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Electrodeposition of bronze–PTFE composite coatings and study on their tribological characteristics

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Abstract

The aim of this paper is to obtain lubricant composite coatings of bronze (copper with 10–15% tin) with PTFE (polytetrafluoroethylene) particles over mild steel substrate and to evaluate their tribological properties. The electrodeposition was carried out from an alkaline bath containing cyanide. The composite coatings were prepared by means of CECD (Conventional Electrodeposition) and SCD (Sediment Co-deposition) techniques. PTFE suspension with an average particle size of 0.3 μm was used. The incorporation of PTFE in the composite coatings was investigated with respect to the PTFE concentration in bath, cathode current density, and mode of deposition. The cathode efficiency of the coating was calculated. The PTFE distribution in the composite coatings, as examined with SEM, are uniform at low concentration of PTFE in the bath and agglomerated at high concentrations. The PTFE incorporation in the SCD technique is higher than that of the CECD technique. Physical properties of the composites including hardness, wear resistance and roughness etc., were measured.
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1. Introduction

Extensive research work has been carried out in the past in composite coatings produced by chemical or electrochemical deposition techniques. Interest in such composites has increased substantially during the past two decades due mainly to the fact that they can enhance properties, such as wear resistance, high temperature corrosion protection, oxidation resistance and lubrication properties of a metallic coating.

Co-deposition of particles in a metal matrix is the result of the adsorption of metal ions at the particle surface and thus making them attracted to the cathode [1]. The influence of the particles' presence in the electrolyte on mass transfer enhancement and the effect of hydrodynamic conditions on the particle content in co-deposits has also been investigated [2,3]. The kinetics of the deposition of inert particles from electrolytic baths has been investigated by Guglielmi [4] and Celis and Roos [5]. Celis et al. [6] proposed a mathematical model for electrolytic co-deposition of particles with a metallic matrix. Stankovic and Gojo [7] reviewed electrodeposited composite coatings of copper with inert, semi-conductive and conductive particles.

Different metal matrix composites containing second phase particles have been electrodeposited to improve mechanical and physiochemical properties of the material. A different approach to improve wear characteristics is based on the reduction of the coefficient of friction between relatively moving surfaces by the

Table 1
Composition and deposition parameters of Cu–Sn bath used

Deposition parameters	Concentration
CuCN	30 g/l
NaCN	45 g/l
Na_2SnO_3	42 g/l
NaOH	10 g/l
Temperature	40 °C to 60 °C
pH	12.5
Current density	1–5 A/dm^2

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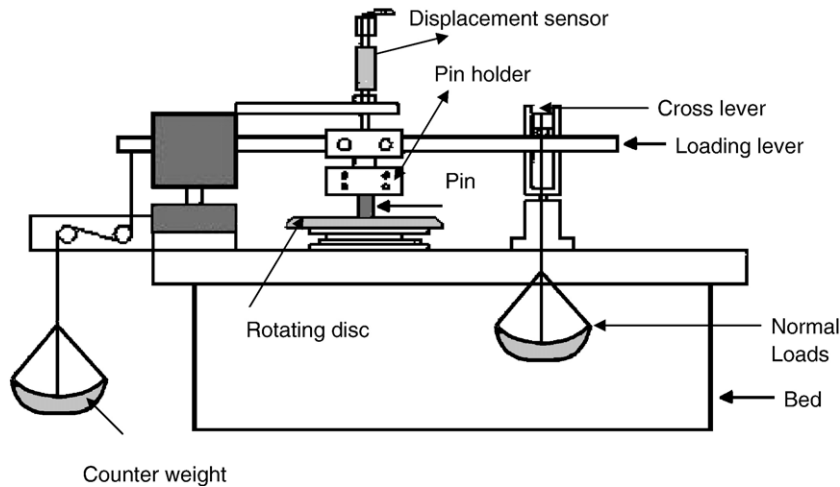*E-mail address:* malathypush@yahoo.com (M. Pushpavanam).

Fig. 1. Pin on disc wear testing set up.

introduction of a dry lubricant in the metal matrix [8]. Polymers especially polytetrafluoroethylene (PTFE), with their non-stick properties are used mainly for dry lubrication. Research on the electrodeposition of nickel–PTFE has been carried out during the past one decade and is also compared with the electroless coatings [9,10]. Research on Au–PTFE composite coating has also been carried out by Serhal et al. [11]. Numerous studies have been devoted to electrodeposited copper composites [12]. Bhalla et al. have studied the properties of copper–PTFE composites [13]. Addition of PTFE particles in the deposition baths decreases the coating's hardness but gives good self-lubrication properties [11–15]. Occlusion plating of a second phase particle with a metal matrix has been carried out by both CECD and SCD techniques [15]. Particles were kept in suspension by continuous agitation in the CECD technique whereas particles were suspended intermittently in the electrolyte and allowed to settle onto the horizontal cathode as sediment and co-deposited in the SCD technique [16]. Co-deposition of particles in a metal matrix is the result of the adsorption of metal ions on the particle surface thus making them attracted to the cathode [17].

For bearing applications the coating selected must possess high ultimate tensile strength, hardness and low dry coefficient of friction. Since, bronze containing copper and 10–15% tin, has the

above properties [18–20], it is widely used in the automotive industry [18–20]. PTFE is a material that possesses non-stick and sliding properties, chemical inertness etc., Hence, co-deposition of PTFE along with bronze should provide an excellent load carrying capacity and solid lubrication. Reports are available on electro-co-deposition of Al_2O_3, CaF_2, talc particles and graphite along with brass (Cu–Zn) and bronze (Cu–Sn) alloy [21–24]. In this paper electro deposition of bronze–PTFE composite coatings on mild steel substrate and its characterization has been discussed.

2. Experimental

The electrolyte used in this study is a cyanide–stannate system, containing PTFE suspension. The composition of the bath and operating parameters for electrodeposition are as given in Table 1. PTFE concentration in the electrolyte was varied between 10 and 60 g/l. Electrodes were positioned in horizontal plane (SCD) or vertical plane (CECD) with dual anodes. The distance between anode and cathode was maintained as 7 cm.

Both plain bronze and bronze–PTFE coatings (PTFE suspension with a particle size of 0.3 μm supplied by M/s. Dupont India Pvt Ltd) are produced on mild steel substrates using the CECD and SCD techniques. The duration of plating was 1 h. Steel specimens of $25 \times 75 \times 1$ mm were used for the studies. Before each experiment, cathodes were mechanically polished, degreased with trichloroethylene, cathodically cleaned in alkaline solution, dipped in acid solution (HCl) and rinsed with distilled water. Experiments were performed in a beaker of 500 ml capacity with magnetic stirring in order to keep the PTFE particles in suspension. Stirring speed was varied from 50–300 rpm for the CECD technique and maintained at
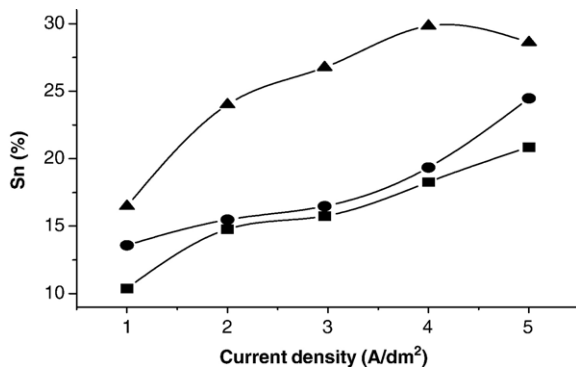

Fig. 2. Effect of current density and temperature on composition of bronze deposit. C.D: 2 A/dm^2; agitation: 300 rpm; temperature °C:–■– 40;–●– 50;–▲– 60.

Table 2
Effect of stirring rate on the composition and CCE of the alloy

Rotational speed rpm	Cu (%)	Sn (%)	CCE (%)
50	76.00	24.00	65.71
80	79.10	20.90	72.14
300	89.60	10.40	82.10

2 A/dm^2; 40 °C.

Table 3
Effect of bath temperature on the composition and CCE of the alloy 2 A/dm^2; 300 rpm

Bath temperature °C	Cu %	Sn %	CCE %
40	89.60	10.40	82.10
50	84.20	14.80	77.45
60	77.45	22.60	65.87

300 rpm intermittently for the SCD technique. Experiments were conducted with and without PTFE addition.

Cathode efficiency of the deposits was calculated knowing the mass of the deposit and the composition of the alloy. The deposits were stripped electrolytically, the solution centrifuged and the PTFE content was estimated gravimetrically. Copper and tin contents of coatings were determined by using X-ray fluorescence spectroscopy. The total mass of the deposit, its composition and density of the constituents were used to determine the volume percent of PTFE in the deposit. Surface morphologies of composite coatings were examined by scanning electron microscope and phase types were examined by XRD using Cu Kα radiation.

Hardness of the deposits was determined using a Mitutoyo microhardness tester at a load of 25 g. Surface roughness of the composite was determined by means of a Mitutoyo Roughness testing instrument.

The wear was determined using a pin on disc machine in dry conditions. The flat samples made from mild steel were plated with bronze–PTFE composite coating. For comparison bronze coatings were also tested. The pin used for testing was SAE 200 high speed steel containing 5% of cobalt with 6 mm diameter, and a hardness of 65 HRC. The tests were done at various loads, distances and speeds and rotating track diameter was around 14 mm. The wear resistance of the composite coatings was characterized by weight loss. It was obtained by weighing the specimen before and after each experiment. Fig. 1 shows the apparatus used for testing wear and friction of composite coatings.

3. Results and discussion

3.1. Bronze deposition

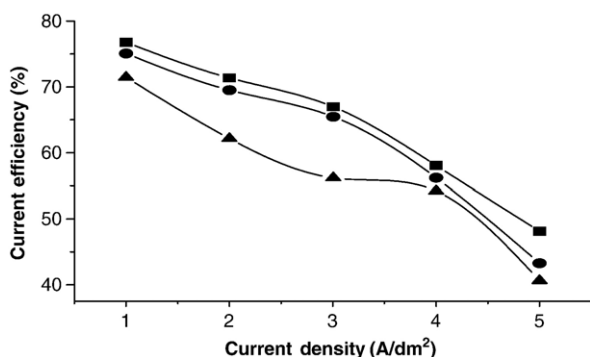In order to produce the composite, the conditions for producing the alloy of the desired composition have to be stan-
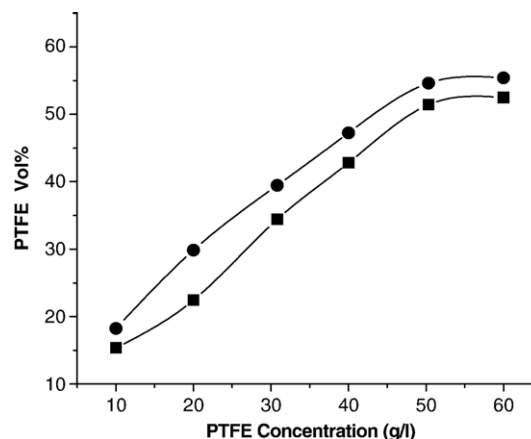

Fig. 4. PTFE volume percent as a function of PTFE concentration in the bath and plating techniques. C.D: 2 A/dm^2; agitation: 300 rpm; temperature 60 °C.–■– CECD;–●– SCD.

dardized. Fig. 2 shows the composition of bronze deposit as a function of current density at 40°, 50° and 60 °C at 2 A/dm^2. An increase in current density generally helped in increasing the tin content of the alloy. Increasing the electrolyte-stirring rate decreased the tin content of the alloy (Table 2). With increasing bath temperature the tin content rose up further, as given in Table 3. Thus the alloy composition is dependent on temperature, current density and stirring rate. For producing bronze alloy containing 10–15% tin, it would be advisable to operate the bath at ambient temperature and at 1–2 A/dm^2 the rotational speed being 300 rpm.

The variation in cathode efficiency of the bronze bath with current density at different temperatures is shown in Fig. 3. The cathode efficiency decreases with the increase in current density. The efficiency is higher at 40 °C than at 60 °C at a given current density (Table 3). In other words, the cathode efficiency increases with decreasing operating current density and temperature. Decrease in cathode efficiency with increasing operating current density can be attributed to increased cathode polarization and mass transfer limitations. Normally, deposition from complex baths result in lower efficiency due to higher over potential required. Tin deposition from stannate bath occurs
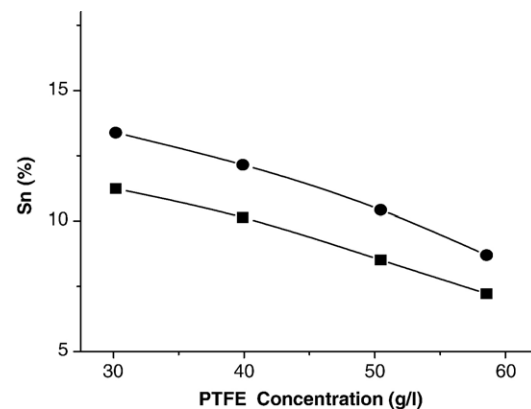

Fig. 3. Effect of current density and temperature on cathode current efficiency of bronze plating agitation: 300 rpm; temperature °C:–■– 40;–●– 50;–▲– 60.

Fig. 5. The dependence of the percentage of tin in the deposit with PTFE concentration in the bath. Conditions as above. Mode of deposition:–■– SCD;–●– CECD.

Table 4
Effect of PTFE concentration on the alloy composition and CCE

PTFE conc.	Cu (wt.%)	Sn (wt.%)	PTFE (wt.%)	CCE (%)
20	76.07	16.48	7.45	65.37
30	76.57	11.24	12.19	68.60
40	74.15	10.14	15.71	75.52
50	69.41	8.83	21.76	78.37
60	67.76	7.2	25.04	79.41

SCD:2 A/dm^2; 300 rpm; 40 °C.

Table 5
Surface roughness measured at different PTFE contents in deposit

PTFE percent in deposit (vol.%)	Surface roughness (μm)
0	0.3
15.35	1.33
23.32	1.38
35.64	1.84
42.79	2.32
50.87	2.74
53.51	3.92

through tetravalent tin and associated with lower efficiency. Hence, with increase in tin content the alloy deposition efficiency decreases.

3.2. Bronze–PTFE composite deposition

Electroplating of the bronze–PTFE was carried out by both CECD and SCD techniques. The PTFE volume percent in the deposit as a function of PTFE concentration in the bath is shown in Fig. 4.

At constant stirring rate (300 rpm), an increased concentration of particles in the bath corresponded to an increased incorporation of particles in the coating (Fig. 4). With increase in PTFE concentration above 50 g/l in bath, the PTFE percent in composite coating becomes almost constant which is similar to that observed for graphite–bronze and graphite–brass composites [22–25]. This is partly because of the agglomeration of particles in the bath; also, it corresponds to the maximum particle adsorption on the substrate surface thus resulting in constant PTFE percent in the composite coating.

Fig. 4 also shows that the amount of PTFE in the composite coating is higher in the SCD compared to the CECD technique at constant PTFE concentration in the bath. This is similar to that observed by Ghouse et al. for Cu–graphite, and Cu–SiC composite coatings [15–17]. In sedimentation technique, the horizontal cathode allows co-deposition of particles easily due to the positive influence of gravity on the particles. In the CECD method, the particles should get adsorbed on to the surface against gravity till they are engulfed into the growing metal deposit.

The dependence of the tin content in the composite with the PTFE concentration in the bath and the mode of deposition, at cathode current density of 2 A/dm^2 is shown in Fig. 5. Tin content
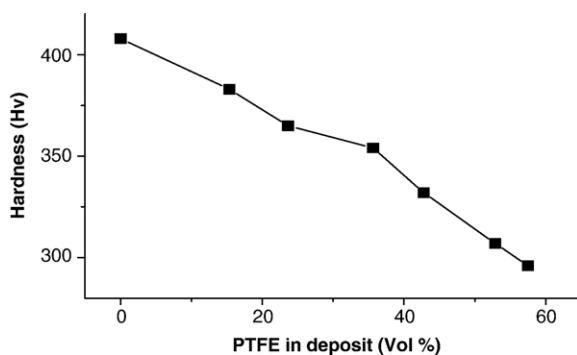
increases initially (Table 4) with the addition of PTFE and then decreases with increase in PTFE concentration. As the concentration of particles in the bath increases, more of electrode area is covered by the particles and hence the area available for metal deposition is less. This makes the actual current density applied to be considerably higher than what is expected from the geometrical area of the substrate. So, at such higher current densities tin content decreases. However, the tin content obtained with the SED technique falls within limits and hence, considering higher particle incorporation and the desired tin content in the alloy, SED deposition appears to be more preferable than the CECD method. Table 4 shows the composition of the alloy composite produced with different PTFE concentration in the bath and the current efficiency of deposition.

3.3. Hardness of the composite

As shown in Fig. 6, hardness of the bronze–PTFE composite depends on the volume percent incorporation of PTFE particles. Increasing PTFE content in the deposit decreases the hardness of the deposits. This can be attributed to the soft nature of the lubricating particles.

3.4. Surface roughness

Table 5 shows the variation of surface roughness with the PTFE content of the deposit. The arithmetic mean average R_a values vary from 0.3 μm for the pure bronze deposit to 1.33 and 3.92 μm for the composites containing 15.35 and 53.5% PTFE
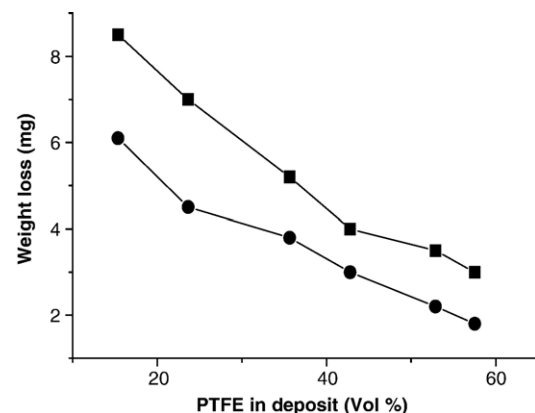

Fig. 6. Effect of PTFE in the deposit on the hardness of deposits.

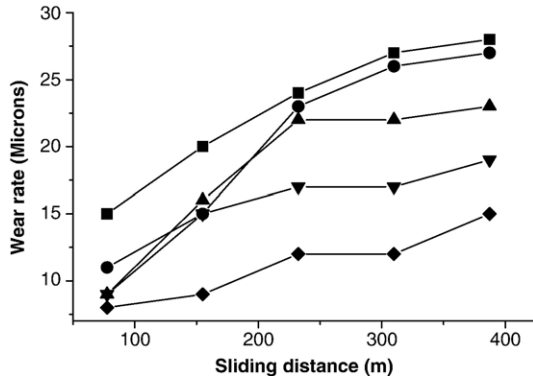Fig. 7. Effect of PTFE content on the wear loss of deposits.–■– CECD;–●– SCD.

Fig. 8. Wear rate as a function of sliding distance. Deposits containing PTFE, vol.% :–■– 15.35;–●– 23.64;–▲– 35.64;–▼– 42.79;–◆– 52.87.

respectively. This should be due to the increased current density at the surface due to the blocking effect of the particles.

3.5. Wear resistance

As seen in Fig. 7, wear loss decreases with increase in PTFE concentration in the deposit due to the lubrication contributed by the particles. It is also seen that the wear loss estimated for coatings produced by the CECD technique is higher than those produced by the SCD technique. It has been already observed that the extent of co-deposition is higher in coatings produced by the SED technique. So, the decreased wear loss despite the higher roughness of the surface is due to the higher lubrication prevailing due to higher particle absorption. The wear rate in microns versus
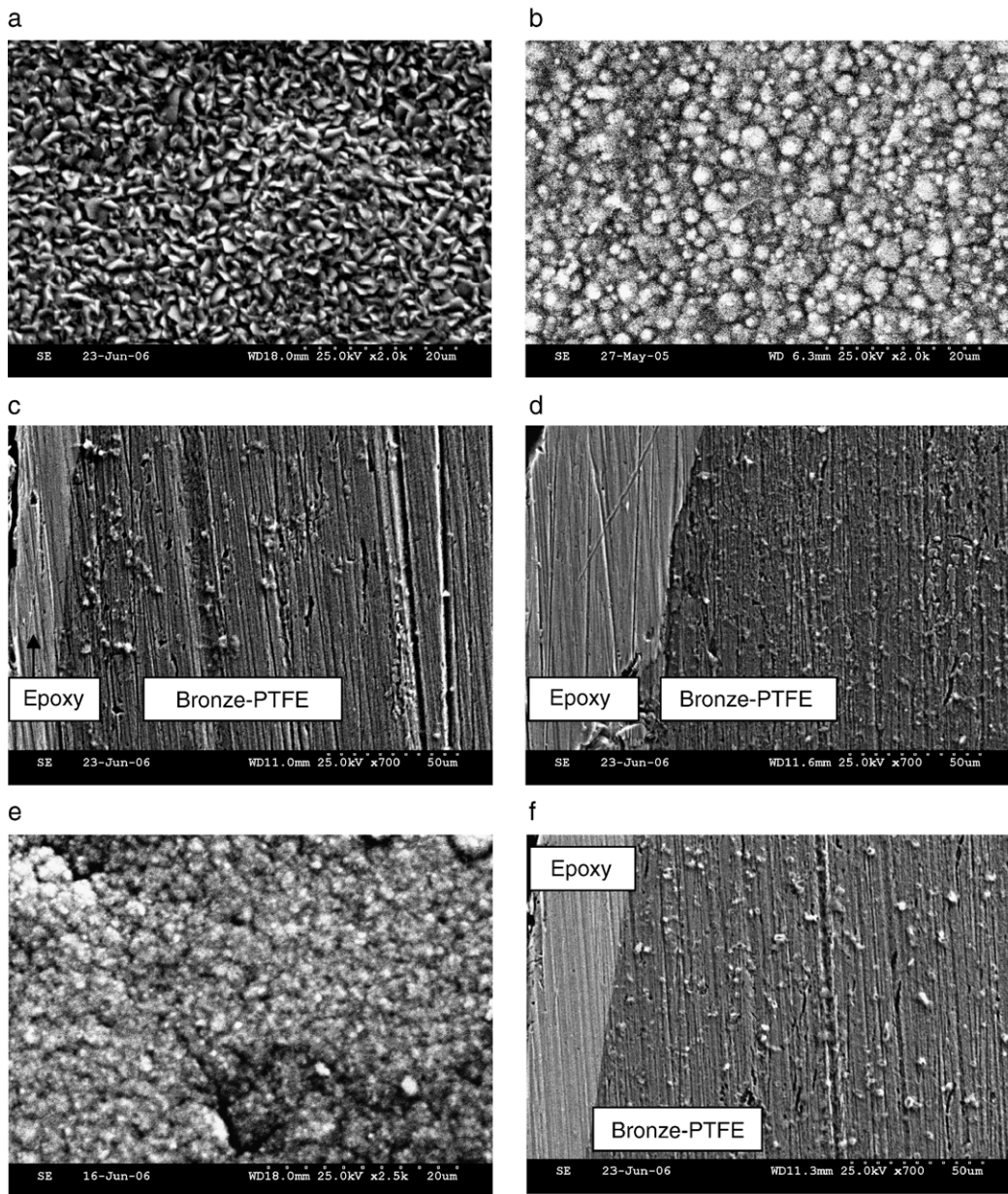

Fig. 9. a SEM micrograph of bronze without PTFE. b SEM micrograph of bronze with 42.79% PTFE (CECD). c Cross section of bronze 23.6% PTFE composite (CECD). d Cross section of bronze 52.8% PTFE composite (CECD). e SEM micrograph of bronze with 55% PTFE (SED). f Cross section of bronze 52.8% PTFE composite (SCD).
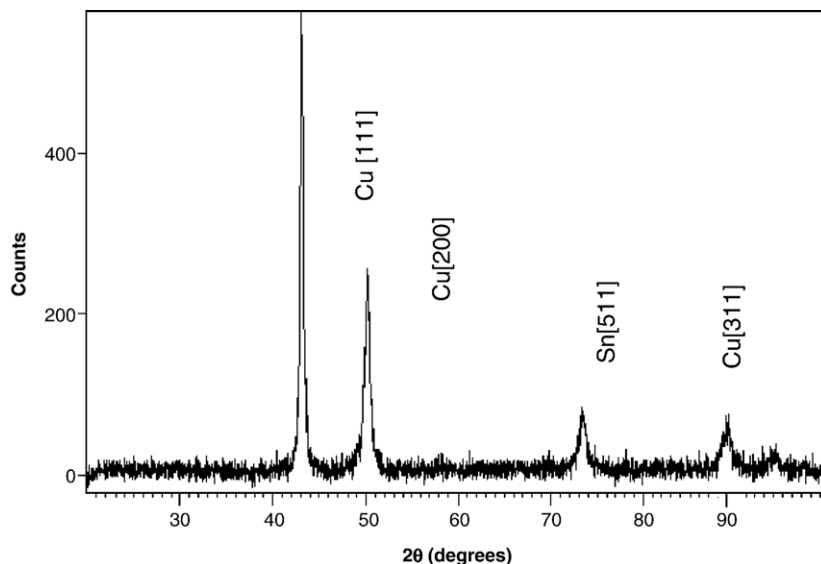
Fig. 10. X-ray diffractogram of bronze deposit with PTFE.

the sliding distance for deposits produced by the SCD technique is shown in Fig. 8. When wear occurs, the top layer of the composite having a higher roughness wears off easily showing a higher wear rate and a high slope. As wear proceeds, a glaze develops on the surface and wear rate drops considerably. Therefore, with increase in distance, the slope decreases.

3.6. Morphology of bronze PTFE

The surface morphology of the bronze–PTFE composite coatings with varying PTFE concentration produced by the CECD and SCD techniques are shown in Fig. 9a–f. PTFE particles are distributed in the deposit as white spherical globules. In the CECD technique at higher concentrations, agglomeration of the particles is more compared to that observed in the SCD technique in which PTFE is present as much smaller globules distributed throughout uniformly. The SEM cross sections of the deposits indicate that in the CECD technique, the particles are randomly distributed at lower concentrations. The distribution is improved at higher concentrations. In the SCD technique, the particle distribution is uniform.

X-ray diffractogram shows no marked change in the structure of the Cu–Sn alloy and Cu–Sn–PTFE composite (Fig. 10). The alloy should correspond to ά-bronze.

4. Conclusion

Bronze–PTFE composite coatings containing copper with 10–15% Sn can be obtained from a cyanide bath at 40 °C. The current density, stirring rate and PTFE content in the bath influence the cathode efficiency and deposition rate. The cathode efficiency is optimum at 2 A/dm^2.

PTFE particles can be successfully co-deposited with bronze alloy by both CECD and SCD techniques. The amount of PTFE obtained by the SCD technique is greater than that obtained by the CECD technique.

Comparison of SEM micrographs obtained by the examination of the deposits both on the surface and in the cross section show better uniformity in the distribution of particles in the coating obtained by the SCD technique. Agglomeration of particles was more prevalent in the CECD technique. At lower concentrations the cross sectional view of the deposit obtained by the CECD technique shows random distribution of particles and at higher concentrations the distribution is improved. The SCD technique shows better particle distribution in the cross section also.

The bronze–PTFE coating exhibits a marked decrease in the hardness compared to the bronze coating and the hardness slightly decreases with increase of the PTFE content. While bronze alloy coating has a smooth surface, the bronze–PTFE coatings have high roughness, which becomes rougher with increase of PTFE concentration in the bath.

The wear resistance of the bronze–PTFE composite coatings can be improved by the presence of dry lubricant PTFE particles. The wear rate for CECD obtained composite coatings are higher than that obtained by the SCD technique. The wear resistance increases by increasing the PTFE particles in the deposit.

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