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Development of cadmium-free silver metal-oxide contact materials

S. C. DEV, O. BASAK, O. N. MOHANTY
National Metallurgical Laboratory, Jamshedpur 831 007, India

A cadmium-free silver-base alloy has been developed to substitute the standard Ag–12% CdO contact alloy which is widely used in electrical and electronics industries. Substitution of cadmium was attempted through the addition of zinc as the basic and major alloying element and with minor additions of tin and copper. The developed alloy, after internal oxidation, possesses better electrical contact characteristics than the standard alloy.

1. Introduction

The Ag–Cd group of contact alloys are widely used in tonnage quantities in electrical and electronics industries because of high electrical and thermal conductivities, high resistance to arcing, high welding adhesion resistance, low contact resistance, high hardness and strength. However, toxic cadmium vapour is released during melting and operation of the contacts, causing a serious pollution problem [1, 2].

Keeping in view the toxicity of cadmium vapour and also the ever-increasing demand for good contact materials in the growing energy sectors, world-wide attempts are underway to develop cadmium-free electrical contact materials [3].

There is evidence in the literature that Ag–Zn binary alloy responds well to internal oxidation treatment. This produces zinc oxide having physical properties similar to those of cadmium oxide [4]. However, one of the disadvantages that this alloy suffers is the production of laminated microstructure that has detrimental effects on electrical characteristics [4].

Some efforts have been made [5], through the addition of small amounts of copper, tin and tellurium to the binary Ag–Zn alloy, to modify the morphology, shape and size of the oxide precipitation. It is also known [5] that the welding adhesion resistance increases in the presence of finer oxide particles, while the erosion resistance and contact resistance depend to a large extent on the oxide content, as well as its distribution.

The present work was directed towards developing a cadmium-free alloy with Ag–Zn base, bearing other alloy additions such as copper and tin. Processing parameters were to be optimized to induce desirable properties such as high hardness, high welding adhesion resistance, high electrical conductivity, high erosion resistance and low contact resistance.

2. Experimental procedure

2.1. Materials

Silver, copper, tin and zinc of 99.9% purity were taken for preparing the alloy. The compositions of the new and the standard alloys are given in Table I.

TABLE I Composition of the alloys (wt %)

Alloy designation	Alloy description	Zn	Cu	Sn	CdO	Ag
A	Cadmium-free alloy	3.00	1.75	1.25	–	Bal.
B	Standard Ag–Cd alloy	–	–	–	12	Bal.

2.2. Melting and casting

Melting of the alloys was done in a pot-type electric furnace using a clay-bonded salamander crucible and the melt poured in to a preheated steel mould in the temperature range 950–1000 °C. Experimental heats, each of 0.5 kg were made.

2.3. Processing

2.3.1. *Homogenization and rolling*

The cast slabs were homogenized at 450 °C and subsequently rolled with intermediate annealing.

2.3.2. *Internal oxidation*

The rolled products were internally oxidized in air in an electrically heated muffle furnace in the temperature range 800–830 °C for 24 h. Subsequently, the time period for internal oxidation was reduced considerably by prior cold-reduction.

2.4. Evaluation of physical properties

2.4.1. *Electrical conductivity and hardness*

Electrical conductivity was measured by a Foster Sigmatest instrument using a probe of 10 mm diameter. For hardness measurement, a Vicker's hardness tester was used.

2.4.2. *Measurement of contact properties*

Contact properties were measured using a laboratory developed apparatus [6, 7]. In this system two pairs of

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contact tips, one pair made of test material and the other made of a reference material, were placed in a contactor. A number of make-and-break operations were performed and the contact properties such as contact resistance, contact weldability and amount of arc erosion were measured.

2.4.2.1. Measurement of contact resistance. For this, initially a 10 A current in the d.c. mode was passed through the pair of contacts (as per ASM specification) for about 1 h for stabilization, and the millivolt drop was measured for monitoring the initial contact resistance. Then a specified number of make-and-break operations were carried out with a nominal current in the a.c. mode. Following this, again a 10 A current was passed through them for 1 h and the millivolt drop measured. The changed value of the contact resistance due to the deterioration of the contact tips was thus noted. This was repeated a number of times. The variation of the contact resistance was measured as a function of the number of make-and-break operations over a wide range of values (10×10^3–50×10^3).

2.4.2.2. Measurement of arc erosion. Loss in weight of the contact tips was monitored as a function of the number of make-and-break cycles (10×10^3–50×10^3).

2.4.2.3. Measurement of contact weldability. A specified amount of current was passed through both the reference pair and the test pair of contact tips. Making-and-breaking operations of the electrical circuit was continued until a weld occurred. The number of operations when the first weld occurred was noted.

2.5. Structural characterization

The microstructure of an internally oxidized layer of the alloy was observed using an optical microscope. Additionally, some observations with TEM and electron probe micro analysis (EPMA) were also made.

3. Results and discussion

From a preliminary study with varying amounts of alloying elements, it was observed that when the total alloy content exceeds 6%, laminated structure is produced that results in undesirable contact properties. It is known [8] that the concentration of less-noble alloying elements plays an important role during internal oxidation. The literature also shows that concentration beyond a critical value is adversely affected by the formation of laminated structure [9].

The electrical conductivity and hardness showed a wide scatter in the as-cast condition, but were smoothened considerably after homogenization. Table II contains these values (for the homogenized condition) as well as those upon internal oxidation. It is evident from the table that electrical conductivity and hardness values of Alloy A are higher compared to those for Alloy B. Further, it is observed that the internal oxidation time is drastically reduced from 24 h to 10 h by preceding it with cold rolling. The beneficial effect of initial cold reduction in improving the kinetics of oxidation may be understood on the basis of the reduction in the effective diffusion distances that in turn lowers the relaxation time [10].

Contact resistance of the Alloys A and B, measured as a function of the number of make-and-break cycles, is shown in Fig. 1. It is evident from this figure that the contact resistance of Alloys A and B are in the same range. Moreover, Alloy A shows a more uniform range during the make-and-break operations.

Fig. 2 shows the arc erosion as a function of the number of make-and-break cycles. Alloy A displays a slightly higher erosion rate compared to Alloy B.

Table III shows the weldability data. It is seen from the table that neither Alloy A nor Alloy B shows any welding phenomenon up to 50×10^3 cycles of make-and-break operations, thus indicating similar anti-welding properties.

Fig. 3 shows the microstructure of the Ag–Zn binary alloy specimen internally oxidized in air at 800 °C. A pronounced laminated structure of the oxides is found. This observation supports similar behaviour reported by earlier investigators [4].

Fig. 4a and b show the microstructures of specimens of Alloys A and B internally oxidized in air at 830 °C. The oxide particles were found to be uniformly dispersed in the silver matrix of both Alloys A and B. From the absence of laminated structure in Alloy A, one can justify the necessity of adding other alloying elements into the Ag–Zn binary system as others have also observed [11]. The presence of copper in Alloy A disperses oxide particles uniformly. The addition of tin

TABLE II Electrical conductivity and hardness values of the alloys

Treatment	Alloy A		Alloy B	
	Electrical conductivity (% IACS)	Hardness (VPN)	Electrical conductivity (% IACS)	Hardness (VPN)
Homogenized	22–25	38–40	35–40	30–35
Internally oxidized (24 h)	75–78	72–75	70–72	63–65
Cold work and internally oxidized (10 h)	75–78	73–75	70–72	62–65

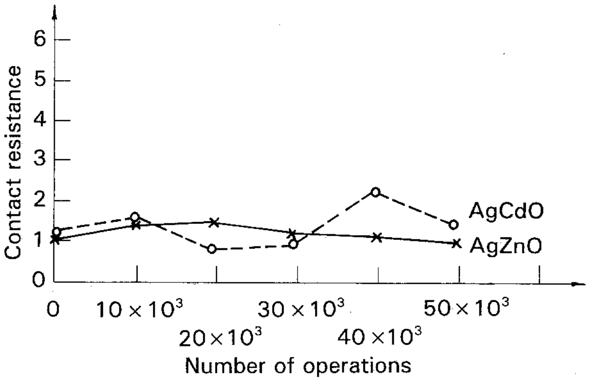


Figure 1 Contact resistance of alloys as a function of the number of make-and-break cycles.

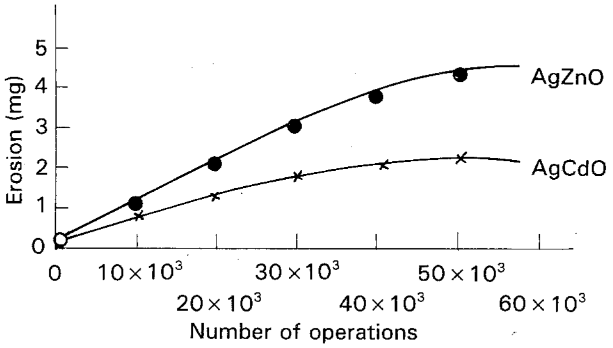


Figure 2 Arc erosion of alloys as a function of the number of make-and-break cycles.

TABLE III Weldability data of the alloys

Alloy	Number of operations taking first weld
A	50 000
B	50 000

Figure 3 Microstructure of Ag–Zn binary alloy internally oxidized at 800 °C in air.

possibly results in finer oxide particles, again reported elsewhere [11].

The EPMA results on internally oxidized samples are given in Fig. 5a and b. It may be noted that barring a few large precipitates, the average particle size is

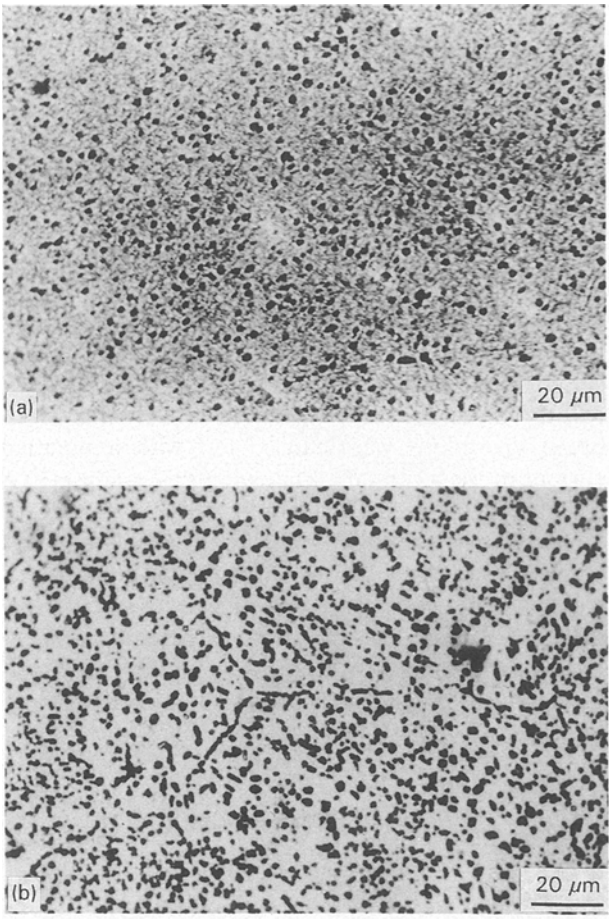


Figure 4 Uniformly distributed globular oxide particles in (a) Alloy A, and (b) Alloy B, internally oxidized at 830 °C in air.

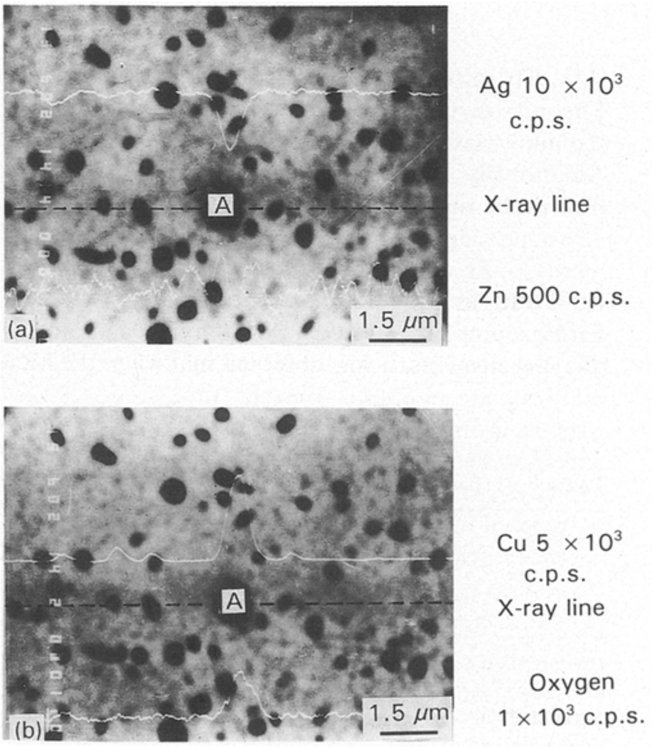
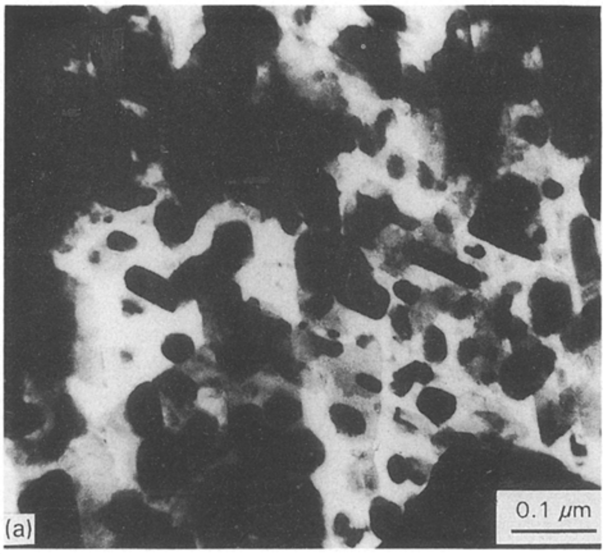
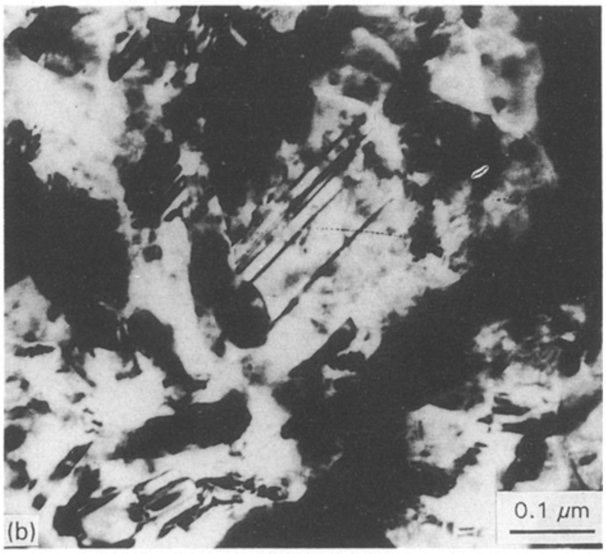


Figure 5 a, b EPMA results on internally oxidized samples (830 °C) of Alloy A: globular oxides and X-ray profiles.





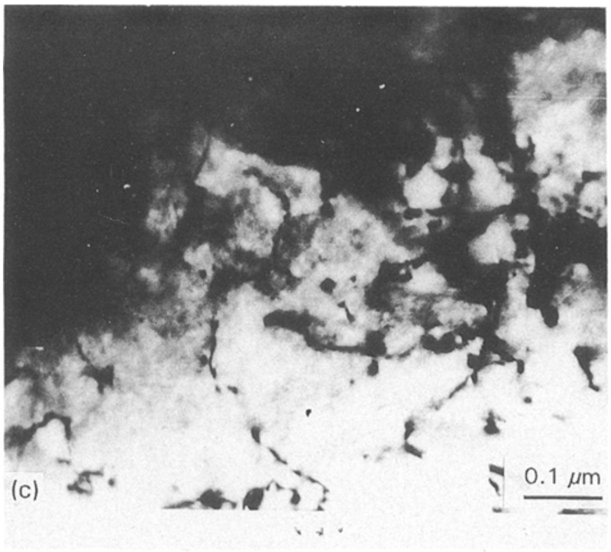


Figure 6 Transmission electron micrographs of Alloy A, internally oxidized at 830 °C. (a) Globular oxide particles and some elongated particles. (b) Mostly elongated precipitates and twins in the matrix. (c) Precipitates seen to decorate dislocations.

around 0.3–0.4 μm. The precipitates (such as marked "A" in Fig. 5a and b) on the basis of the X-ray lines, show impoverishment in silver and enrichment in copper, zinc and oxygen. Thus, these are the complex Cu–Zn oxides.

The transmission electron micrographs are shown in Fig. 6a–c. From Fig. 6a, one notes that apart from the spherical particles, some elongated geometrical particles are also seen. Further, the average particle size is around < 0.05 μm. Compared to the precipitates encountered in Fig. 5a and b, these precipitates are much finer. In Fig. 6b, one can observe a number of twins: these are annealing twins formed as a result of deformation followed by internal oxidation. In Fig. 6c the dislocations, decorated by precipitates, can be seen. In all these cases, however, the composition of the precipitates could not be ascertained. While concluding the observations on EPMA and TEM investigations, it may be noted that the relatively coarser (0.3–0.4 μm) precipitates are Cu–Zn oxides. The finer (< 0.05 μm) particles could be complex oxide containing tin. It is reported in the literature [5] that the addition of tin results in the appearance of finer oxide particles. Further work is required to resolve this situation.

4. Conclusion

A cadmium-free silver-base alloy shows higher electrical conductivity and hardness values than those of the conventional Ag–12% CdO contact alloys.

The new alloy possesses comparable contact properties such as arc-erosion, contact resistance and anti-welding to those of the standard alloy. Thus, an Ag–Zn binary base alloy with minor additions of tin and copper should be a potential substitute for the conventional Ag–12% CdO contact alloy which is toxic.

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References

1. I. SIGEMATSU, in "Proceedings fourth international cadmium conference", edited by D. Wilson and R. A. Volpe, (Cadmium Association, London, 1983) p. 97.
2. D. M. DHIZIHKOV, "Cadmium" (Pergamon Press, London, 1966) p. 10.
3. S. C. DEV, P. BASAK and O. N. MOHANTY, a research report, National Metallurgical Laboratory, Jamshedpur, India (1987).

4. M. SATO and M. HIJIKATA, *Trans. Nat. Res. Inst. Metals* **24** (2) (1982) 67.
5. M. SATO and M. HIJIKATA, *Trans. Jpn Inst. Metals* **23** (1982) 267.
6. P. N. MISHRA, S. C. DEV, P. BASAK, A. ROY and O. N. MOHANTY, Ind. Pat. No 763/DEL/90, Nat. Met. Laboratory, India (1990).
7. P. N. MISHRA, S. N. SINGH, S. C. DEV, P. BASAK, A. ROY and O. N. MOHANTY, *Meas. Sci. Technol.*, **4** (1993) 221.
8. P. KOFSTAD, "High Temperature Oxidation of Metals" (Wiley, New York, 1966) p. 285.
9. M. SATO, M. HIJIKATA and I. MORIMOTO, *Trans. Jpn Inst. Metals* **15** (1974) 180.
10. P. G. SHEWMON, "Transformation in Metals", McGraw Hill Series Material Science and Engineering (McGraw Hill, New York, 1969), p. 88.
11. M. SATO and M. HIJIKATA, *J. Jpn Inst. Metals* **43** (1979) 1095.

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