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# Some Properties, Inhomogeneities, and Applications of Plasma Sprayed Electroconductive Cu-Based Coatings

M. Brezovsky, V. Palka, and V. Chovanec

This article reports on the effects of inhomogeneities on properties of plasma sprayed electroconductive copper and CuSn coatings. These coatings, in combination with aluminum-alloy-based substrates, are of interest for applications in the power industry, particularly for the production of diverse types of power clamps and armatures for switching stations of high and very high tension electrical equipment. The properties of an aluminum alloy substrate with an electroconductive coating were examined, including coating structure, character of coating substrate boundary, strength, hardness and adhesion of the coating, as well as electrical conductivity and contact resistance between the substrate and coating.

## 1. Introduction

COPPER and aluminum alloys are the most widely used electroconductive materials. To distribute electricity in high tension and very high tension switching stations, there is often the need to conduct electrical power from copper connecting points of power sources to the copper connecting points of electric appliances, for example, by aluminum or aluminum-steel cables. Many types of power armatures and clamps are manufactured for joining aluminum and copper conductors by casting of dissimilar metals, pressing or embedding the copper parts into aluminum alloy, resistance welding, etc. For example, Fig. 1(a) shows a clamp for a copper flange 100 mm in diameter and an aluminum tube (100 mm in diameter with a 5-mm wall thickness), and Fig. 1(b) shows a clamp for a copper bolt 36 mm in diameter and a cable, consisting of a copper (smaller) part embedded in an aluminum alloy. The problem encountered in manufacturing these clamps is a suitable mechanical and electrical connection of both parts. The main concern is that the contact resistance at the junction of the aluminum and copper parts may be a significant portion of the total resistance of the node, thus determining the overall properties of the clamp. The higher the contact resistance, then the higher the heat of production, which leads to temperature increases in the clamp and subsequent power losses. Significant power losses, when such types of instrument clamps and armatures are used, and also the high demands placed on their production, led to further development of the clamps.<sup>[1,2]</sup>

The new method of production is based on fabrication of the body (armature, clamp, etc.) with an aluminum alloy, whereas the contact area for attachment of the copper member is covered by a plasma sprayed coating of copper or copper alloy (Fig. 2). The suggested solution is based on a study of properties of copper-based coatings deposited on aluminum alloys by plasma

**Key Words:** aluminum substrate, clamp application, contact resistance, copper-based coatings, electroconductive coatings, structure/property relationships

M. Brezovsky and V. Palka, Slovak Academy of Sciences, Institute of Materials and Machine Mechanics, Bratislava, Slovakia; and V. Chovanec, ELBA Kremnica, Slovakia.

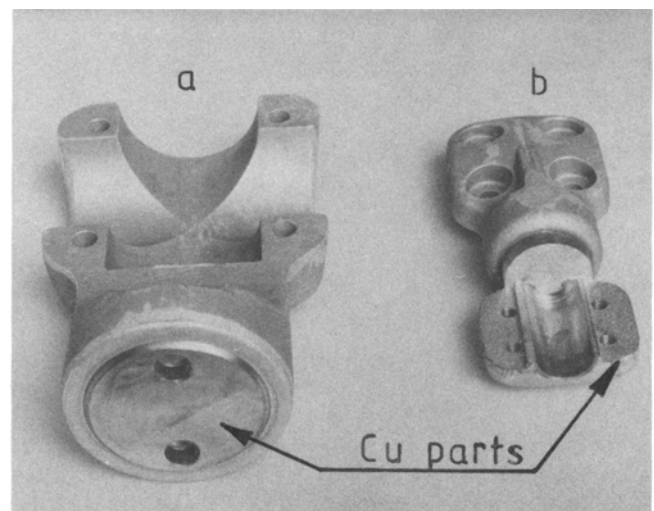


Fig. 1 Clamps with copper part embedded into an aluminum alloy

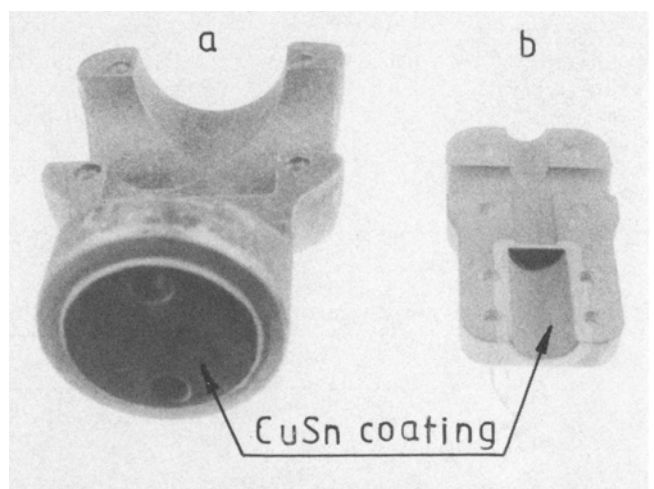


Fig. 2 Clamps with a CuSn coating

spraying.<sup>[2,3]</sup> This method allows uniform and reproducible properties of current transition between the connecting member and the body of an armature or clamp, and at the same time, suppresses corrosion at the aluminum-copper boundary. Test measurements were made of the contact resistance between the copper and aluminum parts using the current-voltage method for the different types of joining. The lowest contact resistance was obtained by using a copper coating deposited by plasma spraying.<sup>[2]</sup> Inhomogeneities, occurring in the substrate coating and the substrate/coating boundary, exert a significant effect on the physical and mechanical properties of such components prepared by plasma spraying. This article identifies some inhomogeneities that result from the properties of feedstock materials, pretreatment procedures of the substrate material, the plasma spraying process, and characterization of the coating structure, which affects the serviceability of the copper-based coatings.

## 2. Experiments

The plasma sprayed coatings were electrolytically prepared copper powder and a powder of tin bronze (CuSn<sub>10</sub>) obtained by atomization. The coatings were fabricated with a Plasma-Technic AG F4-HB torch (Table 1). Metallographic study was performed by light microscopy and scanning electron microscopy (SEM) on a JEM 100C microscope with EDAX and KEVEX DELTA IV analyzers. Quantitative metallographic analysis was performed on Epiquant equipment, and X-ray diffraction analysis was done on Siemens D 500 equipment with CuK<sub>α</sub> radiation. Details on other experimental methods are also presented.

## 3. Results and Discussion

### 3.1 Powder Materials

Powder materials were selected to ascertain the suitability of two powders prepared by different production technologies as

**Table 1 Parameters of plasma spraying for copper and CuSn<sub>10</sub> powder consumables**

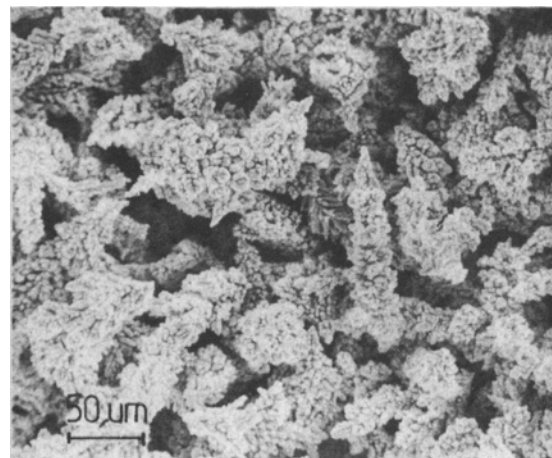
Spraying parameter	Parameter value	
	Cu	CuSn <sub>10</sub>
Plasma current, A	360	500
Plasma arc voltage, V	46	62
Plasma gas	Ar + 14.3wt% H <sub>2</sub>	Ar + 16.3wt% H <sub>2</sub>
Plasma gas flow rate, l min <sup>-1</sup>	39.7	46.6
Carrier gas, l min <sup>-1</sup>	Ar 2.6	Ar 2.6
Spraying distance, mm	130	130

**Table 2 Chemical composition of materials used**

Material	Composition, wt%							
	Sn	Al	Si	Fe	Mn	Mg	Ni	Cu
Copper powder	...	...	...	0.01	...	...	0.07	Bal
CuSn <sub>10</sub> powder	10.8	...	...	0.07	...	0.01	0.01	Bal
CuSn <sub>10</sub> coating	4.1	0.09	...	...	...	...	...	Bal
Silumin	...	Bal	9.59	0.23	0.21	0.03	...	0.03

well as from the requirement of their availability. The copper powder was prepared electrolytically and had a specific weight of 8.96 g cm<sup>-3</sup> and a grain size below 40 μm, with 10 wt% below 5 μm. Figure 3 shows the configuration and surface appearance of the copper powder. The powder particles were of irregular shape with an articulated surface with branched projections and internal pores. From the standpoint of plasma spraying process requirements, such a powder seems unsuitable. Irregular particles result in imperfect and nonuniform heating and fusion of particles during their flight in a plasma. Small copper powder particles also adversely affect powder transport to the plasma beam. This fact was verified by a flow factor test, suggesting that the copper powder has six times less flow behavior compared to the CuSn<sub>10</sub> powder.

The chemical composition of the powders is shown in Table 2. Commercial CuSn<sub>10</sub> powder is delivered in the particle size range of 0 to 100 μm. The specific density of the powder is 8.74 g cm<sup>-3</sup>, with 59 vol% ranging from 0 to 40 μm, 39.2% in the 40 to 63 μm fraction, and the remainder greater than 63 μm. The large proportion of the fine fraction and the wide range of particle sizes makes the selection of optimum spraying process parameters problematic. The CuSn<sub>10</sub> powder (Fig. 4) is of spherical shape with a dendritic structure. Analysis of the CuSn<sub>10</sub> powder indicated other nonmetallic particles composed of Al-Si-O, Fe-FeO, Ni-Ca-P-O, Ca-P-Fe-Pb-O, and Ca-P-O. These particles will become incorporated as impurities (inclusions) in the coating layer and influence the properties compared to the bulk material of the coating. Other properties of these powders and their effects on the coating structure have been studied previously.<sup>[4,5]</sup>



**Fig. 3** Copper powder

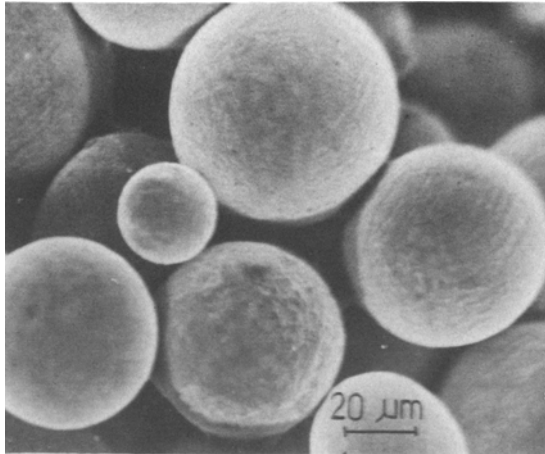


Fig. 4 CuSn<sub>10</sub> powder

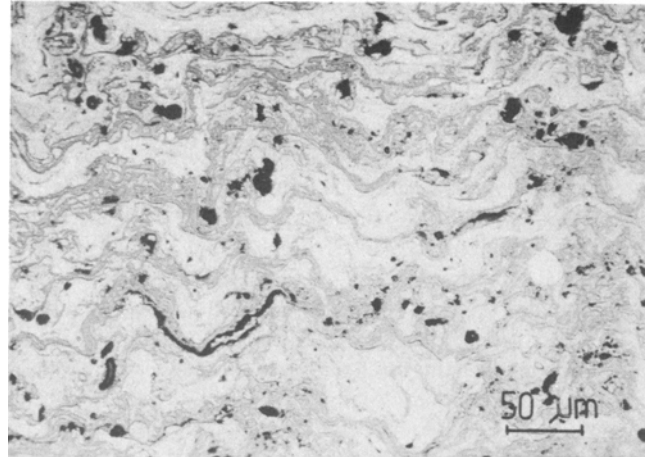


Fig. 6 Microstructure of copper coating

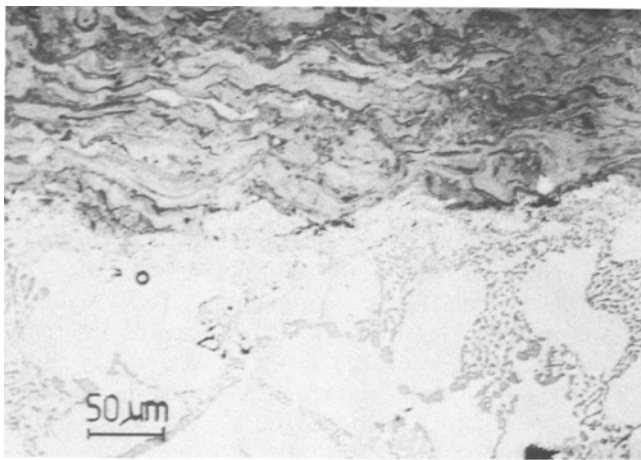


Fig. 5 Microstructure of substrate and CuSn coating

### 3.2 Characteristics of the Substrate Material

The aluminum alloy "Silumin" (CSN Standard 424330) was used in the study. The density of this alloy was  $2.6 \text{ g cm}^{-3}$ , with silicon content ranging from 9 to 13%. It was suitable for casting, with 0.4 to 0.6 vol% shrinkage, and it was also corrosion resistant. The electrical conductivity of aluminum depends on chemical composition, structure, and heat treatment. For example, for a similar type of Silumin,<sup>[6]</sup> electrical conductivity was  $18.2 \times 10^6 \Omega^{-1} \text{ m}^{-1}$ , and this is about 36% of copper conductivity.<sup>[7]</sup> The minimum tensile strength of sand cast AlSi<sub>13</sub>Mn alloy is 150 MPa; the ductility is 4%, and minimum hardness is 45 HB.<sup>[8]</sup> Figure 5 shows the base metal structure of a plasma sprayed CuSn coating. The microstructure and chemical composition suggest that this is a slightly subeutectic modified alloy with a slight addition of magnesium. Some inclusions were observed, and these inhomogeneities may be detrimental if they occur in the vicinity of the sprayed coating.

The character of the coating/substrate boundary is related to the electrical contact resistance between the substrate and

sprayed coating. Occurrence of any inhomogeneities in that boundary results in a considerable reduction of contact resistance. Because plasma spraying requires sand blasting of the substrate, attention must be paid to this problem. In the present case, the specimen surfaces were degreased in perchlorine and alcohol prior to coating and were grit blasted with brown artificial corundum of 600 to 700  $\mu\text{m}$  grain size at a pressure of 0.3 to 0.5 MPa. Forces greater than about 0.5 MPa may cause cracks in the surface layers. Corrosion may occur preferentially in such places. Also, residual corundum particles, anchored in the boundary, were observed as artifacts of the grit blasting procedure. Their occurrence is undesirable. The aluminum-based alloys also form oxide films on the blasted surface after a very short time.

Tests were performed by spraying the CuSn<sub>10</sub> coating on the cylindrical surface of specimens 30 mm in diameter and 50 mm long. If the time between sand blasting and spraying was longer than 1/2 h, then adherence was poor. The effect of temperature was studied on two series of specimens. One series was sprayed with six passes deposited in alternating directions without changing the parameters and without cooling. The temperature of the specimen surface reached about 200 °C. In the second series, the specimens were cooled after each pass to maintain the temperature of specimens after individual passes in the 90 to 96 °C range, followed by cooling to 33 to 40 °C. The boundaries of specimens prepared in this manner did not show any significant differences in the amount of corrosion products. However, the first series of specimens with a surface temperature of about 200 °C exhibited local zones with partial decomposition of the silicon phase. The occurrence of local or more continuous zones with oxides at the boundary may, in addition to lowering contact resistance, also exert an unfavorable effect on coating adhesion to the substrate. Thus, it is necessary to select spraying procedures so that the occurrence of oxides is minimized.

### 3.3 Structural Properties of Copper and CuSn Coatings

The microstructures of copper (Fig. 6) and CuSn (Fig. 5) coatings are similar and are layered, which is typical for plasma sprayed coatings. The microhardness of the individual layers

was measured according to CSN Standard 420375. At a 0.049-N load, the microhardness of the bright layers attained 24.1 VPN and that of the dark layers 28.7 VPN, with measurement error of less than 10%. The structure of the copper coating was mono-phase and layered, caused by the irregularity of the shape and dimensions of the grains and cooling conditions at particle impingement on the substrate. The solubility of tin in the individual layers varied from 0 to a maximum of 5 wt% and suggests that evaporation of tin takes place during spraying, as confirmed by chemical analysis of the coating (Table 2).

X-ray phase analysis of the sprayed coating, performed by the Debye-Scherrer technique with  $\text{Cu}_{K\alpha}$  radiation, determined that the coating contains a copper-based fcc phase with a lattice parameter of  $a = 36.1$  nm. Another phase analysis performed on the Siemens D-500 diffractometer revealed the 4-836 (JCPDS)-copper phase and, moreover, an amorphous peak for  $d = 73$  nm (unidentified). Phase analysis of the initial  $\text{CuSn}_{10}$  powder performed on the same equipment showed that the powder was a mixture of 4-836 copper phase and the CuSn alloy with a different lattice parameter than pure copper, but with the same crystalline structure (solid solution). The CuSn phase in the coating could not be identified due to a lower tin content compared to the initial powder.

The feedstock  $\text{CuSn}_{10}$  powder also contained particles in the form of inclusions.<sup>[4-6]</sup> After spraying, these particles may form inclusions of different shapes and sizes, as shown in Fig. 7. The compounds were of diverse chemical composition, with higher or lower content of iron, aluminum, and oxygen forming the complex oxides, and in some cases,<sup>[9]</sup> they can form amorphous phases, as suggested by X-ray phase analysis.

Microhardness measurements of the bright layers of the CuSn coating, measured in a similar manner as the copper coating, obtained the value of 178 VPN, whereas the dark layer was 184 VPN with an error of less than 10%.

The porosity of both coatings was evaluated on Epiquant equipment by the linear statistic method. The CuSn coating contained an average of  $7.2 \pm 2$  vol% pores, and the copper coating contained  $12 \pm 3.3$  vol% pores. The relatively high porosity of the copper coating indicates the unsuitability of the copper powder. Similarly, the high porosity is related to the inappropriate 0 to 100  $\mu\text{m}$  particle size range. The  $\text{CuSn}_{10}$  coatings manufactured with 70  $\mu\text{m}$  powder size and copper powder with 50  $\mu\text{m}$  powder exhibit about 6% lower porosity.

Higher porosity of CuSn powder sprayed with powder of 0 to 100  $\mu\text{m}$  grain size is directly related to inhomogeneities of the coating.<sup>[2,10]</sup> It was shown that these particles of  $\text{CuSn}_{10}$  powder are spread a relatively great distance (more than 120 mm from the spraying jet center) on contact with the substrate. Mostly small particles (up to 1  $\mu\text{m}$ ), with little deformation, are captured on the rough profile of the surface. The irregularity of the coating formation toward the center of the sprayed coating is characterized by the presence of particles deformed to a different extent and particles that do not deposit uniformly on the rough substrate surface but form clusters. The articulated substrate surface, irregular distribution of particles after spreading on the substrate, and the undeformed particles in the marginal zone of the plasma stream are gradually covered with the fused and deformed particles. This results in the formation of pores of various zones that exhibit different adhesion throughout the

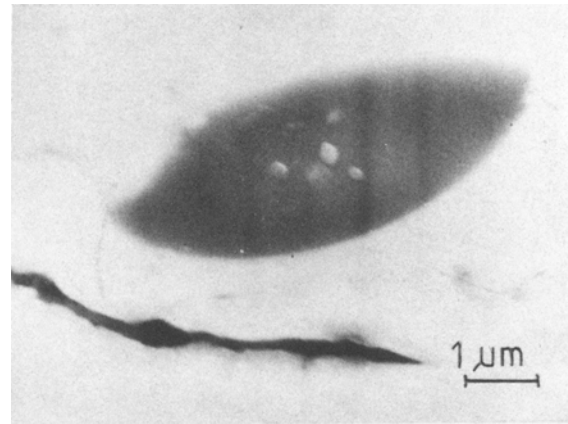


Fig. 7 Inclusions in CuSn coating

coating.<sup>[10]</sup> The inhomogeneities and pores may significantly affect coating properties and, for instance, account for the variable resistance against the degrading effects of environment in different zones of the coating.

#### 3.4 Adherence, Strength, and Hardness of Copper and CuSn Coatings

Adhesion testing allows coating optimization. However, there is some confusion in such testing as a consequence of different theoretical explanations concerning the coating and substrate bonding, as well as the existence of more than 30 experimental methods for the study of adhesion. The DIN 50160 test, with specimens in form of cylinders 30 mm in diameter and 40 mm long, was selected. The yoke test was also used on cylinders 30 mm in diameter.<sup>[11]</sup> The results showed that the adhesion of a copper coating to the substrate was 19 to 25 MPa, and that of the CuSn coating was 23 to 31 MPa.

There are no special demands placed on the hardness and strength of coatings for the intended service conditions studied in the present work (primarily power clamps and armatures with clamped attachments). The hardness of the coatings, for example from the viewpoint of indentation evaluation in clamped connections, should not be lower than the substrate hardness. Similarly, extremely high coating strength is not required in a clamped connection, because loading is primarily compressive in nature and is distributed more or less uniformly over the entire area of the clamped connection. The copper coating at 49-N loading was  $105 \pm 6$  VPN, and the CuSn coating was  $128 \pm 7$  VPN. Both coatings exhibit higher hardness values than Silumin or other metallurgical electroconductive materials such as copper or bronze.

The strength of coatings was determined from tensile tests according to CSN 420320 using modified specimens. The average ultimate tensile strength for the CuSn coating was  $126 \pm 8$  MPa, and that of the copper coating was  $53.8 \pm 3$  MPa. The lower strength of the copper coating was caused by higher porosity and higher inclusion or oxide contents. Tensile tests have shown that the ductility of CuSn coatings was never greater than 1.2%, whereas the ductility of copper coating specimens was approximately 50% lower. Both coatings are relatively brittle.

**Table 3 Electrical conductivity of copper-based coatings and materials**

	Electrical conductivity, $\Omega^{-1} \text{ m}^{-1}$						
	CuSn coating Specimen No.			Cu coating Specimen No.			
Current work	1	2	3	4	5	6	7
IMMM-laboratory	7.3	7.5	7.1	14.9	15.4	15.4	15.2
1st firm	8.4	7.2	6.2	...	...	17.2	15.6
2nd firm	...	6.6	6.4	12.2	13.9	...	13.9
	<b>Cast Materials</b>						
Reference			Cu	CuSn	CuSn <sub>6</sub>	CuSn <sub>8</sub>	CuSn <sub>10</sub>
7			50	33.3	6.7	7.14	...
14			55.5	...	...	...	5.55
15			57	9.5	7.5	...	...

**Table 4 Electroconductive properties of the coatings**

Coating	Losses, W		Contact resistance, $\Omega \times 10^{-6}$	
	Prior to test	After	Prior to test	After
Cu	0.225	1.38	3.660	6.615
CuSn <sub>10</sub>	0.146	0.31	1.682	2.168

### 3.5 Electrical Conductivity of Copper and CuSn Coatings

The four-point (four-probe) method was selected to measure the electrical conductivity of the test materials.<sup>[12,13]</sup> The coefficient of electrical conductivity is calculated from the relationship:

$$\sigma = \frac{4 \cdot L_x \cdot U_N}{\pi \cdot d^2 \cdot R \cdot U_x} \left( \Omega^{-1} \text{ m}^{-1} \right) \quad [1]$$

where the relative error  $[\Delta d/d \cdot 100\%]$  is less than 2.4% and  $L_x$  is the distance between the voltage contacts (m);  $d$  is the specimen diameter (m);  $R$  etalon (i.e., standard resistor) resistance (0.01  $\Omega$ );  $U_N$  is the voltage on resistance standard (V); and  $U_x$  is the voltage on the contacts (V).

Four specimens of the copper coating and three specimens of the CuSn coating in the form of plate (30  $\times$  10  $\times$  1 mm) were prepared. Equation 1 was adapted into the following form:

$$\sigma = \frac{L_x \cdot U_N}{S \cdot R \cdot U_x} = \frac{100 \cdot L_x}{a \cdot b} \cdot \frac{U_N}{U_x} \left( \Omega^{-1} \text{ m}^{-1} \right) \quad [2]$$

where  $S$  is the area of the rectangular cross section of the specimen.

Measurements were also taken by two independent companies to ensure that there were no specimen geometry effects. The measured values of electrical conductivity of the copper and CuSn coatings together with the values of some copper-based materials in the cast condition (from experimental literature sources) are summarized in Table 3. The average electrical conductivities of copper coatings is 14.8  $\Omega^{-1} \text{ m}^{-1}$  and that of CuSn coating is 7.1  $\Omega^{-1} \text{ m}^{-1}$ . The scatter in the  $\sigma$  coefficient arises from the type of specimens used and the accuracy of individual measuring equipment.

The experimental values of the electrical conductivity coefficient, when compared to values from the literature, indicate that the sprayed copper coating attains only 30% of the electrical conductivity of the cast electrolytic copper. On the other hand, the CuSn coating, which after spraying contains 5% Sn, has about the same conductivity as that of cast bronzes containing 6 to 8% Sn.

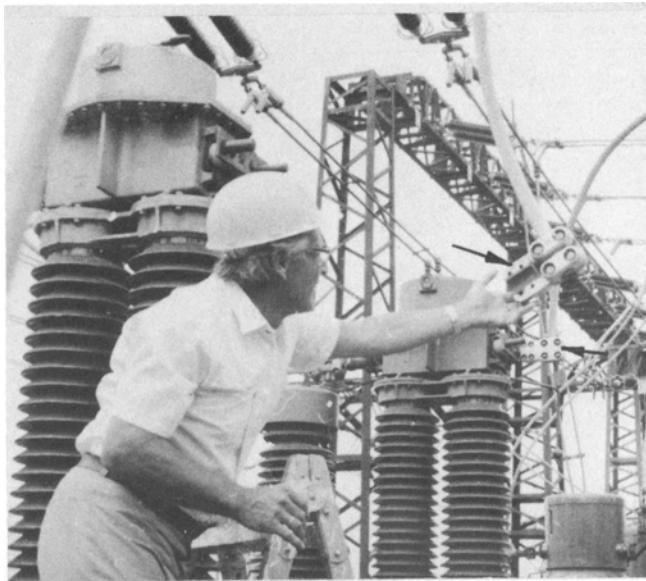
The results support the theoretical findings concerning the effect of material inhomogeneities and porosity on changes in electrical conductivity. This was true for the copper coating rather than the CuSn coating. If a higher quality of copper coating structure is attained, then the electrical conductivity will also be improved.

### 3.6 Contact Resistance of Silumin-Plasma Sprayed Coating System

The contact resistance between the two parts is an important factor for the service performance of power clamps and armatures produced from aluminum and copper parts. Approval tests have shown that the clamps with a plasma sprayed coating exhibited lower contact resistance by one order compared to those fabricated by other technologies.<sup>[1,2]</sup>

A series of cylindrical specimens of Silumin, 30 mm in diameter and 150 mm long with the coatings sprayed on the cylinder surface, were prepared to determine the contact resistances of the Silumin plasma sprayed coating system, as well as the effect of corrosion on the change in contact resistance. The effect of corrosion of the Silumin coating system on the contact resistance was studied using an accelerated corrosion test in a condensation chamber in accordance with CSN Standard 038130. The corrosive medium was  $\text{H}_2\text{SO}_3$  solution at 40  $^\circ\text{C}$ , and the corrosion test lasted 45 days.

The contact resistance on the specimens was measured by the volt-ampere technique. The contact resistances expressed by



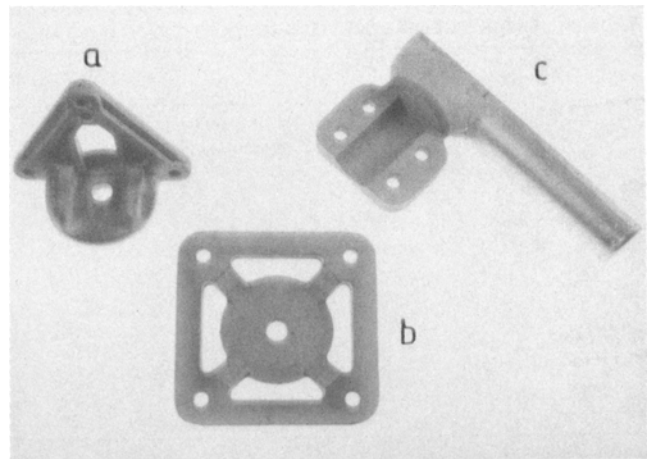
**Fig. 8** Clamps installed in a switching station

power losses and calculated in ohms prior to and after the corrosion test are given in Table 4. It shows that, prior to the corrosion test, higher contact resistances were observed on copper-coated specimens. This results from the poor bond quality of the copper coating to the substrate and the higher porosity of the copper coating compared to the CuSn coating. A higher amount of  $Al_2O_3$  oxides was observed at the coating/substrate boundary after corrosion testing, compared to the coating prior to the test. The corrosive medium can reach the boundary either through the unprotected lateral surfaces of the coating or through the pores in the coating. A more intense corrosive attack on the coating/substrate boundary was observed for the copper and CuSn coatings than on Silumin. Therefore, contact resistance of copper-coated specimens increased by 1.8 times after corrosion testing compared to 1.3 for the CuSn-coated material. The copper coating prepared from 50- $\mu m$  particles, as well as the coating of  $CuSn_{10}$  of 50 to 70  $\mu m$  feedstock, exhibited a 10 to 20% lower contact resistance compared to the commercial powders.

The effects of the corrosive environment were also examined by tests in a condensation chamber with 100% humidity for 6 months. No significant corrosion was observed, and corrosion products were observed only on the unprotected faces of the Silumin specimens. Similarly, no significant traces of corrosion were observed in specimens that were subjected to aggressive industrial corrosion for 3 years. The penetration of corrosive medium into the substrate surface area can be eliminated by sealing the coating.

#### 4. Practical Experience

Based on the study of selected properties of plasma sprayed copper-based coatings, the  $CuSn_{10}$  coating is the most suitable, and therefore, it was recommended for production of clamps and armatures. Verification of the effects of corrosive environment on service and functional reliability is extremely time consuming. Therefore, other than laboratory studies, several innovative



**Fig. 9** Typical clamps and armatures. (a) Vertical band holder for copper conductor. (b) Horizontal band holder for copper conductor. (c) Press clamp for copper bolt (36 mm in diameter) and AlFe cable

clamps were used under actual service conditions in high-tension switching stations for electricity distribution (Fig. 8). The clamps were installed in the switching stations in October 1987. The first inspection after 10 months of continuous service did not show any traces of corrosion or mechanical damage. Current loadings with peaks over 1000 A did not cause any changes on the working surfaces of the coatings. Heating measurements of the installed clamps were performed by thermovision cameras at least once per year and have shown that the new clamps exhibited better service properties than the classical ones. No unfavorable changes in the functional properties of clamps under service conditions have been observed.

#### 5. Conclusion

The encouraging results attained with plasma sprayed copper-based coatings have led directly to a practical implementation in the power industry. Electroconductive copper-based coatings can now be recommended for diverse types of instrument power clamps and armatures.

Industrial application of the new power clamps and armatures with plasma sprayed electroconductive coatings will considerably reduce power losses in distribution systems of high and very high tension applications, mainly due to reduced contact resistances. Considerable reduction of copper consumption results by replacement of bronze castings with electroconductive coatings that are deposited onto the aluminum parts of the clamps. Moreover, the merits resulting from the simplified design and production technology of clamps and armatures, reduced weight, and overall improvement of utility properties are of economic merit.

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