New Technique for Metal Bonding and Cleaning

Laboratory soldering tests show that hydrazine vapor is an excellent flux, producing residue-free bonds at moderate temperature

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ABSTRACT. A novel process* is described for cleaning and joining metal surfaces. The process uses gaseous hydrazine, N_2H_4, as the active reducing agent or flux. The hydrazine catalytically decomposes on the metal oxide surface, thereby reducing the metal oxide to the metal with all reaction products being volatile gases. This process, when carried out in the presence of low melting metals or alloys, such as solder, results in excellent metal-to-metal bonds without producing nonvolatile, corrosive, or electrically conducting residues.

The combination of a gaseous, noncorrosive, residue-free flux with relatively low working temperatures renders this process ideal for applications such as cleaning metal surfaces, diffusion bonding, soldering, or reflowing of electronic circuit boards, or of very small, inaccessible, or temperature-sensitive workpieces. The feasibility of this process is demonstrated for cleaning and reflowing printed copper circuit boards, for soldering copper to copper, or copper to gold using lead-tin solder, and for soldering inside the bore of beryllium-copper capillaries.

Introduction

For joining metals by soldering, fluxes must be used to remove nonmetallic surface films in order to promote flow of the solder and to achieve wetting of the metal surface. Commonly used are the solid, pasty, or liquid fluxes of the chloride or "acid" type, the organic, and the resin fluxes.[1] Their main disadvantages are the nonvolatility and in some cases the corrosiveness of the residues formed requiring thorough cleaning of the workpiece after completion of the soldering process. Furthermore, these fluxes are frequently difficult to apply to and to remove from very small or inaccessible workpieces. These problems might be overcome by using gaseous fluxes, such as forming gas (15% H_2 and 85% N_2) or NF_3.[2] These gaseous fluxes, however, are either rather inactive and therefore require high operating temperatures or corrosive (NF_3), making their application impractical. From these considerations, it is obvious that for many applica-

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tions, the ideal flux would exhibit a combination of the favorable properties of each flux type without their shortcomings. In this paper, we report on the existence of such an "ideal" flux, i.e., gaseous hydrazine. It is shown that hydrazine, (N_2H_4), is a noncorrosive and highly active gaseous flux permitting good metal-to-metal bonds without formation of residues.

Materials and Procedures

Pure hydrazine, N_2H_4, is a stable liquid at ambient temperature, having melting and boiling points of 2 and 113.5 C (35.6 and 236 F), respectively. It is commercially available.

Operators not familiar with its properties and handling are cautioned to consult the appropriate literature[3-5] prior to its use. Due to its flammability[3-5], the use of aqueous solutions is preferred, which at concentrations of less than 40 wt % of N_2H_4 are completely nonflammable. Hydrazine should be used only in well ventilated areas and effluents containing large amounts of unreacted hydrazine vapors should be neutralized.[5]

The apparatus used for the experiments is shown by Fig. 1. It uses pure hydrazine together with dry nitrogen as a diluent and inert carrier gas. The composition of the N_2-N_2H_4 gas mixture was regulated by adjusting the temperature of the hydrazine container. The composition of the mixture can be easily calculated from the known vapor pressure of hydrazine at a given temperature.[3,4] A convenient concentration of about 4% by volume of hydrazine can be obtained by maintaining the hydrazine vessel at 38 C (100 F). The system was equipped with stopcocks to allow bypassing of the hydrazine container and purging of the apparatus with dry N_2 prior to its use.

The gas flow was monitored by means of a flowmeter. The reaction chamber consisted of a 25 in. long Pyrex glass tube, 1 in. in outside diameter. It was heated by a variable temperature electric tube furnace (Lindberg, Hevi Duty, Model 55035A.) The temperature inside of the glass tube was monitored by a thermocouple. Samples were introduced from the exit end of the tube. The heated sections of the apparatus should be constructed of a material (such as glass or ceramics) which does not catalyze the decomposition of hydrazine, to avoid premature decomposition of the hydrazine before it reaches the workpiece.

For the use with aqueous hydrazine solutions, the apparatus was modified as shown in Fig. 2. The hydrazine bubbler was eliminated and the aqueous hydrazine was slowly injected by a motor driven, variable speed one ml syringe (Sage Series 255). The aqueous hydrazine was vaporized by electrically heating the injection port to about 150 C (302 F).

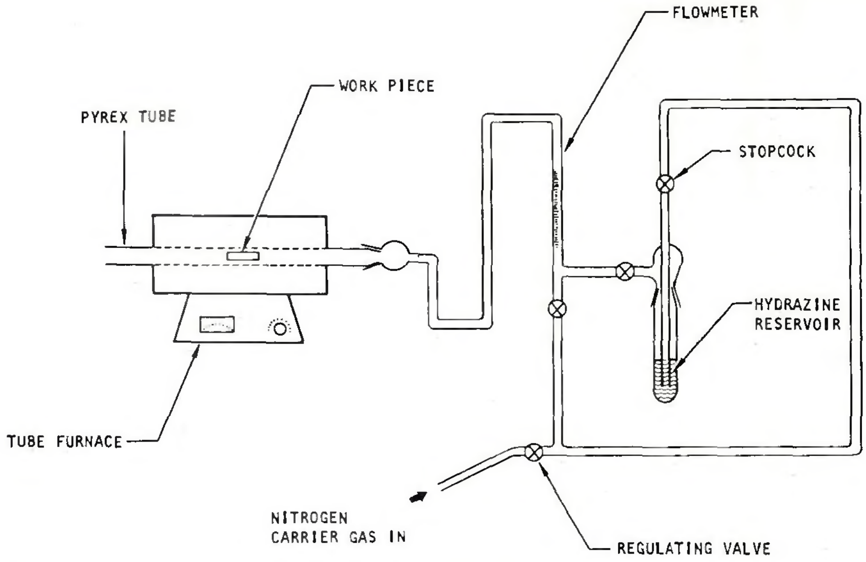

Fig. 1—Apparatus employed for the experiments using pure hydrazine

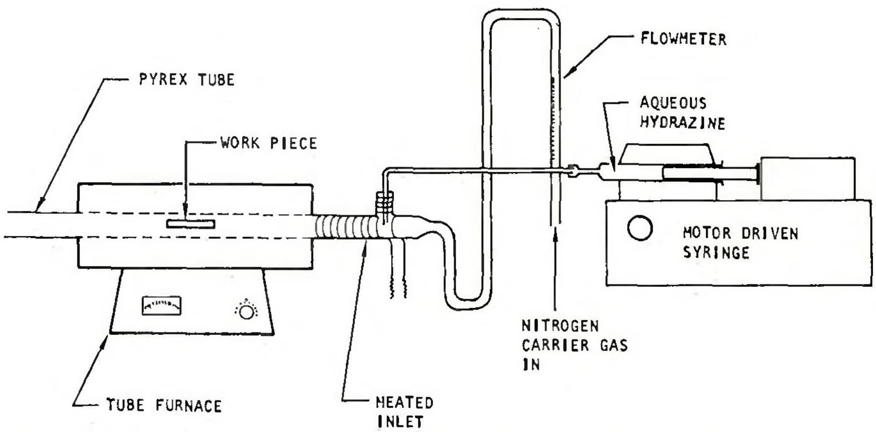

Fig. 2—Apparatus employed for the experiments using aqueous hydrazine

The circuit boards used in some of our experiments were constructed of copper clad epoxy glass resin (G-10). The surface consisted of copper circuitry which was plated with tin-lead alloy, with resin between the circuit lines. The thickness of the copper circuitry ranged from three to five mils.

Cleaning of Copper Surfaces

A badly tarnished piece of copper sheet was precleaned with acetone. It was placed in the glass lined furnace at 260 C (500 F). After purging with N_2 for several minutes, the copper sheet was exposed to a hydrazine (5%)-N_2 flow of 180 cc/min. Visual inspection of the workpiece after a hydrazine exposure time of less than one minute showed a bright clean surface.

Solder Flow on Copper

A piece of solder wire (63% Sn, 37% Pb) was placed on a piece of badly tarnished, acetone rinsed copper sheet. The specimen was exposed at 260 C to a hydrazine (5%)-N_2 flow of 180 cc/min for 3 min. After removal from the furnace, the copper sheet showed a bright clean surface and visual inspection showed that the solder had formed a good metallurgical bond with the copper sheet.

Soldering of Copper to Copper

A piece of copper wire, a solder washer (63% Sn, 37% Pb) and a piece of copper circuit board were rinsed with trichloroethylene and methanol. The copper wire and solder were placed in contact with the copper circuit and exposed at 232 C (450 F) for

5 min to a hydrazine-containing nitrogen flow of 150 cc/min. The hydrazine-containing gas was generated by injecting one ml of aqueous hydrazine (40% N_2H_4) per hr into the heated injection port of the glass reactor (see Fig. 2). Visual inspection of the workpiece showed that a good metal-to-metal bond had formed.

Soldering of Copper to Gold

A pre-tinned (50% Sn, 50% Pb) copper circuit board was brought in physical contact with the untinned gold leads of a conventional integrated circuit pack. After rinsing with trichloroethylene and methanol, the workpiece was exposed at 232 C for 5 min to a hydrazine-containing gas flow as described in the preceding experiment. Visual inspection of the workpiece showed that good metal-to-metal bonds had formed.

Reflowing of Copper Circuit Boards

An acetone-rinsed, pretinned (50% Sn, 50% Pb) copper circuit board was exposed at 260 C for 10 min to a hydrazine (5%)-N_2 flow of 180 cc/min. Visual inspection of the workpiece showed a clean, shiny, solder surface and that reflow of the solder had occurred. The epoxy board showed no signs of damage or discoloration.

Soldering of Beryllium-Copper

A piece (0.031 in. diam, 0.070 in. long) of solder wire (60% Sn, 40% Pb) was placed in a hole (0.032 in. diam, 0.150 in. deep) drilled into a piece of beryllium-copper (Brush alloy No. 10). The specimen was exposed at 260 C for 10 min to a hydrazine-containing argon flow of 150 cc/min. The hydrazine-containing gas was generated by injecting one ml of aqueous hydrazine (40% N_2H_4) per hr into the heated injection port of the glass reactor (see Fig. 2). Cross-sectioning and microscopic inspection of the workpiece (see Fig. 3) revealed a good metal-to-metal bond.

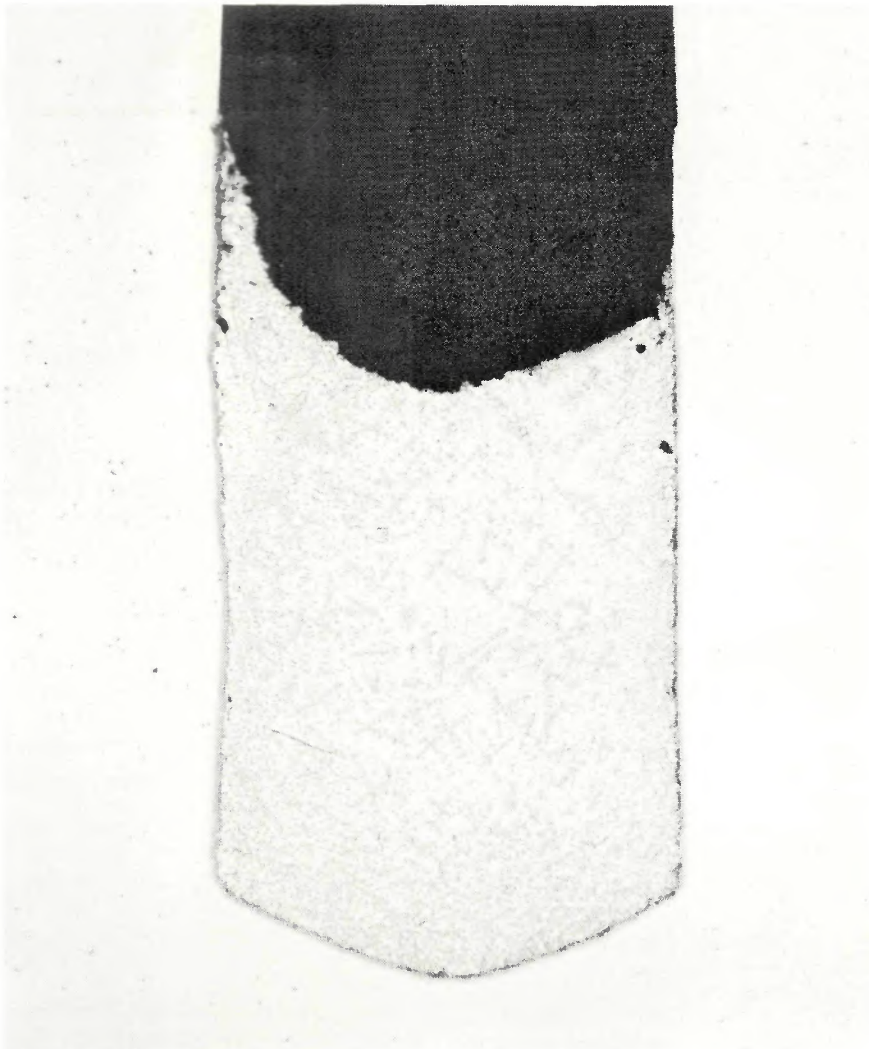

Fig. 3—Cross-sectional view of a tin-lead solder-containing beryllium-copper capillary showing a good metal-to-metal bond (X50, enlarged 31%)

Discussion

The above examples demonstrate the great advantages of using gaseous hydrazine for the cleaning of metal surfaces with or without subsequent soldering or brazing operations. Hydrazine is commercially available and due to its use as a propellant in rockets, detailed handling procedures have been worked out. In particular, the possibility of using aqueous hydrazine solutions significantly simplifies the handling procedures. No effort has been made to screen metals or alloys other than those reported here for their potential applications. However, it can be seen from the example involving the use of beryllium-copper, that hydrazine is not just a replacement for conventional fluxes, but gives excellent metal-to-metal joints in cases where conventional fluxes fail. An obvious application for our hydrazine process would be diffusion bonding since it generates clean, residue-free metal surfaces. The low level of impurities introduced during metal joining should make this process ideal also for work on semiconductors. The advantages due to the relatively low temperatures required when using hydrazine as a gaseous flux for soldering, are obvious from the above examples involving epoxy circuit boards. Work on electronic microcircuits should also be greatly facilitated by the use of gaseous hydrazine as a flux.

Conclusion

A huge number of applications can be foreseen where the use of gaseous hydrazine would revolutionize our present metal joining technology.

Acknowledgment

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