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CONSTRUCTION OF THERMO-ELEMENTS BY ELECTRODEPOSITION

By H. Kersten and Roland Schaffert [Dept. of Physics, University of Cincinnati, Cincinnati, Ohio. Received January 4, 1932]

INTRODUCTION

Several years ago Wilson and Epps¹ developed a method of constructing thermocouples by the use of electrodeposition. This method, which was devised to overcome the difficulty of making satisfactory soldered joints between the elements, consisted of using a continuous wire of one of the elements and coating those parts of it which were to form the other element with an electrolytic deposit of the other metal. However, the range of metals to which this method is applicable is very limited due to the fact that the deposited metal must have a much greater conductivity than the wire upon which it is deposited.

In the ordinary methods of thermocouple construction, the two metals are joined either by soldering or welding. In this paper the authors describe a method for joining the metals by electrodeposition, making use of the fact that most metals plated on stainless steel may be peeled off easily.

SINGLE JUNCTIONS

A sheet of polished stainless steel, used as the cathode, is placed in a plating bath (e.g., a nickel bath) in such a way that half of it is immersed. It is electroplated to the desired thickness, removed, and placed in a different (e.g., silver) bath in such a way that the unplated half of the sheet and a narrow margin along the edge of the nickel are immersed. The sheet is removed when the desired thickness of silver has been deposited and the metals, which are now joined together at the junction, peeled off with the aid of a safety razor blade as is shown in Fig. 1.

In order to make a more definite junction with a minimum of lap, a thin sheet of brass, A, Fig. 2, may be placed so as to cover about half the stainless steel sheet D. The brass sheet may be held in place with a piece of hard rubber clamped over it. When the second metal is plated the brass sheet is reversed so that it covers the other half and allows only a small lap over the first deposit.

The number of different metals which may be combined to form junc-

¹ Wilson and Epps, Proc. Lond. Phys. Soc., 32, 326; 1920.

tions in this way is limited to those which can be successfully plated and stripped from stainless steel. Junctions using combinations of the following metals have been made: Fe, Co, Ni, Cu, Ag, Cd, and brass.²

To produce very thin couples it is necessary to have a good polish on the stainless steel. To remove these very thin layers it was found best



FIG. 1. Peeling the junction from the stainless steel.

to cover the deposit with a light coat of varnish³ or lacquer, allowing the varnish to dry and then peeling the metal and varnish off together. The varnish may then be dissolved away by placing the junction in turpentine or some other solvent. In this way nickel-silver junctions were produced less than 0.0005 cm in thickness without difficulty.



FIG. 2. Arrangement for getting a minimum of lap.

These single junctions may be cut into strips of the desired width with a sharp knife or razor blade before removing them from the stainless steel, or, with a scissors, after removing. The strips may be used to con-

 2 The brass had a composition of about 30% zinc and 70% copper. Thermocouples made of bismuth and bismuth-tin alloys give a much greater thermoelectric power than any of the combinations tried. Bismuth has not been electroplated in a form suited to the uses here described. The authors are attempting to electroplate it and the bismuth-tin alloy, in a workable form.

³ Valspar varnish was used.

struct thermopiles of the type described by Moll⁴ as well as others, depending on the purpose for which the thermocouple is to be used. It is quite probable, also, that by plating two junctions on each plate, this method may be used in the construction of thermo-relays of the Moll⁴ type.

If it is desired to have a receiver of large area, with small leads, these junctions may be cut into the form shown in Fig. 3.

PLATING BATHS

The following plating baths were used. With each is given a current density and a bath temperature which was found suitable. Some of the baths, especially the cobalt, if operated under improper conditions, tends to adhere either too well at the junction so that it cannot be removed, or not well enough so that the junction cracks apart before it



FIG. 3. Junction with large receiver area.

can be removed. In each case a certain amount of experimenting was necessary in order to deposit ductile metals. Brittle metals are difficult to remove from the stainless steel.

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Cobalt(1):	
Water	1 liter,
Cobalt sulphate, CoSO4:7H2O	300 gm,
Sodium chloride, NaCl	20 gm,
Boric acid, H_3BO_3	30 gm,
Temperature	10°C,
Current density	25 amp/dm^2 .
Cobalt(2):	
Water	1 liter,
Cobalt formate (to make a saturated sol.)	
Temperature.	25°C,
Current density	0.5 amp/dm^2 .
Nickel:	
Water	1 liter,
Sodium citrate, $2Na_3C_6H_5O_7$: $11H_2O$	35 gm,
Nickel sulphate, NiSO4:7H2O	40 gm,
Temperature	50°C,
Current density	0.25amp/dm^2

4 Moll, Proc. Lond. Phys. Soc., 35, 257; 1922-23. Phil. Mag., 50, 618-26; 1925.

it.

Copper:	
Water	1 liter,
Cuprous cyanide, Cu ₂ (CN) ₂	22.5 gm,
Sodium cyanide, NaCN	34 gm,
Sodium carbonate, Na ₂ CO ₃	15 gm,
Temperature	25°C,
Current density	0.3 amp/dm^2 .
Cadmium:	•
Water	1 liter,
Cadmium oxide, CdO	32 gm,
Sodium cyanide, NaCN	75 gm,
Temperature	30°C,
Current density	1 amp/dm^2 .
Iron:	
Water	1 liter,
Ferrous chloride, FeCl2:4H2O	450 gm,
Calcium chloride, CaCl ₂	500 gm,
Temperature	100°C,
Temperature Current density	100°C, 3 amp/dm².
Temperature Current density (If the electrolyte becomes coated with a brown film, add dilute	100°C, 3 amp/dm ² . HCl to dissolve it.
Temperature Current density (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces-
Temperature	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces-
Temperature Current density (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver:	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces-
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² .
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density. Brass (copper-zinc alloy):	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² .
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density. Brass (copper-zinc alloy): Water.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density. Brass (copper-zinc alloy): Water. Copper cyanide, CuCN.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter, 27 gm,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density. Brass (copper-zinc alloy): Water. Copper cyanide, CuCN. Zinc cyanide, Zn(CN) ₂ .	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter, 27 gm, 9 gm,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water. Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density. Brass (copper-zinc alloy): Water. Copper cyanide, CuCN. Zinc cyanide, Zn(CN) ₂ . Sodium cyanide, NaCN.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter, 27 gm, 9 gm, 54 gm,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature Current density. Brass (copper-zinc alloy): Water Copper cyanide, CuCN. Zinc cyanide, XaCN. Sodium cyanide, Na2CO3.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter, 27 gm, 9 gm, 54 gm, 30 gm,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature Current density. Brass (copper-zinc alloy): Water Copper cyanide, CuCN. Zinc cyanide, XaCN. Sodium crabonate, Na2CO3. Temperature.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter, 27 gm, 9 gm, 54 gm, 30 gm, 80°C,
Temperature. Current density. (If the electrolyte becomes coated with a brown film, add dilute The solution should have a clear bright green color. If two much acid sive amount of hydrogen will be evolved.) Silver: Water Silver cyanide, AgCN. Potassium cyanide, KCN. Temperature. Current density. Brass (copper-zinc alloy): Water Copper cyanide, CuCN. Zinc cyanide, XaCN. Sodium carbonate, Na ₂ CO ₃ . Temperature. Current density.	100°C, 3 amp/dm ² . HCl to dissolve it. is added, an exces- 1 liter, 31 gm, 27 gm, 25°C, 0.5 amp/dm ² . 1 liter, 27 gm, 9 gm, 54 gm, 30 gm, 80°C, 2 amp/dm ² .

METHOD FOR PLATING JUNCTIONS IN SERIES

For some types of thermopiles it is desirable to have a number of junctions in series. These may be produced electrolytically, as follows: A stainless steel rod is polished and hung in a horizontal position between two adjustable supports mounted on cork floats as is shown in Fig. 4. The float is placed on the surface of the electroplating bath (e.g. nickel) with the rod adjusted so that half of it is immersed. When the desired thickness has been plated it is placed in another (e.g. silver) bath, with the rod adjusted so that half of it and a narrow margin along the edge of the nickel is plated. The rod is next placed in the chuck of a lathe and threads cut on it, to whatever width of junction is desired,

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by means of a special tool, shown in Fig. 5. This tool consists of a safety razor blade, clamped to a lever arm on the end of which a weight just heavy enough to make the blade cut through the electroplated layer, is



FIG. 4. Floating rod holder.



FIG. 5. Tool for cutting junctions.

hung. When the junctions are very thin they are easier to remove if they are covered with a light coat of varnish before cutting, as has been mentioned above.

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CONSTRUCTION OF A THERMOPILE USING JUNCTIONS IN SERIES

The following is a description of a thermopile for measuring spectral intensities: A piece of brass is cut in the form shown at A, Fig. 6, and of such dimensions that the junctions come into alignment when wound around it. Two insulated copper leads B, Fig. 6 are placed in the holes at the ends of the piece of brass.



FIG. 6. Thermopile details.

After the brass has been insulated by a coat of lacquer, one end of the series is soldered to one of the copper leads, and the whole series wound around the piece of brass, each junction being just far enough away from the adjoining one to insure insulation (C, Fig. 6). The loose end of the series is then soldered to the other copper lead. The holder is then



FIG. 7. Mounting for the thermopile.

placed in a copper plating bath so that the back, or cold junction side, is heavily plated with copper to increase the mass of the cold junction and reduce the electrical resistance of the series. The brass holder is mounted in a heavy brass rod, A, Fig. 7, which is prepared by boring a hole, somewhat larger than the brass holder near the edge of the rod and cutting an opening through the side, large enough to insert the holder. The two copper leads are placed in the small holes in the brass rod and serve to hold the junctions in place (B, Fig. 7). The cap, C, to which is soldered a small tube, T, is mounted on the top and held in place by two small screws. A fluorite or mica window may be placed over the opening and fastened with wax to make the enclosure air-tight. The tube T, may be connected to a vacuum pump if it is desired to increase the stability and sensitivity of the thermopile by evacuation. A nickel-silver thermopile constructed in this manner with twenty junctions had a resistance of about 18 ohms. It was found to be very stable and reached equilibrium in about one second in air.

Conclusions

The method described has the following advantages:

1. It eliminates the difficulties encountered in soldering together a number of small wires and simplifies the construction of sensitive thermocouples.

2. The mass of the junction may be reduced to a minimum.

3. The junctions may be used at higher temperatures than soldered junctions.