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Studies of the SLT Chip Terminal Metallurgy

Abstract: The thin film metallurgy used for SLT chip terminal contacts has been studied with respect to the soldering procedure used for chip-to-module joining. A simple solder immersion test was used to study wetting and dewetting effects on Cr films overlaid with films of Cu and other metals. It was found that the initial soldering reaction (consisting of the conversion of the Cu film to a Cu-Sn metallic layer) proceeds to completion in only a few seconds. Thereafter, the intermetallic layer starts to disintegrate and become thinner by a mechanism identified as solution-assisted spalling. Removal of the intermetallic layer by this mechanism is not limited by simple solubility considerations. From metallographic observations and the inability to produce direct wetting of Cr films by solder, it was concluded that the basic cause of solder dewetting is the excessive loss of intermetallic from the underlying Cr film. Dewetting is accelerated if the Cu film is deposited on an oxidized Cr surface. These observations underscore the importance of the manufacturing practice of overlapping the Cr and Cu depositions so as to obtain an adherent and interlocked structure which is resistant to spalling. Other studies have shown that Al films are relatively inert to molten pure Pb-5% Sn solder, but are susceptible to rapid attack if gold is added to the solder. Appreciable delay of such attack is afforded by an overlying film of Cr, provided both surface and edge coverage are achieved.

Introduction

The objective of this study was to examine some of the metallurgical factors involved in the use of solder joining for SLT (Solid Logic Technology) chip-to-module contacts. In a companion paper,[1] Totta and Sopher have traced the history of solder joining from its adoption in SLT, through the period of this work (1965), to the later development of the "controlled-collapse" technique for use with monolithic circuit chips. In the latter technique, the copper ball used in SLT as a stand-off between the module and the chip has been eliminated. The multilayer Cr-Cu-Au thin film chip contact metallurgy, with which this report is largely concerned, has however been retained and is consequently now of importance for both types of solder terminal contact.

The essential features of an SLT chip terminal contact and the Cu ball prior to joining are shown schematically in Fig. 1. It will be observed that the system contains a considerable array of materials, the primary functions of which are listed in Table 1. The soldering of the ball to the contact is performed by heating in a hydrogen atmosphere to 350°C for a few minutes, using only the solder already provided in the form of the vacuum deposited Pb-Sn "pad." At this stage, therefore, the system is effectively closed in the sense that the components of the system are fixed and of known amounts. In contrast, the subsequent joining of the chip to a module presents a less clear situation, since the extent to which the relatively large reservoir of the module solder (Pb-10% Sn) mixes with the chip solder is not easily defined. The duration of the module joining is a few minutes at about 330°C, a temperature high enough to assure remelting of the previously formed chip-to-ball joint.

Significant changes occur in the thin film metallic structure depicted in Fig. 1, as a result of the ball joining operation. After joining, the gold and copper films are replaced by a layer of intermetallic compound formed by reaction with the Sn. The dominant compound is basically the intermetallic Cu_6Sn_5, with perhaps some Au substituting for the Cu. The experiments described below show that this reaction occurs in a matter of seconds, and thereafter the intermetallic layer has a tendency not only to dissolve but also to spall into the molten solder. Excessive removal of the intermetallic is deleterious, since it produces solder dewetting at the exposed Cr surface. Solder immersion experiments on copper films deposited on glass substrates clearly reveal the existence of an interaction between the processes of spalling and true solution. Specifically, the tendency to spall, which is promoted initially by the stresses generated when the copper film is converted to the intermetallic form, can be triggered by localized solution attack. As a consequence of this "solution-assisted spalling," the removal of the intermetallic layer is not simply governed by the limited solubility of the intermetallic in the solder, which by

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itself is demonstrated to be an unimportant factor in the SLT geometry. Thus, the prevention of solder dewetting is largely dependent on those factors which ultimately inhibit or arrest the spalling process. These factors are optimized in production by the use of the Cr-Cu phasing-in or overlap procedure described by Totta and Sopher.[1]

The starting point adopted in this work was to ascertain whether a Cr film could in fact be wetted by the Pb-Sn solder. The reasoning for such a choice was that, if the Cr could not be directly wetted by solder, any mechanism that resulted in the excessive removal of the intermetallic film from the Cr surface would automatically cause dewetting. The initial experiments, and the later ones they stimulated, are described and discussed in the second following section; experimental procedures are outlined below.

Procedure

Most of the experiments involved immersing thin film specimens, prepared on either glass or oxidized Si substrates, into a crucible of molten solder held at 350°C. Periodic withdrawal for visual or microscopic surface examination enabled the occurrence of solder dewetting to be observed conveniently, while the use of glass substrates permitted an examination of the back side of the first deposited film. These observations were supplemented, where appropriate, by metallographic examination of 10:1 taper sections. The majority of the films used in these "immersion tests" were prepared by successive deposition, without breaking vacuum, within a multiple-source (rf-heated) vacuum deposition system which was equipped with deposition rate and substrate temperature control facilities.[2] As many as eight substrates of 1-in. diameter could be accommodated during one deposition cycle. Individual specimens for the immersion tests were generally obtained by splitting each wafer into two or more portions. Details on some of the batches of specimens prepared in this evaporator are given in Table 2. In addition, immersion tests were also performed on various blanket film specimens prepared by the IBM Components Division.

The immersion test apparatus is depicted in Fig. 2. The 1-in. diameter alumina crucible, which held a solder charge of approximately 150 gm, was located in a temperature-controlled pot furnace. To prevent oxidation of the solder, the crucible was placed inside a Pyrex tube through which forming gas (95% N_2-5% H_2) was continuously flushed at a rate of 1 liter/min. The specimen was held by stainless steel tweezers, and was lowered into or raised from the solder pot by manipulation of the slide rod passing through the top flange. The solder alloys were prepared from high-purity materials and thoroughly stirred prior to use. The temperature of the solder was obtained from a sheathed thermocouple inserted directly into the

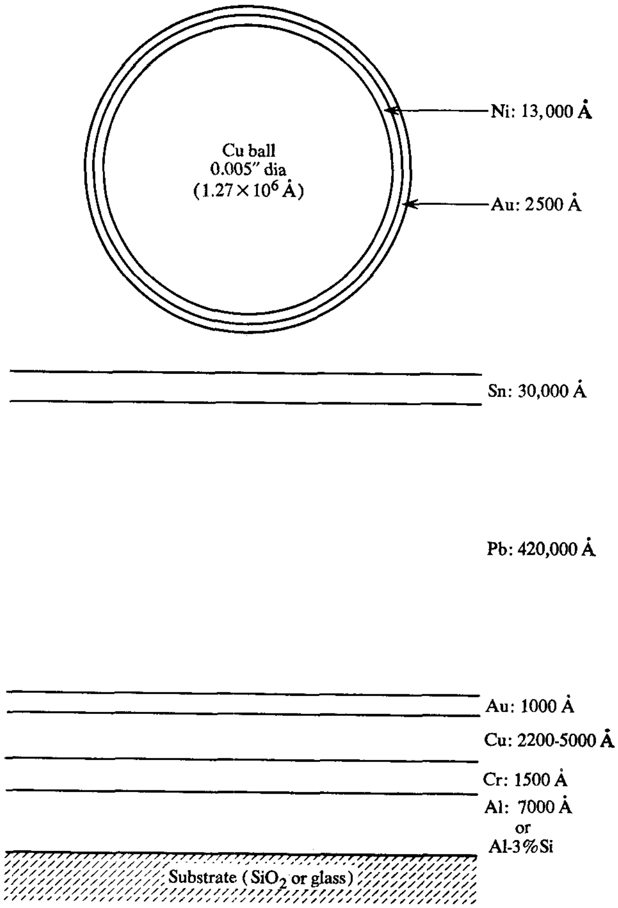


Figure 1 Schematic illustration of the chip contact and ball prior to melting. The figure has been drawn far out of scale for clarity.

Table 1 Primary functions of the elements shown in Fig. 1.

Element	*Function*
Al (or Al-3% Si) film	To provide ohmic contact to the Si device and act as a conductive stripe extending to the terminal area.
Cr film	To bond to both the Al film and the glass layer (not shown). Also, to provide a diffusion barrier between the Al Film and the solder contact.
Cu film	To provide a solderable layer above the Cr film.
Au film	A protective surface film to assure easy wetting of the Cu film surface.
Pb and Sn films	On subsequent melting, to provide a Pb-5% Sn solder for ball joining. (The stratification of the Sn on top of the Pb follows from the deposition method used, and is a result, rather than the intent, of this procedure.)
Au layer on ball	A protective surface to maintain ball solderability during storage.
Ni layer on ball	To prevent thick Cu-Sn intermetallic formation on the surface of the ball during soldering.
Cu ball	To provide a stand-off between the chip and the module.

Table 2 Summary of principal samples and testing conditions.

Code (in numerical order)	*Description*	*Substrate temp. during film deposition, °C*	*Film thickness, Å; deposition rate, Å/sec.; dep. pressure range, torr.*	*Remarks*	*Composition and temp. (°C) of solder*
823	Cr, Au, and Cr-Au on oxidized Si wafers	250	Cr:1000, 6, 10^{-7} Au-4ppp, 10, 10^{-7}	Cr source: crucible containing powdered Cr	Pb-5%Sn-2%Au 350
830	Cr, Au, and Cr-Au on oxidized Si wafers	200	Cr:1700, 5, 10^{-7} Au:1700, —, 10^{-7}	Cr source: as for 823.	Pb-5%Sn-2%Au 350
832	Combinations of Cr, Cu, Au on oxidized Si wafers	200	Cr:1200, 5, 10^{-7} Cu:5000, 3, 10^{-7} Au:1000, 1, $<10^{-7}$	Cr source: as for 823. Outgassing of Cu source judged inadequate.	Pb-5%Sn-2%Au 350
843	Cu on glass	200	$\left.\begin{matrix}2000\\5000\\8000\end{matrix}\right\}$, 10, 10^{-7}	Different thicknesses obtained by use of shutter.	Pb-5%Sn 350
863	Cr-Cu-Au on oxidized Si wafers (Test and control samples	200	Cr:1500, 5, $<10^{-7}$ Cu:2600, 10, 10^{-7} Au:1000, 1, $<10^{-7}$	Test samples cooled to room temperature after Cr deposition and exposed to 1/2 atm. of pure O_2 for 1-1/2 hours. System repumped and substrates reheated for Cr deposition on control samples, followed by Cu and Au depositions on both sets of samples.	Pb-5%Sn-2%Au 350
866	Cr-Cu-Au on oxidized Si wafers (Test and control samples)	215	Cr:1500, 5 Cu:2600, 10, $<10^{-7}$ Au:1000, 1, $<10^{-7}$	Test Cr deposited at 1.6×10^{-6} of O_2. Control Cr deposited at 10^{-7}. Single layer pellet sources for Cr.	Pb-5%Sn-2%Au 350
874	Cu-Au on glass	200	$\left.\begin{matrix}\text{Cu:5500,}\\\text{and}\\10{,}000\end{matrix}\right\}$, 30, 10^{-7} Au:1000, 1, 10^{-7}	Solder pot fitted with copper foil lining.	Pb-5%Sn-2%Au saturated with Cu; 350
910	Cr-Sn on oxidized Si wafers	50	Cr:1500, 5, 10^{-7} $\left.\begin{matrix}\text{Sn:5000}\\\text{and}\\11{,}000\end{matrix}\right\}$, 60, 10^{-7}	New single layer pellet source for Cr.	Pb-5%Sn-2%Au 350
913	Cr-In on oxidized Si wafers	50	Cr:1500, 5, 10^{-7} $\left.\begin{matrix}\text{Sn:5000}\\\text{and}\\11{,}000\end{matrix}\right\}$, 60, 10^{-7}	Single layer pellet source for Cr, previously used for code 910.	Pb-20%In 300
925	Al-Cr-Cu-Pb on glass	200 for Al, Cr, Cu. 50 for Pb.	Al:14,000, 40, 10^{-7} Cr:1500, 5, 10^{-7} Cu:2500, 40, 10^{-7} Pb:7500, —, 10^{-7}	1st pattern: Al blanket, Cr dots, Cu dots, Pb blanket. 2nd (reverse) pattern: Al dots, Cr blanket, Cu blanket, Pb dots.	Pb-5%Sn-2%Au, Pb, Pb-5%Sn, Pb-2%Au; 350 for all

Notes: Substrates were either oxidized Si wafers or Corning 710 cover glass of 1 inch diameter. The substrate preparation procedure was as follows: (a) Clean in hot chromic-sulphuric acid. (b) Step rinse in 3 baths of demineralized water. (c) Etch 100 Å from substrate surface using mild HF etch. (d) Repeat step rinse. (e) Hot water ultrasonic rinse at 90°C. (f) Methanol-acetone ultrasonic rinse. (g) Freon vapor degrease.

melt. Although the pure binary Pb-5% Sn solder* was sometimes used, most of the immersion tests were performed with a solder of the composition Pb-5% Sn-2% Au. (Referring to Fig. 1, we note that solution of all the Au on the ball and in the standard Cr-Cu-Au layer configuration by the Pb-5% Sn pad would produce the Pb-5% Sn-2% Au composition.) The melts of solder were discarded and replaced at appropriate intervals to ensure that no serious drift in composition accrued from the solution of materials from the immersed specimens.

Results and discussion

The experiments are grouped and discussed below under a number of different headings. To refer to the specimens listed in Table 2, use will be made of the code number shown in the first column of that table. The temperature and composition of the solders employed in the immersion tests are also entered in Table 2.

• *Immersion tests on Cr films, with and without overlays of Sn, In, or Au.*

No wetting was obtained on the bare Cr films of Codes 823 and 830. These films were smooth, uniform, highly reflective and free of surface discoloration both before and after a solder immersion for several minutes. The absence of wetting cannot, however, be taken as evidence that solder does not wet pure, clean Cr, since exposure of the film to the air may be expected to oxidize the surface. Accordingly, immersion tests were performed on Cr films protectively overlaid in the same pump-down cycle with Au (Codes 823 and 830), or Sn (Code 910), or In (Code 913). The latter two metals (like Pb itself) have a very restricted solubility in Cr and do not form compounds with it; thus they appear suitable as inert overlays to protect the Cr from oxidation until they are dissolved from its surface after immersion in the solder. The Sn-overlaid samples readily dewetted down to the Cr upon immersion in the solder. The In-overlaid samples showed a high resistance even to wetting of the In film (both in Pb-20% In and Pb-5% Sn-2% Au solders). This effect was traced to surface oxidation of the In overlay, since application of a diluted flux did cause prompt solution of the In film. Again, however, no wetting was obtained on the underlying Cr film. In view of these results, it has been concluded that pure Cr films, even when substantially free of surface oxide, cannot be wetted either by Pb-Sn or Pb-In solders.

The immersion tests on the Cr films overlaid with Au (Codes 823 and 830) presented an interesting contrast to those described above using overlays of Sn or In. With the Au overlay, an immersion time of 5-10 minutes was usually required to produce gross dewetting. The appearance of a specimen on which little dewetting had occurred after 5 min is shown in Fig. 3. In contrast, Fig. 4 shows another sample where major dewetting had occurred after the same immersion time. Despite the variability in the dewetting rate, the point of major significance is that wetting on these samples did exhibit a temporary but noticeable persistence. This behavior, in contrast to that for the Cr-Sn and Cr-In films, is believed to arise from the fact that the Au film is not wholly dissolved by the solder, but in part reacts with it to form the intermetallic compound AuSn,* which then gradually dissolves and spalls off the Cr surface. Dewetting is thus attributed to the removal of the intermetallic and the inability of the solder to wet the underlying Cr film. Evidence for this suggestion is presented in Fig. 5, which shows a taper section through a solder globule adhering to an otherwise dewetted area of the specimen. Only in the area under the solder is there intermetallic present on the Cr film.

These results indicate that a fundamental distinction should be drawn between the types of materials that might be useful as overlays on the Cr layer. Only materials like Au, Cu or Ni (all of which react to produce solid intermetallic compounds with Sn) appear to be of potential use

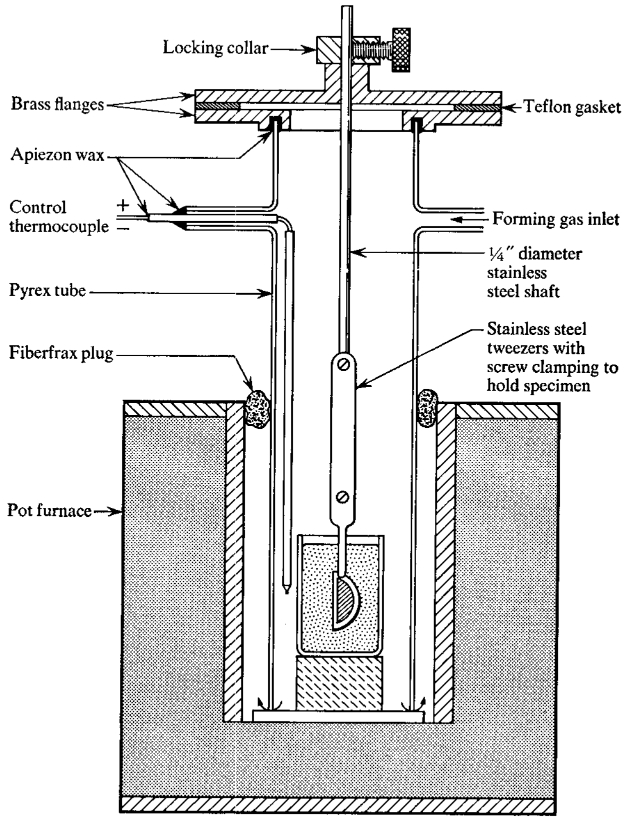


Figure 2 The immersion test apparatus.

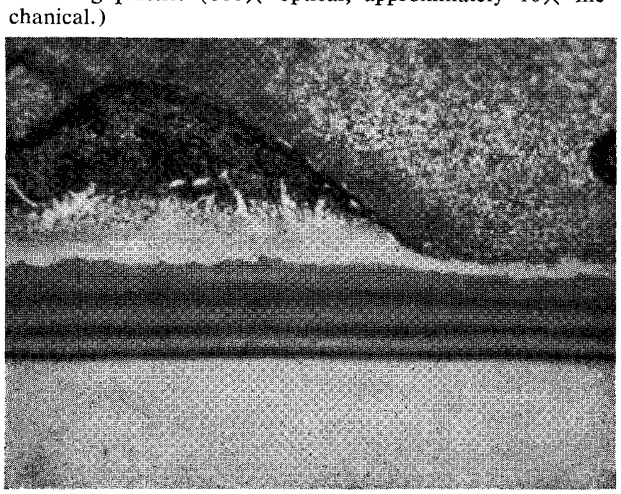
* Throughout this paper, all compositions are quoted in weight percent.

* The compounds $AuSn_4$ and $AuSn_2$ are not stable at 350°C.

Figure 3 A Code 823 Cr-Au specimen after 5 min of immersion in Pb-5%Sn-2%Au. Wetted except for some pinholes. (4.5×.)

Figure 4 Another Code 823 Cr-Au specimen exhibiting major dewetting after 5 min of immersion in Pb-5%Sn-2%Au. (4.5×.)

Figure 5 A taper section (10:1) through a Code 830 Cr-Au specimen after 700 sec of immersion in Pb-5%Sn-2%Au. The oxidized Si substrate appears at the bottom. The SiO_2 layer exhibits interference fringes as a result of the taper sectioning, which produces a wedge of oxide between the polished surface and the Cr film. Part of the section goes through a solder globule (dark area at left) which interfaces with an intermetallic compound on the Cr surface. The sectioned Cr film shows as a thin light band running through the middle of the picture; the light grey mottled area above this is the dewetted Cr surface viewed slightly off-normal through a wedge of transparent mounting plastic. (600× optical; approximately 10× mechanical.)



for soldering purposes. Although the persistence of wetting is poor for a direct Au overlay, in SLT it is a Cu film that is in contact with the Cr. For this reason, attention was switched at this stage to the behavior of Cu films upon immersion in solder. Results for single Cu films deposited directly on glass substrates are described below.

• *Immersion tests on Cu films, and the solubility of Cu in Pb-5% Sn at 350°C.*

The specimens used for these immersion tests are identified as Codes 843 and 874 in Table 2. Glass substrates were used to permit visual inspection of the backs of the films. The initial wetting of these films was found to occur patchily and in some areas rather slowly (~30 sec), indicating the presence of a surface barrier film. This supports the experience of others (in the Components Division) that exposed Cu films do not provide such easily wettable surfaces as do Au films. A second observation concerns the unexpected rapidity with which a change in color occurred on the back side of the film once wetting had occurred on the front face. Even for films 10,000 Å thick, the time delay between front surface wetting and the back side color change was only a few seconds. This color change was from the distinctive color of the original copper to a shiny silvery appearance. It is believed that this change

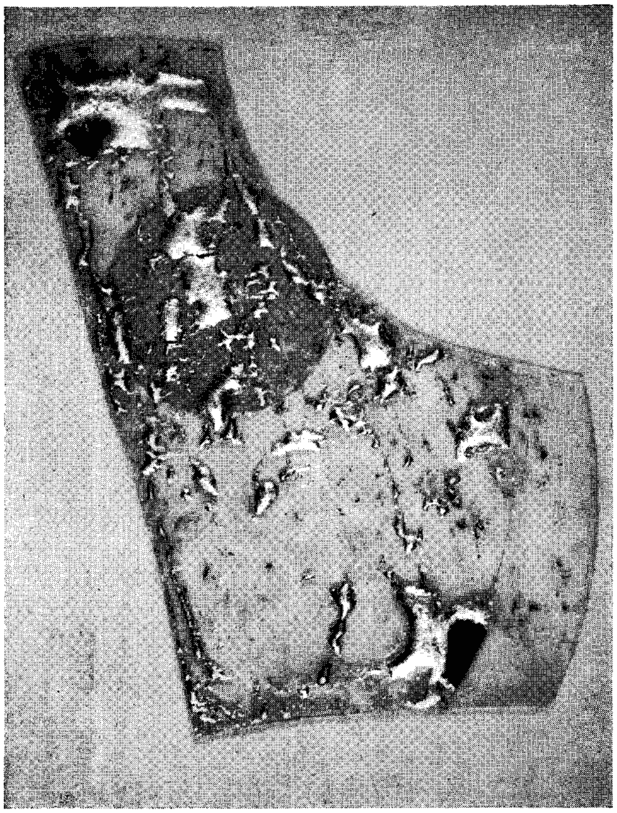


Figure 6 Removal of a Code 843 (Cu on glass) specimen after 10 sec of immersion in pure Pb-5%Sn solder. (4.5×.)

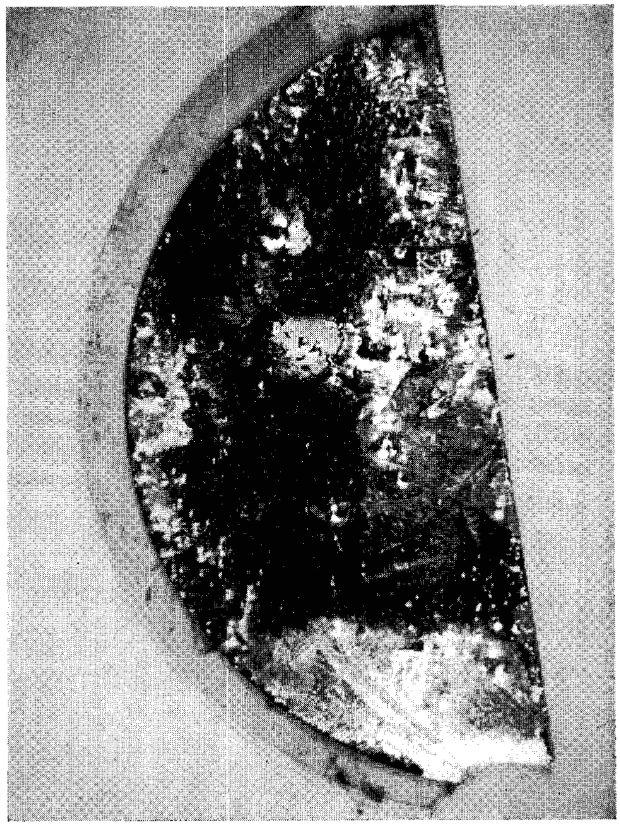


Figure 7 Persistence of a Code 874 (Cu-Au on glass) specimen after 1400 sec of immersion in copper saturated Pb-5%Sn solder. (4.5×.)

marks the total conversion of the Cu film to the intermetallic form. Support for this contention was later obtained by metallographic examination of immersed Cr-Cu-Au films, which confirmed that conversion of the Cu film to the Cu-Sn intermetallic does proceed with the rapidity noted for the color change.

The observations cited above describe only the early behavior of the films. At that stage, no significant difference was noted in the immersion behavior of films immersed in the different solder compositions noted in Table 2. In contrast, the behavior upon continued immersion was found to depend critically on the copper content of the solder. With pure Pb-5% Sn solder, the film was rapidly removed from the glass substrate, as may be seen from Fig. 6, which shows the appearance of a sample after an immersion time of only 10 sec. Two reasons can be thought of to account for the rapid disappearance of the film. One is that adhesion to the glass substrate may be lost once the Cu is totally converted to the intermetallic, with the result that the intermetallic may bodily spall off and float away into the solder. A second possibility is a true solution of the intermetallic film in the solder, a process which may be expected to be operative until such time as the copper content of the solder has risen to the solubility limit at the temperature in question (350°C). Experiments were performed to shed some light on the relative importance of these two alternatives. For these tests, use was made of a solder pot to which a lining of Cu foil had been added to ensure that, after a suitable equilibration, the solder was saturated with Cu. This procedure does not prevent the previously noted rapid conversion of the Cu film to the Cu-Sn intermetallic; it does, however, prevent the intermetallic from being taken into solution. Hence a disappearance of the intermetallic film in this case must be attributed entirely to a tendency of the intermetallic to flake off the substrate. The lifetimes of films immersed in the Cu-saturated solder proved to be at least 20 times greater than was the case when the pure (non-Cu doped) solder was used. For example, Fig. 7 shows a sample which remained essentially intact after 1400 sec of immersion in the saturated solder. These experiments, therefore, demonstrated rather conclusively that the removal rate of the intermetallic is greatly accelerated by the ability of the intermetallic to go into solution in the solder.

At this stage, consideration may be given to the relevance of these results to SLT. The primary question prompted by

Figure 8 A Cr-Cu-Au specimen after 1200 sec of immersion in Pb-5%Sn-2%Au. Good bulk wetting, with some edge dewetting. (4.5×.)

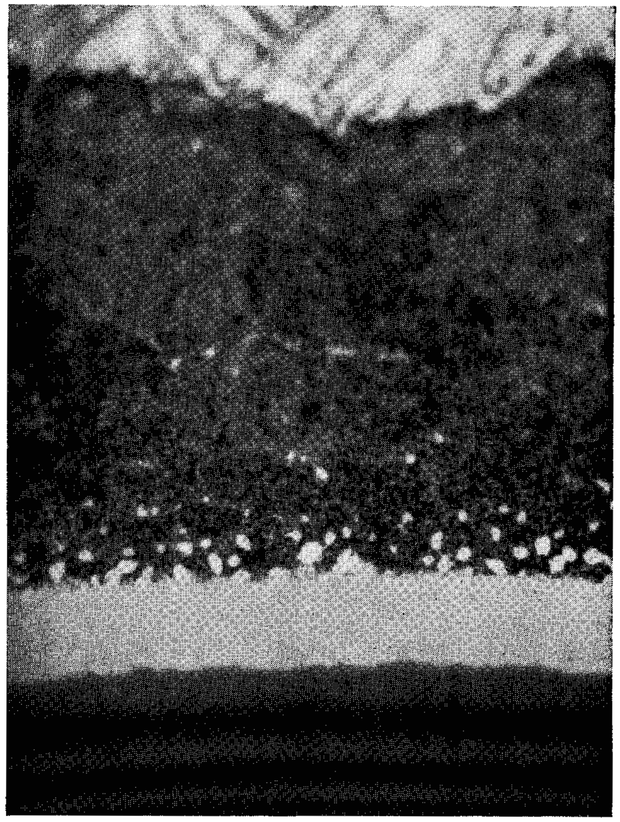


Figure 9 A taper section through a Code 866 Cr-Cu-Au sample after a 1200-sec immersion in Pb-5%Sn-2%Au. Note the sparse globular nature of the residual intermetallic. (1000× optical; approximately 10× mechanical.)

these tests is whether or not it is thermodynamically possible in the SLT ball-joining operation to take all the copper into solution in the molten solder pad. (If this were the case, the possible danger of dewetting from too prolonged a soldering time is apparent.) To answer the above question, the value of the solubility of Cu in Pb-5% Sn solder at 350°C must be known. Since this could not be found in the literature, an experimental determination was undertaken. Because the solubility can be expected to be small,[3] the scheme adopted consisted of adding small weighed pieces of Cu foil to a bath of pure Pb-5% Sn. It was anticipated that eventually a piece would be added which would not completely dissolve, and that by subsequent chemical analysis for the weight of copper in this residual piece (which is mostly converted to intermetallic), it would be possible to determine the total weight of copper taken into solution by summing the weights contributed by the final and the preceding foil additions. Actually, the experiment turned out to be complicated by the fact that a clear "end-point" was not obtained. This arose from the tendency of the intermetallic formed on the Cu foil to spall off. The exposed Cu was then converted to more intermetallic, and the cycle repeated. Fortunately, this turn of events did not render the experiment ineffective since, once the solubility limit was exceeded, the spalled off intermetallic floated up to the surface to form a thin but visible and persistent scum. Using the point at which the scum was detected as an indication of saturation, the solubility was estimated to be no greater than 0.14%. Allowing for the uncertainties involved, a final value of $0.12 \pm 0.02\%$ appears to be a reasonable estimate of the solubility of Cu in Pb-5% Sn at 350°C.

Using the thicknesses indicated in Fig. 1, we observe the weight of the combined Pb and Sn layers in the contact region to be 3.15×10^{-7} gm/mil^2 of surface area. With the copper solubility figure of 0.12%, this weight of solder is capable of taking 3.8×10^{-10} gm of copper into solution. Per mil^2, this weight corresponds to a Cu film thickness of 650 Å. (Bulk densities are assumed throughout.) Since the Cu film employed in SLT is at least several times this thickness, it would appear at first sight that a substantial removal of the intermetallic layer could not occur during the ball joining operation. However, such a conclusion is based on the assumption that the amount of material disappearing from the intermetallic layer is just equal to the amount taken into solution. This assumption is not valid if solution of the film occurs inhomogeneously and induces an accompanying spalling action. If, for example, the intermetallic is subject to preferential intergranular attack by the molten solder, the actual solution of a relatively small amount of intermetallic may serve to detach solid nodules of intermetallic from the layer. These detached nodules would be free to float away in the solder, without being taken completely into solution before more nodules are detached from the intermetallic surface. This process, which can be described as the "solution-assisted spalling" of the intermetallic, can clearly result in the disintegration of a much thicker intermetallic layer than would be possible by a true solution action only. The importance of this mechanism is obvious by reference (for example) to Fig. 10, which shows the top of the intermetallic layer disintegrating in this fashion after an immersion time of only 50 sec.

- *Immersion tests on Cr-Cu-Au films*

Having described the immersion tests on separate films of Cr and Cu, we turn now to the immersion tests on Cr-Cu-Au composite films. The first specimens prepared (Code 832, Table 2) can now be judged to have behaved very poorly in the immersion test. Most specimens in this batch showed major areas of dewetting after 40-80 sec of immersion. This behavior was quickly found to be unrepresentative, and in retrospect can be attributed to inadequate film preparation conditions. Later batches of samples behaved in a distinctly superior manner. With only one exception, samples immersed from 1200 to 1500 sec showed no dewetting except at the edges of the specimens. Figure 8 shows the appearance of a specimen after a 1200-sec immersion. The surface solder film will be seen to have frozen into a large-grained structure exhibiting a well-defined dendritic surface topology. (The edge dewetting, visible around the circular periphery, was an almost universal result of the immersion tests, and was ascribed mainly to a combination of shadowing and misregistration effects.) The microstructure of a similar sample is shown in Fig. 9. After 1200 sec of immersion, the intermetallic was reduced to a porous residue which provided incomplete coverage of the Cr film. Nevertheless, attempts to force dewetting to occur, by further prolonging the immersion time first to 3000 sec and eventually to as long as 17 hr, were unsuccessful.

To investigate in more detail the initial rate of formation of the intermetallic layer and the rate at which it is subsequently thinned upon continued immersion in the solder pot, a series of taper microsections was prepared from samples immersed for a series of different times. For these tests, use was made of Cr-Cu-Au samples prepared by the Components Division (without use of the overlap technique), and identified here as the F-1 series. No dewetting occurred on any of these samples. It was observed (Fig. 10) that the total conversion of the copper film to the intermetallic form was fully completed after the shortest (50 sec) immersion time. At this stage the onset of spalling is evident only near the top of the layer. After 100 sec of immersion, the breakup of the film extended down to the Cr surface (Fig. 11). Thereafter, prolonging the immersion time merely had the effect of slowly thinning down the amount of residual intermetallic. The relative slowness of this stage can be appreciated from Fig. 12, which corresponds to an immersion time of 4000 sec.

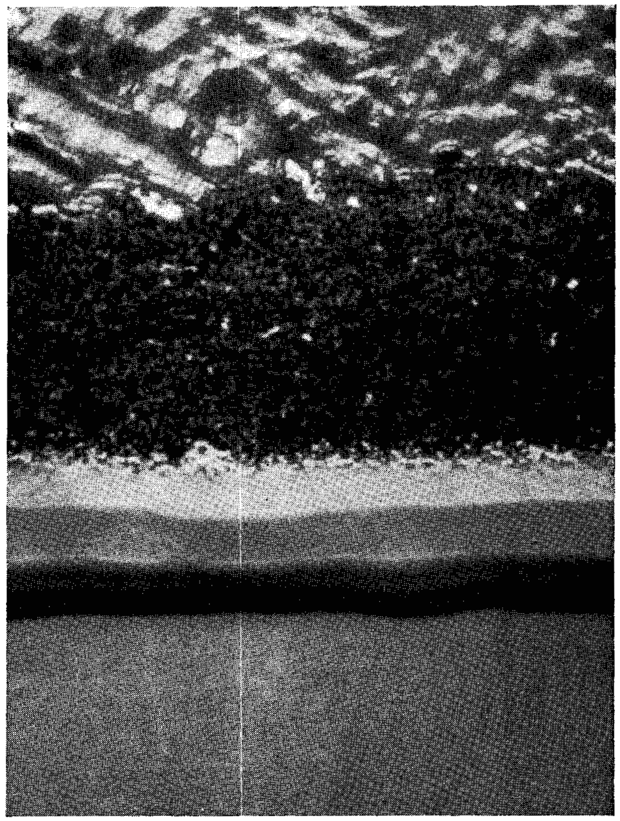


Figure 10 A taper section through an F-1 Cr-Cu-Au sample after 50 sec of immersion in Pb-5%Sn-2%Au. At this stage the intermetallic layer is relatively thick and continuous, with evidence of spalling only near its top surface. (600× optical; approximately 10× mechanical.)

In discussing these results, it is appropriate to start with the finding that prolonged solder pot immersions do lead to incomplete coverage of the Cr film by the residual intermetallic (c.f. Fig. 9). Hence the possibility must be considered that the observed persistence of wetting is not due solely to the retained intermetallic, but may arise also from the ability of the solder to wet the exposed Cr underlay. The available evidence relating to this question is as follows. First, the experiments on Cr failed to produce direct wetting of Cr films. Secondly, an improvement of

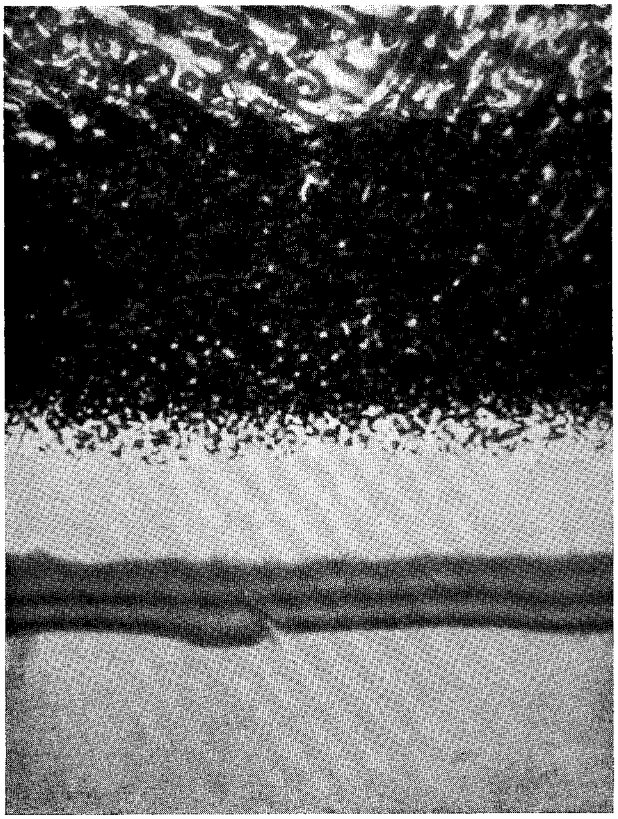


Figure 11 A taper section through an F-1 Cr-Cu-Au sample after a 100-sec immersion in Pb-5%Sn-2%Au. By comparison with Fig. 10, spalling of the intermetallic can be seen to have advanced rapidly. (600× optical; approximately 10× mechanical.)

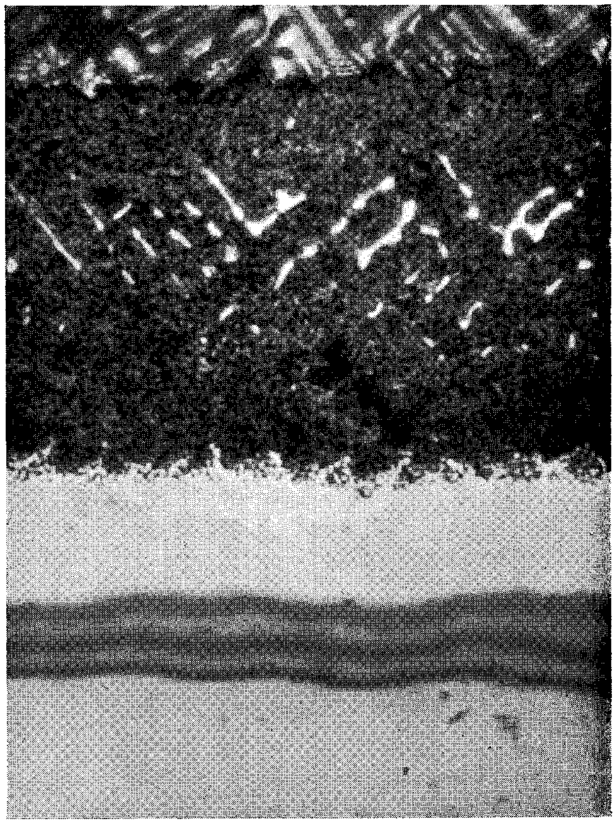


Figure 12 A taper section through an F-1 Cr-Cu-Au sample after a 4000-sec immersion in Pb-5%Sn-2%Au. A significant amount of porous intermetallic is still present. (600× optical; approximately 10× mechanical.)

the wettability of the Cr surface by the interdiffusion of Cu cannot be expected, owing to the extreme immiscibility of these two metals. In this connection, there is no microscopic evidence of Cr-Cu interdiffusion. Furthermore, a decrease of the substrate temperature for the deposition of copper from 250°C to 100°C was found to have no effect on the persistence of wetting. These points, coupled with the additional result that microscopically observable intermetallic was always present in wetted specimens, and was absent in dewetted specimens, lead to the conclusion that direct wetting between Cr and solder does not occur in the Cr-Cu-Au configuration. This conclusion has the corollary that the retention of some intermetallic is essential for the prevention of dewetting.

We may now seek to explain the observation that, despite a rapid initial attack and breakdown of the intermetallic layer in the first minutes of immersion, a persistent residue of intermetallic remains at the Cr surface for many hours. This is interpreted to mean that the internal stresses which engender the initial stage of solution-assisted spalling in the intermetallic are relieved by the breakdown of this layer, and thereafter removal of the intermetallic proceeds much more slowly by the process of true solution. On this basis, the prevention of dewetting is seen to require that the chemical adhesion and/or mechanical interlocking of the intermetallic at the Cr interface must be adequate to withstand the initial stress in the film. Otherwise, instead of an inward self-limiting attack, the intermetallic may spall off bodily at this interface immediately following conversion of the copper film. The evidence presented in the next section indicates that the presence of an oxide at this interface can weaken the bonding to the point where this mode of failure can be produced.

• *Dewetting produced by oxidation of the Cr underlayer*
Early concern over the state of oxidation of the Cr film surface in SLT was promoted by the greenish color sometimes seen on used Cr-source filaments,* which indicated the possibility of substantial evaporation of Cr_2O_3 in the final stages of the film deposition. Immersion tests were

* The Cr source referred to here, used at the time of this investigation, was a chromium-plated tungsten filament from which the Cr source was sublimed.

performed on the Cr-Cu-Au specimens specially prepared by the Components Division by running a Cr-plated filament source to completion. The results confirmed the suspicion that an oxidized surface on the Cr film does not act as an adherent base for the intermetallic film. Most of these samples dewetted over roughly 70% of their area after immersion times of only 40-100 sec. Corroboration of this effect was also obtained from the Code 863 specimens listed in Table 2. These samples were of two kinds; one set consisting of control samples prepared under optimum conditions. The other set was prepared identically except for the exposure treatment administered to the Cr film prior to the deposition of the Cu and Au films simultaneously over both the test and control samples. For Code 863, the exposure treatment consisted of 1.5 hr of exposure to 0.5 atm of pure oxygen at room temperature. Whereas all the control samples exhibited no bulk dewetting after a 20-min immersion, the exposed samples dewetted completely in less than 80 sec. Visually, the exposed Cr films on the dewetted samples appeared clean and highly reflecting, thus giving no hint of the surface oxidation which was presumed to account for their early dewetting behavior.

Since the exposure used for the Code 863 specimens resulted in such prompt and complete dewetting, ensuing experiments were designed to investigate the sensitivity of dewetting to less drastic oxidation treatments. The exposure conditions investigated are listed below.

Code	*Significant "Exposure" Variable*
866	Cr deposited with a controlled O_2 leak giving a gauge reading of 1.6×10^{-6} torr during deposition; no subsequent exposure.
869	As above but with O_2 leak set to give 1×10^{-5} torr.
877	As above but with water vapor leak set to give 1×10^{-5} torr.
879	Deposition at a background of 1×10^{-6} torr. After deposition, some samples exposed to 3×10^{-4} torr of water vapor for 200 sec; others to 1×10^{-4} torr for 30 sec.
899	Deposition at below 10^{-6} torr. After deposition, some samples exposed to 1×10^{-4} torr of water vapor for 300 sec; others to 1×10^{-4} torr of water vapor for 3000 sec.

All the specimens listed above behaved satisfactorily in a 20-min solder immersion test. Thus, Cr films evaporated from a "clean" source appeared to be quite tolerant of poor vacuum conditions as far as subsequent dewetting was concerned. On the other hand, the experiments first described in this section do demonstrate that, in sufficient amount, surface oxide on the Cr film can cause rapid dewetting. For this reason, the inadvertent evaporation of Cr_2O_3 directly from the Cr source should be avoided.

• *Immersion tests on composite films containing an aluminum underlayer.*

It is to be recalled from Fig. 1 that the Cr-Cu-Au composite provides an overlay for the Al or Al-3% Si film[1] that is used to achieve contact to the planar device on the silicon chip. If the Cr film were both continuous and an impenetrable diffusion barrier, there would be little need to examine the Al film from the viewpoint of the soldering operations. However, from a more realistic point of view, it is desirable to know what changes may occur (a) if the solder interfaces an Al film directly (as could happen if the Cr film contained discontinuities), or (b) if the Cr film is not an adequate diffusion barrier to one or more of the constituents of the solder. The experiments prompted by these questions were performed on the specimens of Code 925. As indicated in Table 2, specimens of this code were of two types, one being the reverse pattern of the other. In one type, a blanket film of Al was first deposited on a glass substrate. This was followed by a pattern of Cr dots (0.030-0.050 in. dia.), which in turn were overlaid by Cu dots put down through the same mask. The mask was then rotated out of position without breaking vacuum, and a final blanket film of Pb deposited over the specimen. The purpose of the Pb film was simply to provide an inert overlay to minimize oxidation of the otherwise exposed areas of the Al film, on breaking vacuum. The reverse pattern specimens prepared concurrently with those described above contained the sequence: Al dots, blanket Cr, blanket Cu, Pb dots. It will be convenient to designate the two types of sample as "Al-blanket" and "Al-dot" specimens, respectively.

Immersion tests were performed first on the Al-blanket films, using Pb-5% Sn-2% Au solder at 350°C. After the first few seconds of immersion, the back side of the Al film showed discoloration in circular arcs corresponding to the edges of the overlying Cr-Cu dots. This was followed a few seconds later by the appearance of discolored areas in the non-Cr-Cu overlaid part of the film. These areas spread rapidly, and discoloration of the non-protected part of the Al film was complete in about 60 seconds. By that time, the discoloration had also advanced appreciably under the Cr-Cu dots. Under the microscope, the discolored areas had a light tan or beige color, in contrast to the white appearance of the original Al film. This discoloration was taken to be evidence of a rapid diffusion of some constituent of the solder into the Al film. In an attempt to identify the constituent responsible, similar films were given immersion treatments in pure Pb, in Pb-5% Sn, and in Pb-2% Au. For pure Pb and Pb-5% Sn, no discoloration appeared even though the immersions were prolonged to the point where solution of the Al film in the solder became evident (9000 sec for pure Pb; 6600 sec for Pb-5% Sn). However, the discoloration was produced by immersion in Pb-2% Au, although in this case the rate of discoloration was noticeably slower than for Pb-5% Sn-2% Au. Whether this difference reflects some difference between the specimens or some effect related to the presence of Sn is not known. However, the main point established by the tests is that the discoloration occurred only with the presence of Au. It is considered significant that of the three elements Pb, Sn and Au, only Au forms intermetallic compounds with Al. Furthermore, work by King[4] has shown that the dominant compound produced in Al-Au diffusion couples also has a beige appearance under the microscope. There is thus indirect evidence to suggest that the discoloration resulting from immersion represents conversion of the Al film to an intermetallic compound.

Since the Al-dot (reverse pattern) films contained blanket overlays of Cr and Cu, immersion tests on these specimens permitted an evaluation of the effectiveness of the Cr-Cu composite as a diffusion barrier for the protection of the underlying Al dots. As before, no discoloration resulted from prolonged immersion of these films in pure Pb or Pb-5% Sn. However, with both Pb-5% Sn-2% Au and Pb-2% Au, small random patches of discoloration did become visible on the back side of the Al dots, but only after 1200 sec of immersion at 350°C. Compared with the discoloration rate on the unprotected areas of the Al-blanket specimens, this represents a reduction in the rate of attack of roughly two orders of magnitude. The Cr (plus residual intermetallic) film therefore appears to act as a substantial diffusion barrier, to the point that no attack of the underlying Al film should be anticipated during ball and module joining in SLT production (provided of course that the Cr film is continuous and masks the Al completely).

Conclusions

Lead-tin solders will not wet a Cr film, whether or not its surface has been protected from oxidation. Consequently, the use of a Cr film in SLT terminal contacts makes mandatory the addition of a suitable solderable overlayer such as copper. During soldering, the conversion of the Cu film to a Cu-Sn intermetallic proceeds with great rapidity and is complete in less than 10 seconds. After this, the remaining minutes of the soldering operations lead to thinning of the intermetallic layer by a process of solution-assisted spalling. This process is self-arresting, and the residue of intermetallic left adhering to the Cr surface is normally sufficient to prevent dewetting. However, adherence of the intermetallic can be greatly impaired by the presence of a surface oxide on the Cr film. Thus, from the viewpoint of preventing oxidation, and also for the purposes of promoting adhesion and mechanical interlocking between the Cr film and the intermetallic, the process of overlapping the Cr and Cu depositions described by Totta and Sopher[1] is highly desirable.

The addition of Au to Pb-5% Sn solder was found to produce rapid discoloration of an unprotected Al film, possibly as a result of the formation of an intermetallic compound (not, however, the purple compound $AuAl_2$). An overlying Cr film, which provides both surface and edge protection, retards such attack for a time appreciably longer than the duration of the SLT ball and module joining operations. Thus, apart from its role in securing good adhesion of the terminal contact to the glass layer on the chip, the Cr film performs a significant function as a protective diffusion barrier in the terminal configuration.

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References

1. P. A. Totta and R. P. Sopher, *IBM J. Res. Develop.* **13**, 226 (1969, this issue).
2. I. Ames, J. Hoekstra and G. Folchi, "Modular Thin Film Deposition System," in preparation.
3. The solubility of Cu in pure Pb is accurately known from the work of O. J. Kleppa and J. A. Weil, *J. Am. Chem. Soc.* **73**, 4848 (1951).
4. W. J. King, private communication.

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