

Development of a New High-Temperature Solder System

Sacrificial metal coating technique as opposed to plating opens a completely new range of metal-to-metal joining possibilities

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ABSTRACT. A new high-temperature soldering system has been developed for use on copper, copper alloys, and low-carbon steel. The method is applicable to automobile radiators and home appliances. The system uses a unique sacrificial metal coating method to promote spontaneous wetting and spreading of zinc and zinc alloy solders on metallic substrates. The 10^{-5} to 10^{-6} cm thick, electroplated or sputtered, sacrificial nickel coating is absorbed by the molten filler alloy during soldering and produces a direct solder-substrate metallic bond. Preliminary measurements on butt joints with copper members give tensile strengths over 32,000 psi at room temperature using 95Zn-5Al alloy as solder. Spontaneous wetting, spreading, and capillary penetration are extremely rapid and produce joints as easily as 50-50 tin-lead solders. Recrystallization or annealing of the wrought copper joint members is negligible at the soldering temperatures of 450 to 490 C and lower. A list of

typical fluxes and solder alloys is included.

Introduction

For the past 50 to 60 years attempts have been made to close the so-called "solder gap." Maximum practical operating temperatures for tin-lead solders are below 284 F (140 C),¹ and lowest practical brazing temperatures are around 1,000 F (538 C). Between these limiting temperatures no practical solders or soldering systems exist for use with copper, copper alloys and iron alloys. This range of temperatures can be designated as the "solder gap."

Both solders, consisting primarily of tin-lead alloys, and brazing filler

metals, mainly silver-copper alloys, work best when used in the form of pure binary alloys. Although solder alloys having melting points above 360 F have been developed,² none have received wide acceptance in industry. Many of these higher melting point alloys have very limited application. Solder producers consider that any modification of the basic binary is just adding impurities to the alloy.³ Although lead, cadmium, aluminum, and zinc base alloys have melting points in the range required, they are unsatisfactory for solder uses because they do not wet or spread on substrates such as copper, brass, and iron when standard soldering methods are used.

Extensive research in the past in an attempt to develop either higher temperature solders or lower temperature brazing alloys has been directed mainly toward development of alloys starting from the tin-lead solder base, or from the silver-copper brazing filler metal base.⁴ The soldering research started several years ago on these same lines. Since then, however, the approach to the problem of higher temperature solders has changed completely.

The present approach is based on two fundamental hypotheses: (1) The filler metal (solder) in a soldered joint must fulfill the requirements of

Editor's Note: The authors have graciously consented to changes involving AWS terminology. Thus, tin-lead "soft-solders" and silver-copper "hard solders" were changed to "solders" and "brazing filler metals" respectively. The expression "high-temperature solder system" might well have been stated "low-temperature brazing system" were it not for the authors' contention that their contribution suggests a need for new thinking in this field of joining.

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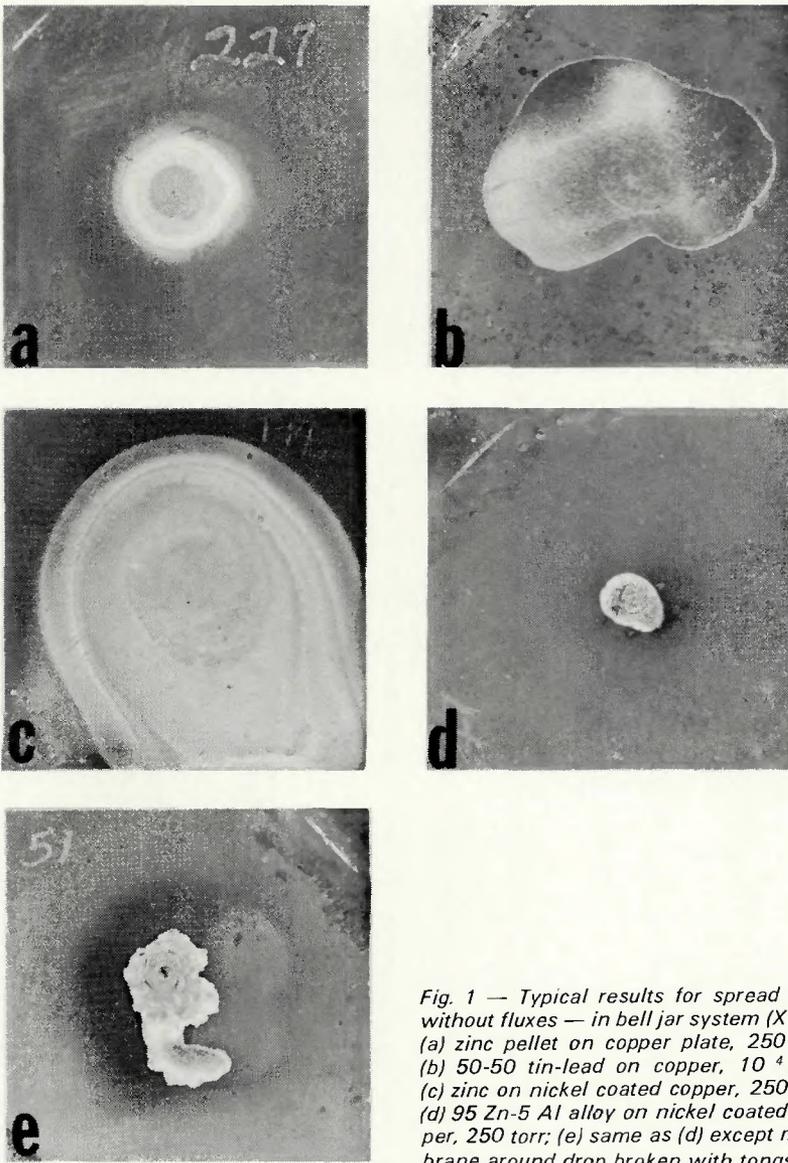


Fig. 1 — Typical results for spread tests without fluxes — in bell jar system (X 1.5): (a) zinc pellet on copper plate, 250 torr; (b) 50-50 tin-lead on copper, 10^{-4} torr; (c) zinc on nickel coated copper, 250 torr; (d) 95 Zn-5 Al alloy on nickel coated copper, 250 torr; (e) same as (d) except membrane around drop broken with tongs

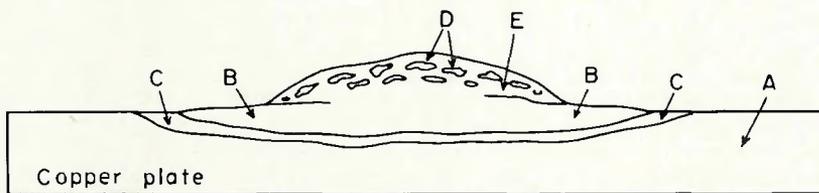


Fig. 2 — Schematic drawing of zinc pellet melted on copper plate. (For explanation of lettered phases see text and Table 1)

an adhesive.⁵ Therefore, it must make intimate contact to the metallic substrate; in other words, it must "wet" and spontaneously spread on the substrates or members to form the joint. (2) Any liquid metal or alloy should wet and adhere to the surface of any other metal or alloy that melts at a higher temperature provided proper conditions for intimate liquid-metal to solid-metal contact exist.

The term "wetting" here used does not imply the need for substan-

tial alloying at the interface, but does admit that intimate association of metal cations will result in interpenetration of the two materials (metal and solder). This may be referred to as a solution action, or even alloying, but not in the usual metallurgical connotation involving substantial alloying or diffusion processes. The first premise has received incidental recognition, and the second follows from the basic quantum mechanical definitions of the structure of metals.

Literature on wetting and soldering states either that zinc will not wet copper or that zinc in solders reduces the wetting abilities of solders conspicuously,^{3,6} (p. 2 of ref. 2). A sacrificial metal coating system for promoting wetting and spontaneous spreading has opened a completely new realm for soldering development. The purpose of this report is to outline the salient facts leading to the development of the system, to describe some of its probable capabilities, and to indicate the present status of the research.

Experimental Work

Because the initial requirement for a solder is that it spontaneously wet and adhere to the metallic substrate to which it is applied, the research started with tests for wetting and spreading.

Earlier work with tin-lead solders has been reported previously⁷ where a simple wetting test for tin-lead alloys on copper is described. "Wetting" used here was defined as the initial stage when a small measured quantity of molten metal or alloy applied to a solid metal surface clings and spreads over the surface rapidly and eventually adheres to withstand tensile or shear forces of the order of 1,000 psi or better at room temperature. It is not necessary to subject each wetting test (essentially a sessile drop test) to such forces. With a sessile drop resting on a substrate, wetting can be related to the contact angle between the substrate and the free surface of the drop measured inside the drop. An angle of less than 90° designates some degree of wetting; more than 90° implies nonwetting. In addition to the contact angle, a quantitative measure of the amount of wetting can be determined by measuring the area over which the molten drop (a controlled amount of material) spreads on the substrate; that is, if wetting occurs.

The first experiments were performed inside a vacuum bell jar system. The substrates were $1\frac{1}{2}$ -in. squares of $1/16$ -in. thick, rolled, oxygen-free, high-conductivity copper. The soldering materials were either commercial solders (tin-lead) or alloys prepared from high-purity materials in the foundry. The soldering materials were rolled into strips having a standard thickness of 0.100 in., and $3/16$ -in. diam pellets were punched from the strip to furnish the controlled amount of material for each spread test. All procedures observed the necessary precautions for handling high-purity materials.

Various methods were used to prepare the surfaces of the copper

Table 1 — Composition of Phases in Figure 2 by Zones

Element	A	B			C	D	E
		Bottom	Center	Top			
Zn	0	60.3	61.9	85.8	36.7	98.5	83.7
Cu	100	39.7	38.1	14.2	63.3	1.5	16.3

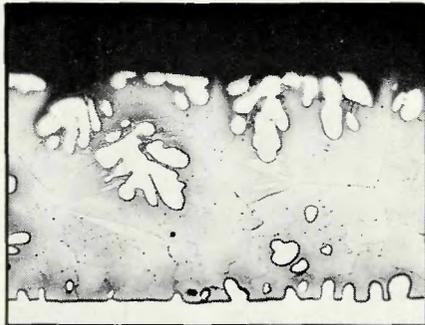


Fig. 3 — Micrograph of zinc pellet spread on nickel coated copper. (X 500, reduced 40%). See Fig. 4 for details of phases shown.

plates for wetting tests — acid cleaning and etching, ion bombardment, electrolytic polishing, mechanical polishing, electroplating and vacuum sputtering. With tin-lead solders the wetting tests were performed at about 10^{-5} torr vacuum, and without using fluxes. With zinc and zinc alloys the tests were performed in an atmosphere of high-purity de-oxidized helium at about 250 torr.

The copper plates were heated by placing them on an electrically heated, solid copper hotplate inside the bell jar system. As proper conditions for a test were obtained, the solder pellet was placed in the center of the test plate and allowed to melt. After the necessary time selected for the experiment had elapsed, the test plate was removed carefully from the hotplate and set aside on another metal block to cool. Spread areas were measured by circumscribing the drop 10 times with a planimeter. Where necessary to prevent scratching, a 1:1 reproduction of the plate was made on the proper paper and this image was measured with a planimeter.

Spread tests were also performed in the open atmosphere using various fluxing mediums. The procedures were about the same as those used inside the bell jar system. The hotplate, a nickel alloy, was heated with a propane-air burner.

After a method for using zinc and zinc alloys as solders in the open atmosphere was developed, various joint forms were made in the laboratory. These assemblies were usually heated with a small hand-held propane-oxygen torch.

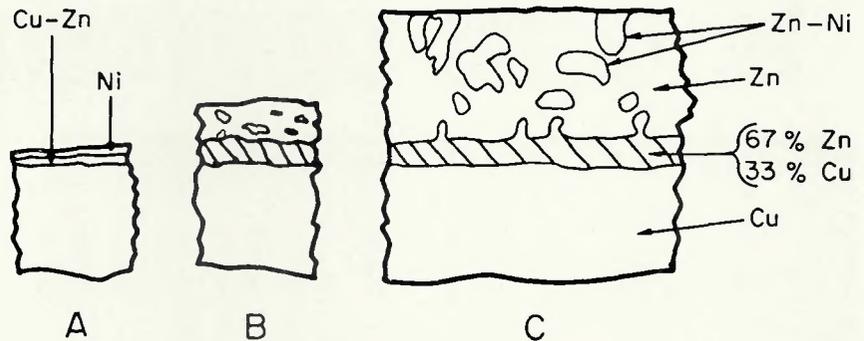


Fig. 4 — Schematic drawing of sections of zinc spread on nickel-coated copper plate without flux at 250 torr. (approx. X 75): (a) near edge of spread area; (b) about midway between edge and center of spread area; (c) center of spread area

Results

Spread Tests in Vacuum System

Fig. 1(A) verifies that zinc will not wet copper. This characteristic form has been designated as the "fried-egg-effect," because the central dull-zinc-colored pellet is surrounded by a bright silver ring, which is in turn surrounded by a bright yellow (brass-colored) ring. Surrounding this, the surface has varying shades of brass coloring out to the edges of the plate.

Fig. 2 is a cross-section schematic drawing of a typical zinc pellet allowed to melt on a copper plate. Microprobe analyses of the components of the drop are given in Table 1. Of main interest are the yellow ring (zone C, Fig. 2) and the silver-colored ring (zone B). The analyses showed that zone C, an α -brass, completely separated the drop from the copper plate. Copper was found, to some extent, in all five phases. This shows that copper readily diffuses into the zinc from the plate. Diffusion and alloying, as opposed to wetting, seem to be the predominant mechanisms in this system. The test was performed at 600 C in a 250-torr helium atmosphere. The zinc drop was retained in the molten state for about 8 minutes.

For comparison, Fig. 1(B) shows the spread of the same quantity of 50-50 tin-lead solder on a copper plate at 10^{-4} torr.

Fig. 1(C) shows the spread of zinc on a nickel-coated copper plate at 250 torr and 914 F (490 C). The coating of nickel, applied by electroplating, was approximately 10^{-5} cm thick. The contact angle for zinc on copper was reduced from approx-

imately 65 deg., Fig. 1(A), to essentially zero deg. by the addition of the thin nickel coating. The spreading of the zinc over the plate was quite rapid; complete spreading was attained within 30 seconds after melting started.

A micrograph of the interfacial region of a typical spread test of zinc on nickel-coated copper is shown in Fig. 3. The micrograph was not taken at the center of the drop. Schematic diagrams of cross-sections of zinc spread on nickel-coated copper are shown in Fig. 4. The data for this drawing were taken from microprobe analyses. Fig. 4(A), a cross section near the edge of the drop, shows that the zinc flowed out beneath the nickel coating to join with the copper plate and form a brass alloy. Fig. 4(B) shows the cross section about one-half the distance from the center of the plate to where Fig. 4(A) was made. Here sufficient zinc was available to dissolve the nickel, and the nickel appears as a dispersed second phase in the zinc. The height of the drop at this point is about 0.003 in. A thin layer of brass about 0.0015-in. thick has formed at the copper-zinc interface. This brass layer is continuous through the spread drop. Fig. 4(C) is the cross section at the center of the drop. Maximum thickness of the drop is about 0.011 in.

The 67Zn-33Cu, or brass, zone is shown with sharp edges. Actually the composition varies as the edges of the zone interface with the other constituents. The etching procedures to delineate the various zones of the cross section for metallography produce the sharp lines. Other brass

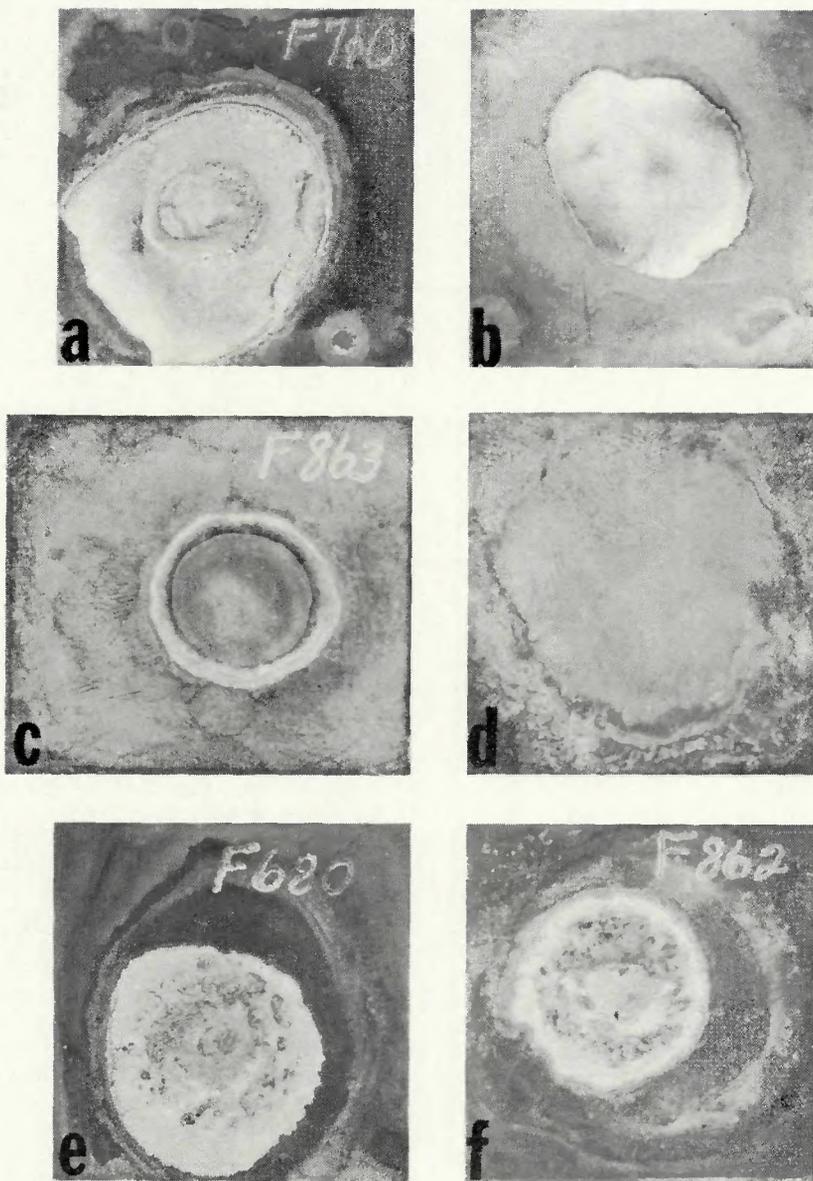


Fig. 5—Typical results for spread tests with fluxes in open atmosphere. (X 1.5). (a) Zinc on nickel-coated copper plate; (b) 50-50 tin-lead solder on copper; (c) Zinc on bare copper, nickel in flux; (d) Flux containing nickel salts, heated to 400C on copper plate; (e) 95 Zn-5 Al on nickel-coated copper plate; (f) 95 Zn-5 Al on bare copper, nickel in flux

phase diagram could occur.

The microprobe analyses of the interfacial regions show that the copper and zinc have alloyed and that the nickel has been absorbed into the zinc. The nickel coating that promoted the wetting has been displaced, allowing a metal-metal bond to form between the copper and zinc. Thus the term "sacrificial metal coating" has been applied to this system. It is important to note that the nickel coating must be thin, of the order of 10^{-4} to 10^{-5} cm thick. Experiments have shown that 1×10^{-5} cm thickness is sufficient to promote complete spontaneous wetting in the bell jar system where the spread takes place without fluxes.

Although pure zinc may have some applications as a solder, it has some disadvantages. Therefore, the research turned toward alloys of zinc, mainly the 95 Zn-5 Al and other zinc die casting alloys. Pure zinc becomes brittle at low temperatures and exhibits excessive creep at temperatures not too far above room temperature. The die casting alloys, although somewhat brittle, are much stronger and more ductile at low temperatures than pure zinc.

Upon testing the 95Zn-5Al alloys for wetting in the bell jar system, a tenacious film or membrane, probably aluminum oxide, formed around the molten alloy drop and prevented it from contacting and spreading. Typical results are shown in Fig. 1(D). If the membrane surrounding the drop was broken mechanically, the molten alloy would run out and wet the plate as shown in Fig. 1(E). The spread area in Fig. 1(E) is relatively small, but if the membrane was broken quickly enough as the pellet melted, much larger spreads could often be obtained.

Many other details of the properties of the sacrificial coating method were investigated using different substrates (brass, low carbon steel, etc.), and other zinc-base alloys for the solder. Even some soldered joints, typically a butt joint between a plate and a $\frac{3}{8}$ -in. diam cylinder, have been made in the bell jar system. However, these studies in special atmospheres and without fluxes are not generally applicable to practical soldering operations.

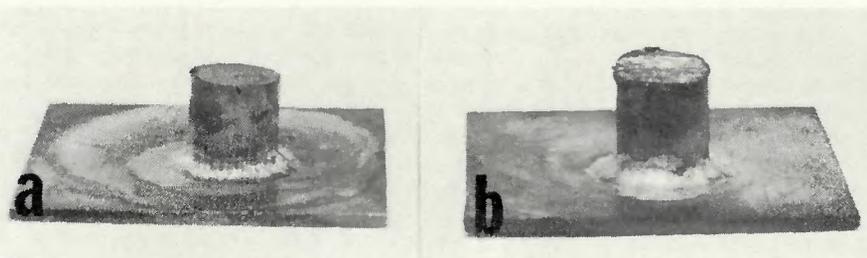


Fig. 6—Plate to cylinder solder joints. (a) Zinc solder on nickel-coated copper; (b) Zinc solder on bare copper, nickel in flux

compositions occur as the 67Zn-33 Cu blends into the two separate metals. For example, the lower edge of the 67-33 brass zone may gradually blend through α -brass (30Zn-70 Cu) toward the substrate (100Cu). The other side of the band may show

areas of ϵ -brass (85Zn-15Cu) or even an 85Zn-15Ni alloy or a ternary of Zn-Cu-Ni. The second phase scattered throughout the zinc, often floated up to the top of the bubble, is usually about 85Zn-15Ni. All possibilities shown on the copper-nickel-

Wetting Tests in the Open Atmosphere

With proper fluxes the sacrificial metal coating system should work in the open atmosphere. Spread tests with commercial brazing fluxes verified this possibility. Fig. 5(A) shows a typical spread test using a zinc pellet

on a nickel-coated copper plate with flux containing metal fluorides. Fluxes consisting of mixtures of metal chlorides and fluorides will also produce the required wetting and spreading of zinc on nickel-coated copper. For comparison, Fig. 5(B) is typical of a spread test made with 50-50 tin-lead solder on an uncoated copper plate with a zinc chloride-ammonium chloride mixture for the flux.

Earlier studies on soldering⁷ showed that when ammonium chloride-zinc chloride fluxes are used with tin-lead solders on copper the solder actually spreads on a thin layer of tin deposited or plated out ahead of the spreading solder. This plating action involves tin chloride ions developed by reaction between the tin in the solder and the flux. Nickel salts added to the fluxes for the zinc soldering system produce a similar effect as shown in Fig. 5(C). The spread is not as good as that obtained with the precoated copper, but is applicable where repairs to previously soldered assemblies might be required. That the plating action truly takes place is shown in Fig. 5(D). Here a flux with added nickel salts was heated on a clean copper plate and allowed to cool. The nickel coating on the copper was verified by microprobe analysis. This experiment was performed in the open atmosphere with the plate held at 400 C for about 1 minute. The plate did not recrystallize or anneal in this time and retained practically its original wrought strength.

The only obstacle to the spreading of the 95Zn-5Al alloy on the nickel-coated copper is the oxide membrane that forms around the molten drop. Active fluxes can rupture this membrane so that the drop can spread. This is shown in Fig. 5(E). Fig. 5(F) shows that the flux containing nickel salts will also work with Zn-Al alloys.

Solder Joints

Fig. 6(A) shows a butt joint between a copper cylinder and a spread plate. After the flux and the nickel-coated 3/8-in. diam cylinder were placed on the plate, the pellet of zinc to be used as the solder was placed beside the cylinder. The assembly was heated with a small propane-oxygen torch from below the plate or from above diametrically opposite the pellet with the flame directed to strike the juncture of the cylinder and plate. When the pellet melted, the molten solder immediately flowed around and under the cylinder. In many of these tests, the capillary action of the molten zinc

was great enough to float the cylinder above the plate and move it a short distance across the plate. The wetting was instantaneous upon melting of the pellet. A few seconds only were required to form a smooth joint. Fig. 6(B) shows a joint made without initial plating, but using flux containing nickel salts. The rate of wetting was not as rapid, and the final appearance of a joint made with the nickel in the flux was not as good as that of the one made with precoated members.

Joints have also been made with brass members. Fig. 7(B) shows a cross section of a zinc-soldered joint between a 1/8-in. diam brass rod (nickel-coated) and a nickel-coated brass plate. Note that the rod was floated up slightly from the surface by the molten solder. The small void at the bottom of the rod is due to a small bubble of flux trapped beneath the rod. All solder joints have varying amounts of porosity depending upon the fluidity or mobility of the flux, heating time, and other variables.

Fig. 7(A) is a joint made the same way as that shown in 7(B) except the parts are copper. The joint shown in Fig. 7(C) was made with brass parts but using 50-50 tin-lead solder and zinc chloride-ammonium chloride flux. All the joints show the usual small voids typical of soldering practice.

Fig. 8(A) is a cross section of a lock-seam joint using nickel-coated brass sheet, zinc solder, and fluoride fluxes. The brass sheet was 0.0162-in. thick. The solder (zinc) was introduced on only one side of the joint. Capillary action carried it through to the other side. Fig. 8(B) is a brass lock seam without preliminary nickel coating, but soldered with flux containing added nickel salts. The solder was zinc.

Fig. 9 shows a micrograph of a joint as pictured in Fig. 6(A). The lower interface is that between the plate and the solder. The upper interface is that between the solder and the bottom end of the 3/8-in. diam cylinder. The lower joint is properly made because the nickel coating was thin enough to be penetrated and displaced by the molten solder. The plating on the cylinder was too thick, and so a layer of nickel remains attached to the cylinder face. The strength of this upper interface will be low because it depends upon the bond between the copper and the nickel plating. This bond will give way before the bulk of the solder. The dark line across the upper interface resulted from the polishing and etching. The residual nickel layer is faintly visible above the dark area.

The bond to the copper, when

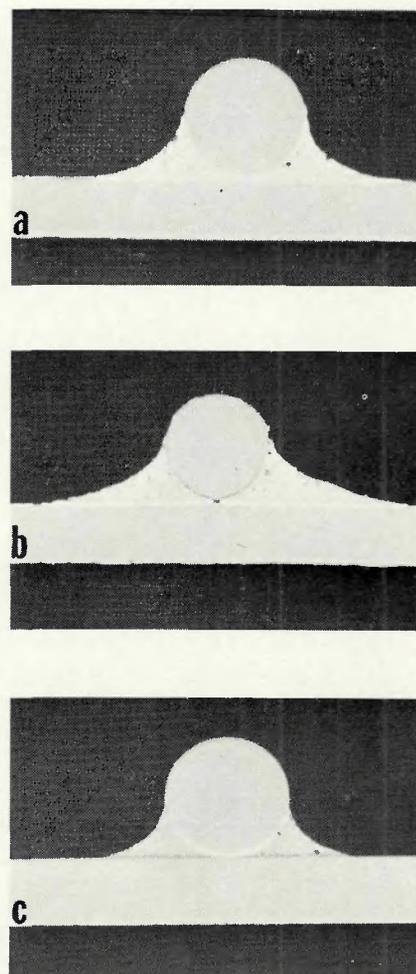


Fig. 7—Cross section of solder joints (approx. X 5); (a) Copper parts with zinc solder; (b) Brass parts with zinc solder; (c) Brass parts with 50-50 tin-lead solder

properly made, is stronger than the bulk of the solder, and the joint will fracture in the solder instead of at one of the interfaces.

Microprobe analyses of the plate to solder interface, on the side where the joint was properly made, gave the following compositions:

- A. 100% copper
- B. 67% zinc-33% copper
- C. 85% zinc-15% nickel
- D. 100% zinc (with dispersed particles of 85 Zn-15 Ni).

The analyses show that the zinc has flowed beneath the nickel, washed it away, and alloyed with the copper to form a brass bond with the substrate.

A cross-section of the fillet at the edge of the cylinder is shown in Fig. 10. The contact angles are essentially zero degrees. Crude tests with a bench vise and a pair of pliers have shown that, although the soldering temperatures were close to 900 F (about 460 C), the copper plate was not annealed. Yet, with properly made joints (both interfaces), it was

Table 2—Zinc-base Solder Alloys for Sacrificial Metal Coating System

Alloy No.	Alloy composition, weight-percent				Spread on Ni-coated Cu, etc.	Remarks
	Zn	Al	Cu	Other		
1	100	—	—	—	Excellent	Spontaneous wetting
2	95	5	—	—	Excellent	Spontaneous wetting
3	90	10	—	—	Excellent	Spontaneous wetting
4	78	22	—	—	Excellent	Spontaneous wetting
5	70	30	—	—	Excellent	Spontaneous wetting
6	95.96	4	—	0.04 Mg	Excellent	Spontaneous wetting
7	94.89	5	—	.11 Ti	Excellent	Spontaneous wetting
8	90.5	5.1	0.1	4.3 Fe	Excellent	Extremely bright, Spontaneous wetting
9	89	7	4	—	Excellent	Spontaneous wetting
10	75	20	5	—	Excellent	Spontaneous wetting
11	95	4	1	—	Excellent	Spontaneous wetting
12	94.96	4	1	.04 Mg	Excellent	Spontaneous wetting
13	98	—	2	—	Good...	Sluggish— not spontaneous
14	98	—	—	2 Cd	Excellent	Spontaneous wetting
15	75	—	—	25 Cd	Very good	Less spread than above
16	60	—	—	40 Cd	Fair...	Spread not as good
17	70	—	—	30 Sn	Excellent	Spontaneous wetting
18	80	—	—	20 Pb	Excellent	Spontaneous wetting
19	43	—	—	14 Cd } 35 Sn } 8 Pb }	Excellent	Spontaneous wetting
20	99.1	—	—	.9 Ag	Fair to poor	Sluggish, small spread

necessary to bend the plate to peel the cylinder away from the plate.

To obtain more quantitative data on the strengths of the joints, especially those with 95Zn-5Al solder,

butt joints of copper were made and tested in a standard tensile testing machine. The specimens were made from two pieces of copper rod, 3/8-in. in diameter. The pieces of rod were

turned down to have a 1/4-in. diam section about 1 1/4 in. long for the joint and a 3/8-in. diam shoulder for gripping in the tensile machine.

If the plating or coating has the proper thickness (or thinness in this case), and the flux has sufficient activity and fluidity, a good joint may be obtained. Preliminary work on these butt joints, performed primarily to develop methods and procedures, has produced tensile joints that fracture two ways. Where the nickel plating is too thick (10^{-3} cm or more), the joint fails at the plating interface. The fracture face is smooth and shows the machining marks on the face of the part. Fig. 11(A) is typical of this type of fracture. Tensile strength is usually around 12,000 to 13,000 psi at room temperature. If the nickel plating is thin enough to be displaced, a requirement of this soldering system, the joint will fracture in the filler metal, leaving a rough surface as shown in Fig. 11(B). Properly made joints have recently shown tensile strengths from 28,000 to over 36,000 psi at room temperature. The joint spacing before soldering was usually set at 0.025 in. when cold. The final thickness of the joint varied somewhat as the result of the method of holding the joint pieces and the expansion of the copper during heating. A final method for heating and a fixture for holding the joints have not yet been developed.

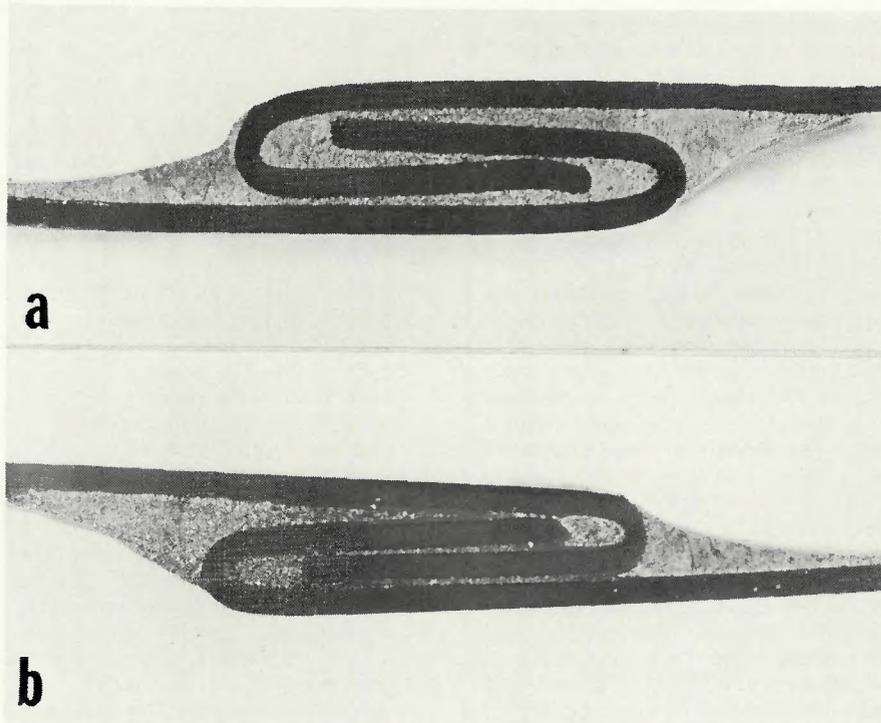


Fig. 8 — Cross-section of soldered lock seam (approx. X 8): (a) nickel-coated brass parts, zinc solder; (b) brass parts, nickel in flux, zinc solder. (Upper surface of seam during soldering is shown at the top)

Table 3—Fluxes for Sacrificial Metal Coating System

Flux No.	Composition, weight-percent							Approximate liquidus, °C	Remarks*
	KCl	NaF	LiCl	LiF	ZnCl ₂	NH ₄ Cl	As shown		
For Use on Ni-coated Copper									
							NaCl		
1	48.0	9.5	31.0	—	11.5	—	—	330	Good HRT
2	28.0	6.0	42.0	—	24.0	—	—	337	Good HRT
3	31.0	5.0	16.0	—	37.0	5.0	6.0	330	Fair HRT—removes Ni
4	32.6	5.3	16.8	—	39.0	—	6.3	—	Poor HRT
5	33.0	5.3	17.0	—	39.4	5.3	—	—	Good HRT—removes Ni
6	37.0	5.0	15.0	—	33.0	10.0	—	—	Poor HRT—removes Ni
7	10.0	4.0	30.0	—	50.0	6.0	—	—	Poor
8	30.0	2.0	16.0	—	44.0	8.0	—	—	Good LRT—removes some Ni
9	—	—	1.0	2.0	89.0	8.0	—	—	Good LRT for Al alloys
10	—	—	2.0	1.0	89.0	8.0	—	—	Excellent for Al alloys
11	—	—	—	2.0	90.0	8.0	—	250	Excellent LRT—no Ni removal
12	—	—	—	4.0	88.0	8.0	—	255	Excellent LRT—no Ni removal
13	—	—	—	8.0	84.0	8.0	—	260	removal
14	—	—	—	6.0	70.0	24.0	—	—	Good LRT—some Ni removal
For Use on Uncoated Copper									
							NiCl ₂		
15	32.55	5.25	16.8	—	38.85	5.25	1.30	327	Good HRT—Ni coat too heavy
16	32.75	5.3	17.0	—	39.0	5.3	.65	—	Excellent but HRT
17	32.4	—	17.0	—	42.0	8.0	.6	—	Poor
18	—	—	—	4.0	85.2	10.0	.8	260	Poor—Ni coat inadequate
19	—	—	—	—	91.4	8.0	.6	—	Poor

*HRT means high reaction temperature; LRT means low reaction temperature.

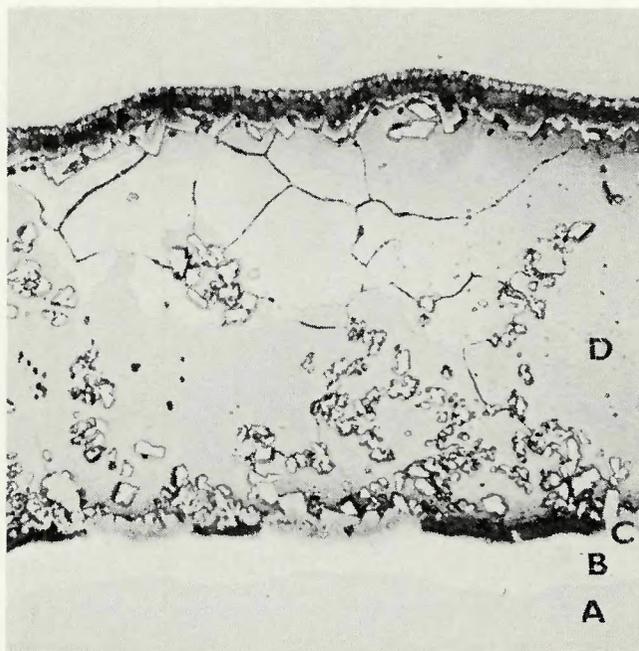


Fig. 9 — Micrograph of solder joint (X 500). Plate-cylinder joint; lower interface is nickel-coated copper plate, upper interface is nickel-coated copper cylinder. Approx compositions: A — 100% Cu; B — 67 Zn-33 Cu; C — 85 Zn-15 Ni; D — 100% Zn (containing 85 Zn-15 Ni particles).

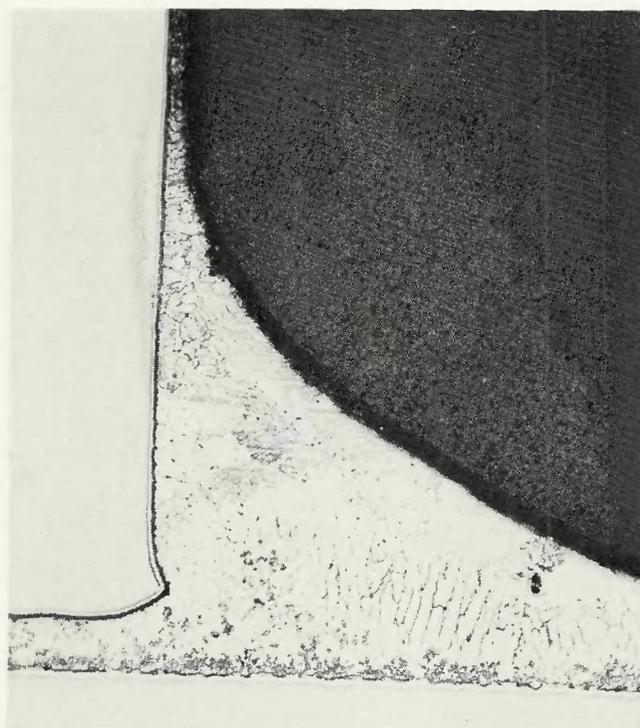


Fig. 10 — Cross-section of fillet at edge of plate-cylinder joint (X 75). (Part of joint shown in Fig. 9.)

For purposes of comparison, the tensile strength of butt joints made with 50-50 tin-lead solders averaged around 18,000 to 20,000 psi at room temperature.⁷ A listing of some of the alloys that have been used for solders is contained in Table 2. A representative list of fluxes is given in Table 3. Many other alloys and fluxes have been used successfully.

The actual thickness of the sacrificial coating of nickel on the substrate is not critical providing the solder penetrates the coating and makes contact to the substrate metal. Three methods of coating have been tried, but only two have been useful so far. Most coatings for this work have been electroplated from standard nickel electroplating solutions. Coatings applied by sputtering in a vacuum system have given results equally as good as the electroplated coatings. Standard procedures for sputtered coatings, such as etching, cleaning, and ion bombarding, have been used. Chemical deposition, or electroless plating, has not proved successful for this soldering system up to the present time. The electroless methods available deposit a compound or mixture of nickel with other elements and so purely metallic interactions seem to be absent.

Experiments on the required thickness for wetting and spreading in the open atmosphere using fluxes have shown that a coating as thin as 10^{-6} cm is sufficient to produce good wetting. This is in contrast to the 10^{-5} cm thickness required in the bell jar experiments without fluxes.

Discussion

The sacrificial metal coating system for soldering is truly a breakthrough in this field. The results of this work suggest the need for a re-assessment of the traditional approaches to solder development. Plating surfaces of so-called unsolderable metals to make them solderable is used extensively.⁸ Actually, the "unsolderable" metal is not made solderable with his approach. Instead, a bond is made to the plating only, and the strength of the joint becomes the strength of the substrate-plating bond as shown in Fig. 11(A). The point here is not that plating methods are necessarily inferior, but that the plating approach is limited. Wetting of the substrate is prevented by plating, and the user is always cautioned to be sure that the plating is thick enough to prevent penetration⁸ (p. 5). The sacrificial metal coating technique opens a completely new range of metal-metal bonding possibilities that re-

quire thorough investigation.

Some references in the literature suggest that improvements in solder technology are the result of the cleaning action of the flux or solder; for example, the use of reactive fluxes for aluminum,^{9,10} or the addition of titanium to the solder alloy as an oxide scavenger. The fluxes used with the pre-coated metal may have these same reactions. The sacrificial metal coating system might conceivably be called an additional fluxing action of some nature. It might also be characterized as a capillary penetration action. Other references in the literature assert that the solder alloy should be improved by the addition of metals with appropriate solubility behavior to improve wettability. As an example, Klein-Wassink¹¹ reports wetting enhancement for silver on iron with the addition of palladium. Greater wetting is achieved, according to Klein-Wassink, because palladium is soluble in both iron and silver, while silver is not soluble in iron. The same thinking is implied in his mention of the addition of copper to silver brazing alloys for use on iron.

In the system here, zinc is soluble in both nickel and copper to about the same degree, forming the same type of alloys, whereas nickel and copper are completely soluble in each other. Thus, the solubility relationship noted by Klein-Wassink does not appear to be the most important feature in this application. Also, it is known that lead added to tin as the basis for solders enhances the wetting of copper by tin, whereas lead is completely insoluble in copper.¹² (Solubility here is used in the normal connotation for metallurgy and does not fit the statement of the original hypotheses in the introduction of this report.) The entire literature on this subject implies that it is the composition of the solder alloy that solves the wetting problem, but the reports indicate that extensive search for the answer through alloy studies has not been successful.⁴

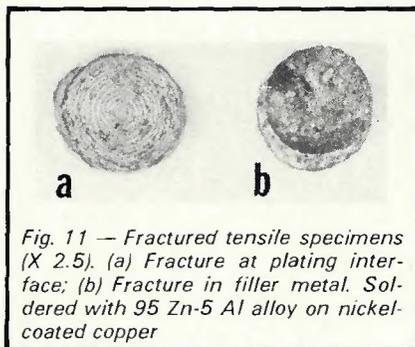


Fig. 11 — Fractured tensile specimens (X 2.5). (a) Fracture at plating interface; (b) Fracture in filler metal. Soldered with 95 Zn-5 Al alloy on nickel-coated copper

An example of a study that had results somewhat similar to these early experiments is that by Kageyama.¹³ Kageyama showed how coatings of cadmium, silver, copper, and nickel (by electroplating) enhanced the spread of soft solders. He even reported on the effects of a thin layer of tin electroplated on copper and steel and noted that it spread better when the coating lifted off the substrate¹³ (p. 12). However, he did not realize the possibilities of applying this technique to spreading by other metals or alloys.

Basic research on the spontaneous wetting, spreading and adhesion in metal-metal systems has been currently recessed in favor of further development work on the present Zn-Cu-Ni system to make it practical for general use. The research is continuing toward developing better fluxes, developing more filler alloys based mainly on zinc, and further testing of the capabilities of the system. Many areas remain to be investigated:

1. Fluxes with greater fluidity and activity at lower temperatures are needed. Ammonium chloride lowers the operating temperatures of fluxes, in general, but attacks the nickel coating to some extent and prevents the necessary spreading.
2. Although the system has been used on low-carbon steel, time has not been available to make quantitative measurements.
3. The corrosion and fatigue properties are yet to be measured.
4. Application to other filler metals and systems is yet to be investigated.

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