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# Mechanical and dry-sliding wear properties of boronized pure cobalt using boronizing powders with SiC as diluent

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# 1. Introduction

Co and Co-based alloys are widely used in gas turbine aircraft engines, valve pump shafts of pressure vessels and hip implants, due to its high flow stresses and outstanding resistance to oxidation, wear up to temperatures closing to its melting point and wear properties [1–3]. In order to further enhance the surface properties of Co and Co-based alloys, a variety of surface treatments or coating processes have been tried in the past such as plasma transferred arc (PTA) [4], plasma spray [5], plasma nitriding [6] and laser cladding [7]. However, for most ordinary applications, these coatings may be somewhat expensive and hence not feasible for large volume applications.

Boronizing is a thermochemical treatment that diffuses boron through the surface of metallic substrates. As boron is an element of relatively small size it diffuses into a variety of metals; including ferrous, non-ferrous and some super alloys [8–11]. On the other hand, very little information exists on boride coatings obtained on Co and Co-based alloys [12–15]. The authors have reported their findings of boronizing Co using the powder-pack method [16]. Due to the composition of the boronizing powders which contain SiC and KBF<sub>4</sub> as a diluent and an activator, respectively, experiments and thermodynamic calculations of the reaction processes involved show that two competing processes occur during boronizing of pure cobalt, namely, boronizing and siliconizing. During this process, a dual-layer coating consisting of an outer layer of silicide, and an inner layer of boride is formed. The report does not cover the dry-sliding wear behavior of boronized pure

# ABSTRACT

In this study, boronizing of 99.95% pure cobalt was performed in a solid medium by using Commercial LSB-II powders (that contain SiC) at 850, 900 and 950 °C for 2, 4, 6 and 8 h, respectively. The surface modified samples were examined by means of scanning electron microscopy (SEM)–energy dispersive spectroscopy (EDS), X-ray diffraction, microhardness tester and ring-on-block wear tester. Samples boronized had Co<sub>2</sub>B phase or Co<sub>2</sub>B plus Co<sub>2</sub>Si phases depending on the process temperatures. The depth of modified layer ranged from 40 to 186 µm, depending on treatment temperature and time. The hardness of boride layer is much higher than that of silicide layer and substrate, and the wear resistance of the boride layer is more excellent than that of the silicide layer. © 2013 Elsevier B.V. All rights reserved.

cobalt. Therefore, the wear properties and the mechanisms of pure cobalt with boride and silicide coatings were investigated using a ring-on-block wear tester under dry-sliding conditions in this study.

# 2. Experimental details

# 2.1. Substrate materials

The substrate material used for this study was 99.95% pure cobalt and had a dimension of 10 mm  $\times$  10 mm  $\times$  10 mm. Before boronizing, all the samples were ground using 600 grid emery papers to get surface finish and degreased ultrasonically in acetone and dried.

# 2.2. Boronizing

Boronizing was performed in a solid medium by using Commercial LSB-II powders that contained the boriding source  $(8\% B_4C)$ , the activator (4% KBF<sub>4</sub>) and the diluent (88% SiC). All samples to be boronized were packed in the powders and sealed in a medium steel container. Boronizing was performed in an electrical resistance furnace under atmospheric pressure at 850, 900 and 950 °C for 2, 4, 6 and 8 h, respectively.

# 2.3. Characterization

The microstructures of the polished and etched cross-section of the samples were observed by scanning electron microscopy (SEM, JSM5910LV) equipped with energy dispersive spectroscopy.

Different phases formed on Co substrates were identified by X-ray diffraction analysis on a Philip X-ray diffractometer using

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Fig. 1. Schematic illustration of the wear test device.

Cu-K $\alpha$  radiation ( $\lambda = 0.1541$  nm, voltage 40 kV, and current 25 mA) with continuing scanning at a rate of 2° 2 $\theta$ /min in the range of 20–80° 2 $\theta$ . The hardness measurements of the layers formed on the surface were performed using the Vickers microhardness tester (SHIMADZU/HMV-2) with the loads of 25 g.

Wear tests were carried out on a Type M200 ring-on-block wear tester. A schematic view of the tester is shown in Fig. 1. The tests were performed at a constant speed of 200 rpm (equating to a linear sliding velocity of 52.3 cm/s) for duration of 900 s. A normal operating load of 30 N was used. For the counter body, 50-mm-diameter GGr15 rings (HRC52) were selected. The wear losses were measured by Type TG328A analytic balance with sensitivity of 0.1 mg. The wear rates of the unboronized and boronized samples were calculated using the equation of K = W / S where W is the wear weight in mg, and S is the total sliding distance in km. The worn surface morphologies of the samples were also observed by scanning electron microscopy (SEM, HITACHI S-3400N).

# 3. Results and discussion

# 3.1. Material properties

SEM and SEM–BSE micrographs of the boronized pure cobalt at 900 °C for 4 h are shown in Fig. 2a and b. The modified layer is composed of four distinct regions; these are (I) a silicide layer formed on the surface of the coated sample, (II) a diffusion zone (DZ) occurred between silicide layer and boride layer, (III) a boride layer and (IV) a substrate. The boride formed on the cobalt substrate has a needle-shaped structure, whereas the silicide has a nearly smooth morphology.



Fig. 3. Relation between the boronizing temperature and time on the thickness of modified layer formed on pure cobalt.

Fig. 3 indicates the thickness of modified layer as a function of boronizing time. The thickness of modified layer ranged from 40 to 186 µm. As it is well known, thickness of the boride layer is closely related with the process temperature, treatment period and chemical composition of substrate [17]. As the boronizing time and temperature increased, the depth of modified layer increased.

# 3.2. Phase analysis

Fig. 4 shows the results from the X-ray diffraction (XRD) analysis of the specimen treated by boronizing for 2 and 8 h at various temperatures. As shown in Fig. 4a, peaks from the Co<sub>2</sub>B boride were observed. When increasing the boronizing temperature, as shown in Fig. 4b, a small quantity of Co<sub>2</sub>Si is detected. Fig. 4c shows that the strongest peak from the Co<sub>2</sub>Si silicide was detected, suggesting that a large amount of Co<sub>2</sub>Si is formed on the surface of the boride layer when pure cobalt was boronized at 950 °C. However, no peaks of boride phase can be observed when pure cobalt was boronized at 950 °C for 8 h. The reason is that the silicide phase covers outside of the boride layer whose thickness is thick, and boride phase exists inside of modified layer.

There are three cobalt borides (Co<sub>3</sub>B, Co<sub>2</sub>B, and CoB) according to Co–B phase diagram. This was the consequence of the presence of Co<sub>2</sub>B as determined by X-ray diffraction (Fig. 4). The formation of Co<sub>2</sub>B can be explained by the fact that Co<sub>3</sub>B acts as a diffusion barrier. Hence, the supply of boron for the continued growth of Co<sub>3</sub>B is reduced. Boron atoms accumulating behind the layer of Co<sub>3</sub>B react with it, forming Co<sub>2</sub>B on the cobalt substrate. When the boronizing powders (that contain SiC) were packed in air, SiC can oxidize at temperatures greater than 600 °C to form a sheath of SiO<sub>2</sub> on the surface [18]. The



Fig. 2. SEM and SEM–BSE micrographs of the boronized pure cobalt at 900 °C for 4 h: (a) SEM micrograph; (b) SEM–BSE micrograph.

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