JOURNAL OF MATERIALS SCIENCE 28 (1993) 1758–1764

A study of the tribological properties of cobalt–titania composite

E. P. RAJIV, S. K. SESHADRI
Department of Metallurgical Engineering, Indian Institute of Technology, Madras 600 036, India

The frictional and wear behaviour and hardness of cobalt and cobalt–titania (anatase) particulate composites, developed by sediment electro-codeposition method, were studied. Frictional and wear studies, performed on a disc-on-disc type machine, show that the microhardness of the composite increases as the titania content in the composite increases. A decrease in both the coefficient of friction and specific wear rate was observed for the composites with increasing titania content in the cobalt matrix. The effect of sliding velocity and load on the coefficient of friction and specific wear rate of cobalt and cobalt titania composites was also investigated. The optical microphotographs and X-ray diffractogram reveals that the tribo-deformation is oxidation dominated for cobalt. A probable mechanism is discussed.

1. Introduction

Wear of metals at high temperatures due to high loads and/or speeds, is of special interest in a variety of applications such as cutting tools, metal-forming dies, press fits, automotive brakes, etc. Friction and wear in such cases can be reduced by using a metal or alloy that forms an oxide film having a low brittle to ductile transition temperature (about 400 °C), such as cobalt and its alloys [1]. Above this temperature these oxides become lubricious. These tribological properties can be further improved by ceramic inclusions [2]. Cobalt (an hexagonal close packed metal) based-particulate strengthened composites have an *a priori* advantage over composites based on cubic metals [3, 4] as an anti-wear, anti-friction and anti-seizure material, because their restricted slip does not allow the rubbing surface to conform perfectly even after running in [5]. Over and above this, it is a good high-temperature material with high melting point (1495 °C) and low stacking-fault energy. Cobalt composites containing fine dispersions of Cr_2O_3, Al_2O_3, ThO_2, SiO_2, Cr_3C_2, etc., have been prepared by a variety of methods, such as mechanical blending of metal and oxide powders [6–8], co-precipitation [9–13], flash drying, selective reduction [14–16], internal oxidation [17] and electrolytic co-deposition methods [18–20]. As a method of producing composite materials, electro-co-deposition is particularly attractive in that it allows for the production of composites in the form of a coating, which is specially suited for tribological applications, where surface reactions are of paramount importance.

In the present investigation, studies have been carried out to understand the wear and frictional behaviour of cobalt and cobalt–titania composites of various compositions. The form of titania used was anatase (a tetragonal system). These composites were prepared by the sediment-electro-co-deposition (SECD) [21] method from a sulphate bath [22].

2. Experimental procedure

A plating solution was prepared with 400 g/l $CoSO_4 \cdot 7H_2O$, 30 g/l H_3BO_3, 0.15 g/l dodecyl sodium sulphate (stress reducer and anti-pitting agent) and 1–30 g/l TiO_2 particles (about 1 μm size). The plating bath was maintained at pH $\simeq 2$ and at a temperature of 30 °C. A cathodic current density of about 400 A m^{-2} was used. The solution was agitated intermittently by a magnetic stirrer to keep the titania particles in suspension, while the duration of agitation and quiescent periods (both 30 s each) were controlled by a solid state timer.

In SECD, the second-phase particles kept in suspension during the stirring period are allowed to settle on to a horizontally placed cathode during electrodeposition. The cathodes used as substrates for coating were of mild steel. Co-deposition was carried out for a time sufficient to obtain a minimum coating thickness of 100 μm.

Vickers hardness was measured on samples in the as-coated condition using a Leitz Wetzlar micro-hardness tester under a 200 g load and the average of five replicate samples were recorded.

The coatings were tested for wear resistance and coefficient of friction under dry sliding conditions by the disc-on-disc method. A schematic diagram of the testing rig is shown in Fig. 1. The counter disc was a unidirectionally rotating hardened steel disc (697 VHN), finished to a roughness of $R_{max} = 0.9$ μm. The relative sliding speed at the interface was changed by varying the rotational speed of the counter disc. Loading of the sample was achieved by compressing a spring using load-adjusting screws. The frictional

0022-2461

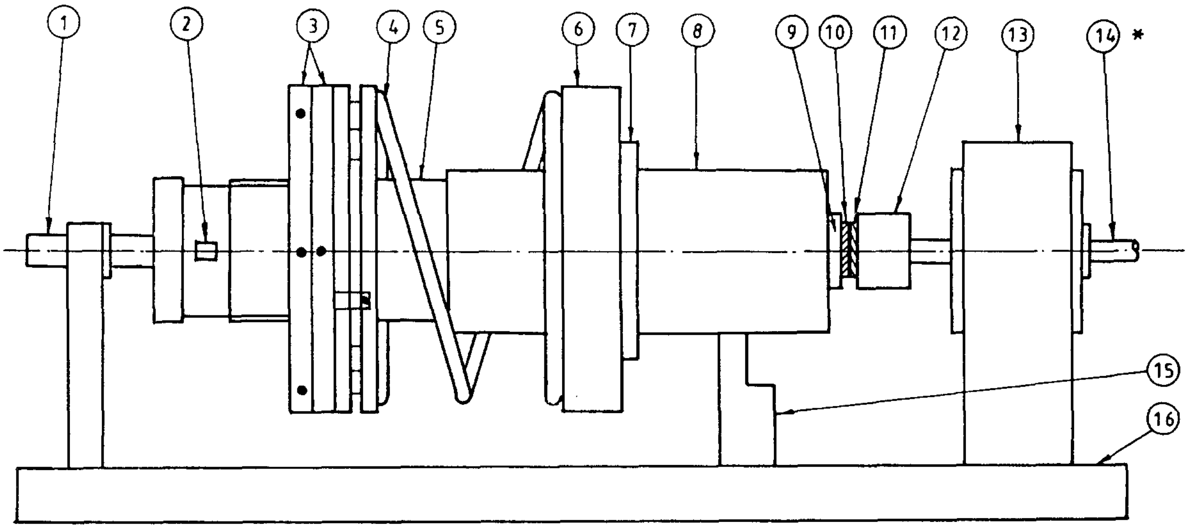

Figure 1 Schematic diagram of the wear testing rig. 1, Stationary shaft; 2, slot for inserting leaf spring; 3, locknuts; 4, spring; 5, inner hollow cylinder; 6, cap; 7, collar; 8, outer cylinder; 9, sample holder; 10, specimen; 11, counter disc; 12, cap; 13, support column for driving unit; 14, shaft (connected to speed variable/1/4 HP AC/DC motor); 15, support column; 16, base plate.

torque, which the thrust-bearing disc imposes, acts against the test piece and is measured by a strain gauge–carrier frequency amplifier arrangement. The specific wear rate was calculated by the weight loss measurement after an experiment lasting 20 min.

Before starting the new experiment, the counterface was cleaned, polished with 1/0, 2/0, 3/0 and 4/0 grades of emery papers, cleaned and degreased with acetone so that starting conditions for every run were identical. The weighed coated specimen was mounted against the loaded and rotating counterdisc of the same diameter, and tested; the specimen was removed, cleaned with trichloroethylene, dried and weighed. The experiment was repeated under identical conditions and average values of weight loss and amplifier readings were taken for evaluation. The wear tracks were examined under an optical microscope.

Cobalt and cobalt composite coatings were analysed before and after wear testing by means of a semi-automatic microprocessor controlled X-ray diffractometer, Philips PW 1710. The X-ray analyses were made on the upper side of the coatings. The mean value of the CuK_α radiation was 0.154 18 nm. Qualitative phase determination was made by constructing X-ray diffraction diagrams within the angular range $2\theta = 5°–120°$.

3. Experimental formulae

3.1. Coefficient of friction

If F (N) is a certain force acting at a point "B" (Fig. 2) on the surface of the specimen holder, and f is the frictional force on the specimen, then about the axis of rotation,

$$\text{moment of } f = \text{moment of } F \tag{1}$$

If a load L acts on a supporting surface of radius r with a uniform pressure, p, over the supporting area, A, the infinitesimally small frictional force, df, over the area dA is

$$\mathrm{d}f = p\ \mathrm{d}A\mu \tag{2}$$

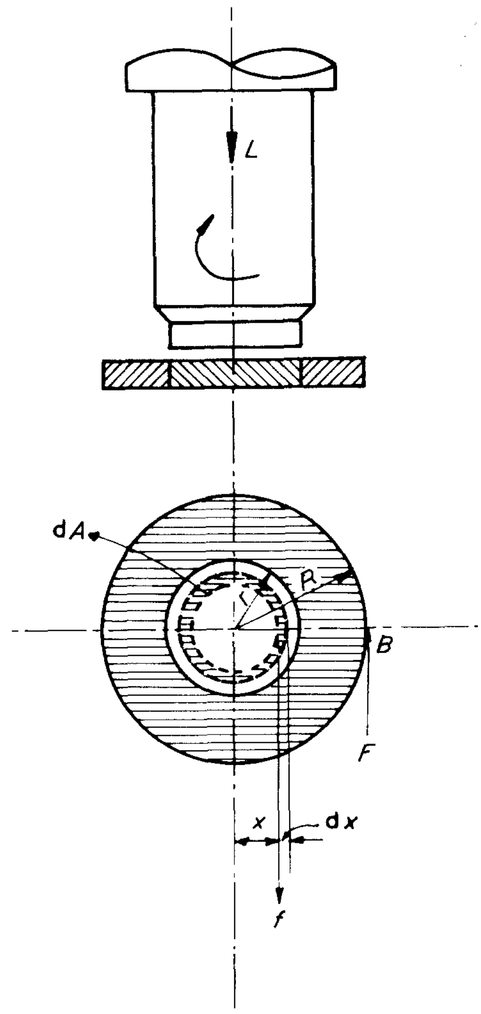

Figure 2 Geometry of torque-lever arrangement.

(because, $\mu = f/L$) and the frictional moment, $\mathrm{d}M_\mathrm{f}$ at the surface is given by

$$\mathrm{d}M_\mathrm{f} = \mathrm{d}f\,(x + \mathrm{d}x) = p\mathrm{d}A\ \mu x$$
$$= 2\Pi p\mu x^2\mathrm{d}x \tag{3}$$

(because $\mathrm{d}f\mathrm{d}x$ is negligible).

The total frictional moment, M_f, is given by

$$M_f = dM_f = (2/3)\ L\mu r \quad (4)$$

and the moment of the force

$$F = FR \quad (5)$$

therefore, from Equations 1, 4 and 5 we have

$$\mu = 3RF/(DL) \quad (6)$$

where $D = 2r$, and μ is the coefficient of friction.

3.2. Specific wear rate

The specific wear rate was calculated by the expression

$$w_s = w/(lL) \quad (7)$$

where w is the wear mass, L is the normal load and l is the sliding distance. In this study the sliding distance was calculated at the mean radius of the specimen.

4. Results

The variation of Vickers hardness of the cobalt–titania composites with increasing weight per cent incorporation of the dispersoid (titania) is shown in Fig. 3. The microhardness of the composites increases with increasing weight per cent incorporation of the dispersoid in the metal matrix.

The effect of increasing incorporation of titania on the coefficient of friction of cobalt, at a constant sliding velocity of 0.78 $m\,s^{-1}$ and a load of 8.16 N, is shown in Fig. 4. The coefficient of friction decreases with increasing weight per cent incorporation of titania in the cobalt matrix. The variation of the coefficient of friction of cobalt with load is very small. In composites, however, for each composition initially, there is a significant increase in the coefficient of friction with load, which becomes marginal at higher loads.

The variation of the specific wear rate of cobalt with increasing weight per cent TiO_2 incorporation, at constant load (8.16 N) and sliding velocity (0.78 $m\,s^{-1}$) is shown in Fig. 6. The specific wear rate decreases with increasing titania incorporation. The effect of load on the specific wear rate of the cobalt metal and its composites at a constant sliding velocity of 0.78 $m\,s^{-1}$ is shown in Fig. 7. There is a gradual decrease in the specific wear rate, as the load increases,

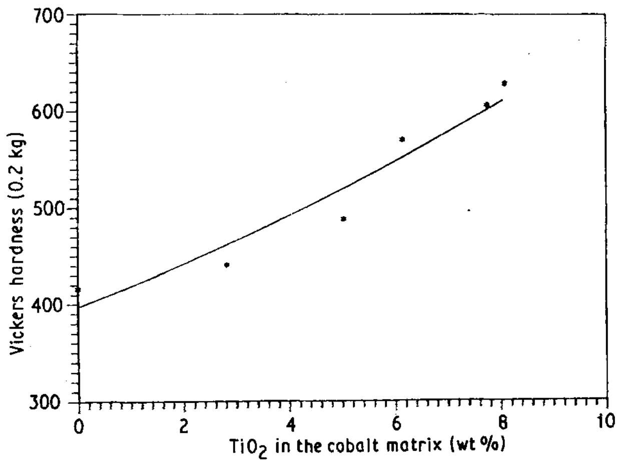

Figure 3 Dependence of the cobalt composite hardness on the weight per cent of TiO_2 in the cobalt matrix.

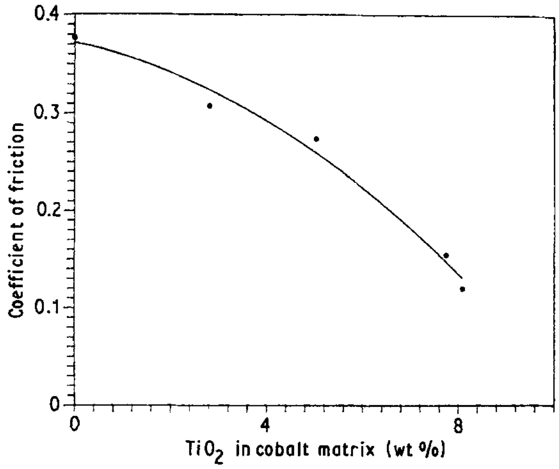

Figure 4 Variation of coefficient of friction of cobalt–TiO_2 composite with weight per cent of TiO_2 in the matrix. Load = 8.16 N, sliding velocity = 0.78 $m\,s^{-1}$.

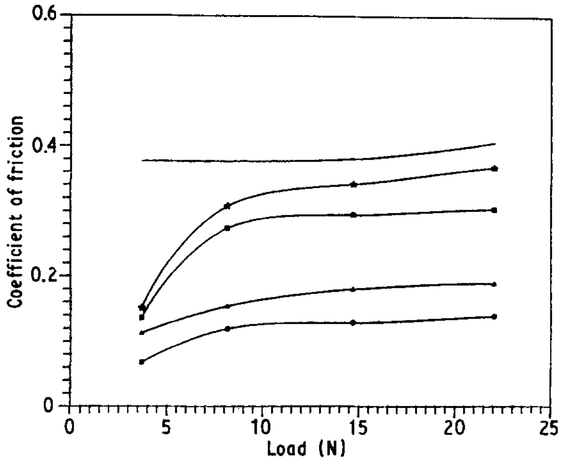

Figure 5 Effect of load on the coefficient of friction of cobalt (—) and cobalt–titania composites: TiO_2 (wt %): (★) 2.82, (■) 5.035, (▲) 7.750, (●) 8.094. Sliding velocity = 0.78 $m\,s^{-1}$.

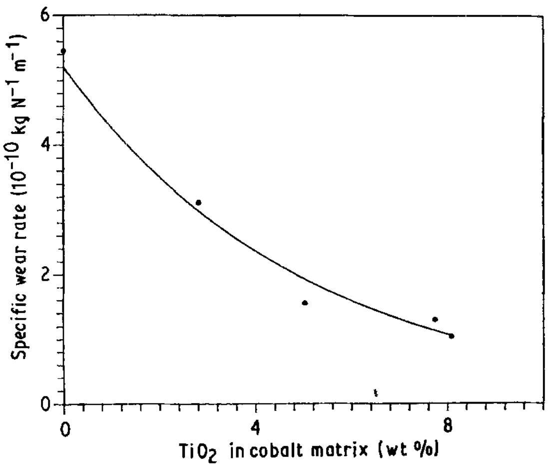

Figure 6 Variation of specific wear rate of cobalt–TiO_2 composite with weight per cent of TiO_2 in the matrix. Load = 8.16 N, sliding velocity = 0.78 $m\,s^{-1}$.

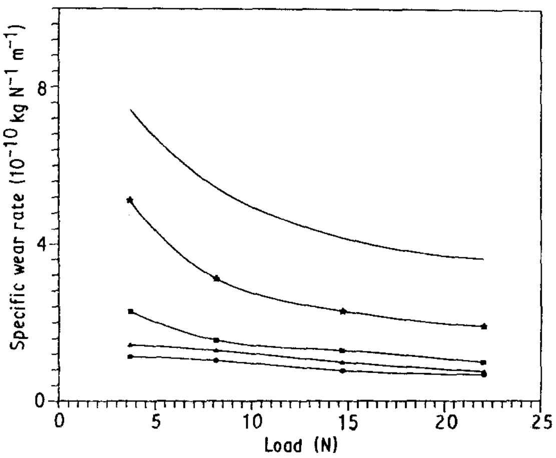

Figure 7 Effect of load on the specific wear rate of cobalt and cobalt–titania composites. For key, see Fig. 5. Sliding velocity = 0.78 m s^{-1}.

in all cases. A large material transfer as blackish brown oxides was observed in the friction and wear experiments for the cobalt metal, as can be seen from the optical micrographs (Fig. 8). X-ray diffraction studies reveal that cobalt metal, in the as-plated condition from a sulphate bath at room temperature, contained a mixture of hexagonal close packed and face centred cubic lattice structures (Fig. 9). Cubic (1 1 1)

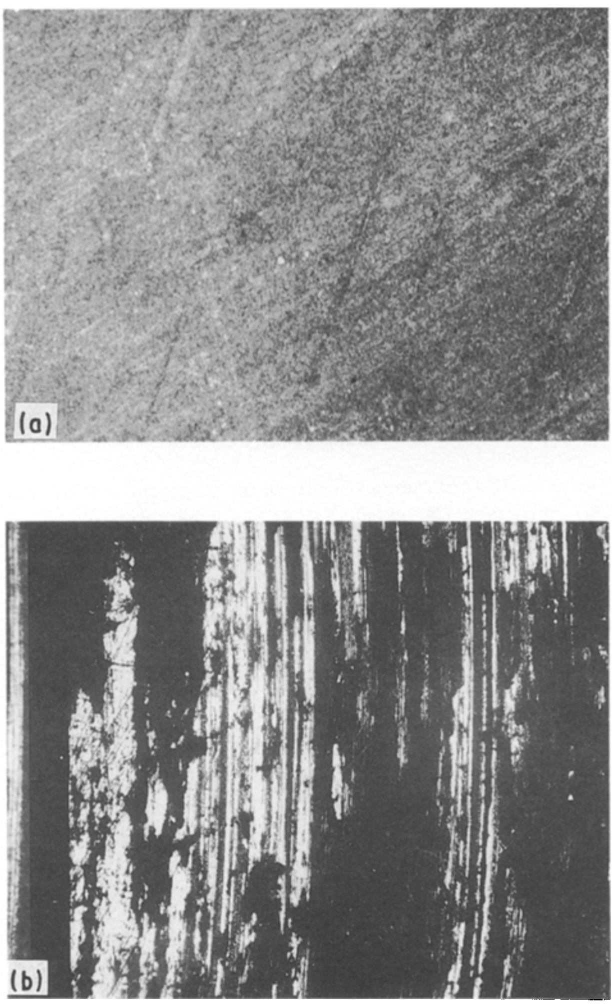

Figure 8 Optical microphotographs (X1000) of cobalt (a) before and (b) after the wear test.

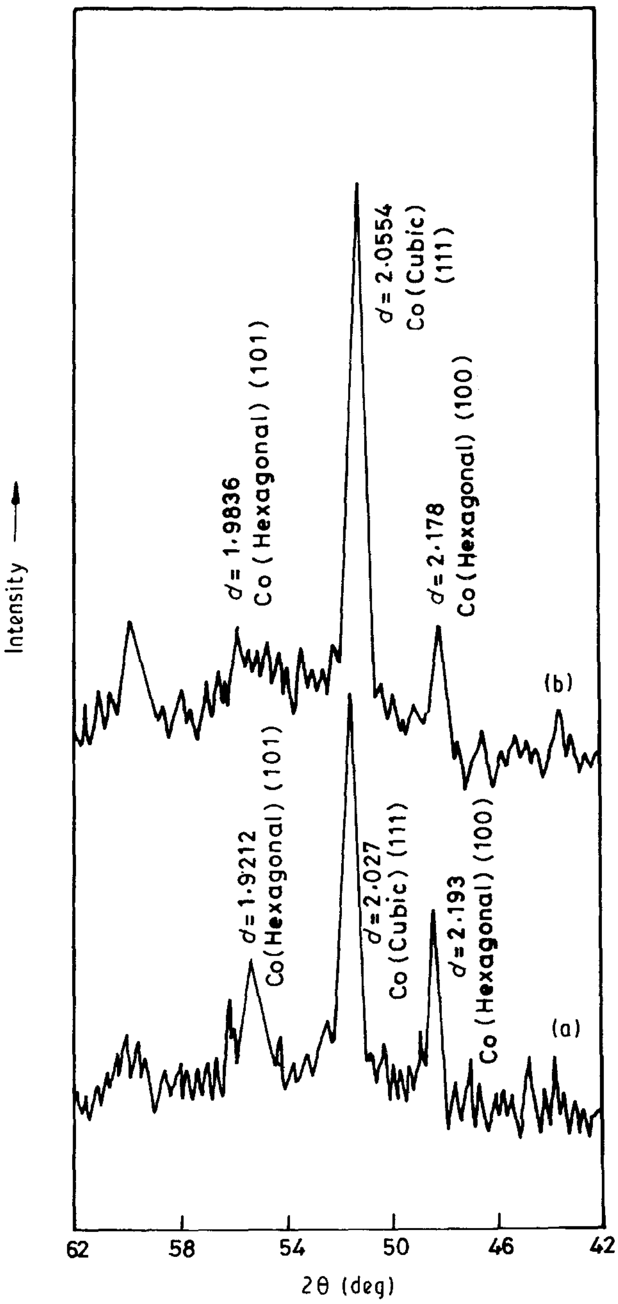

Figure 9 X-ray diffractogram of cobalt (a) before and (b) after the wear test.

plane shows peak at 2θ = 52.4°, whereas hexagonal close packed (1 0 0), (1 0 1) and (1 1 0) planes show at 2θ = 49.87°, 55.5° and 91.2°, respectively. However, after the tests, the coating predominantly contained a face centred cubic structure, as the increased intensity of the cubic peak shows. The transition from hcp to fcc may be assisted by a martensitic transformation, the starting temperature for which is 388 °C. The hcp structure is stable at room temperature, while the fcc structure is stable above 390 °C. The X-ray diffraction study (Fig. 10) also confirmed that the oxide debris formed during the tests was predominantly Co_3O_4 and Fe_3O_4. On the other hand, the material transfer as metal oxides was found to be insignificantly small in similar tests with cobalt composites (Fig. 11).

Fig. 12 shows the variation of co-efficient of friction of cobalt and its composite containing 8.09 wt % titania, with sliding velocity at a constant load of

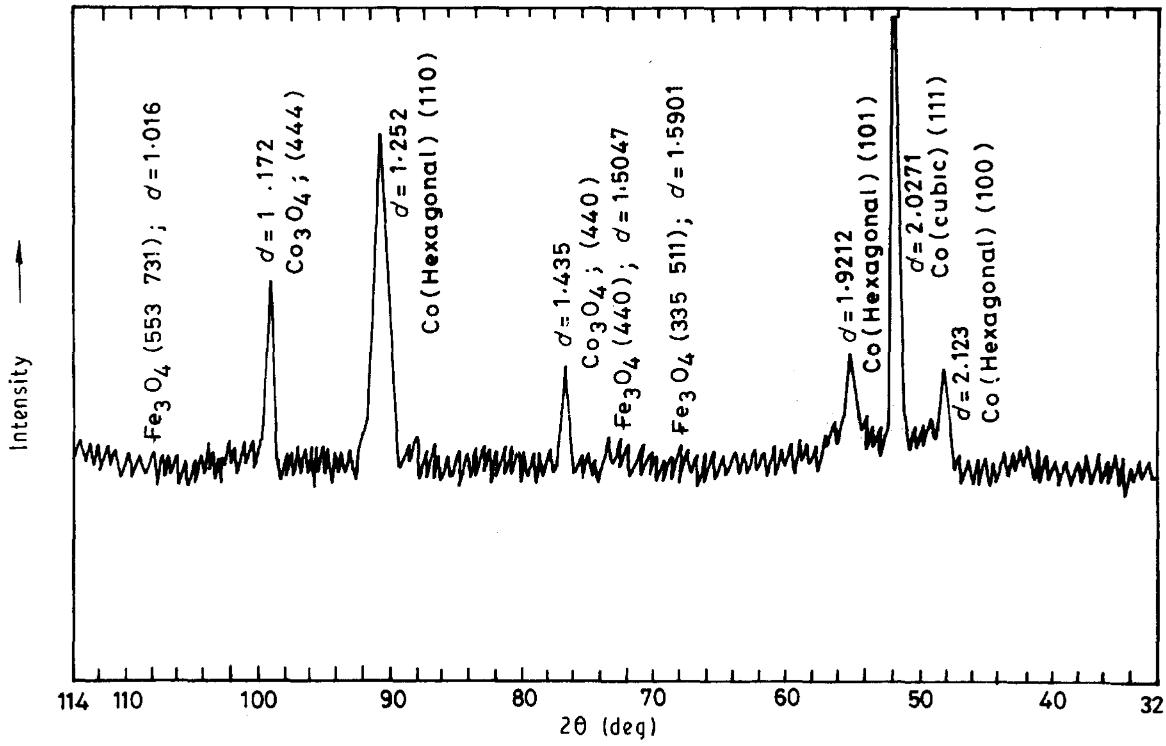

Figure 10 X-ray diffractogram of wear debris of cobalt on the coating.

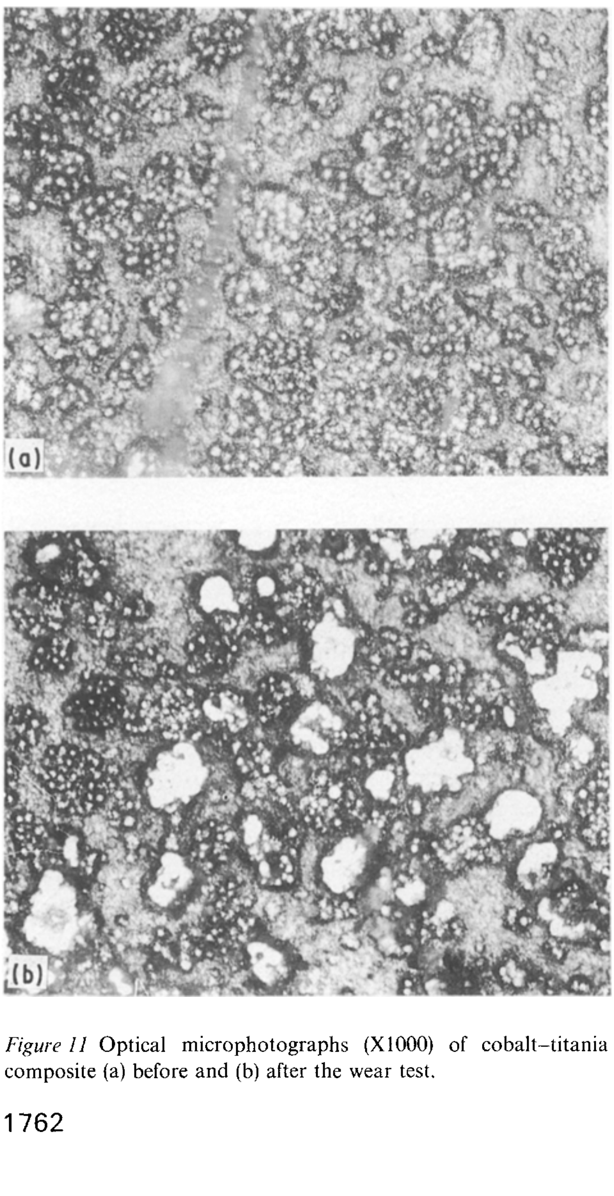

Figure 11 Optical microphotographs (X1000) of cobalt–titania composite (a) before and (b) after the wear test.

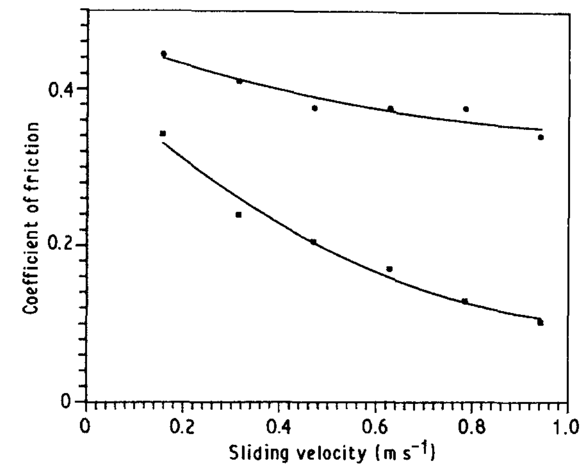

Figure 12 Effect of sliding velocity on the coefficient of friction of (●) cobalt and (■) cobalt–8.09 wt % titania composite. Load = 8.16 N.

8.16 N. The coefficient of friction decreases continuously in both cases.

The effect of sliding velocity on the specific wear rate of cobalt metal and its 8.09 wt % titania composite at a constant load of 8.16 N are shown in Figs 13 and 14, respectively. At low values of the sliding velocities, the specific wear rates were found to increase with increasing sliding velocities. However, at higher sliding velocities (after about 0.48 $m\,s^{-1}$), both cobalt metal and its composite, show a decrease in the specific wear rate.

5. Discussion

The hardness of the composites depend upon the nature and number of the dispersoid in the metal

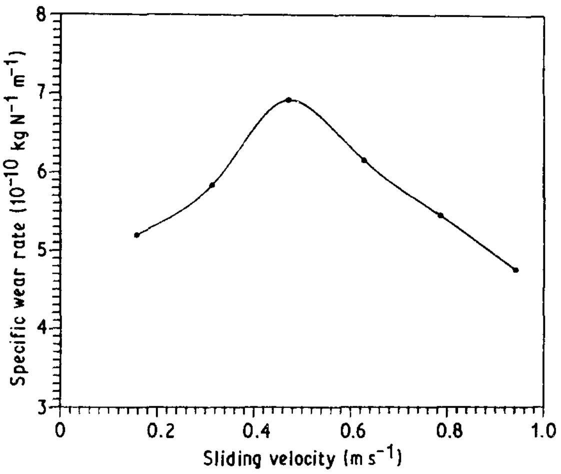

Figure 13 Effect of sliding velocity on the specific wear rate of cobalt metal. Load = 8.16 N.

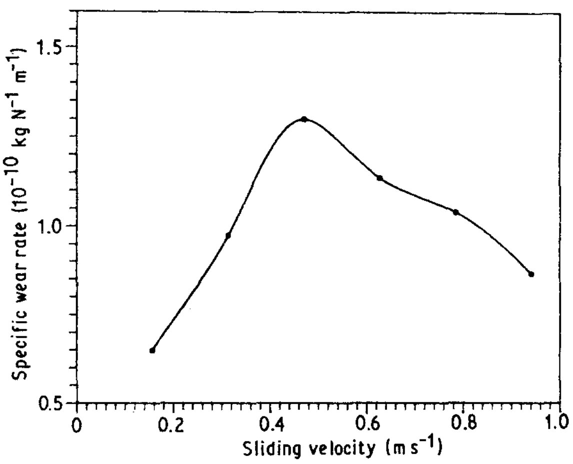

Figure 14 Effect of sliding velocity on the specific wear rate of cobalt–8.09 wt % TiO_2 composites. Load = 8.16 N.

matrix. The softer dispersoids such as graphite, molybdenum disulphide or hexagonal boron nitride, increase the microhardness only slightly, whereas oxides, carbides and nitrides, which are hard ceramics, increase the microhardness of the cobalt–titania composites with increasing weight per cent titania occlusion in the cobalt metal matrix (Fig. 3), also confirming the above trend. Because the dispersoids used in this composite are relatively large in size (about 1 μm), they cannot interfere with dislocations and the strengthening effect is manifested by the hydrostatic restrainment of the matrix in the proximity of the dispersoid.

The wear and frictional performance of a material depends on such intrinsic properties of the mating surfaces as their hardness [23], mutual solubility and surface energy [24], and crystal structure [25]. For a composite, the hardness further depends on such factors as shape, size, volume content and distribution of the dispersoids in the metal matrix [26]. In general, a material possesses good wear resistance when it has a low mutual solubility and a low surface energy to hardness ratio [24]. Cobalt has a hardness, h, of approximately 4177.35 MN m^{-2} and surface energy, Y, of 1.530 Jm^{-2}, which gives the Y/h value of $\sim 3.67 \times 10^{-10}$ m and most of the ceramics like titania have a Y/h value less than 0.5×10^{-10} m. This fact explains the cause of the substantial decrease in the friction coefficient and specific wear rate of the composite *vis-à-vis* the cobalt metal with increasing weight per cent incorporation of titania in the cobalt metal matrix (Figs 4 and 6).

The wear mechanisms occurring in metals are broadly classified in two categories [27]: plasticity-dominated wear and oxidation-dominated wear. When the mating surfaces slide at speeds below about 0.1 m s^{-1}, and under high load, the wear mechanism is plasticity dominated, i.e. by adhesion and delamination, and above a speed of 1 m s^{-1}, the wear is oxidation dominated. In the intermediate condition, i.e. at low load and a sliding velocity below 1 m s^{-1}, the wear mechanism is mainly mild delamination type, which is the condition in the present study. Here, the direct metal to metal contact is conceived to be absent owing to an ultrathin (tenths of a nanometre), but tough, layer of oxide [28]. This thin layer can undergo elastic deformation without rupture under light loads, thus resulting in a low specific wear rate. Because this oxide layer is lubricious at the same time, the coefficient of friction also remains low. The black oxide debris of Co_3O_4 and Fe_3O_4 observed (Fig. 8) in mild wear is produced from this layer and perhaps from small metallic fragments which are removed and oxidized [29–34]. The damaged surface quickly re-oxidizes, avoiding further metal to metal contact between the sliding surfaces. Beyond a critical load, the oxide layer is penetrated because of high surface tensile forces. This causes an increase in the coefficient of friction (Fig. 5). The surface tensile forces (frictional forces) cause a drastic increase in the plastic shear strain accumulation in the oxide layer, initiating cracks transverse to the sliding direction, and resulting in increased wear rate (Fig. 7) [1]. The drop in the specific wear rate of cobalt may be associated with the surface hardening of the cobalt coating. The surface cooling rate from the temperature produced by sliding at high speed and load conditions, is high enough to cause hardening [35]. Hence, there is a lower specific wear rate at higher loads for cobalt metal. Similar transition from high to low specific wear rate with increasing load under dry sliding conditions for a variety of metals has been reported by Arnell *et al.* [36].

When the electrodeposited composite is brought into contact with a sliding counterface, initially hard particles are exposed and completely support the wear load (Fig. 11). Consequently, the friction and wear pattern will be determined mainly by the tribological properties of the hard dispersoid and will be of low magnitude. As the load increases, because of elastic and then plastic yielding of the composite as a whole under the compressive stress, the real area of contact increases, thus increasing the coefficient of friction and wear (Figs 5 and 7) [26]. Composites being much harder, and also because of surface hardening as above, however, the load has very little effect on its specific wear rate. So, with increase in load, the specific wear rate of composites continuously decreases.

The decrease in the coefficient of friction of cobalt with increasing sliding velocity (Fig. 12) may be due to the thickening of the oxide layer on its surface. This thickening is caused by heating of the surface at high sliding velocity under load [37–40]. For composites, the continuous decrease in the coefficient of friction may be because of the increased ductility of titania embedded in the metal at higher temperatures.

The initial increase and subsequent decrease in specific wear rate of cobalt coating (Fig. 13) may be due to the combined effect of surface hardening and thickening of the oxide layer as the sliding velocity increases. In the beginning, hardening of the surface and thickening of the oxide layer is less, and so, there is a higher specific wear rate. Subsequently, these factors predominate, and that causes a reduction in the specific wear rate. In the composite (Fig. 14), the specific wear rate is high initially, because surface hardening of the cobalt matrix has yet to set in, while titania becomes softer because of the temperature produced at the interface. Later, however, because of the hardening of the matrix, the overall specific wear rate of the composite decreases.

6. Conclusion

Cobalt–titania composites have much better frictional and wear resistance than the cobalt metal alone, which in turn is better than any cubic metal coatings. Therefore, for tribological applications, cobalt–titania composites can be used with advantage.

References

1. H. E. SLING, *Surface Coating Technol.* **33** (1987) 243.
2. H. E. SLING and C. DELIACORTE, *ASLE Trans.* **30** (1) (1987) 77.
3. D. H. BUCKLEY and R. L. JOHNSON, *ibid.* **8** (1965) 123.
4. *Idem, ibid.* **9** (1966) 121.
5. P. G. PARTRIDGE, *Met. Rev.* **12** (1969) 169.
6. E. F. ADKINS and R. STICKLER, *Phys. Status Solidi* **35** (1969) 11.
7. A. S. BUFFERD and N. J. GRANT, "Journees Internationales des Applications du Cobalt", 9–11 June, CRM -CIC, Brussels (1964) p. 251.
8. J. W. HANCOCK, D. COUTSOURADIS and L. HABRAKEN, AFML Technical Report no. 69–145, September 1969.
9. A. L. MINCHER, *Cobalt* **32** (1966) 119.
10. A. L. MINCHER and I. PERLMUTTER, in "97th Annual Meeting of the Metallurgical Society of AIME", New York, 25 February–1 March 1968.
11. A. L. MINCHER and D. B. ARNOLD, AFML Technical Report no. 68–95, April 1968.
12. J. M. DRAPIER, D. COUTSOURADIS and L. HABRAKEN, *Cobalt*, **53** (1971) 197.
13. J. M. DRAPIER, D. COUTSOURADIS and L. HABRAKEN, AFML Technical Report no. 69–145, September 1969.
14. B. H. TRIFFLEMAN, NASA Control Report no. 54516, December 1967.
15. R. F. CHENEY and W. SCHITHAUER, NASA Control Report no. 54599, December 1967.
16. B. H. TRIFFLEMAN and K. K. IRANI, NASA Control Report No. 72591, Dec. 1969.
17. D. P. WHITTLE and M. E. EL DAHSHAN, *Corr. Sci.* **17** (1977) 879.
18. E. S. CHEN and F. K. SAUTTER, *Plating Surface Finishing* **63** (9) (1976) 28.
19. MARTIN THOMA, *ibid.* **71** (9) (1984) 51.
20. MICHEL RUIMI and ROBERT MARTNOU, *Metal Finishing* **87** (7) (1989) 7.
21. M. VISWANATHAN and K. S. G. DOSS, *ibid.* **70** (2) (1972) 67.
22. S. ARMYANOV and G. SOFIROVA, *Surface Coating Technol.* **34** (1988) 441.
23. W. HIRST, in "Proceedings of the Conference on Lubrication and Wear", (Institute of Mechanical Engineers, London, 1957) p. 674.
24. E. RABINOWICZ, "Friction and Wear of Materials", (Wiley International, New York, 1965) pp. 10–18, 51–108.
25. D. H. BUCKLEY, *Cobalt* **38** (3) (1968) 20.
26. E. C. KEDWARD, *Metallurgia* **79** (1969) 225.
27. S. C. LIM and M. F. ASHBYS, *Acta. Metall.* **35** (1) (1987) 1.
28. M. FINK, *Trans. Amer. Soc. Steel. Treat.* **18** (1930) 1026.
29. R. M. FARRELL and T. S. EYER, *Wear* **15** (1970) 359.
30. T. F. J. QUINN, A. R. BAIG, C. A. HOGARTH, and H. MULLER, *ASLE Trans.* **16** (1973) 239.
31. N. C. WELSH, *Phil. Trans. R. Soc. Ser. A* **257** (1965) 31.
32. J. F. ARCHARD, *Wear* **2** (1958/59) 438.
33. N. C. WELSH, *Phil. Trans. R. Soc. Ser. A* **257** (1965) 51.
34. H. UETZ and K. SOMMER, *Wear* **43** (1977) 375.
35. N. C. WELSH, *J. Appl. Phys.* **28** (1957) 960.
36. R. D. ARNELL, A. P. HEROD and D. G. TEER, *Wear* **31** (1975) 237.
37. S. JAHANMIR, E. P. ABRAHAMSON and N. P. SUH, *ibid.* **40** (1976) 75.
38. R. W. BERRY, P. M. HALL and M. T. HARRIS, "Thin Film Technology" (Van Nostrand, Reinhold, New York, 1968).
39. N. P. SUH, "Coated Carbides – Past, Present and Future; Advances in Hard Material Tool Technology" (Carnegie Press, Pittsburgh, PA, 1976).
40. N. P. SUH and T. NAGAO, *CIRP Amer. Inst. Proc. Eng. Res.* **25** (2) (1976) 513.

Received 19 July 1991
and accepted 11 March 1992