CHAPTER 2

REVIEW OF LITERATURE

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Review of Literature

2.1 Role of contact materials in electrical industry :

Any electrical apparatus is essentially, an assembly of electrically interconnected parts and conductors. The point at which the circuit current passes from one current -carrying part to another is called a point of electrical contact ; and the cooperating parts involved are known as contact materials or contact members. Thus at least two contact members are needed to establish an electric contact. The contact members may be classified as stationary contacts, switching contacts and sliding contacts according to their arrangement and possible relative displacement.

Stationary contacts constitute a permanent electrical connection and do not move with respect to each other during operation of the assembly . Switching contacts make, break or change the connections of the circuit carrying electrical current. Sliding contacts are a version of switching contacts where one of the contact members is slid over the other without interrupting the continuity of the electrical circuit. Fig.2.1 gives a pictorial view of the configurations of commercially used contacts with base -plates.

Contact materials are incorporated in various switchgear devices such as contactors, circuit breakers, relays, switches etc. so as to connect, interrupt or isolate electric circuit.

Fig. 2.1 : Pictorial view of the configurations of commercially used contacts with base-plates. (Courtsey Modison, Bombay)

Switchgear is a general term which covers a wide range of electrical equipment concerned with switching and interruption of currents during normal and abnormal conditions. It also includes the equipment associated with controlling, regulating, protecting and measuring electrical power. The switchgear devices are thus used in generation, transmission and distribution of electric power.

Various switchgear devices may be grouped into two broad categories [12]

(i) Low-voltage switchgear (for applications involving voltages upto 600V) such as

- air circuit breakers.
- a.c. and d.c. contactors.
- various switches like rotary switches, knife switches and selector switches.
- various types of relays such as electromagnetic relays, thermal relays and induction relays.

(ii) High-voltage switchgears (for voltages of 1000V and above) such as

- oil circuit breakers.
- air blast circuit breakers.
- sulfur hexafluoride circuit breakers.
- vacuum circuit breakers
- isolating switches
- current limiting switches
- earthing switches

No single contact material can cater such a wide spectrum of contact applications in both low and high-voltage switchgear devices in terms of the diversity of their operating conditions and hence a host of materials starting from pure metals; alloys to composites are developed or under development as contact materials.

An ideal electrical contact material would be one which satisfies following requirements:

- high electrical conductivity since this would lead to a low contact resistance and consequently reduce heat generated during the passage of current.
- high thermal conductivity which would enable both resistive and arc heat developed at the contact surface to be conducted away to the backing material.
- high melting and boiling points so as to reduce any tendency to arcing.
- high reaction resistance to all environments in which the contact material is to be used to avoid the formation of insulated oxides, sulfides and other compounds.
- high hardness to provide good wear resistance and yet enough ductility to ensure ease of fabrication.
- finally the material should be available at low cost in desired form.

Since no single material can have an ideal combination of all these properties; some compromise is necessary and a selection based on availability, reliability, life and cost is made for each specific application. Accordingly some of the pure metals developed and used as contact materials are platinum, palladium, gold,silver and copper. They have low strength, low hardness and hence poor wear resistance; high tendency to welding and sticking. The silver and copper base alloy systems used as contacts are Ag-Cd, Ag-Ni, Ag-Cu, Be-Cu, Cr-Cu, Cu-Cd, etc. which in general suffer from relatively lower electrical conductivity values. The materials developed in last few decades are silver-base composites such as Ag-CdO, Ag-NiO, Ag-SnO_2, Ag-W, Ag-WC, etc. which offer superior combination of contact properties to those of pure metals and alloys.

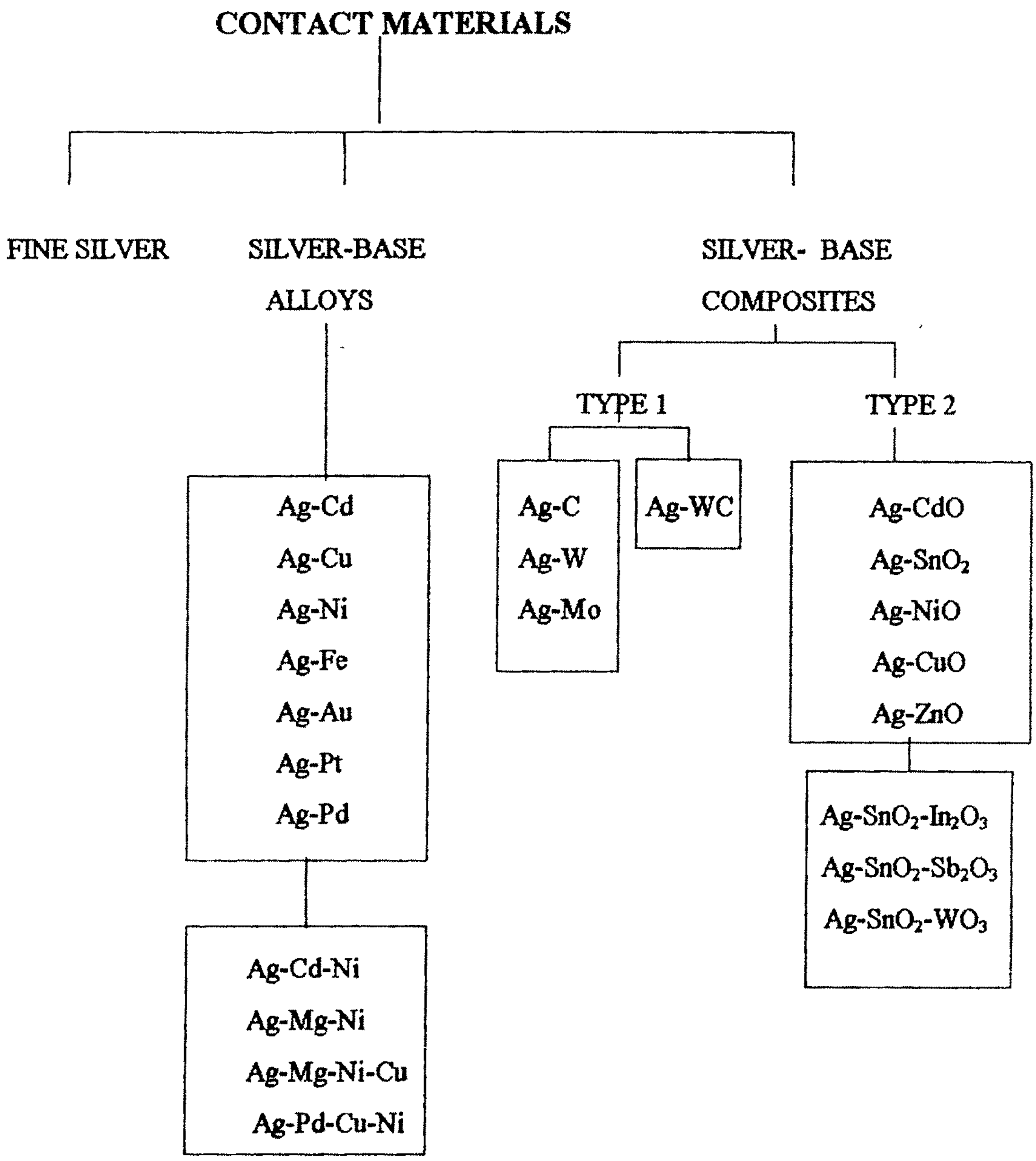
2.2 Classification of contact materials:

2.2.1 Classification on the basis of composition for silver-base contacts:

Silver-base contacts are made of either elemental metal, alloys or composites of silver. Table2.1 gives a broad classification of different silver-base contacts.

Fine silver or pure silver (99.9% Ag) has the highest electrical and thermal conductivity of all the metals. However, due to low melting and boiling points, fine silver contacts tend to weld easily and have high arc erosion tendency. Low hardness and low strength of fine silver lead to mechanical wear of contacts. Fine silver contacts are therefore used in low-current applications such as switches and relays in appliances and automotive products, slip rings and brushes in telecommunication equipment and microelectronics systems operating at max. 25V and 0.01A current.

Table 2.1: Classification on the basis of composition



Ag-Cd, Ag-Cu, Ag-Ni and Ag-Fe; the binary alloys of silver; have greater hardness and strength as compared to pure silver owing to solid solution strengthening and hence offer superior arc-erosion resistance and anti-welding properties than pure Ag contacts. However, they give lower electrical conductivity values. They are used in wall switches, thermostats, appliance switches. Silver-base alloys like Ag-Au, Ag-Pt and Ag-Pd are used in AC and DC relays with current capacity of less than <0.5 Amp. These noble metal systems have an added advantage over other silver- base alloys in terms of their greater oxidation and corrosion resistance.

Some of the silver-base multicomponent systems like Ag-0.25 Mg-0.20 Ni and Ag-0.18 Mg-0.20 Ni-0.15 Cu are used in low-current DC applications because of their low material transfer characteristics.

In case of silver-base composites, the second phase forms discrete particles that are dispersed in silver matrix. Dispersed phase imparts matrix-strengthening, resistance to mechanical wear and anti-welding properties to contacts. Silver-base composites are grouped into two types - type 1 use refractory metal or metal carbide as dispersed phase whereas type 2 contain oxide as dispersed phase.

Ag-W or Ag-WC type contacts are used as current carrying contacts in circuit breakers, low-voltage switches, heavy-duty circuit breakers, etc.

Silver-metal oxide type composites have an edge over silver-base alloys in terms of their higher electrical conductivity than latter. Conductivity in a silver-composite depends strictly on the percentage of silver by volume in the composite and not on the weight percentage of silver as in the case of silver-base alloy. For instance, the volume of silver in Ag-15wt% CdO composite is less than that in Ag-15 wt% Cd alloy, yet the electrical conductivity of former (65%IACS) is much greater than that of latter (35% IACS) [1]. Silver-metal oxide type composites like Ag-CdO are used in aircraft circuit breakers, aircraft relays, automotive relays, truck controls, circuit breakers, motor starters, etc.

Silver-graphite contacts are used in automotive regulators, low-voltage make-break contacts and sliding contacts.

2.2.2. Classification on the basis of current rating :

Different contact materials can be broadly classified into four types on the basis of their current carrying capacity as under[13].

(i) very light (feeble) current contacts:

These contacts are used in electromagnetic current and voltage relays, radio and telephone relays, miniature microswitches and contactors used in electronic applications. They carry current in the range of milliamperes to 1 ampere.

(ii) light duty contacts:

These are used for interrupting current upto 10 Amp. in devices like contactor relays, control switches etc.

(iii) medium duty contacts:

They are used for medium current make and break contact operations in the current range of 10-300 Amp. This category covers contacts that remain closed for long period of times; contacts subjected to occasional sliding like rotary switches and low resistance sliding contacts such as slip rings.

(iv) heavy duty air or oil break contacts:

They deal with large units of power with current ranging from 300 Amp to several thousand amperes. They include devices such as high-voltage circuit breakers, low-voltage circuit breakers, air-blast circuit breakers, oil-circuit breakers, SF6 circuit breakers, current-limiting reactors, etc.

2.2.3. Classification on the basis of specific performance

Contact materials can also be classified on the basis their specific attribute such as threshold welding current, arc-extinguishing characteristics, erosion behaviour, etc. [14]. Following tables give a brief account of the same.

Table 2.2 : Classification on the basis of erosion on make [14]

Ag-SnO_2	lowest erosion
Ag-CdO	low erosion
Ag-C	medium erosion
Ag-Ni	high erosion
Ag	highest erosion

Table 2.3 : Material classification according to threshold of welding current I_{SG}.[14]

Material	I_{SG}	Group
Ag/C 5 Ag/C 3	>5000 A	Gr.1
Ag/ZnO 8 Ag/SnO_2 10;12 Ag/CdO 10;12;15	1000 A	Gr.2
Ag/WC Ag/W Ag/Cu Ag/Ni Ag	150 A	Gr.3

Table 2.3 gives the optimum material on the basis of threshold of welding as a result of overheating and subsequent welding of contacts taking place due to pre-breakdown of arc and bouncing during contact operation. According to above table, pure silver contacts have the highest tendency to weld whereas Ag/C, the lowest.

Contacts can weld due to too high contact resistance when short circuit or over current occurs. Table 2.4 gives the welding behaviour of different contacts in which pure Ag and Ag/C contacts show the lowest tendency and the tungsten-based materials the highest tendency to welding.

Table: 2.4 : Tendency to welding of closed contacts [14]

Ag Ag/C	Lowest tendency to welding
Ag/CdO 10;12;15 Ag/SnO_2 10;12 Ag/ZnO 8 Ag/Ni 10;20 Ag/Cu 3;10	Low tendency to welding
Ag/WC Ag/W	Relatively high tendency to welding

Contacts are also classified according to their arc extinction capacity. According to Table 2.5, silver-metal oxide composites have very good arc extinction property whereas silver-base refractory contacts show poor arc-extinction characteristics.

Table:2.5 Classification on the basis of arc-extinction property[14]

Material	Self-extinotion behaviour
Ag/SnO_2 Ag/CdO Ag/Ni	Gr.1 very good behaviour
Ag/Cu Ag	Gr.2 Fair behaviour
Ag/W Ag/WC Ag/C	Gr.3 Bad behaviour

On the basis of above specific performance attributes, optimum material recommended for switching devices for various current ranges are as per Table 2.6.

Table 2. 6 : Optimum material for switching devices [14]

Current range	Optimum material
Upto 10 A	Ag/Cu
10-100 A	Ag/Ni 10 SP
100-300 A	Ag/CdO SP
300-3000 A	Ag/SnO_2 SP
3000-5000 A	Ag/ZnO SP
> 5000 A	Ag/w 80, Ag/WC 60

SP = sintered and extruded

2.3 Manufacturing processes for silver-base contacts :

2.3.1. Powder production :

The following review covers the methods of powder production for Ag-MeO composite contacts.

2.3.1.1. *Silver powder production :*

Silver powder is used in P/M electrical contacts for production of pseudo-alloys or mixtures of materials such as Ag-W, Ag-Fe, Ag-Mo, Ag-WC, Ag-CdO, Ag-SnO_2, etc. Methods employed for production of metal powders in general may be employed for silver powder production [15,16]. These include physical methods,chemical methods, electrochemical processes and thermal decomposition. Table 2.7 gives a comparative account of physical properties of silver powders obtained by these methods[1]. Physical methods employed are atomization and various communition routes such as ball-milling, vibro-milling or attrition milling, etc. The chemical methods mainly involve reduction of silver oxide by organic reducing agents like alcohol, sugar or aldehydes. Inorganic reducing agents like hydrazine, potassium sulfate or sodium formate are used to reduce silver nitrate to silver powder. The electro-chemical methods cover silver powder production by cementation process or by conventional electro-deposition route. Silver oxide or silver carbonate is used to produce silver by thermal decomposition at temperatures greater than 250 ^{0}C.

Table 2.7 : Physical properties of silver powders [1]

Method of preparation	Apparent density g/cc	Tap density g/cc	Particle size microns	Surface area m^2/g
Atomization	3.0-7.0	4.0-7.0	>40	<0.2
Chemical				
Organically reduced	0.4-1.5	0.8-3.0	0.5-3.0	0.2-4.0
Inorganically reduced	1.0-2.0	1.0-3.0	3.0-20	<0.3
Galvenic reduction	1.5-4.0	2.0-4.5	>100	<0.2
Electrolytic reduction	1.5-3.0	2.5-3.5	40-1000	<0.2

2.3.1.2. *Production of dispersoid constituent :*

The commonly used dispersoid or second phase constituent in Ag-MeO contacts are CdO, SnO_2, NiO, CuO, ZnO, etc. The dispersoid may be produced either as elemental powder followed by its oxidation or it may also be produced by thermal decomposition route directly as an oxide [17,18]. A variety of techniques including atomization, electrodeposition, carbonyl method, mechanical communition methods, chemical precipitation, etc. are available for production of elemental powders for subsequent conversion to oxide as a dispersoid.

2.3.1.3. *Alloy powder production :*

Alloy powders of Ag-Cd, Ag-Cu, Ag-Sn, Ag-Ni, Ag-Zn, etc. may be produced by atomization route, conveniently and economically. K. Sakarai & coworkers have produced Ag-7.1 wt % Sn alloy powder by atomizing a melt of silver and tin [6]. In a study on manufacturing Ag-MeO contacts by Yuan-Shou Shen and Lawrence Gould [19], the water atomized powders were made by tapping the silver alloy (with cadmium or tin) at 1200 ^{0}C through the water-jets at 34 MPa. Alloys of three different compositions (Ag-9 wt % Cd, Ag-13.5 wt % Cd and Ag-7 wt % Sn) were atomized for this investigation. It is claimed that the atomized alloy powders make the process of oxidation of silver-base alloy powders simpler and more economical.

2.3.2. Powder Synthesis :

Powders for contact materials are synthesized by a variety of methods. Some of them are conventional and adopted for this purpose since long whereas others are novel and recent. Following is a brief account of various powder synthesis techniques.

2.3.2.1. *Mixing or blending :*

ASTM standard B243 defines the term “mixing”as the thorough intermingling of powders of two or more materials whereas the term “blending” means the thorough intermingling of powders of same material.However, the two terms are used interchangeably.

Powder mixing is carried out in variety of mixers such as cylindrical drum mixers, double-cone mixers, Y-blenders, etc. The interior of such mixing devices is important in determining the mixing efficiency. Baffles, intersifiers, spinning blades and dividers are possible internal additions which enhance degree of mixing[20]. The variables governing blending or mixing of powders include the material, the particle sizes, the type of mixer and its size, the speed and the time of mixing, relative powder volume in the mixer,etc.[21]. H.H. Hausner has studied the effect of various parameters of mixing such as volume ratio of powder to mixer; time of mixing for different speeds of rotation and baffle-design on degree of mixing or mixedness [22].

In the conventional P/M process of silver-base contact production, silver and metal oxide powder such as Ag and CdO are mixed in double-cone blenders or Y-blender for several hours. Yet uniform mixing of extremely fine silver and cadmium oxide is practically impossible. N.T. George and coworkers [23] have found that the density differences between silver and cadmium oxide powders lead to segregation of cadmium oxide resulting into coarse and nonuniform distribution of oxide particles in the final powders. Not only this, chemically precipitated or vapour deposited cadmium oxide being extremely fine, tends to form a continuous coating on silver particles during mixing. The cadmium oxide coating so developed hinders metal to metal contact during pressing and sintering and makes densification difficult. Network of cadmium oxide along grain boundaries of silver, besides lower final compact density, is the cause for the relatively low electrical conductivity exhibited by the contacts processed by this route.

2.3.2.2. *Milling :*

Milling of silver and metal oxide powders in stoichiometric proportions may be carried out in ball mills, vibratory mills or tube mills. Conventional ball milling is however not advocated for silver-base systems as fine silver tends to leaf. Milling poses several problems-firstly it requires so fine powders that it becomes pyrophoric; secondly it does not disperse oxide phase well enough and finally it introduces contamination problems.

2.3.2.3. *Mechanical Alloying :*

The mechanical alloying (MA) was developed in late 1960's for the production of oxide-dispersion strengthened superalloys [24,25]. The early understanding of the process was empirical and greatly limited by analytical techniques available then. Later on the MA process was modified and adopted for producing a wide range of materials such as amorphous/nanocrystalline materials, intermetallic compounds, metal matrix composites, solid solution alloys etc. The resulting powders are characteristically dense, cohesive and homogeneous.

The MA process is not simply mixing on a fine scale; but involves true alloying. Benjamin and schelleng [26] during the studies on mechanical alloying of Al- 4% Mg.alloy monitored the progress of alloying by x-ray diffraction of powder samples after varying times of processing. They found that the relative peak height of Mg continued to decrease throughout the processing and dropped essentially to zero after 12 h of processing. Elimination of Mg diffraction peak indicates that the Mg is substantially dissolved in Al.

In mechanical alloying, required blend of powders is introduced into high energy mill such as Szegvari type Attrition mill [27,28] in which ball and powder charges are held in stationary, vertical, water-cooled vessel and agitated by impellers radiating from a rotating central shaft. During the process of attrition the particles of metal powders are repeatedly flattened, fractured and welded. MA involves a dynamic balance between welding and fracturing of composite powder particles. Fig.2.2 shows a schematic view

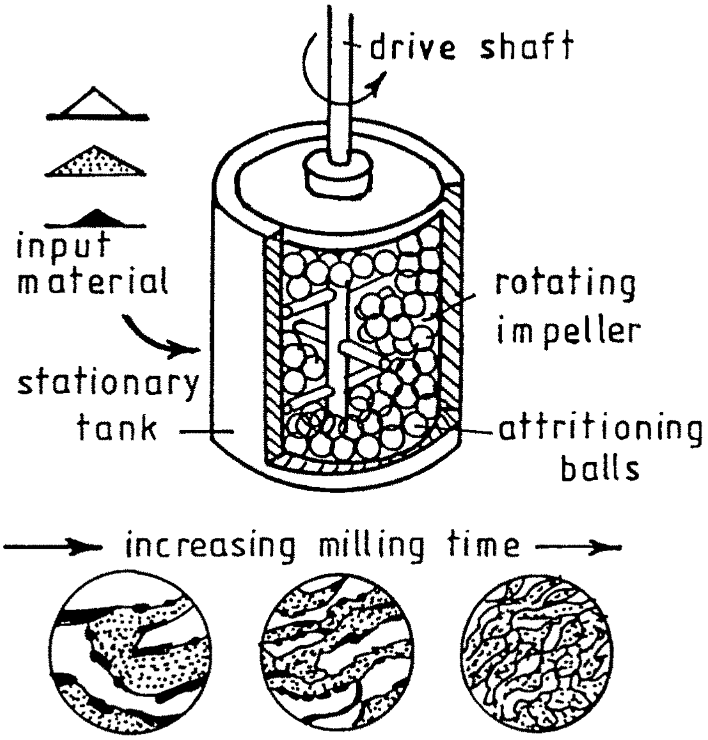


Fig.2.2: Schematic view of mechanical alloying set-up alongwith the resultant micro-structural changes taking place during alloying [15].

of mechanical alloying set up alongwith the resultant microstructural change taking place due to alloying.

Considerable amount of work has been reported on MA of aluminium alloys and aluminium powder composites [29-32]. Mechanical alloying is also a very promising route for processing of oxide-dispersion strengthened (ODS) alloys. Earlier these materials were processed by internal oxidation or chemical co-reduction method. SAP, thoria-dispersed nickel, thoria-dispersed nickel- chromium alloys, nickel-base superalloys with and without yittrium are some of the systems processed by MA [33,34]. Prakash and E. S. Bhagiradha Rao studied the mechanical alloying of thoria-dispersed nichrome [35]. They found that conventional ball milling cannot achieve the dispersion of oxides in practical time periods. According to these authors, the mechanically alloyed product approximates to a truly alloyed state, for which evidence is provided by optical microscopy and electron probe microanalysis (EPMA). E. S. Bhagiradha Rao and coworkers in another investigation examined the effect of attrition speed on the alloying in MA of Ni-20 Cr-2 ThO_2 system [36]. They have observed that there appears to be an optimum speed of attrition milling below which the degree of alloying is poor, and above which also the alloying begins to become increasingly inhomogeneous when compared on the basis of common number of revolutions performed by the attritor impellers. Table 2.8 reports batch compositions and milling conditions for a few representative systems processed by MA.

Present work explores the possibility of applying these fundamental concepts of MA to achieve highly dispersed Ag-MeO composites by MA.

Table 2. 8 : Typical batch compositions and milling conditions for MA

Batch Composition	Milling time (hrs)	Attrition speed (rpm)	Ball to charge ratio	Ref.
Ni-Al-Ti-ThO_2-Y_2O_3	40	132	17.5:1	24
99% Al	10	1200	30:1	30
Al-Mg-Si	10	1200	30:1	30
Al-ferrochrome	36	500	10:1	31
Ni-20Cr-2ThO_2	40	160	18:1	35
Ni-20 Cr-2.3 ThO_2	42	154 260 450 850	18:1	36
7010- 10 SiC	21	430	5:1	32
7010- 10 SiC	11	620	10:1	32

2.3.2.4. *Coprecipitation method :*

The physical methods of powder synthesis such as mixing or milling give rise to segregation of oxide phase in silver matrix. The resultant heterogeneous microstructure adversely affects the performance of the contact material during its use[37]. To overcome this problem "L-Type" silver-cadmium oxide contacts were developed by Lever [11] which involve the use of the coprecipitation technique. The process involves the dissolution of silver and cadmium in nitric acid. Compounds of the metals are coprecipitated by reaction with alkaline carbonate or hydroxide solution, washed and dried to form homogeneous powder of submicron size. This coprecipitated powder is then calcined at temperatures above 500°C so that the compounds decompose, leaving a composite powder of metallic silver and cadmium oxide that may be compacted, sintered and coined in the usual way. Fig 2.3 compares the microstructure of "L-type" sintered compact with conventional PM part and an internally oxidized part. L-type material offers a relatively fine dispersion of cadmium oxide in silver matrix. Coprecipitated powders are extremely fine and do not give any oxide coating on silver as in the case of mixed powders. The powders offer excellent cold & hot workability, good hardness of compact and higher electrical conductivity [23].

B.A.Yudin and coworkers in two separate investigations have examined the effect of various process parameters over the particle size of coprecipitated silver-cadmium carbonate and silver-nickel oxalate powders [38,39]. According to them, factors leading to fine particle size of mixed composite powders are ~ 1 mole/litre as the concentration of mixed nitrate solution, 3-5 pH of mixed nitrate solution, rapid mixing of mixed nitrate and precipitant solution, use of Na & K bicarbonates or Na & K oxalates as precipitant and 20°C as the temperature of precipitation.

Douglas et.al .[40] have patented the processes for making Ag-CdO, Ag-CdO-Li_2O, Ag-MgO, Ag-ZnO, etc. by coprecipitation method from mixed nitrate solutions using potassium carbonate, potassium bicarbonate, sodium carbonate, sodium bicarbonate, sodium hydroxide & potassium hydroxide as precipitants. The powders so produced are found to be suitable for making electrical contacts for switching applications.

T.I. Stewart, P.Douglas and others have produced powders for silver-metal oxide contact materials by spray-coprecipitation technique [41]. Ag-10wt% CdO, Ag-7.6wt%SnO_2 , Ag-6.55wt%ZnO and Ag-2.1wt%La_2O_3 are processed by this modified technique. Here

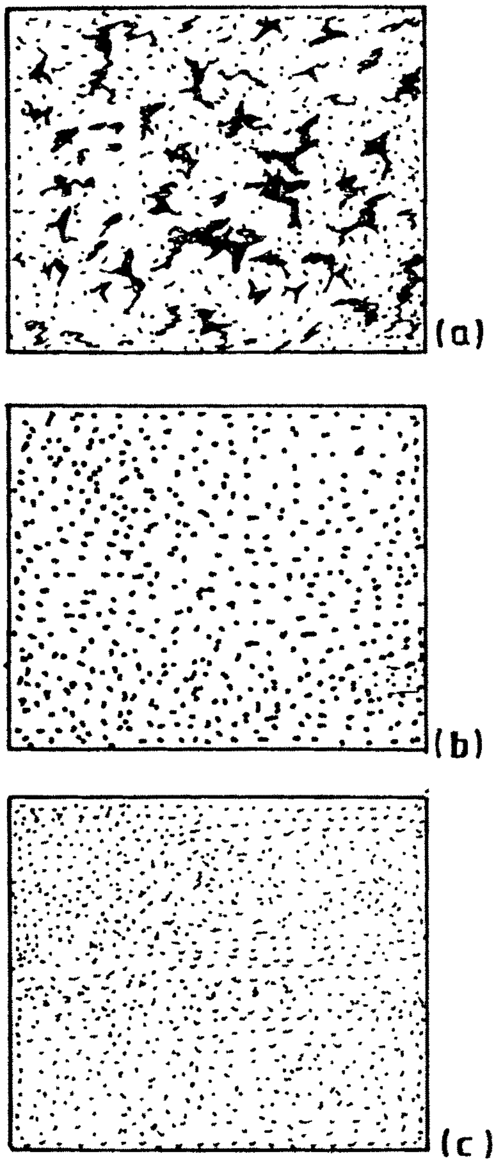


Fig. 2.3 : Schematic microstructures of Ag- CdO contacts prepared by (a) conventional PM route, (b) internal oxidation process and (c) L-type contacts at 650X magn. [11].

the mixed nitrate solution is sprayed, using a conventional glass capillary spray nozzle, into large excess of bicarbonate solution than necessary stoichiometrically. The method mainly concerns with converting the intimate dispersion provided on a molecular scale in mixed nitrate solutions to the solid state by instantaneous coprecipitation from small sprayed droplets of mixed nitrates. It is claimed that spray-coprecipitation route offers uniform fineness and long range homogeneity of oxide dispersion; unlimited composition with respect to both quality and type of oxide and ease of doping with ternary additions.

2.3.2.5. *Freeze-drying route :*

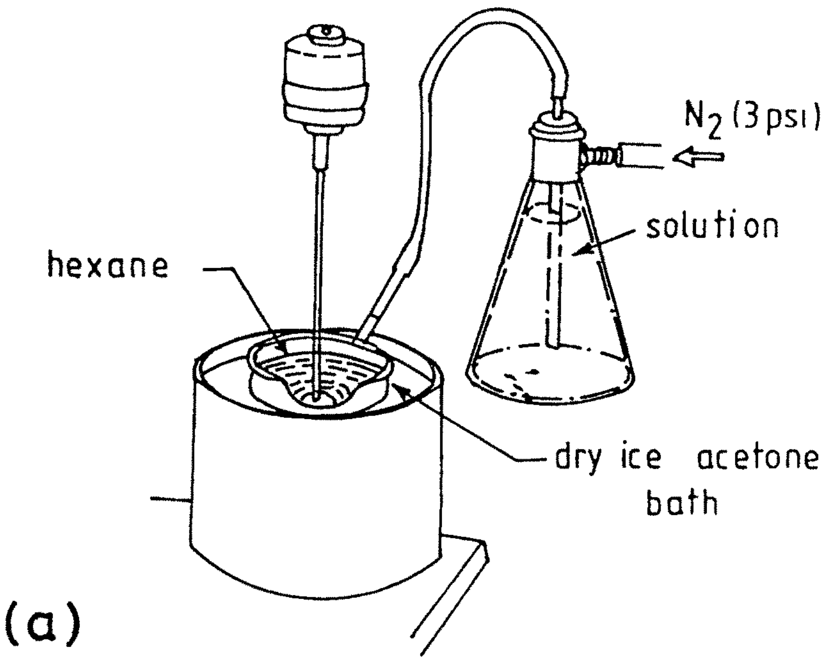
Freeze-drying or cryochemical preparation of ceramic oxides was introduced by Schnettler et.al. [42]. The technique involves the separation of a solution into small droplets by spraying it through a hydraulic nozzle at a pressure of a few psi into a bath of immiscible liquid, such as hexane chilled by Dry Ice-acetone or by spraying directly into liquid nitrogen[43]. The rapid freezing is essential to minimise ice-salt segregation. Frozen mass is then subjected to drying which involves the sublimation of water from frozen solution without melting. This is ensured by introducing frozen sample into a vacuum chamber that is evacuated to a pressure of about 1 Torr or less to maintain the partial pressure of water below triple point. (approx. 4mm of Hg at 0°C). The process leads to anhydrous sulphates, nitrates,etc., which when calcined produce highly reactive homogeneous sinterable powders with crystallite size in the range of 0.1 to 0.5 microns. However, since most freeze-drying is accomplished from frozen aqueous solutions, some degree of agglomeration is inevitable and say about 30% powder having an equivalent diameter in the range of 5-30 microns is produced. The process of freeze-drying has been used for the production of fine powders, homogeneous powder mixtures and dispersion-strengthened materials having unusual properties [44 -47].

D.J.Anderton and F.R.Sale[48] used freeze-drying technique to make silver- cadmium oxide electrical contact materials from aqueous nitrate solutions having improved microstructural morphologies. They found that the contact material developed by this route is very similar to that obtained by conventional P/M route ; although the freeze-dried material produced a significantly greater proportion of cadmium oxide particles in the size range of 0-5 microns than the one obtained in silver-cadmium oxide produced by just decomposition of mechanical mixture of nitrates. However, the maximum benefits of freeze-drying were not achieved as the silver nitrate melts prior to its decomposition ultimately leading to loss of freeze-drying morphologies.

Recently it has been recognized that the freeze-drying of the precipitates from a solution (other than water) is a good way to avoid shrinkage and formation of hard agglomerates in precipitates normally encountered as a consequence of small capillary dimensions of the fine particles and the high surface tension of the water[49]. Use of non-aqeuous solvent or suspension liquid such as tertiary butyl alcohol in freeze-drying is claimed to offer two advantages: (I) attainment of melting point close to room termperature (thereby simplifying freezing procedures and reducing the risk of any melting during the evaporation stage) and a high vapour pressure (to accelerate the drying stage). Fig. 2.4 shows the schematic of a laboratory scale freezing setup and the freeze-dryer.

2.3.2.6. *Electroless coating method :*

Electroless deposition of metals has received over the last decade full recognition as a valuable industrially applicable coating technology [50]. It is based on the principle of deposition of a metal or an alloy by controlled chemical reduction of metal ions and the process is catalysed by metal ions being deposited. Electroless coating of silver is done using propritory reducing baths like Brashear (sugar), Rochelle salt or Formaldehyde [51]. In order to develop silver coating on the substrates like powder particle surfaces



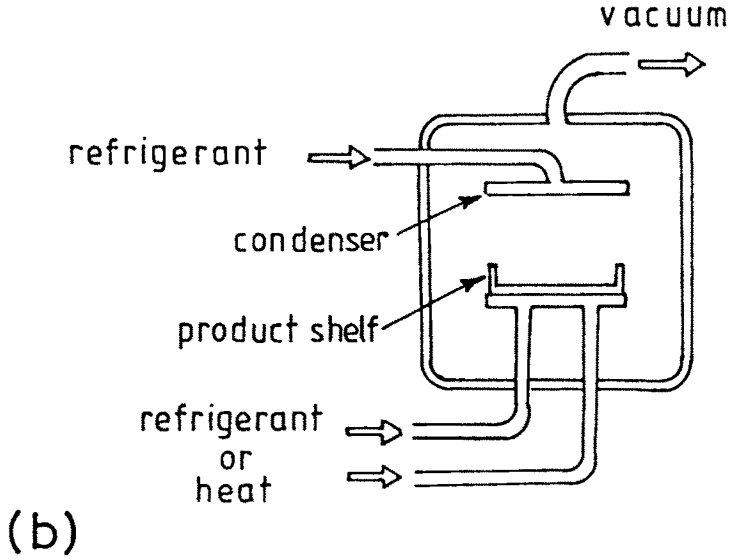


Fig. 2.4 : Schematic of **(a)** laboratory scale freezing set-up and **(b)** freeze-dryer [42].

such as those of metal oxide, excess charge is first developed on the oxide particle surfaces. Oxide surfaces have a marked acid-base character. It has been found with a number of oxides[52] that the surface contains a definite number of ionizing sites from which H^+ (acid dissociation) or OH^-(basic dissociation) may be released, giving rise to a net surface charge. The state of ionization of the surface depends on the nature of the oxide and on the $_pH$ of the aquous phase with which it is in equilibrium.The charge on the hydrated surface of a pure oxide particle dispersed in water is determined by its reaction with H_3O^+ ions or OH^- ions. The addition of H_3O^+ ions will reduce the $_pH$ and will cause the uncharged oxide particle surface to be positively charged. The addition of OH^- ions will raise the $_pH$ and will produce negative surface charge when $_pH$ exceeds PZC of the surface; PZC being the point of zero charge.

The excess +ve or -ve charge on the oxide particle surfaces promotes interaction with positive or negative ions from the solution. The ions from the solution are attracted and adsorbed over the oppositely charged surfaces of oxide particles. M+ or A- ions can neutralize the charge on the oxide particle surfaces as per following reactions [53].

$$MO^-\text{(surface)} + M^+\text{ (solution)} \rightarrow MOM\text{ (surface)}$$
$$MOH^{2+}\text{ (surface)} + A^-\text{ (solution)} \rightarrow MOH_2A\text{ (surface)}$$

H. Chang and coworkers [54] as well as Verma and others [55] have developed novel method of coating tin oxide particles with silver by an electroless coating process to produce silver-tin oxide electrical contact materials. The method consists of in-situ reduction of silver from silver nitrate solution over the negatively charged surfaces of highly dispersed tin oxide particles in aqueous medium. The coating is carried out under controlled conditions of temperature, silver ion concentration, silver ion feed rate and pH of solution having tin oxide particles dispersed in it. Formaldehyde was used as reducing agent to reduce silver nitrate to silver in electroless reduction mode. Contacts prepared from electroless coated powders exhibited excellent silver to silver continuity and hence better electrical conductivity than those processed by conventional blending route or internal oxidation method.

2.3.2.7. *Other miscellaneous processes :*

Ceramic and composite powders may be prepared by using different solution techniques which by and large consist of a common step of solution preparation so as to achieve molecular level of chemical homogeneity amongst various species present in the solution; followed by various means of solvent removal and finally a salt decomposition step[56,57]. Based on the method of solvent removal, a large number of processes including simple evaporation, spray drying, spray roasting, fluidised-bed drying, emulsion drying, liquid mix technique, sol-gel process etc, are developed [58]. Highly dispersed mixed oxides or oxide solid-solutions are developed for applications in areas of piezoelectrics & ferroelectrics by pyrolysis of amorphous organic precursor [59]. M.P. Pechini [60] has patented this process for preparing lead and alkaline earth titanates and niobates and their combinations for end use as dielectrics. Another novel preparative technique is Liquid Drying which involves dehydration of the aqueous salt solution by hygroscopic liquids like acetone & alcohol [61-63]. K.S. Mazdiyasni has given a complete account of use of gel technology in ceramics through alkoxide route [64].

In general these techniques offer a greater degree of chemical homogeneity and control of stoichiometry in the oxide powders. Powders are finely divided, possess improved reactivity and sinterability as compared to powders processed by conventional routes. These techniques may even be extended to production of silver-metal oxide composite powders such as Ag-CdO & Ag-ZnO. The product obtained while using these techniques at an intermediate stage would typically be a mixed oxalate, acetate, citrate, hydroxide or carbonate of silver and metal like cadmium or zinc. The silver compound in these mixtures is highly unstable and decomposes on heating to silver oxide and finally to silver. For instance, literature reports that the silver carbonate is fairly stable in air at room temperature but, at temperatures above 100 ^{0}C, it dissociates into silver oxide and carbon dioxide [65].

$$Ag_2CO_3 \rightleftarrows Ag_2O + CO_2$$

At 218 ^{0}C the equilibrium pressure of the carbon dioxide is equal to that of atmosphere, and in air decomposition proceeds to completion. Same way silver oxide is very easily decomposed into silver and oxygen by simple heating. At temperature above 300 ^{0}C and at atmospheric pressure in air the decomposition goes to completion.

This high thermal instability of silver compounds ultimately would yield final powders as silver-metal oxide powders,with an improved dispersion of metal oxide in silver matrix in the final compact.

2.3.3. Consolidation processes :

Different consolidation processes of silver-metal oxide contact manufacturing can be grouped into two:

- Internal oxidation processes (IO)
- Powder metallurgy processes (PM)

2.3.3.1. Internal oxidation processes :

There are two sub-divisions of this group namely internal oxidation of silver-base alloy and internal oxidation of alloy powder.

2.3.3.1.1 *Internal oxidation of silver-base alloy :*

The process consists of transforming silver-alloy strip (such as that of Ag-Cd alloy) produced by melting, casting and rolling; into composite silver-metal oxide by heating it in an oxidizing atmosphere at suitable temperature for several hours [66]. The internal oxidation of binary alloy takes place whenever:

(i) solubility of matrix metal (silver) is large.

(ii) rate of diffusion of oxygen is faster than that of alloying metal (cadmium)and

(iii) the free energy of formation of alloying metal oxide (cadmium oxide) is considerably larger than that of the matrix metal (silver).

Silver with its high solubility of oxygen and its unstable silver oxide at elevated temperatures is thus an ideal metal for internal oxidation for many of its alloys.

Fig.2.5 shows the diagram of stages of manufacture of silver-cadmium oxide contacts by internal oxidation [67]. The basic processing steps are as under:

* melting of Ag/Cd ingot.
* rolling out to sheet.
* folding the sheets to form a "bag" and welding the edges.
* oxidation in air, oxygen or special oxygen bearing atmosphere at temperatures in the range of 750-850 ^{0}C, sometimes under pressure, depending on conditions upto four weeks.
* termination of the oxidation, when the oxidation front is about 2/3 advanced into the material.
* sawing the edges off, such that each produces two sheets. Each sheet consists of two layers, one with 2/3 of thickness of Ag/CdO and another 1/3 thickness of Ag-Cd.

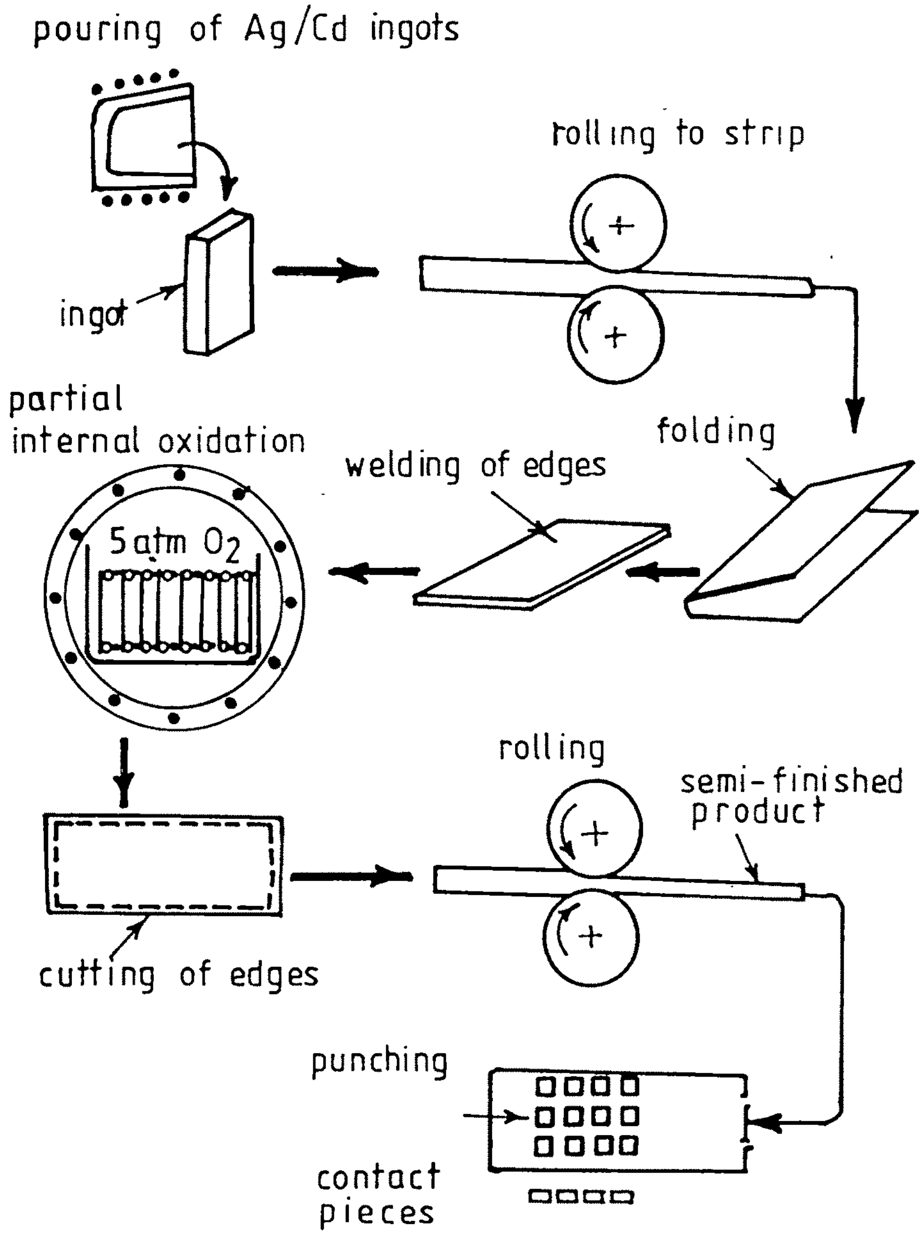


Fig. 2.5 : Diagram showing stages of manufacture of silver-cadmium oxide contacts by internal oxidation [67].

* further fabrication into strips, tapes,profiles by rolling,cutting, pressing, stamping, etc.

IO process has several limitations. First of all it is limited to sections of about 6 mm thickness, due to the fact that the rate of internal oxidation decreases exponentially with the depth of oxidation. High oxidation temperature (~800 ^{0}C for Ag/Cd alloy) and longer oxidation times, lead to grain growth of CdO precipitates which is highly detrimental to both electrical & mechanical properties of Ag-CdO contacts. Since the process of oxidation proceeds essentially from the surface, the central portion remains low in oxide content. Thus particularly in case of thick sections, an oxide depleted zone is developed at the centre. Such a non-uniform distribution of CdO leads to non-uniform wear of contacts [23].

A few modifications of conventional internal oxidation process aiming at reducing the size of oxide depleted zone are reported [68]. They are internal oxidation from both sides in air; use of preoxidized material and tiger-stripe material; and use of pressure-oxidized internal oxidation route.

Internal oxidation of Ag/Sn alloy has been studied by K Sakarai and coworkers [6]. According to these authors, though the process yields finer dispersion of tin oxide in silver matrix, it has two major limitations. First due to high interdiffusion coefficient of tin into silver matrix (about 10^7 times as much as that of Cd at 750 ^{0}C), an oxide enriched zone is formed on the surface which retards further oxidation inside the zone. Secondly it is too difficult to extrude and draw the alloy of Ag/SnO$_2$ due to its high hardness. Not only this, the conductivity of silver-tin oxide contacts is very low when prepared by internal oxidation route. These problems are taken care of by doping Ag/SnO$_2$ system with additives like indium and bismuth compounds.

A. Verma & T.R. Anantharaman [69] have developed an alternative to doping Ag/SnO_2 with additives. They have proposed a scheme to internally oxidize silver-tin alloy in the increased partial pressure of oxygen, giving rise to both internal & external oxidation effects.

New electrical contact materials of silver-metal (Sn,Cd,Zn,etc) oxide systems are successfully developed by M. Ohta & others by using a new process technology [70]. The process basically involves heat treatment under much higher oxygen partial pressure (higher than 10 MPa) than that used in conventional IO process (~0.02 to 0.3 MPa). The new contact materials are found to have oxide precipitates ranging from several nm to several tens of nm in diameter and hence have high arc erosion resistance and anti-welding properties. Not only this, it is claimed that the process permits the reduction in thickness of contacts to one half that of existing ones, because there is no depleted zone produced in new process.

2.3.3.1.2. *Internal oxidation of alloy powder (IOAP) process :*

In order to have a fine and uniform dispersion of oxide phase in silver matrix; Pedder, Douglas & McCarthy [71] developed a novel process known as I.O.A.P. process. The novel technique essentially combines IO and PM methods of compaction and densification. It avoids the central denuded zone in the core of the contacts and uses oxidation times which are several orders of magnitude less than in the conventional IO method. The first stage of the process is the formation of silver-cadmium alloy powder of fine particle size by the low temperature reduction and alloying of a silver & cadmium oxide powders mixture. Internal oxidation of fine alloy powder is then carried out at relatively low temperatures in times typically 10^3 times shorter than are required in conventional internal oxidation.

Both IO and IOAP processes have been used for a variety of Ag-MeO systems other than Ag-CdO and Ag-SnO_2. Silver base contacts containing magnesium, aluminium, manganese, zirconium, lanthanum and cadmium oxide were prepared by internal oxidation by heating in the temperature range of 480 ^{0}C to 750 ^{0}C [72]. The material transfer or erosion characteristics of these contacts were investigated in the range of applied voltages from 40 to 212 V and currents from 6.4 to 80.1 A in direct current, alternating current and rectified full sinusoidal wave current circuits. Sato and Coworkers [73] prepared four silver base alloys containing two kinds of oxides, namely, manganese and zirconium oxide, magnesium and zirconium oxide, magnesium and lanthanum oxide, and lanthanum and zirconium oxide by internal oxidation in air at 650 ^{0}C. The characteristics of the erosion resistance, resistance to welding, and the contact resistance have been investigated for these systems under an applied voltage of 100 V and amperage from 10 to 50 A in alternating current.

2.3.3.2 Powder metallurgy (PM) processes :

Since the internal oxidation processes tend to promote an uneven distribution of metal oxide particles as well as an oxide depleted zone in the core of the contacts, efforts were made to overcome these limitations by going for various powder metallurgy (PM) processes for processing of Ag-MeO type materials.

The conventional PM process comprises of mixing the powders of the constituent materials in required proportions, compacting of the powder mix, followed by its sintering. The product of superior quality is obtained by repressing or coining of the sintered part; or; hot-pressing, rolling or extrusion of the sintered part. Resultant powder metallurgy processes are as under:

(i) *Press - sinter - repress (PSR) route :*

This is the oldest process of making silver-base contact materials, and in its modern version, is still an important process. Blended powders of silver and metal oxide are compacted to the required shape and then sintered. The material is further densified to near to theoretical density by a second pressing (repressing). Sometimes the properties are modified by a second sintering or annealing [74]. Fig. 2.6 shows the press-sinter-repress route diagram[7].

(ii) *Press-sinter-extrude (PSE) route :*

Blended powder of final composition is pressed into ingot or billet and sintered. Isostatic pressing is preferred for this purpose. The ingot or billet is then extruded into wires, strips or slabs or any other desired shape. The extruded material is subsequently worked by rolling, swaging or drawing. Material made by this method is usually fully dense. Many a times, the silver-metal oxide strip is co-extruded with silver backing so as to achieve an excellent bond between two layers. Fig 2.7 is a diagramatic representation of press -sinter-extrude route for Ag-MeO contacts [67].

(iii) *Direct extrusion or rolling of loose powders :*

The process continuously compacts a single layer of silver-metal oxide powder or a composite silver-metal oxide mixture along with a fine layer of silver through roll-compacting. Cyclical continuous compacting route may also be adopted. The resulting green strip which is upto 12 mm thick is then sintered to density usually exceeding 95% of theoretical and rolled to desired thickness. The schematic of the roll compaction technique is shown in Fig 2.8 [68].

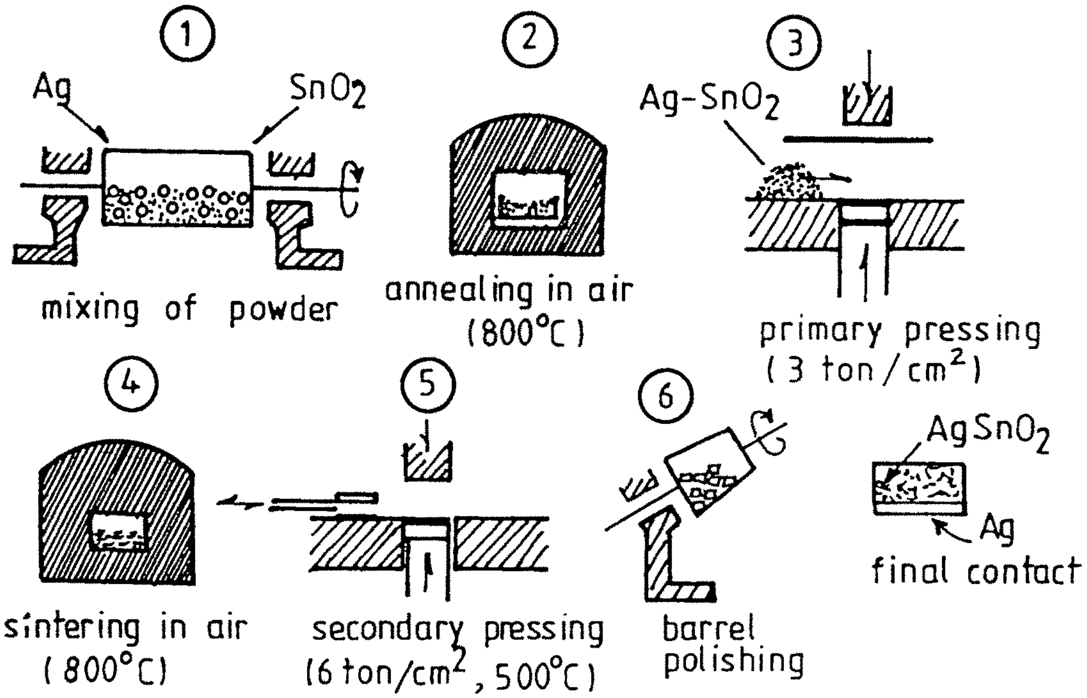


Fig. 2.6 : Diagramatic view of press-sinter-repress route [7].

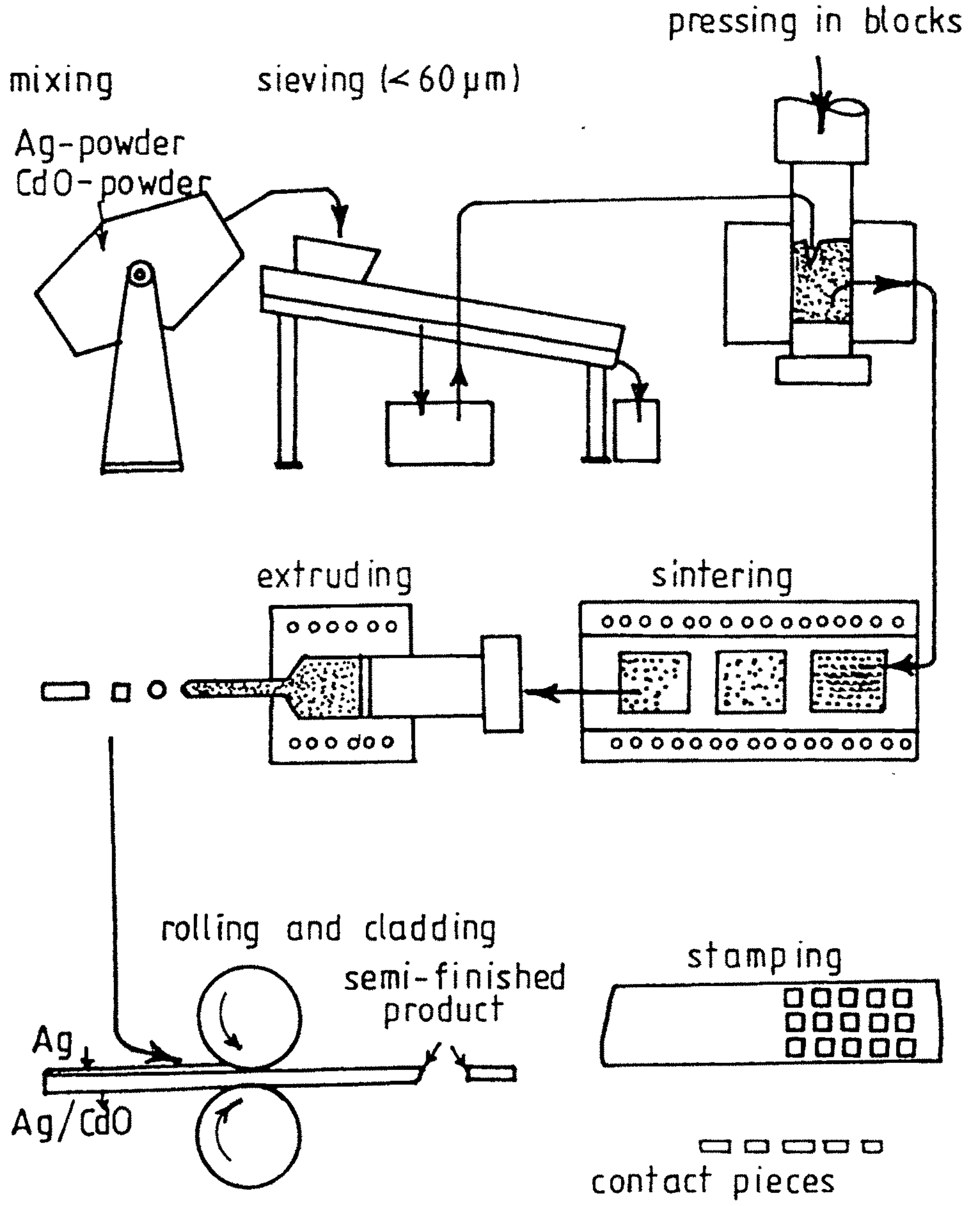


Fig. 2.7 : Diagramatic view of press-sinter-extrude route [67]

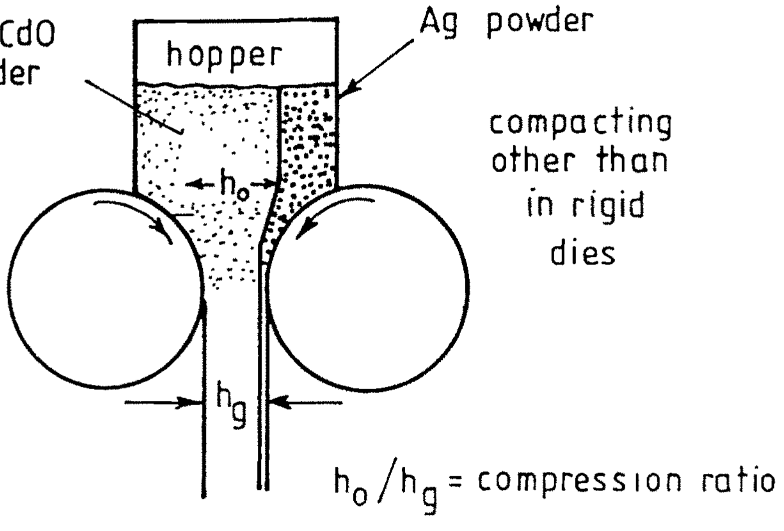


Fig. 2.8 : Schematic of roll-compaction technique [68].

(iv) ***Wollastone technique :***

Poniatowski, Schroder and Schulz [75] during their investigation of finding a replacement material for Ag/CdO, processed and examined a large number of Ag-MeO composite systems. They eliminated the effect of parameter,"method of manufacture" by going for Wollalstone technique. In this technique, the crude silver is filled, bundled, sintered and extruded with the specific metal oxide (such as CdO, SnO_2, CuO, Sb_2O_3, ZnO.etc.) or with another additive. This produced materials with pronounced fibrous structure in which both the diameter of fibre (5-500 microns) and the concentration of metal oxide could be controlled.

A comprehensive review of different competing routes employed for production of Ag/CdO contact materials was undertaken by G.S.Tendolkar [76]. Fig 2.9 gives the flow sheets for various routes of Ag/CdO contact production on a comparative basis.

2.4. Property, testing and evaluation of contacts :

The assessment of quality and reliability of electrical contact materials is done by measuring two types of properties pertaining to contact performance. They are physical properties and electrical contact properties. Physical properties include density, microstructure, hardness and electrical conductivity whereas the major parameters of the electrical contact properties are contact resistance, arc erosion and coantact weldability.

2.4.1. Physical properties:

The evaluation of physical properties is of primary importance to ensure consistency. Following properties are checked on routine basis:

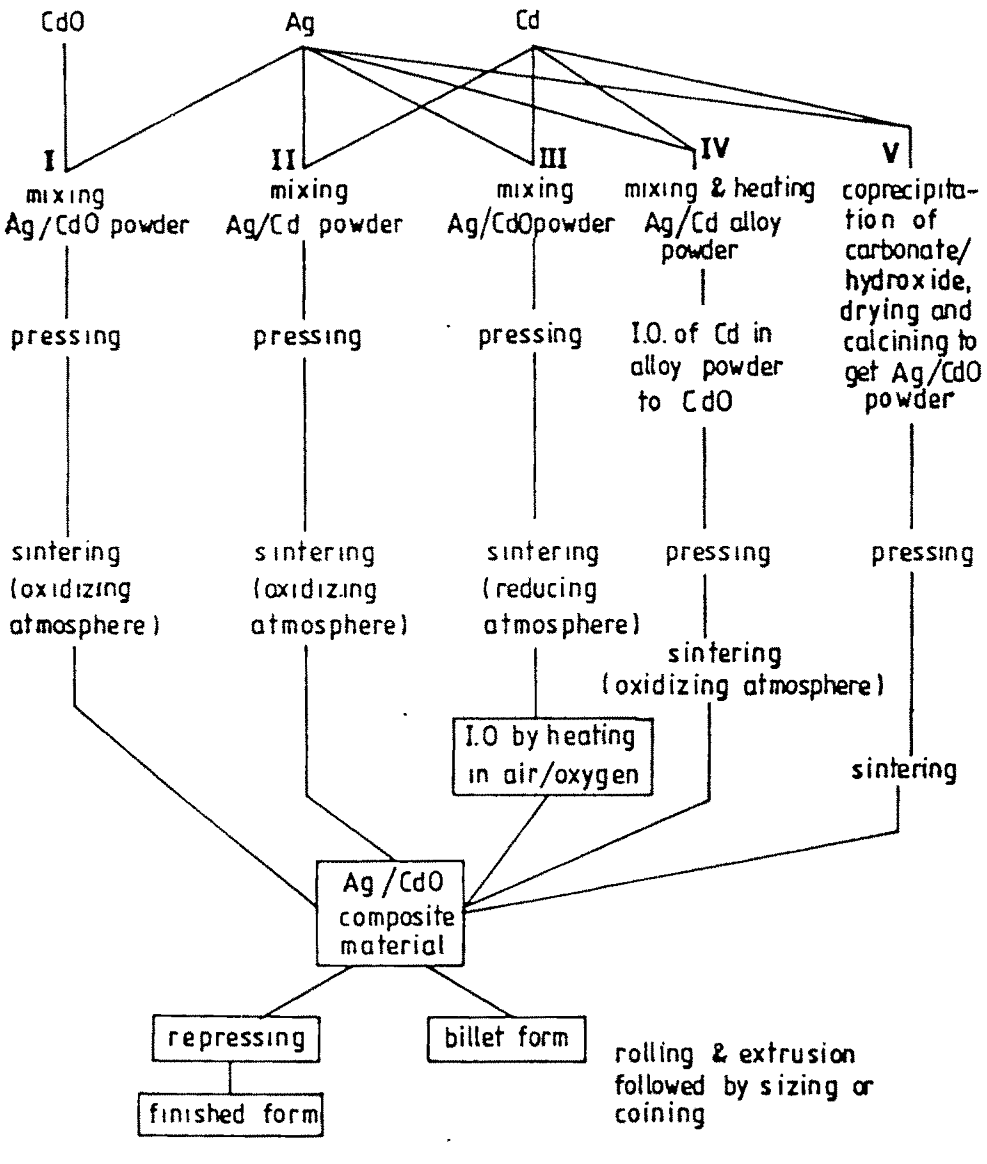


Fig. 2 9 : Flowsheet of various processing routes of Ag/CdO contact materials on a comparative basis [76].

Density: It is an indicator of porosity of compact. Low compact density means higher porosity and higher arc erosion and lower useful contact life.

Density of silver-metal oxide composite contacts is expressed as [77]

$$\gamma = \frac{100}{\frac{C_1}{\gamma_1} + \frac{C_2}{\gamma_2} + \text{--------} + \frac{C_n}{\gamma_n}}$$

Where Cn = Concentration of component n (wt%)

γn = density of component n (gm/cc)

Density of sintered compacts is usually measured by immersion technique.

Microstructure: Optical microscopy in unetched condition (usually at 100X-500X) or scanning electron microscopy is usually recommended for microstructural examination of sintered/hot-pressed compact.The purpose of such a study is to examine the size of dispersed oxide phase particles and the morphology of oxide dispersion.

SEM and EDAX are also employed to evaluate the extent of damage taking place during the use of contacts. The contact decay during service occurs and gives rise to surface changes due to vaporization, oxidation and material transfer between contact members. The progressive decay after a stipulated number of make and break operations and at the end is studied using SEM and EDAX [78-81].

Hardness : The hardness of contact material governs its wear behaviour. It is usually expressed on a microhardness scale or in HRF units.

Electrical conductivity : The conductivity of a two-phase structure in which the conductivities of the two phases are σ_1 and σ_2, respectively, can be given by an expression of the form [74]

$$\sigma_{alloy} = \sigma_1 + \frac{3 f \sigma_1 (\sigma_2 - \sigma_1)}{2\sigma_1 + \sigma_2}$$

where f is the volume fraction of the second phase particles of conductivity σ_2.
This expression is valid provided the second phase particles are greater than 0.1 micron in diameter and f is not greater than about 0.2. For $\sigma_1 >> \sigma_2$., the expression reduces to,

$$\sigma_{alloy} = \sigma_1 (1-1.5 f)$$

Electrical conductivity measurements are usually carried out with conductivity meter which is based on an eddy-current principle and reads conductivity values directly in % IACS units.

2.4.2 Electrical contact properties :

The contact properties usually evaluated are :

- contact resistance
- resistance to arc erosion and
- contact weldability

Contact resistance : Contact resistance is defined as the electrical resistance between the contact surfaces of the two members of a contact pair during the 'make' cycle. It can be measured by a precise milli/micro-ohm meter.

The value of contact resistance not only depends on the electrical conductivity of the contact members but also on the surface topography and the nature of the surface film.

The conducting surface film deteriorates due to erosion and thus the contact resistance may change with time and often rapidly increases towards the end of the switching life of contacts.

The measurement of contact resistance involves passage of a 10 A DC current through the pair of contacts, before starting any make-and-break operation, for about one hour for stabilization and the voltage drop across the contact pair is measured. A specified number of make-and-break operation is then carried out with the nominal AC electric current after which a 10 A DC current is again passed through them for one hour. The millivolt drop is measured once again to evaluate contact resistance.

Another way of evaluating contact resistance is by monitoring the rise in temperature of the contact when a nominal current is passed for a specified time. The termperature difference between the contact terminals in steady state and ambient conditions is monotonically related to contact resistance.

Turner and Turner[82] have developed a simple apparatus, capable of doing reproducible measurements of temperature rise and millivolt drop of contactor contacts with the purpose of comparative testing of contact materials. A linear relationship is observed between millivolt drop and temperature rise at constant current. The ratio of millivolt drop and temperature rise is found to be directly proportional to current, irrespective of material of the contacts.

Testing of electrical contact resistance is also a method for proving the existence of corrosion and reaction products and of adhering and contaminating substances on clean contact surfaces [83]. The measurement is based on the principle of quantitative detection of the effect of layers, which increase the resistance, by measuring the current intensity and voltage of a surface against the reference electrode.

Caven et. al. have developed a personal computer model that predicts contact resistance distributions for clean electrical contacts.[84] .

Recently attempts have been made to use the data of changes in the contact resistance for monitoring the reliability, efficiency and life of contacts [85,86]. The contact resistance of the stationary contact usually increases with time. The cause of increase in contact resistance is the degradation processes taking place on contact spot. The model of spot degradation proposed by these authors enables one to obtain theoretical dependence of contact resistance vs. spot radius, time, temperature and properties of surface film. The time dependence of contact resistance in turn enables the prediction of life time of a contact.

Resistance to arc erosion and wear : Contact surfaces are subject to erosion and wear during the make and break operations of the electrical circuits. Wear is nothing but the general erosion of the contact causing irreversible changes in the shape, size and follow-through of the latter. Wear due to mechanical effects such as impact, friction or rolling is called mechanical wear. Wear produced in contacts when opening an electric circuit is due to the action of the resulting arc. The closure of contacts also produces electrical wear which, in certain cases, may be even greater than wear due to opening. Excessive electrical wear during closure results from the fact that the contact make is not always finished at first touch, but as a consequence of bouncing, the members make and break their contact several times before they reach a permanent state of contact.

The make and break operations of the electric circuit give rise to arcing or sparking across the contacts. When breaking an appreciably heavy current, arcing is produced by an appearance of the bridge of molten metal between the contacts. Due to the high temperature developed by an arc or spark some of the bridge metal is evaporated, some is splashed and ejected from the gap, and some of it is removed from one contact and deposited on the other. The directional transfer of metal from one contact to the other caused by the electric discharge set up between separating contacts is termed as electrical erosion or arc erosion. Arcing transfers the bridge metal from the cathode to the anode and sparking transfers it from anode to cathode. This phenomena leads to the formation of pip on one contact and a crater in the other contact, and with small clearances, may even lead to welding of contacts due to their being bridged while open. Electrical erosion increases linearly with current, voltage and arc duration and depends on the material of contacts.

Arc erosion gives rise to decrease in the weight of contact elements continuously with an increasing number of make - and - break operations. This loss in weight is monitored as a function of number of make - and - break operations, by taking out the contact elements (along with the base plate) and weighing them in a high precision electronic microbalance before and after a specified number of make break operations. The practical units of loss in weight due to arc erosion are microgram per operation or milligram per set of operations.

Powder metallurgically produced silver-cadmium oxide and silver-tin oxide materials with equal volume percentages of oxide were electrically tested to evaluate and compare the effects of different oxides on the arc erosion behaviour [87]. The silver tin-oxide material had less steady-state erosion, better weld resistance but higher contact resistance compared to silver-cadmium oxide contacts. The arc-eroded surfaces of silver-tin oxide material consisted of silver, tin oxide and porosity distributed across the contact surface whereas silver-cadmium oxide eroded surfaces had large, elevated, oxide-depleted areas.

Pravoverov and co-workers [88] investigated the electro erosive wear of contacts made of Ag-CdO composites differing from each other in terms of the dispersivity of the CdO particles. It was established that electroerosive wear of finely dispersed (internally oxidised) contacts is much smaller than that of coarsely dispersed ones.

D. Nath [89] during the studies on comparative behaviour of silver-tin oxide and silver-cadmium oxide contact materials in commercial contactor obtained contradicting results to those reported in the literature. Tests were conducted on block-type contactors under AC-4 conditions at 250 A current for Ag-CdO and Ag-SnO_2 contacts. The contactor fitted with Ag-SnO_2 tips showed higher erosion than the one fitted with Ag-CdO tips. These results are contrary to those reported by some of the other authors in the literature.

Resistance to contact welding : Arcing transfers metal from one contact to the other leading to the formation of pips on one contact and craters on the other. The small clearance between the two contacts combined with a rise in temperature and the force necessary to make the contact, occasionally leads to welding of contacts. The inherent resistance of contact materials to this welding tendency is an important parameter for the continued trouble-free operation of electrical switching devices. There are a number of ways to quantify this welding tendency.

The minimum current necessary is passed through the contacts so that the weld occurs after a specified number of make-and-break cycles. The force required to separate the contacts is one indication of welding tendency i.e.the materials with good anti-welding properties require a smaller force to separate the contacts. The number of occurences of such welding phenomena for a specified number of make-and-break operations is another indication of contact weldability.

Contact weldability can also be evaluated by passing a high current through the contact and determining nominal current when 10 to 100 such welds are recorded in a million operations. The higher the nominal current, the better is the antiwelding behaviour of the contact material.

The evaluation of welding force being a more involved task of using transducers/sensors of contact or non-contact type, it is customary to count the number of operations which give a welding force exceeding a preset value. In some instances, simply number of make-and-break operations after which the welding of contacts occurs is reported. More the number of such weld-free operations better is the welding behaviour.

Welding force is measured by ASTM weld tester which is a test fixture developed by ASTM committee B04.04 [90]. Here a DC current source is energized with the test contacts closed. The contacts are bounced open by a solenoid for a predetermined arcing time and arc gap, after which the contacts close. After closing the contacts and cooling for 30 sec., they are separated, and the force required to break them apart is measured by a spring balance.

M. Huck et al [91], P.Braumann et al [92], W. Rieder [93], B. Dubravec [94], J. Muniesa [95] have investigated the electrical performance of Ag-CdO and/or $Ag-SnO_2$ systems under different test conditions in terms of their contact resistance, resistance to arc erosion and anti-welding properties. It is found that much higher thermal stability of SnO_2 in $Ag-SnO_2$ material (decomposition and/or sublimation of SnO_2 requires temperatures above 1500 ^{0}C as against 900-1000 ^{0}C for CdO) offers higher arc-erosion resistance and better anti-welding properties to $Ag-SnO_2$ materials than Ag-CdO. However, $Ag-SnO_2$ system suffers from higher contact resistance and resultant greater temperature rise than Ag-CdO.

Recently, Behrens and co-workers have developed an advanced silver/tin oxide contact material which utilizes tin oxide powder produced by a novel process so called "spray-roasting" or "reaction-spray process" [96,97]. The contact properties of this new material were tested in a model switch as well as in commercially available contactors of different sizes and designs. The investigation covered tests for service life for different utilization categories, thermal behaviour under continuous current, and welding on make. The new material was found to be superior in performance to conventionally manufactured PM type Ag/SnO_2 materials.

The contact materials are also subjected to DC loads. The contacts are hence evaluated for their electrical performance for a given set of DC voltage-current combinations. C.M.Emmons [98] has carried out life tests at different DC voltage-current ratings and measured contact erosion and contact resistance for a couple of contact materials. T. Kubono [99,100] has done extensive study of Ag-9.3 wt % SnO_2 punched contacts in a DC 30V-10A resistive circuit on a comparative basis with Ag-12 wt % CdO contacts. He found that the arc duration of Ag-SnO_2 contacts was shorter than that of Ag-CdO contacts. It was also found that the contact resistance of Ag-SnO_2 material is equal to or less than that of Ag-CdO and that the temperature rise close to a stationary contact was proportional to the contact resistance. The study also covered the sticking or welding behaviour of contacts. L.H. Matthias et al [101] have patented manufacture and evaluation of Ag-2.5 to 10wt.% ZnO electrical contacts processed by conventional PM route. The performance evaluation was undertaken at a resistive load of DC 24V-100A for 50,000 operations by installing two sets of test contacts in an automatically actuated switch as used in an aircraft.

Table 2.9 gives a comparative account of the different Ag-MeO contact materials in relation to their applications.[114]

Table 2.9 : Properties of AgMeO contact materials [114]

Group	Typical material	Typical application	Switching Performance				
			W	R	E	M	Q
Ag CdO i.o.	Ag CdO 10	contactor	A	E	A	E	E
	Ag CdO 15	MCCB	E	E	E	A	E
Ag CdO p.m.	Ag CdO 10	contactor	A	E	A	E	E
	Ag CdO 12	contactor	A	E	E	A	E
	Ag CdO 15	contactor	E	E	E	A	E
Ag SnO_2 i.o.	Ag SnO_2 In_2O_3 12	contactor, MCCB	E	C	E	A	A
	Ag SnO_2 Bi_2O_3 12	contactor, MCCB	E	C	E	A	A
Ag SnO_2 p.m..	Ag SnO_2 WO_3 12	contactor, MCCB	E	A	E	A	A
	Ag $SnO_2 Mo0_3$ 12	contactor, MCCB	E	E	E	A	A
Ag ZnO	Ag ZnO 8	MCCB	E	C	E	A	A

Note : E = Excellent
A = Acceptable
C = Critical
MCCB = molded-case circuit breaker
i.o. = internally oxidised
p.m. = powder metallurgical

W = Welding
R = Contact resistance
E = Erosion
M = Arc mobility
Q = Arc quenching

Life testing of electrical contacts :

The operation of electrical contacts in different electro-mechanical systems under various operating conditions places requirements on contacts that are as diverse as those on any other material.

Most commercial applications of contacts require that the device which incorporates the contacts meets a set of operating conditions, and tests are run on device to accept or reject it. These tests usually cover all the important conditions of operation in service including life, welding, contact resistance change, corrosion, electrical noise, and reliability under the most critical operational and environmental conditions.

The electrical endurance or life testing of contacts is done as per specified utilization category such as AC-1, AC-2, AC-3, AC-4 in alternating current mode; or DC-1, DC-3, DC-5, DC-6 in direct current mode depending on the intended service conditions of the electrical device (such as contactor, relay, switch, circuit-breaker etc.) on which they are installed.

Life testing is done as per ANSI/ASTM standard B182-49 (Reapproved 1975) which covers the determination of the life and some operating characteristics of the materials used for electrical contacts, as indicated by the loss in weight of the contact material due to arcing, temperature rise of stationary contacts during operation, direct current voltage drop across the pair of contacts at intervals throughout the test, and observation of the welding tendencies.

Life test on devices may be conducted as per International standard CEI/IEC 947 for low-voltage switchgear and controlgear. Some of the tests carried out on electrical device such as a contactor as per standard IEC 947-4-1 (1990) are :

a) test for temperature rise limits
b) test for rated making and breaking capacity
c) conventional operational performance test.
d) test for overload current
e) dielectric property test.

2. 5 Design and testing aspects of different contact testing set-ups :

The quality and reliability of electrical contact materials are more critically dependent on their contact properties. The contact properties, in turn, are quite complex functions of both the physical properties (such as density, composition, microstructure, hardness, electrical/thermal conductivity etc.) and the operating conditions (such as voltage, current, frequency, power factor ; frequency, speed and force of make and break; electromagnetic environment etc.) Specialized techniques are therefore needed to evaluate the contact properties under various operating conditions.

Three types of contact testing systems have been reported in the literature. In the first type, the test systems ensuring make-and-break operations produced by a vibrator mechanism or driven by a motor are covered, [5,13,55,102,103,104]. The operating conditions of make-and-break are varied in these systems in a controlled manner over a range of values. The test set up of this group thus permits evaluation of contact material over a wide range of operating conditions and is of a more versatile nature.

The second type of system tests the contact materials on actual electrical device with a given set of operating conditions. [6,7,9,10,69,81,87,105-110]. Such systems have the advantage that the testing can be carried out under operating conditions and electromagnetic configurations which are actually encountered during service.

The third type uses a specially constructed test-switch fitted with demountable contacts of the material under test. The switch is surrounded by moulding materials of the type used in practice and is operated electromechanically in a similar manner to the category of switch for which the contact material is intended [73,78,101,111].

Gurlet et al [102] have developed a simple contact testing machine for the evaluation of the main electrical properties of contact materials. In this machine the movement of moving contact is ensured by a vibrator. The lower plate supports the vibrator whereas the upper plate supports the fixed contact. The gap between the fixed and moving contact can be set accurately by a gap trimming system. A force sensor is fitted on the upper side of the connecting clamp of the fixed contact. Fig.2.10 (a) shows the schematic of the principal mechanical components. The test parameters such as contact force, duration and delay of bounce at closing, closing speed, opening speed, mechanical duty cycle,etc. are controlled through vibrator. In order to have the most cost effective design, the impedence of the power circuit are chosen as simple resistors. Fig 2.10 (b) gives the electrical circuit diagram for the test set-up. The test current can be selected from 10A to 100A with 10A steps at 230 VAC, 50 Hz. The overall operational control is through the Rockwell 6502 microprocessor, RAM I/O 6532 and 2716 EPROM. This central unit is connected to all the peripheral functions of the electronic circuitary such as keyboard, display, triggering circuit, opto-isolators, triacs,etc. A PT 100 thin film Platinum RTD measures the temperature rise of the fixed contact after a predetermined number of make-break operations.

The machine developed at LCIE, France [103] to determine welding and erosion tendencies of electric contacts also has facilities for measuring the other important test

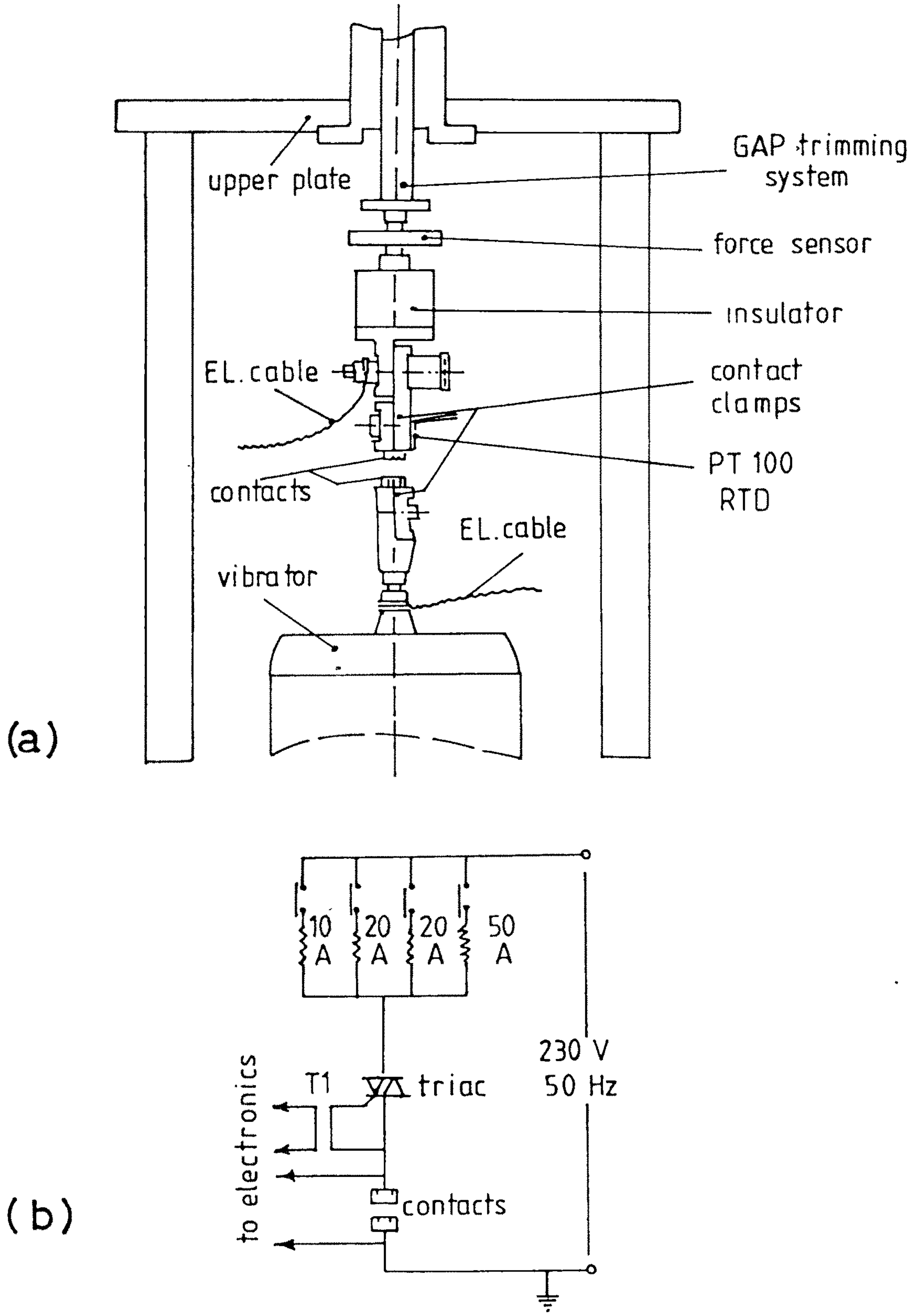


Fig. 2.10: Schematic of **(a)** principal mechanical components and **(b)** electric power circuit of contact test setup [102]

parameters like "contact force", "contact velocity on make" or "break" etc. In this machine the 'open' and 'close' operations of the contacts are mechanically actuated by a striker and cam arrangement driven by an electric motor through a speed reducing gear. The schematic of the various operting parts is as per Fig 2.11 (a). The current, the power factor, and the type and value of the electric load, with which the machine works, may be controlled automatically and the data generated can be logged and processed by a programmable computer dedicated to this machine. As per the electrical circuit given in Fig 2.11 (b) the contacts can be tested for a 'nominal current' range of 5-50 A and power factor of 0.3 to 1.0. Combinations of resistive or inductive loads can be used to adjust the required power factor. More than 80,000 operations can be performed in a day and the entire process is automatic. To simulate AC3 operation of contactors, a current six times the initial or nominal current can be superimposed.

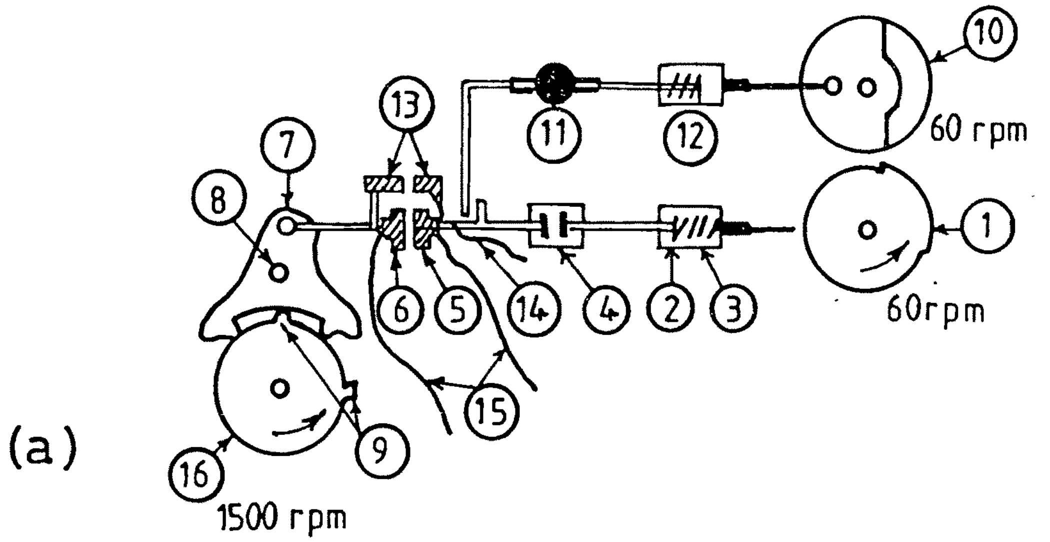
C. Lambert and coworkers [9] conducted electrical tests on an equipment installed with a test contactor as per standard CEI 158-1 and utilization category AC-3 with 100A and 175A nominal currents. The test set up resembles to type two described above. The test details are as under:

Electrical conditions :

* voltage : 230V/50Hz
* rated current : 100A or 175A
* duration of making current : 10 ms
* power factor : 0.35

Mechanical conditions :

* closing speed : 1 cm/s
* bounce duration : 2.2 ms
* opening speed : 6 cm/s
* contact force : 6 N
* operating rate : 30 cycles/min



1. main cam
2. air damping device
3. contact force spring
4. resin damping device
5. moving contact
6. fixed contact
7. tumbler
8. tumbler axis
9. retractable strikers
10. auxiliary cam
11. strain gaugie ring
12. safety spring
13. displacement transducer
14. thermocouple
15. current leads
16. wheel

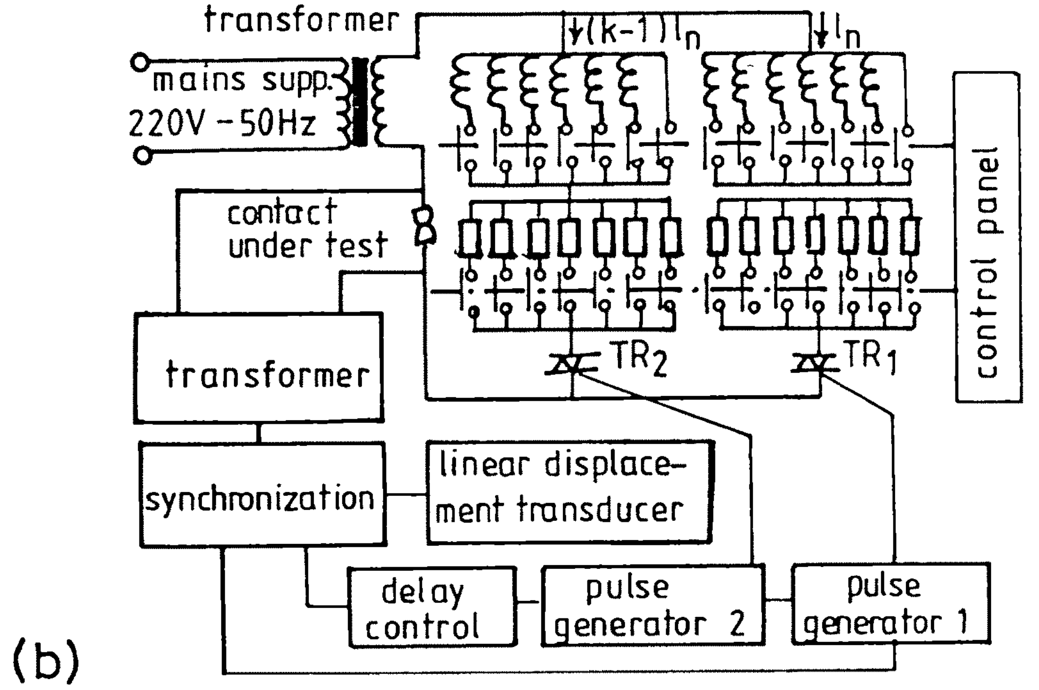


Fig. 2.11: Schematic of **(a)** various operating parts and **(b)** associated electrical circuit for contact test set-up developed at LCIE [103]

Sensors and data aquisition :

- * contact force and welding force : 0 to 64 N range
- * temperature rise of fixed contact : 0 to 50^0 C
- * erosion loss measurement : After every 2,000 op. upto 10,000 operations.

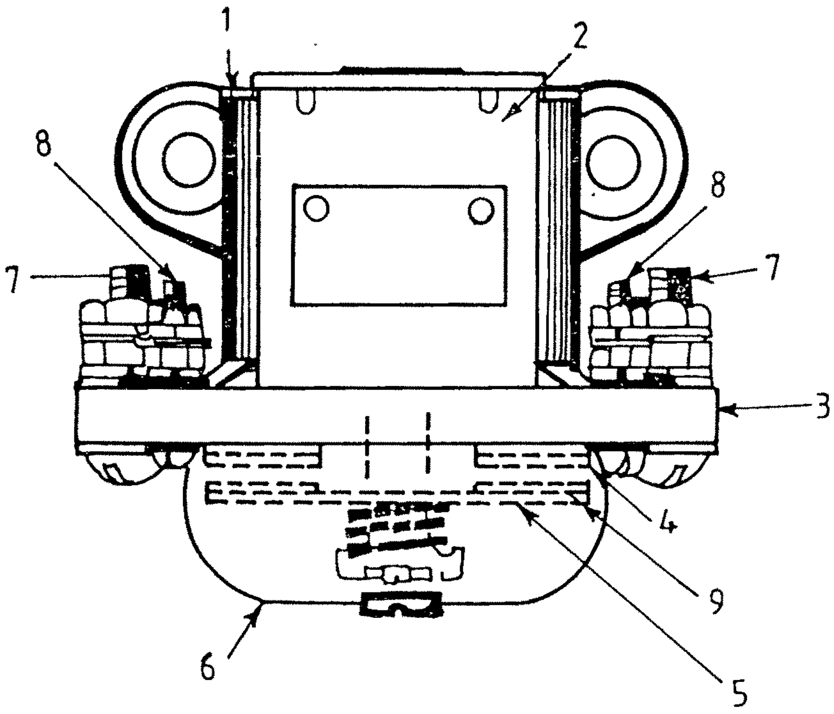
Electrical performance evaluation was done by L.H. Matthias et al [101] using a resistive load of DC 24V-100A for 50,000 operations by installing two sets of test contacts in an automatically actuated switch similar to one used in an aircraft. The switch principally consisted of a magnetic coil, a U-shaped iron field piece, an insulation support, a set of stationary contacts and a set of movable contacts on a bridge bar. Fig 2.12 shows schematic view of this switch used in DC testing.

Table 2.10 gives a summary of various operating parameters of different contact test set-ups reported in the literature.

2.6. Effect of minor alloying additions on performance of electrical contacts :

The relative scarcity of silver throughout the world and its eventual high price has prompted investigations in new alloy systems of silver that would result in reduction in the consumption of silver while achieving improved or at least equivalent performance as conventional contact materials.

It was felt that the additions of a second metal oxide, such as indium oxide, tin oxide, bismuth oxide or tungsten oxide to conventional Ag-CdO system would give enhanced performance [112]. Attempts were also made to develop similar multicomponent systems of Ag-SnO_2 material by adding oxides of indium, bismuth,copper,zinc,tungsten,germanium, tellurium etc.[9,10,81,111,113,114].



1. magnet coil
2. iron field piece
3. insulation support
4. stationary contacts
5. bridge bar
6. enclosure
7. terminal post
8. connection post
9 moving contacts

Fig. 2.12 : Schematic of DC contact test switch [101].

Table 2.10 : Summary of operating parameters of different contact testing set ups.

Applied voltage	Rated Current Ie	Utilization category	Power factor	Duration of make	contact force	Closing speed	Operating speed	Operating frequency	Total switching cycles	Ref.
220 V 50 Hz.	29 A	AC - 3	0.3	20 - 30 ms	7 N	0.3 ms^{-1}	0.1 ms^{-1}	1 S^{-1}	50,000	5
230 V 50 Hz.	10-100 A	—	1. 0	—	4 N	3.0 cms^{-1}	10.0 cms^{-1}	1 S^{-1}	20,000	102
220 V 50 Hz.	5-50 A	upto 6 times Ie	0.35 - 1. 0	500 ms	0.5 – 10 N	1.0 ms^{-1}	—	1 S^{-1}	200 X 10^3	103
100 V A.C.	40-60-80-100 A	—	1. 0	620 ms	40 g	—	—	1/3 S^{-1}	30.000	6
220 V 50 Hz.	375 A	—	0.35	—	—	—	—	—	8 x 10^4	7
380 V	660 A	AC - 3	0.35	200 ms	—	—	—	600 h^{-1}	9 x 10^5	10
380 V	320 A	AC - 4	0.35	200 ms	—	—	—	600 h^{-1}	9 x 10^6	
575 VAC 50 Hz	750 A	AC - 3	0.35	—	—	—	—	300 h^{-1}	50,000	110
100 V	10-50 A	—	1. 0	—	200 g	63 mms^{-1}	63 mms^{-1}	120 min^{-1}	10^5	73
250 V	10 A	As per IEC 328	0.6 +0.05	—	—	—	—	—	40,000	78
415 V 3 ph.	50 A	—	0.65	0. 10 s	3.5 N	250 mms^{-1}	750 mms^{-1}	1 sec^{-1}	30,000	6

However, all such attempts to develop and market such three or more component heterogeneous alloy systems were not successful.

Off late , after a careful consideration of principles of arc physics it has been felt that the electrical performance of Ag-CdO materials can be improved by trace additions of oxides of alkali metals like Na,K or Li. [110,116-121,124-129].

Following discussion pertains to effects of minor additions on the peformance of Ag-CdO and Ag-SnO_2 contact materials.

2.6.1. Alloying additions in Ag-CdO systems :

Improvements in the performance of Ag-CdO materials on alloying are attributed to one or some of the following effects :

i) by refining the cadmium oxide particle size and thereby improving erosion resistance.

ii) within a certain concentration range, the additive minimizes or eliminates precipitation from the grain boundaries or forms divorced grain boundaries.

iii) by acting as a sintering-aid and thereby improving as-sintered density of Ag-CdO.

iv) by changing the morphology of CdO particles to a more uniform and rounded one and giving rise to more isolated particles of CdO to offer continuity to silver matrix.

v) by reducing loss of silver due to splattering and decreasing tendency to thermal stress cracking; finally improving erosion resistance.

Extensive work was carried out by Y. S. Shen and coworkers [37,115] to investigate the effect of single element additions on microstructure and properties of Ag-10 CdO electrical contacts. The authors studied the effect of in all 33 elements, mainly from Gr.IA and Gr.II A. The concentration of additives was varied between 0.05 and 1.0 wt% and was raised upto 2% for Sn and Zn. The effect of additive on microstructure is summed up as under:

(a) Effect on particle size: it was found that elements forming stable oxides, refine the cadmium oxide particles regardless of its alloying behaviour.
(b) Effect on particle configuration: the additives change the configuration of metal oxide particles from anisotropic to isotropic form.
(c) Effect of additives on grain boundary precipitation: some additives lead to grain boundary precipitation and divorced boundaries.

Various aspects of effect of lithium additions have been studied by H.J.Kim and coworkers [116,117], G.J. Witter [119] and F.S. Brugner and others [110,118,120,121].

Mou Chih Lu, Julius R. Sims and F. S. Brugner [118] examined the effect of trace additions of a lithium compound on the oxide particle size and kinetics of growth of CdO particles in Ag-20 wt % CdO material fabricated by IOAP route. The lithium was added to IOAP Ag-CdO powder by following schedule:

* dissolution of the appropriate quantity of lithium carbonate (Li_2CO_3) in a suitable liquid solvent.
* addition of the insoluble Ag-CdO to the Li_2CO_3 solution to form a slurry and followed by thorough mixing.
* drying the resulting Ag-CdO powder particles
* sieving the dry powder mixture through a 100 mesh screen to break-up the agglomerates.

* pressing and sintering to form final compacts.

It was found that the trace lithium additions in the form of Li_2CO_3 decreased the thermal stability of the oxide particles in silver-cadmium oxide which resulted in coarser oxide microstructures. Fig. 2.13 is a plot of mean cross section chord length of oxide particles versus lithium content in Ag-20 wt %CdO.

H.J.Kim and F.J Reid [116,117] investigated the role of lithium nitrate addition as a sintering aid for producing PM Ag-CdO contact materials. Such additions enabled attainment of as-sintered densities of better than 99% theoretical and an improved CdO particle morphology. A minute amount of Lithium nitrate in Ag-CdO powder mixture was found to greatly modify CdO phase through a series of transient physical-chemical reactions with CdO on the particle surfaces during sintering cycle. As a result, improvements in the material properties were obtained; ie (1) higher electrical conductivity, (2) two fold increase in ductility, (3) improved arc erosion resistance when compared with conventional PM Ag-CdO contacts. Fig. 2.14 shows the effect of lithium addition on as-sintered density of Ag-CdO contacts for, varying CdO contents. Microstructural examination of Ag-15 wt % CdO contacts with and without lithium showed finer CdO particle size, uniform distribution and more rounded morphology of CdO for lithium treated Ag-CdO. Improved microstructure is found to be responsible for higher erosion resistance for lithium-treated material.

F. S. Brugner [110] did a comparative study of effect of lithium addition as lithium mitrate and lithium carbonate in IOAP Ag-CdO and coprecipitated Ag-CdO powders, respectively. Despite significant differences in Li dispersion in two cases, very little difference in electrical erosion performance in IEC, AC-3 testing was recorded. Fig.2.15 gives the plot of electrical erosion loss versus number of contactor operations for the two materials.

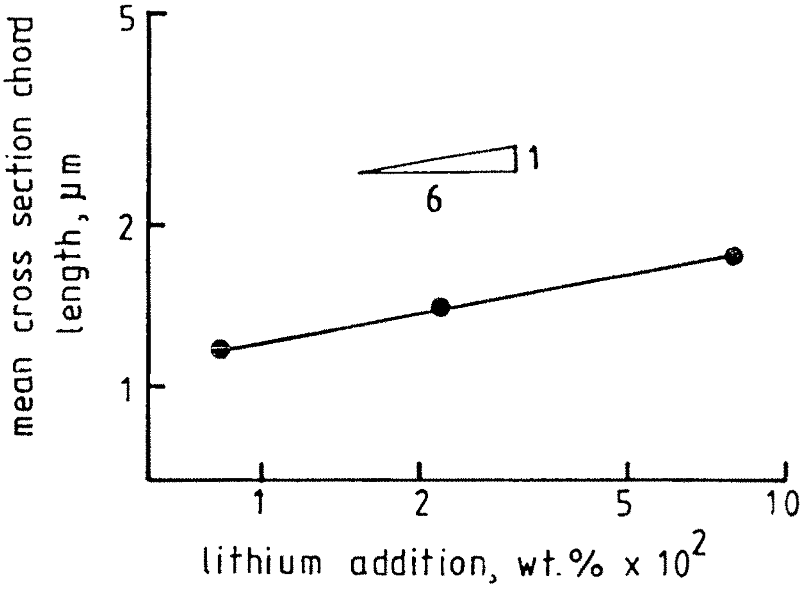


Fig. 2.13 : Plot of mean cross section chord length of oxide particle vs. lithium content [118].

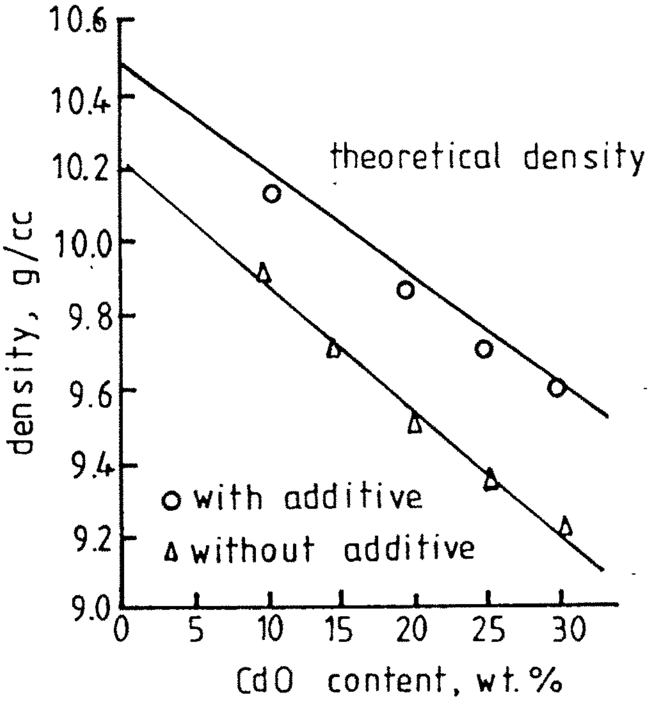


Fig. 2.14: Effect of lithium addition on as-sintered density for Ag-CdO contacts [117].

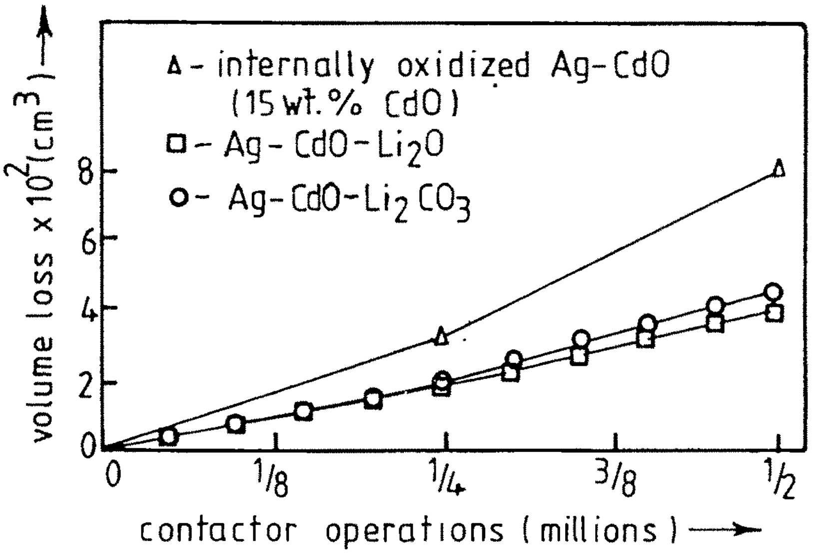


Fig. 2.15: Arc erosion loss for Ag-CdO-Li_2O and Ag-CdO-Li_2CO_3 systems[117]

G. J. Witter and Mou Chih Lu [119] have studied the effect of Li addition on erosion behaviour of silver-cadmium oxide. They have concluded that lithium additions lower contact erosion beyond effects associated with density improvement. From their sintering results, it is seen that Li_2CO_3 activates the sintering process for Ag-CdO. The activation is associated with increased weight (cadmium) loss and cadmium oxide grain growth during sintering, which is contrary to the findings of Kim and Reid [117]. Their study involved $LiNO_3$ as an additive which has a much lower melting temperature and probably a different activation mechanism than Li_2CO_3

Another facet of influence of minor impurities such as Na, K or Li in Ag-CdO on its switching behaviour in terms of its arc reignition voltage and arc interrupting capacity has been studied by several workers [125-129]. It is well known that the chemical methods of silver-metal oxide powder production invariably lead to higher concentration of entrapped impurities such as Na and K. The Na, K as well as Li have low ionization potentials and low work function values (Table 2.11) compared with the components of Ag-CdO, which make these metals a source of added electrons that ultimately tend to reduce the reignition voltage and enhance the reignition tendency of the electric arc. In view of this the recommended levels of these impurities in Ag-CdO are max.50 ppm each so as to control the losses due to erosion.

TABLE 2.11 Ionization potential and work function data [136]

Property	Ag	Cd	Zn	O	Na	K	Li
Ionization potential eV	7.576	8.993	9.394	13.618	5.139	4.341	5.392
work function eV	4.26	4.22	4.33	-	2.75	2.30	2.90

Besides the investigations on effect of additives in elemental form several attempts were made to find the influence of compound additions on matrix strengthening behaviour of Ag-CdO [122,123]. The influence of GeO_2 addition on material loss of Ag-CdO during arcing has been studied [122]. The matrix strengthening due to GeO_2 additions, resulted into somewhat higher steady state material loss rate compared to additive-free Ag-CdO. However, there was a distinct reduction in thermal stress cracking and pronounced blunting of incipient crack tip by inflow of molten silver in GeO_2 added contacts. This resulted into drop in macroscopic material loss and extended operational life of contacts. The GeO_2 additions were found to increase wetting of molten silver on contact surface during arcing and thereby offered more uniform erosion profile.

Similar observations have been reported about the effect of GeO_2 and Ta_2O_5 on switching behaviour of Ag-CdO materials[123]. They reduce thermal stress cracking significantly. Though the overall material loss was higher, the damage with these additives was uniform.Matrix strengthening additives are found to lower the interfacial energy between Ag and CdO and also the surface tension of molten silver on contact surface. This improves wettability between silver and electrode surface and ultimately gives reduction in silver loss due to splattering and contact degradation due to cracking.

2.6.2. Alloying aditions in Ag-SnO_2 system :

As stated earlier, Ag-SnO_2 has been found to be a replacement material to more conventional and toxic Ag-CdO. It has better arc erosion resistance, but has high welding force and high contact resistance i.e.high over temperatures after several thousand contact operations. Such a combination of contact properties of Ag-SnO_2 is owing to higher thermal stability of SnO_2 in Ag-SnO_2 system [130].With a decomposition and sublimation temperature of more than 1500^0C the loss of SnO_2 is no longer balanced by the erosion or evaporation of Ag from the contact surface. This reduces the melting of the contact surface by electric arc and hence gives low erosion rate. At the same time, the dispersion strengthening of welds by SnO_2 increases the welding force and the layer of SnO_2 on contact surface increases the contact resistance.

In order to improve the contact resistance and weldability of Ag-SnO_2, several additives such as In_2O_3 [81,111,131,132], WO_3 [10,114,133], MoO_3[114], TeO_2 [9], GeO_2 [81] etc. have been tried.

Investigations with compounds In_2O_3 and GeO_2 as dopants indicate a marked influence of these additives on crack propagation and rate of erosion. Binary (undoped) Ag-SnO_2 shows relatively poor resistance to crack propagation and an unsatisfactorily high acceleration of erosion rate after extensive switching operations. The doped material shows no better resistance to crack propagation and a deceptively higher initial erosion rate, but its superior surface wetting behaviour results in low acceleration of the erosion rate and satisfactorily low overall material loss.

Tungsten and molybdenum oxides act as wetting agents so that SnO_2 particles remain in suspension in the silver melt formed by the action of arc. Without such a wetting agent the tin oxide particles appear to be rejected by the silver melt. Not only this, WO_3 or MoO_3 addition maintains the higher viscocity of the silver melt that keeps the SnO_2 particles in suspension and reduces the arc erosion loss.

The TeO_2 additions to Ag-SnO_2 system, lowers the welding force by a different mechanism. TeO_2 forms a chemical compound with SnO_2 which has lower thermal stability than SnO_2 alone, and hence improves antiwelding properties.

A systematic evaluation of different additives such as Sb_2O_3, TeO_2, Bi_2O_3,RuO_2, GeO_2, WO_3, CoO_x, In_2O_3, ZnO and La_2O_3 to Ag-11.5 wt % SnO_2 alloy is done by Wingert and Leung [134]. According to them, the best results were obtained with combined additions of GeO_2 and In_2O_3 in amount less than 0.5 wt %. The resultant quarternary alloy shows low erosion rate and much better weld resistance compared to conventional systems.