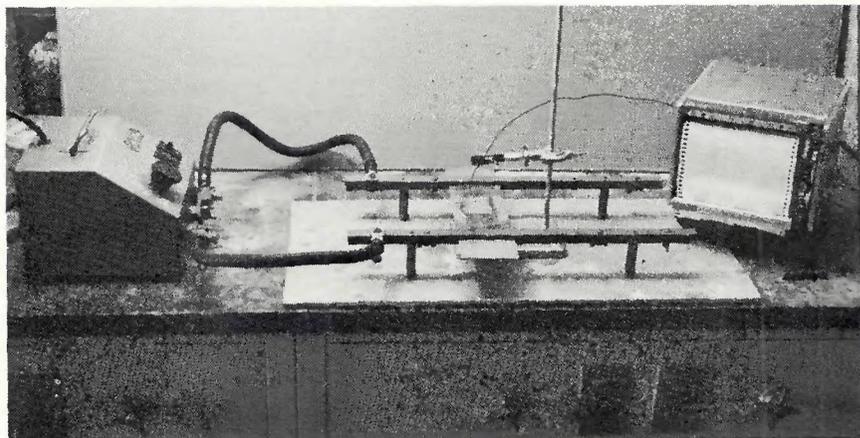


Fig. 1—Apparatus for conducting solder-spread tests



About the Mechanisms of Solder Fluxing on Copper Surfaces

Tests show that a conventional Pb-Sn solder spreads in one of four ways depending on the chemical additive in the flux

BY D. R. LESUER AND R. WEIL

ABSTRACT. The effect of certain chemicals added to rosin flux on the spreading of Pb-Sn solder on oxidized copper was studied. Four types of behavior were observed. In order to attain spreading of the solder immediately after melting, most of the oxide has to be removed by the flux, resulting also in mild attack of the copper especially at grain boundaries. The rate of solder propagation is dependent on the products resulting from the oxide-removal reaction.

Introduction

The fluxing aspects of the soldering operation may have been extensively studied, but there are very few reports of such investigations in the open literature. There are several books^{1,2} dealing with soldering, but

they deal rather superficially with the mechanisms of fluxing or the effect of their chemical compositions. Electrochemical models for the mechanism of fluxing have been proposed by Jordon and Milner³ and by Bailey and Watkins⁴. However, there have been no studies of the degree to which surfaces to be soldered react with the fluxes. The purpose of this study was to investigate the effect of the chemical composition of fluxes on their reaction with oxidized copper surfaces and on the ways that solder spreads subsequently.

Experimental Procedure

The apparatus which was used to conduct the various experiments is shown in Fig. 1 and was essentially the same one used in an earlier study⁵. It consisted of a 0.005-in.-thick tungsten-sheet heating element which was suspended between two copper bus bars. The tungsten sheet was heated by passing a cur-

rent from a step-down transformer unit, shown on the left.

One type of specimen used consisted of a 2 in by 1 in. rolled copper sheet, 0.01-in. thick. The copper specimens were first electropolished in a 50% aqueous solution of phosphoric acid at a current density of 1 amp/cm² to obtain a uniformly bright surface. They were then heated in air for one hour at 500F to produce a uniform and reproducible oxide coating. A thin wire copper-constantan thermocouple was spot-welded to the specimens to monitor the temperature which was recorded on the strip-chart recorder shown on the right in Fig. 1.

Tests were conducted by allowing pieces of 70Pb-30Sn solder, together with various fluxes, to melt and spread over the previously oxidized copper sheet samples. The fluxes were prepared by mixing one of a number of chemicals generally in concentrations of 0.1 to 1% by weight with rosin, plasticizing with 10% turpentine and heating the mixture for several minutes at 400F.

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Several commercially available rosin-core solders were also tested. For comparison, in some experiments the flux was removed from the rosin-core solder and placed around a piece of solid wire. Comparison experiments between rosin-core solder pieces with the ends pinched shut and those with the ends open so that the flux could flow out during heating before the solder melted were also conducted. The amount of solder was always constant in all tests. During several experiments, a 16mm motion-picture camera was mounted over the soldering apparatus to record the procedure and permit a subsequent frame-by-frame analysis.

In order to elucidate the reaction between the flux containing various additives and the oxide on copper, thin-film specimens were prepared for transmission-electron-microscopic and electron-diffraction studies. Two types of copper films which were about 1000 Å thick were used. One type was a single crystal with a [100] plane parallel to its surface grown by epitaxial vapor deposition on potassium-chloride substrates and subsequently dissolving the salt. Pieces of the film were collected on 200-mesh copper grids. Some of these copper-film samples were oxidized by heating them in air for half an hour at 300 F. The second type was a polycrystalline film grown by vapor deposition on a 200-mesh copper grid covered with a thin film of nitrocellulose, which was subsequently dissolved in acetone. These films were very fine grained in the as-deposited state. In order to obtain

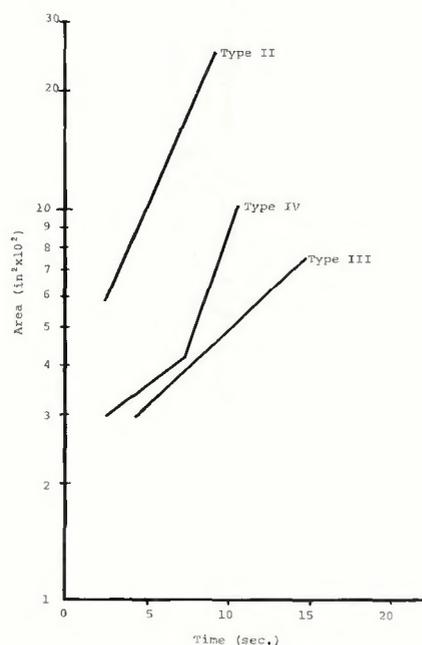


Fig. 2—Spreading of solder exhibiting Types II, III and IV behavior

a somewhat larger grain size the films were heated in vacuum for one hour at 820 F. Some samples were then oxidized in the same manner as the single-crystal films. Films of both types were examined by transmission electron microscopy and electron diffraction in the unoxidized state as well as after heating in air.

Alcohol fluxes were prepared by dissolving rosin and one of three types of additives, respectively, in ethanol. The copper films were then covered with the different fluxes, heated to various temperatures for about ten seconds and after cooling were rinsed successively in methanol, distilled water and acetone. The samples were then examined by electron microscopy.

Experimental Results

The spreading of molten solder on the oxidized copper-sheet specimens which had been in contact with fluxes containing one or several of a large number of different additives could be classified into four types of behavior: I. The solder started to spread slowly as soon as it melted. II. The solder spread rapidly over the copper surface as soon as it melted. III. The solder contracted into an almost spherical shape upon melting and then spread at a uniform rate. IV. The solder started to spread slowly as soon as it melted and for a brief period thereafter the rate of spreading sharply increased. Figure 2 shows graphs of area vs time for solder exhibiting the Types II, III and IV spreading behaviors. Type I was equivalent to a continuation of the first portion of the graph of Type IV. The data for Fig. 2 were obtained from measurements of the areas on motion-picture frames selected at definite time intervals.

The motion pictures also showed that the flux spread over the oxidized copper surface well ahead of the solder. The amount of flux affected the area covered by it, but had essentially no effect on the rate at which the solder spread or its final area. When the ends of a piece of rosin-core solder were pinched closed, the type of behavior did not change, however, graphs like those shown in Fig. 2 would be shifted slightly to the right on the time coordinate.

The purpose of the electron-microscopic and electron-diffraction studies was to determine what changes resulted in the structure of oxidized copper films due to being in contact with fluxes which produced the different types of solder-spreading behavior. Only the effects of fluxes which resulted in the first three types could be investigated. Because

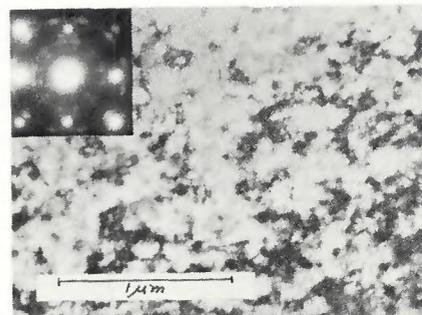


Fig. 3—Transmission electron micrograph and electron diffraction pattern of as-oxidized, single-crystal copper film

it was not possible to follow the changes which occurred in the course of the reaction between the flux and the oxidized metal films, the causes of Type IV behavior did not lend themselves to an electron-microscopic investigation.

Figure 3 shows the structure of the as-oxidized, single-crystal film as seen in transmission electron microscopy and also its electron-diffraction pattern. The diffraction pattern shows the copper reciprocal lattice spots of copper and cuprous oxide (Cu_2O). The spots belonging to cuprous oxide are those which almost form rings.

The effect of contact at 325 F for about 1 minute with a flux which caused a Type I spreading behavior of the solder is shown in Fig. 4. The spots belonging to CuO have almost disappeared in the diffraction pattern. Specimens which were heated to 275 F in contact with the same flux showed stronger oxide diffraction spots. The structure in Fig. 4 is essentially the same as that seen in Fig. 3. The effect of the thin oxide film or its removal on the contrast is negligible. As there was a uniform reduction in the intensity of the oxide reflections in the diffraction pattern rather than the disappearance

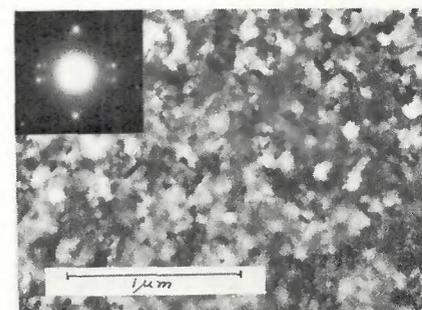


Fig. 4—Transmission electron micrograph and electron diffraction pattern of single-crystal copper film after contact at 325 F with flux containing additive which produced Type I behavior

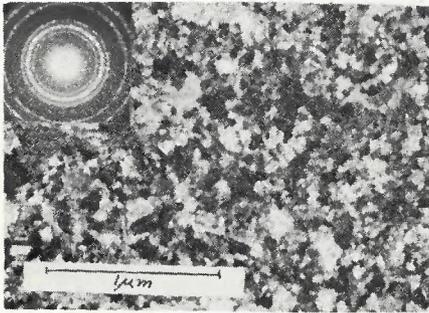


Fig. 5—Transmission electron micrograph and electron diffraction pattern of as-oxidized, polycrystalline copper film

of certain spots, it appears that there was no preferential attack by the flux. Also any attack of the copper by the flux must have been uniform over the whole film.

Contact at 325 F with a flux which produced the Type II behavior again resulted in essentially no change in the structure and a reduction in the intensity of the Cu_2O reflections in the diffraction pattern. However, the diffraction pattern showed several rings which were not present before contact with the flux. These rings were identified as belonging to γ CuI . This product, which apparently was not rinsed away, resulted from a reaction with iodine contained in the flux additive. Increasing the temperature at which the flux was in contact with the film from 275 to 550 F resulted in a decrease in the intensity of the Cu_2O diffraction spots and an increase in those belonging to CuI .

The diffraction pattern of a copper film after contact at 325 F with a flux which produced a Type III behavior, showed that there was still considerable cuprous oxide present on the surface. Again, there was no preferential attack by the flux.

The structure of a polycrystalline copper film after the oxidation treatment and its diffraction pattern are shown in Fig. 5. The diffraction pattern consists of rings belonging to both copper and Cu_2O . Because of the greater thickness of the copper compared to that of the oxide, the rings of the latter are the weaker ones.

The effect of heating oxidized, polycrystalline films in contact with a flux, which produced Type I behavior, to 275 F, 325 F and 400 F is shown in Figures 6(a), (b), and (c) respectively. Attack of the copper by the flux can be seen. The attacked region appears white in the electron micrographs. Examination of the photographic negative of Fig. 6 showed that not all white regions were holes, some areas were only very thin. The progress of the attack can be traced from an initial grain-bound-

ary reaction seen in Fig. 6(a) to considerable corrosion towards the interior of grains in Fig. 6(c). Progressive oxide removal with increasing temperatures was noted in the diffraction pattern. In order to determine that the thin areas or holes in the films were not caused by thermal stresses, samples were heated in the same way as above, but in the absence of flux. No thin regions or holes were observed.

The structure after heating to 400 F in contact with a flux which resulted in Type II behavior is shown in Fig. 7. Again preferential attack is noted. However, it appears to be not as severe as that seen in Fig. 6(c) and not as concentrated along grain boundaries. The diffraction pattern again showed that oxide was being removed and that the reaction product, CuI had formed.

As with the single-crystal films, contact at 400 F with the flux which produced Type III behavior again did not result in substantial oxide removal as indicated by the presence of relatively strong rings belonging to Cu_2O in the diffraction patterns. The electron micrograph shown in Fig. 8 shows only mild, but still preferential attack.

Discussion

The four types of spreading of solder were produced by the chemicals added to the rosin flux. Types I and II behavior differed from Type III in that the solder spread as soon as it melted. The electron-diffraction studies showed that the oxide was removed by fluxes with additives, which resulted in Types I and II behavior. On the other hand, the flux which resulted in the solder first assuming a spherical shape before spreading left considerable oxide on the surface as also shown by the electron-diffraction studies.

It appears that the removal of most of the oxide is required for the initial spreading of the solder. This conclusion can also be reached by a consideration of the surface tensions involved. The surface tensions of a clean copper-air interface is 1730 ergs/cm² ⁶ and that of a copper-solder interface is 370 ergs/cm².⁷ There is a net reduction in energy making the spreading of solder over a clean copper surface thermodynamically favorable. The surface tension of the interface between oxidized copper and air is only about 150 ergs/cm² ⁸ which is less than that of copper and solder making the spreading over oxide unfavorable. Functions of the flux are therefore to remove the oxide and prevent oxidation at the elevated temperature of soldering. The abiatic

acid released by rosin at elevated temperatures is generally agreed⁹ to be responsible for its oxide-removal properties. However, to obtain spreading of the solder, as soon as melting occurs, the oxide-removal properties have to be enhanced by chemicals added to the flux. The iodine-containing additives removed the oxide chemically as the product CuI was found on the surface subsequently. At least in this instance, the oxide was not dissolved in the flux. It also seems that the additive reacted with the oxide independently of the rosin rather than acting as a catalyst.

The difference in the rate of spreading between Types I and II behavior appears to be associated with the formation of the association product CuI in the cases which were investigated. It is possible that a product also formed when flux, which produced Type I behavior, reacted with oxidized copper, but that it was rinsed off. Reaction products can affect the surface tension and the flow

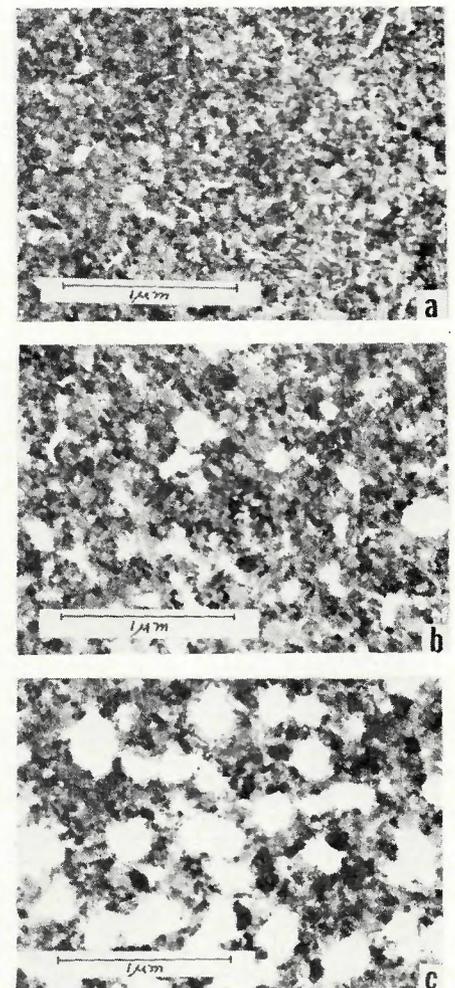


Fig. 6—Transmission electron micrographs of polycrystalline copper films after contact with flux containing additive which produced Type I behavior at (a) 275 F, (b) 325 F and (c) 400 F

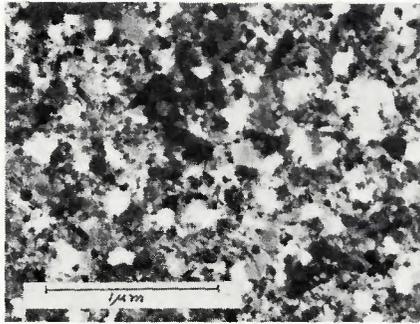


Fig. 7—Transmission electron micrograph of polycrystalline copper film after contact at 400 F with flux containing additive which produced Type II behavior

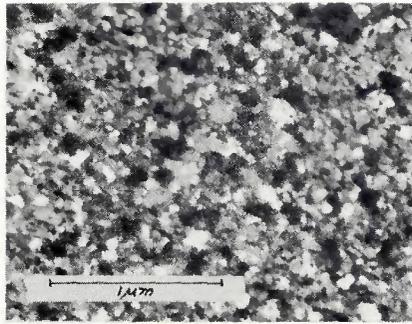


Fig. 8—Transmission electron micrograph of polycrystalline copper film after contact at 400 F with flux containing additive which produced Type III behavior

properties of the flux, that is, the degree to which it can be displaced by the liquid solder. In this way, additives which were equally effective as oxide removers could result in different rates of solder spread, such as Type I and II reactions, respectively.

The two-stage spreading of solder (Type IV reaction) on copper was observed by Bailey and Watkins⁴ when a zinc-chloride flux was used. They attributed the first slower stage to oxide removal. The second stage when there was a more rapid rate of spreading was said to be due to an electrochemical reaction in which the solder was the anode and tin was deposited on the cleaned copper surface. The deposition of tin resulted in more rapid surface wetting by the solder.

For Types I, II or III spreading behavior, the length of time during which the flux is in contact with the oxidized surface appears to have relatively little effect on the spreading of the solder. The motion pictures showed that the flux spread well ahead of the solder. Also it did not seem to matter whether the flux was placed on the solder or whether the rosin-core variety was used. Therefore, the oxide-removal reaction must have been a quite rapid one. It seems that the temperature had a greater effect on the amount of oxide which was removed, as indicated by the electron-diffraction results. It can be seen from Fig. 2, that a larger final area is indicative of a faster rate of solder flow. Therefore, the area of the spread can be taken as a

measure of the spreading tendency of the solder. Similarly, a static contact angle is not a measure of the spreading of the solder. The contact angle varies with velocity.¹⁰ The exponential relationship in Fig. 2 also implies that the contact angle is velocity dependent.

As the excess flux is frequently not washed off after soldering, the corrosive action of the additives is of practical concern. It was seen that there was somewhat greater attack of the copper film, particularly along grain boundaries, by fluxes containing additives which effectively removed the oxide and thereby resulted in immediate spreading of the solder (Types I and II behavior). Apparently, some corrosive attack of the copper is necessary if the oxide is to be removed. Probably, the oxide is first removed over the grain boundaries rendering these areas anodic with respect to the intragranular regions. The studies involving the single-crystal film corroborate this postulate in that the oxide here was uniformly removed. The grain-boundary attack in the polycrystalline films was, however, very mild because contact for several seconds with the flux at elevated temperatures did not result in the complete dissolution of the films which were only about 1000 Å thick. In some instances, as already pointed out, there was even some copper left even in the attacked areas. It thus appears that from a practical viewpoint, there need be no concern about leaving some flux on the soldered part especially as the corrosive

action decreased with decreased temperatures. Thus, at room temperature there should be practically no corrosive action. Some experiments were performed which corroborated this conclusion.

Conclusions

1. Four types of ways in which solder spreads have been observed and these depend on the chemical added to the flux.

2. Immediate spreading of the solder after melting requires that most of the oxide be removed by the flux.

3. The rate of solder propagation appears to be dependent on the products which result from the oxide-removal reaction.

4. The final area appears to be a good indication of the rate of the solder spreading.

5. There is an attack of the grain boundaries of copper by the flux; the degree of attack depends on the flux additives and the temperature.

Acknowledgements

This paper is based on a thesis submitted by D. R. Lesuer to the faculty of the Stevens Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science (Metallurgy). Part of the work upon which this paper is based was supported by Næssou Smeiting and Refining Corporation, New York, New York, and their permission to publish it is gratefully acknowledged. Professor F. S. Clough suggested the various flux additives which were used and offered other helpful advice.

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Correction

The April, 1972 *Welding Research Supplement* article "Ductility of Ferritic Stainless Weld Metal" by B. Pollard contained an error in the captions.

The captions for Figures 2 and 3 should be transposed. Thus, Figure 3 appears first on page 223-s and is concerned with Fe-35Cr welds; Figure 2 follows on page 224-s and represents Fe-26Cr welds.