

STUDIES ON THE PRODUCTION OF COMPOSITE COPPER LEAD POWDER AND BEARING SLEEVES

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The paper describes a new technique for the production of copper-coated lead powder and its subsequent use for making bearing sleeves.

The investigations outline the advantages of fluoborate over acetate process for the preparation of Cu-Pb powders and relate also how the different Cu-Pb composition and sintering temperature bring about variations in physical properties of the bearing sleeves.

The bearing materials mainly required for internal combustion engines consist essentially of a steel backing with a lining of copper-lead alloy. The lining serves to impart anti-frictional properties, a fairly good proportion of softness and an adequate load-carrying capacity. The bearings are produced by casting the alloy on steel or by sintering process. The inherent difficulties involved in the casting process are that of poor wettability between steel and copper-lead; segregating tendency of lead and therefore local variations in composition.

The sintering process which involves preparation of Copper-Coated lead powders and sintering of the powder on the steel has been found to be more efficient and eliminate the difficulties encountered in the casting method (Figs. 1 and 2).

The purpose of this paper is to work out the details for the preparation of different compositions of Cu-Pb powders and to study the effect of sintering temperature and other conditions responsible for marked variations in physical properties of the bearing material.

A reference regarding the preparation of composite copper-lead powder by acetate process¹ is available. In this process, fine lead powder is introduced into copper acetate solution whereby precipitation of copper films on the particles takes place.

Mantell² initiated development work on the preparation of composite metal powders through an aqueous acetate electrolyte, but the details are lacking. Some details of depositing and refining of lead from acetate,³ fluosilicate,⁴ fluoborate,⁵ cyanide⁶ electrolyte are available and so also of copper from cyanide,⁷ acid copper sulphate,⁸ fluoborate.⁹ Kochler,¹⁰ Drouilly¹¹ and Fisher¹² have described the methods of preparation of copper powder by the electrolysis of acid copper

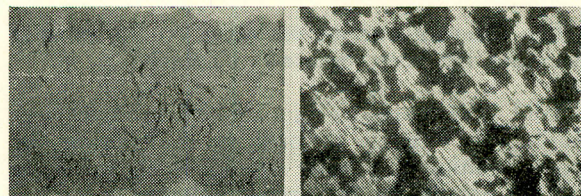


Fig. 1.—indicates sintering on to a mild steel.

Fig. 2.—shows the distribution of copper and lead. The photograph has been taken after rolling and annealing.

sulphate solution but the operating conditions vary very greatly.

Before trying to prepare composite copper-lead powder electrolytically, from a single bath, the general conditions for making copper powder and for depositing lead have been kept in view. The paper also compares the advantages of fluoborate over acetate process.

Experimental

Acetate Process.—Copper and lead acetate solutions were electrolysed between 60:40 cast copper-lead anodes and nickel cathode. The conditions for the preparation of 60:40 copper-coated-lead powder by this process were investigated.

Electrolyte: Copper 15.0 g/l; Lead 3.0 g/l; Free acetic acid 250 g/l.

Current: Cathode current density 125 asf; Anode current density 100 asf; Voltage 12.5 V.

Yield: Total 7.0 g/hr; G/KW/hr 224; Current efficiency 20%.

Sieve Analysis of the Powder (B.S.S.): +200 15%; -200+325 80%; -325 5%.

Fluo-borate Process.—The electrolytes were prepared by mixing hydrofluoric acid and boric acid. The cations were introduced by decomposing their respective carbonates with the acid mixture, i.e. fluoboric acid. The required concentrations were obtained by mixing the calculated quantity of fluoboric acid and copper and lead carbonates and diluting with distilled water.

Nickel sheet ($2 \times 2.4 \times 1/16$ in) was used as a cathode while copper-lead alloy was used as an anode. In an other experiment cast copper-lead alloy was replaced by an assembly comprising ($3 \times \frac{1}{2} \times 1/8$ in) strips of copper and lead. Each assembly consisted of three and two strips of copper and lead respectively.

The effect of various variables on the powder formation has been reported in Tables 1-4.

Mild steel blanks of ($4 \times 1 \times 1/16$ in) size were thoroughly cleaned to prepare the surface for copper plating. A basic cyanide bath was used and the details of which are as follows:

Copper cyanide 25 g/l; sodium cyanide 33 g/l; Rochelle salt 60 g/l; sodium carbonate 30 g/l; current density 4×10^{-2} ; pH 12.6.

Copper-coated lead powder was heaped on the plated side of the blank to form $1/16$ in thick layer. The blank was then placed in a tube furnace in which partially burnt gas atmosphere was maintained. The temperature was raised rapidly. The blank was removed from the furnace and passed through the rolling mill in order to spread the bearing material to form a uniform layer. Coated blanks were finally passed through the furnace maintained at different temperatures to obtain a tenaciously adhering bearing layer on the steel.

The effect of sintering temperatures, time and the composition on the physical characteristics has been investigated and reported in Tables 5,6 and 7.

Results and Discussions

It has been observed that the acetate process has disadvantages for its low current efficiency and relatively coarse particle size of the powder. The obvious reasons are that acetate electrolyte possesses high resistivity and therefore, require high current density. Moreover, since the powder obtained by this process is coarse in size, limits its use for making bearing sleeves.

Starting from the arbitrary amount of copper, lead and free acid contents of the electrolytes, a

TABLE 1.—EFFECT OF VARYING THE COPPER AND LEAD CONTENTS OF THE BATH.

Cathode current density	100 asf
Anode current density	87.5 asf
Free (HBF ₄) acid	600 g/l

No.	Copper g/l	Lead g/l	Composition of powder	
			Copper %	Lead %
1	22.7	3.6	91.0	9.0
2	3.81	6.93	40.0	60.0
3	5.28	6.68	45.5	54.5
4	6.56	6.46	60.5	39.5

TABLE 2.—EFFECT OF VARYING THE FREE ACID CONTENTS.

Cathode current density	100 asf
Anode current density	87.5 asf
Copper contents	6.56 g/l
Lead contents	6.46 g/l

No.	Free acid (HBF ₄) g/l	Yield	
		g/hr	g/KWH
1	550	14.3	715
2	600	15.0	750
3	625	15.48	774
4	650	16.5	825
5	675	16.2	810
6	700	15.1	755
7	725	14.4	720

TABLE 3.—EFFECT OF CATHODE/ANODE CURRENT DENSITIES RATIO VARIATION.

Copper	6.56 g/l
Lead	6.46 g/l
Free (HBF ₄) acid	650 g/l
Total current	10 Amps

No.	Cathode current density asf	Anode current density asf	Composition of the powder	
			Copper %	Lead %
1	87.5	87.5	55.0	45.0
2	100.0	87.5	60.5	39.5
3	112.5	87.5	50.0	50.0
4	125.0	87.5	40.7	59.3

TABLE 4.—EFFECT OF VARYING THE TOTAL CURRENT.

Copper	6.56 g/l
Lead	6.46 g/l
Free (HBF ₄) acid	650 g/l

No.	Total current amps	Cathode current density asf	Anode current density asf	Yield		Composition	
				g/hr	g/KWH	Cu%	Pb%
1	8.75	87.5	76.5	14.9	745	62.4	37.6
2	10.00	100.0	87.5	16.5	825	60.5	39.5
3	11.25	112.5	98.5	16.5	825	59.0	41.0
4	12.50	125.0	109.5	16.4	820	58.9	41.1

series of experiments were carried out with fluoroborate process. During the course of these experiments, a range of current densities falling within the limits of copper and lead powder formation was employed.

TABLE 5

No.	Temperature °C	Composition		Density g/cc	Load carrying capacity lb/in ²	Remarks
		Time	Cu 60, Pb 40 30 min			
1	750	—	—	—	—	Complete break down on rolling
2	800	3.0	299	9.315	3397	
3	850	3.2	307	9.32	3400	
4	900	—	—	—	—	Loss of lead too high

TABLE 6

No.	Time (min)	Composition		Density g/cc	Load carrying capacity lbs/in ²	Remarks
		Temperature	Cu 60, Pb 40 850°C.			
1	15	—	—	—	—	Slight break down on rolling
2	30	3.2	307	9.32	3400	
3	45	3.6	322	9.40	3918	
4	60	3.61	323	9.40	3920	

TABLE 7

Sintering time 45 min, temperature 850°C.

No.	Composition	Tensile strength tons/in ²	Brinell hardness	Load carrying capacity lbs/in ²	Density
1	40 : 60 } Cu Pb	1.2	306	3713	9.53
2	45 : 54 } Cu Pb	1.21	308	3771	9.51
3	60 : 40 } Cu Pb	3.6	322	3918	9.40
4	70 : 30 } Cu Pb	4.12	359	4050	9.25
5	72 : 24 : 4 } Cu Pb Sn	7.2	513	6032	9.01

The cast copper and lead anode proved to be inefficient since salt layers tended to form on the anode surface and thereby caused a steady retarding effect on the electrolysis. The replacement of cast Cu-Pb-anode by an assembly comprising copper and lead strips proved very effective because the electrolysis under similar conditions proceeded undisturbed. These preliminary observations and promising results, therefore, called for a study of the following variables.

Effect of Cu and Pb Contents of the Electrolyte on the Composition of Copper.—Table 1 indicates that higher concentration of Cu to Pb favour transportation of Cu⁺⁺ while higher concentration of Pb to Cu favour transportation of Pb⁺⁺.

60:40 Cu-Pb powder has been obtained with Cu and Pb concentrations of 6.56 g/l and 6.46 g/l respectively. These values of copper and lead electrolyte have been taken as a base for further experiments. The justification to this effect is that bearing sleeves of 60:40 Cu:Pb is the most common variety, although 70:30 are also produced.

Effect of Varying the Free (HBF₄) Acid Contents on the Yield.—Table 2 shows the effect of free acid contents of the bath on the yield of the powder. It is obvious that 650 g/l free acid yields 825 g/KW-hr—an optimum value, while still higher concentrations affect the yield.

Effect of Cathode/Anode Densities Ratio on the Composition of the Powder.—Since the general and relative conditions for making Cu and Pb powders warrant widely differing current densities, the variation in cathode/anode current density ratio has been affected by changing the cathode and anode areas which cause the total current distribution to increase or decrease.

It is obvious from Table 3 that keeping the Cu-Pb concentration; free acid contents and the total current constant, the composition of the powder changes with the changing cathode/anode current density ratio. The appropriate current density ratio for the formation of 60:40 Cu:Pb have been found to be 100 asf and 87.5 asf respectively.

Effect of Varying the Total Current.—Table 4 shows the effect of total current on the yield and composition of the powder.

It further reveals that a total current within a range of 10 amps to 11.25 for which the corresponding cathode and anode current density have been reported against them, favour the formation of 60:40 Cu:Pb with a similar yield of 825 g/KWH.

Sieve Analysis: (B.S.S.) +200=5%; -200+325 =25%; -325 =70%.

Copper-lead can be sintered at about 500°C and if given a considerable sintering time, yields a strong mass, but relatively of lower density as compared to the mass obtained at higher sintering temperature. The obvious co-relation is that of shrinkage and densification. It has been observed during investigation that the sintering carried out at lower temperatures suffer from material transfer and consequently give rise to improperly connected matrix. This phenomena can also be explained on the basis of shrinkage as in the case of 60:40 Cu-Pb, the shrinkage is of the order of about 25%. Sintering at higher temperatures ensures a rapid transfer of material through the liquid and proceeds by the growth of large particles at the expense of small particles. The experiments have been conducted with fine powders (-325 mesh) but in one experiment different particle sizes (+200 to -325) were used. There seems, however, little difference of the two sintered pieces in so far as shrinkage and uniformity in sintering are concerned. Nevertheless fine powders have been employed during investigation on the consideration that for small crystals the interfacial tension between the crystals and their saturated solution is greater than that for large crystals.

Experiments carried out with different compositions of Cu-Pb at different temperatures have revealed their influences on the mechanical properties of the bearing material viz tensile strength, density and conformability etc. The effect of these variables have been discussed in detail.

Effect of Sintering Temperature and Time.—It is evident from Table 5 that 850°C is the optimum sintering temperature for 60:40Cu-Pb composition. Higher temperatures cause severe loss of lead content while a lower temperature brings about a structure which is friable and breaks down on

rolling. The best sintering time has been found to be 45 minute. The influence of time can be gauged from Table 6.

Effect of Composition on the Physical Properties.—Table 7 makes it clear that improvement in the mechanical properties is governed by the lead contents. Addition of small amounts of tin causes great rise in tensile strength, hardness and load carrying capacity. The values recorded in Table 7 help further to interpret that extent of structural consolidation is an inverse function of the lead contents. As a matter of fact the increase in lead contents mean a greater volume of liquid (since sintering is in the liquid phase) and therefore, an unfavourable high contact angle between the solid particles. Weak structure, therefore, results because surplus liquid prevents the spheres from coalescing. In other words phenomenon of structural consolidation may better be understood in the light of volume of liquid. As the addition of tin reduces the volume of lead, better structural consolidation is achieved in addition to the fact that addition of tin strengthens copper.

References

1. E. Fetz, *Metals and Alloys*, **8**, 257 (1937).
2. Charles L. Mantell (U.S. Patent 2, 182, 567); *Chem. Abstr.*, **34**, 1923 (1940).
3. F.C. Mathers, *Metal Finishing*, **38**, 533 (1940).
4. Allen G. Gray, *Modern Electroplating* (John Wiley, New York, 1953), p. 288.
5. A. Kenneth Graham, *Electroplating Engineering Handbook* (Reinhold Publishing, New York, 1954), 2nd ed. p. 244.
6. J. Sullivan, U.S. Patent 2 230 602 (1941).
7. A.K. Graham, *Electroplating Engineering, 2nd Ed. Handbook* (Reinhold Publishing, New York, 1954), pp. 238, 239 and 240.
8. Koehler, U.S. Patent, 1,777,371.
9. Drouilly, U.S. Patent 1,799,157.
10. Fisher, U.S. Patent, 2,216,167.