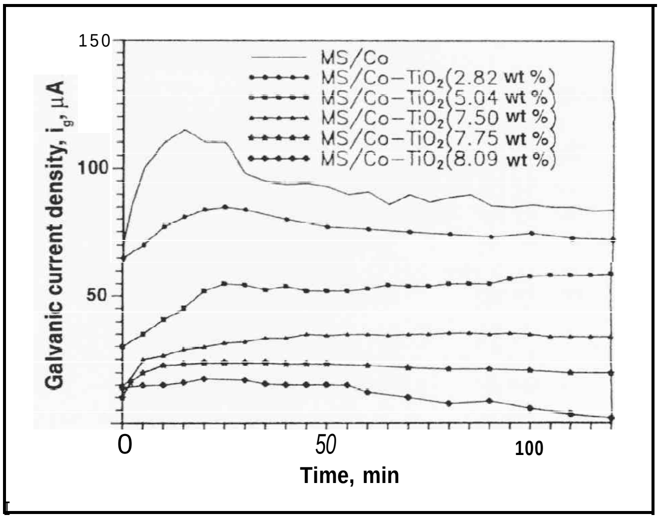

Fig. 6-Variation of galvanic current density i_g with time for galvanic cells, between a medium carbon steel and a cobalt composite mating.

Table 5
Dissolution Current Densities’

Wt. % of titania in cobalt-matrix	i_d $\mu A.cm^{-2}$	r_d $m.m.y^{-1}$
0.00	143.25	1.62
2.82	127.83	1.44
5.04	104.50	1.17
7.50	84.90	0.94
7.76	74.50	0.82
8,09	61.16	0.66

***i_d and corrosion rates, r_d of medium carbon steel (MS) in various MS/cobalt-titania composite galvanic cells in 3.5% sodium chloride solution.**

can be seen in single-metal polarizations of medium carbon steel and cobalt and its composites. This has been attributed to the inherent efficiencies of the metals for oxygen reduction.” For such systems, Mansfeld and Kenkel have shown” that the dissolution current density i_d, galvanic current density i_g and corrosion current density i_{corr} for the anode alone is related as

$$i_d = i_g + i_{corr}$$

Therefore, the average galvanic current density of the anode material may be utilized in computing the average dissolution current density and corrosion rate of the anode material in a galvanic cell. The calculated values are given in Table 5. The results show that a cobalt-titania coating has an advantage over pure cobalt coating in reducing the severity of corrosion of the medium carbon steel as a result of galvanic coupling in the sodium chloride solution.

Conclusions

Cobalt-titania composite coatings have better corrosion resistance and passivation behavior in 3.5-percent sodium chloride solution and 1 N sulfuric acid respectively, compared to cobalt coating alone. Galvanic corrosion of medium carbon steel in the sodium chloride solution is considerably less with a cobalt-titania composite coating than with pure cobalt coating. Thus, this type of composite coating has an advantage over cobalt coating under similar circumstances.

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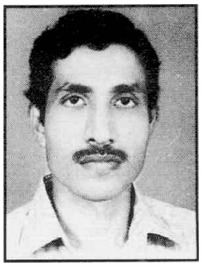
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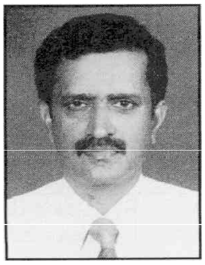
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