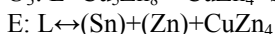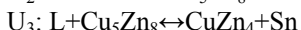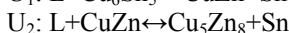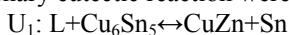# REACTIONS IN THE SN CORNER OF THE CU-SN-ZN ALLOY SYSTEM

D.D. Perovic, L Snugovsky and J.W. Rutter
Department of Materials Science and Engineering
University of Toronto
Toronto, ON, Canada
doug.perovic@utoronto.ca

P. Snugovsky
Celestica Inc.
Toronto, ON, Canada

ABSTRACT
In view of potential damage to heat sensitive electronic components during soldering at the high temperatures required for some Pb-free solders, such as the SAC alloys, it appears likely that more use will be made of solders based on the much lower melting Sn-Zn eutectic alloy. Consequently, it is of interest to determine what reactions can occur in ternary systems derived from the Sn-Zn eutectic. One such system is Cu-Sn-Zn. This paper reports a number of experimentally determined reactions that occur in Sn-rich alloys of this ternary system.

In the expectation of a possible connection between the Sn-Cu_6Sn_5 and Sn-Zn binary eutectics, several alloy compositions were selected along a possible joining path. Samples of each were solidified unidirectionally at a very slow rate, approximating freezing with complete mixing in the liquid (the "Solidification Path" technique). This procedure allows detection of reactions by the change in the phases frozen out with change in composition of the liquid due to segregation. Three quasiperitectic reactions (U_1-U_3) and a ternary eutectic reaction were found:

U_1: $L+Cu_6Sn_5 \leftrightarrow CuZn+Sn$
U_2: $L+CuZn \leftrightarrow Cu_5Zn_8+Sn$
U_3: $L+Cu_5Zn_8 \leftrightarrow CuZn_4+Sn$
E: $L \leftrightarrow (Sn)+(Zn)+CuZn_4$

It is shown theoretically and confirmed experimentally that each of these three quasiperitectic reactions can produce, on a copper substrate, the undesirable effect known as "spalling" in which multiple layers of different phases are formed at the solder-substrate interface during freezing.

Key words: Lead-Free solder, Cu-Sn-Zn system, quasiperitectic reaction, microstructure

INTRODUCTION
With the banning of Pb as a component in solder alloys, much effort has been directed at finding an acceptable replacement for the traditional eutectic Pb-Sn solder alloy previously used in the assembly of electronic components. For reasons of cost, melting point and abundance, the element Sn has been accepted as the only feasible major component of solder alloys. However, the melting point of Sn (232^oC) is substantially higher than that of eutectic Pb-Sn alloy (183^oC), by an amount sufficient to cause damage to heat-sensitive electronic components being soldered. As a result, it is necessary to add alloying elements to Sn to lower the melting point and consequent soldering temperature to an acceptable level. The most popular alloys of this type are the SAC alloys, which contain Ag and Cu and are based on the Ag-Cu-Sn ternary eutectic composition at 0.9 wt% Cu, and 3.5 wt% Ag (balance Sn) with a eutectic temperature of 217^oC. However, problems are sometimes still encountered, due to the relatively high soldering temperatures required, in the mounting of heat-sensitive components using these alloys. As an alternative, the Sn-Zn eutectic alloy, at 9 wt% Zn, 91 wt% Sn, with a melting point of 199^oC, offers substantially lower soldering temperatures than those required for the SAC alloys. However, the use of this alloy has been limited as a result of fears that the higher sensitivity of Zn to oxidation would cause problems, such as poor wetting, during soldering. Nevertheless, Zn-containing solder alloys have been used successfully (1, 2) in the assembly of electronic components and it appears likely that more use of such solders will be made in the future, especially with the addition of a small amount of Al (~100 ppm) to control oxidation of the Zn component. During soldering processes, dissolution of the substrate material, such as Cu or Ni, on which the joint is being made, results in the addition of a third element to the liquid solder. Therefore, it is desirable, for a new ternary solder alloy, to obtain information concerning the possible occurrence of phase equilibria and the corresponding reactions, such as the quasiperitectic reaction, that do not occur in binary systems, but often occur during freezing in ternary systems, influencing the microstructure formed. In particular, it has been reported (3, 4) that the quasiperitectic reaction is responsible for the occurrence of an undesirable effect known as "spalling" (5) during freezing. It is the purpose of the work reported here to examine such an alloy system, possibly created by dissolution from a copper substrate, forming alloys in the Sn corner of the Cu-Sn-Zn ternary system.

BACKGROUND
While Cu-Sn alloys (bronzes) and Cu-Zn alloys (brasses) have been known and used for many years, it is only recently,

with the requirement for Pb-free solder alloys that the Sn-rich region of the ternary Sn-Cu-Zn alloy system has become of interest. In this regard, Chou and Chen (6) have recently determined experimentally three isotherms of the ternary system, at 250°C, 230°C and 210°C. In particular, some detail is shown in their isotherm at 230°C for alloys containing more than 90 at% Sn. While useful in showing what phases exist in regions near the Sn corner, these isotherms do not, however, show what can happen during freezing of various alloys in this region: for this purpose, a liquidus projection is required.

That the solidification behaviour of alloys near the Sn corner must be complex can be seen, starting from a consideration of the binary Sn-Cu and Sn-Zn systems. In the Sn-Cu system, there is a eutectic reaction, $L \leftrightarrow Cu_6Sn_5 + Sn$, at 0.9wt% Cu and 227°C. In the Sn-Zn system, there is a eutectic reaction, $L \leftrightarrow Zn + Sn$, at 9.0wt% Zn and 199°C. Each of these invariant binary reactions must continue in monovariant form into the ternary system and it is probable that they will join, in some form, in that system. The transition from one monovariant binary eutectic to the other cannot be continuous, because Cu_6Sn_5 and Zn do not have the same crystal structure. As a result, there must be one or more reactions on the path from one binary eutectic to the other.

In the 230°C isotherm (Figure 1) of the paper by Chou and Chen (6) is shown the intersection of three monovariant binary equilibria with the isothermal section of the ternary system, suggesting that the corresponding reactions must all be matched to a potential monovariant eutectic valley joining the two invariant binary eutectic reactions and indicating additional complexity in the ternary diagram.

EXPERIMENTAL PROCEDURE

A "solidification path" technique was used to investigate experimentally possible reactions that can occur in this portion of the ternary alloy system. For this purpose, several alloy melts, each weighing approximately 10 grams, were prepared having various compositions near a possible eutectic valley running from the Cu_6Sn_5-Sn binary eutectic point to the Sn-Zn binary eutectic point. Each melt was cast into a graphite mold measuring 17 by 55 mm, and a graphite insert was used to spread the melt into a thin layer, allowing it to freeze into a casting about 1-2mm in thickness. Each sample produced in this way was cut into three sections, which were placed, with spacers between them, in a boron nitride cell in which they were remelted and allowed to freeze unidirectionally at a speed of approximately 4mm per day, with a steep temperature gradient in the liquid. Solidification under these conditions allowed an approximation to complete mixing in the liquid (sometimes referred to as "Scheil freezing" (7)). As a result of solute segregation during freezing, solidification under these conditions allows the detection of phase transformations that can occur during freezing, as the solid phases formed vary during progressive solidification due to the composition change of the liquid.
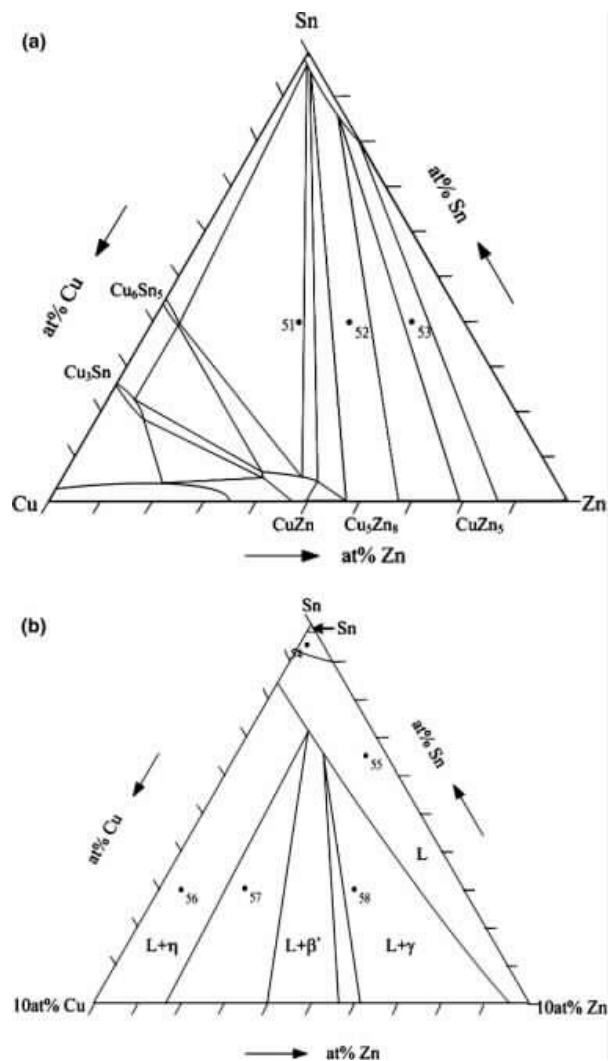
Figure 1: Isotherm of the Cu-Sn-Zn alloy system at 230°C (after Chou and Chen (6)). Note three monovariant binary equilibria shown in this diagram.

In addition to the directionally solidified samples, cooling curves were obtained during freezing of a number of five-gram samples. These cooling curves allowed measurement of the reaction temperatures, as indicated by temperature arrests, of the various transformations that occurred during cooling.

Experiments were carried out in order to determine whether the phenomenon of "spalling", in which regions of different compound phases are formed on the substrate during freezing of a solder joint, occurred during freezing of certain alloys of this system. This was done by melting small samples, with flux, on a copper substrate, holding at 240°C for 60 seconds or 120 seconds, then allowing them to freeze. The samples were mounted in epoxy for metallography. For samples such as these, if it is desired to maintain the Zn phase at the polished surface, it is then necessary during metallography to avoid the use of water, which will lead to electrochemical corrosion of the zinc phase, thereby removing it from the surface of the polished section. For this reason, the polishing
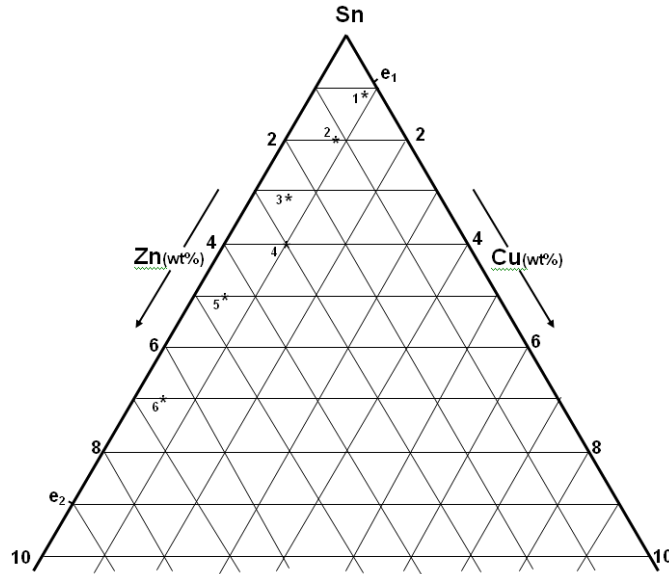
Figure 2: Compositions of samples selected to be near expected monovariant reaction path from binary eutectic e_1 to binary eutectic e_2.

Table 1: Summary of phases formed in Cu-Sn-Zn alloy system

Sample Number	Composition (wt%)			Initial Freezing	Reaction Indicated	Later Freezing
	Cu	Sn	Zn			
1	0.9	98.8	0.3	$L \leftrightarrow Cu_6Sn_5 + Sn$	$L + Cu_6Sn_5 \leftrightarrow CuZn + Sn$	$L \leftrightarrow CuZn + Sn$
2	0.9	98.1	1.0	$L \leftrightarrow CuZn + Sn$	$L + CuZn \leftrightarrow Cu_5Zn_8 + Sn$	$L \leftrightarrow Cu_5Zn_8 + Sn$
3	0.6	96.9	2.5	$L \leftrightarrow Cu_5Zn_8 + Sn$	$L \leftrightarrow Cu_5Zn_8 + Sn$	$L \leftrightarrow Cu_5Zn_8 + Sn$
4	1.0	96.0	3.0	$L \leftrightarrow Cu_5Zn_8 + Sn$	$L + Cu_5Zn_8 \leftrightarrow CuZn_4 + Sn$	$L \leftrightarrow CuZn_4 + Sn$
5	0.5	95.0	4.5	$L \leftrightarrow Cu_5Zn_8 + Sn$	$L + Cu_5Zn_8 \leftrightarrow CuZn_4 + Sn$	$L \leftrightarrow CuZn_4 + Sn$
6	0.5	93.0	6.5	$L \leftrightarrow CuZn_4 + Sn$	$L \leftrightarrow Sn + Zn + CuZn_4$	$L \leftrightarrow Sn + Zn + CuZn_4$

stages were sometimes done with 6µm and 1µm diamond with oil lubrication. Otherwise, the samples were finished with colloidal silica.

Samples were examined in both optical and scanning electron microscopes. Phases were identified by EDX analysis in the SEM.

EXPERIMENTAL OBSERVATIONS
Six sample compositions were selected, in the region between the two binary eutectics $L \leftrightarrow Cu_6Sn_5 + Sn$ and $L \leftrightarrow Sn + Zn$.

The compositions of these samples are shown in Figure 2, along with the Cu_6Sn_5-Sn (e_1) and Zn-Sn (e_2) binary eutectic points. The phases formed in each sample during slow unidirectional freezing are listed in Table 1. The reactions responsible for the introduction of the new phases during unidirectional freezing, as indicated by the phases formed, are listed in the last column of Table 1. It will be noted that three of these reactions are of the quasiperitectic type.
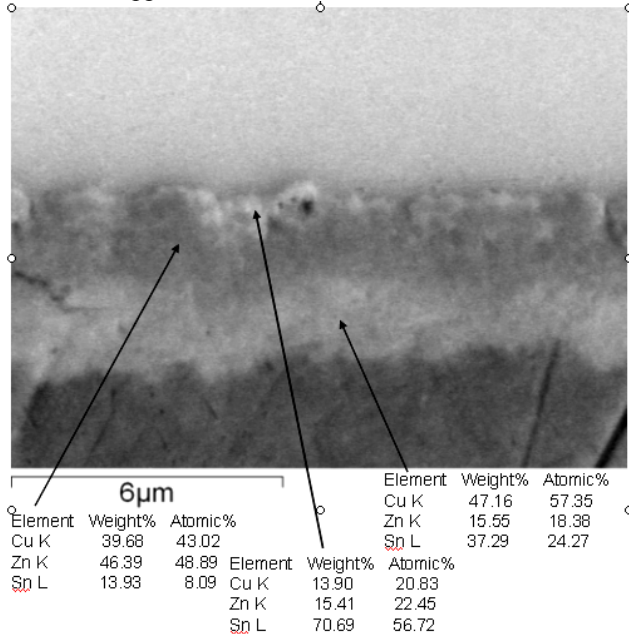
The reactions observed indicated a transition from e_1 to e_2 along a monovariant reaction valley characterized by three quasiperitectic reactions, as the solidifying phases change with falling temperature. This confirmed the original assumption of a monovariant valley from e_1 to e_2 and includes the complexity suggested by the isothermal sections of Chou and Chen (6). The reactions are identified as listed in Table 1. The locations of the three quasiperitectic reactions were determined approximately from the cooling curves measured on the five-gram castings. A temperature arrest gave the temperature of each transformation. The location of the monovariant reaction valley was further obtained from measurement of the copper content of the Sn phase present in a number of samples, giving a value of 0.23 ±0.07 wt% except near the Cu_6Sn_5-Sn and Sn-Zn binary eutectic points. The result is shown in Figure 3. It is estimated that the quasiperitectic reaction points are accurate to ±0.5 wt% in Zn content. The primary phase regions are also indicated in Figure 3.
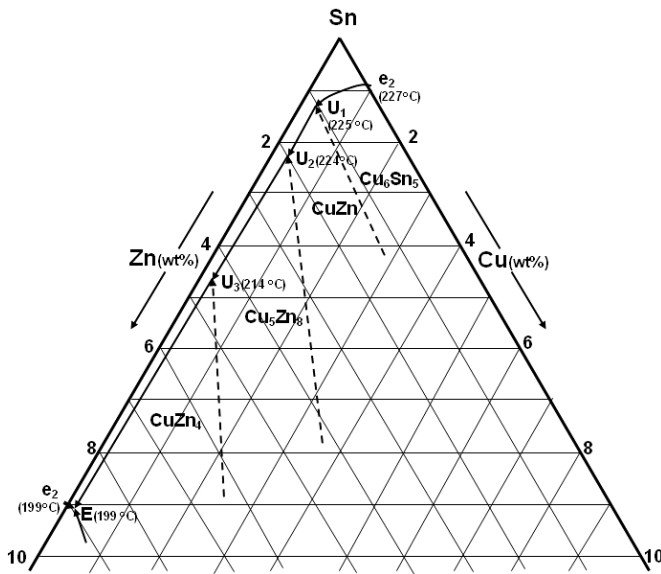
Figure 3: Sn corner of the Cu-Sn-Zn liquidus projection, showing the locations of the three quasiperitectic reactions found in the current study. Regions of primary solidification are also shown.

Experiments carried out to check for spalling were done using sample compositions near the quasiperitectic points U_1, U_2, and U_3. In each case, spalling was observed, as illustrated in Figures 4 and 5 for reaction U_1 and Figure 6 for reaction U_2. The sample illustrated in Figure 4 had the composition 1 wt% Zn, 99 wt% Sn, and was melted with flux on a copper substrate.

Element	Weight%	Atomic%
Cu K	47.16	57.35
Zn K	15.55	18.38
Sn L	37.29	24.27

Element	Weight%	Atomic%
Cu K	39.68	43.02
Zn K	46.39	48.89
Sn L	13.93	8.09

| Element	Weight%	Atomic%
Cu K	13.90	20.83
Zn K	15.41	22.45
Sn L	70.69	56.72

Figure 4: Spalling formed during freezing on a copper substrate of a sample having the original composition 99wt% Sn, 1wt% Zn. Note primary Cu_6Sn_5 phase and two product phases, CuZn and Sn, of the reaction U_1.
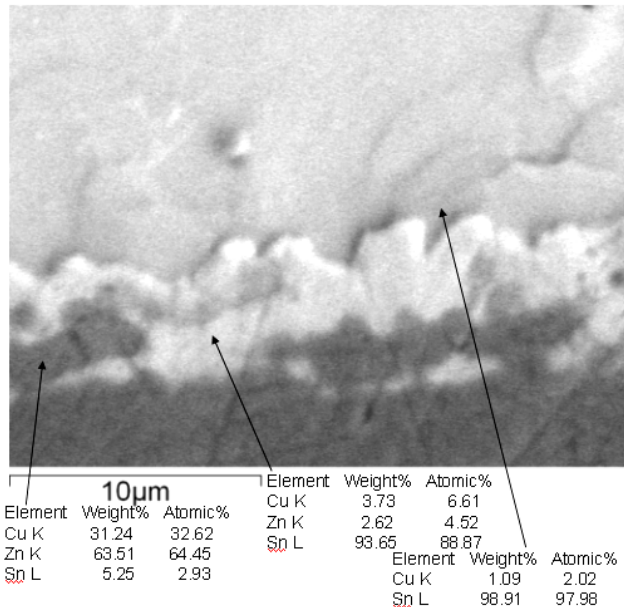
Dissolution of copper from the substrate gave this sample a composition near that of reaction U_1. As seen in Figure 4, a layer of the primary phase, Cu_6Sn_5, of this reaction (see Table 1) was formed on the copper substrate, followed by deposition of layers of the two reaction products, CuZn and Sn. That the quasiperitectic reaction occurred throughout the solder is shown by the partial conversion of a particle of Cu_6Sn_5 in the solder, as illustrated in Figure 5.

The sample shown in Figure 6 had the composition 0.5 wt% Cu, 2.0 wt% Zn, 97.5 wt% Sn, near that of reaction U_2, and was melted with flux on a copper substrate.

| Element	Weight%	Atomic%
Cu K	5.10	8.97
Zn K	2.17	3.71
Sn L	92.74	87.33
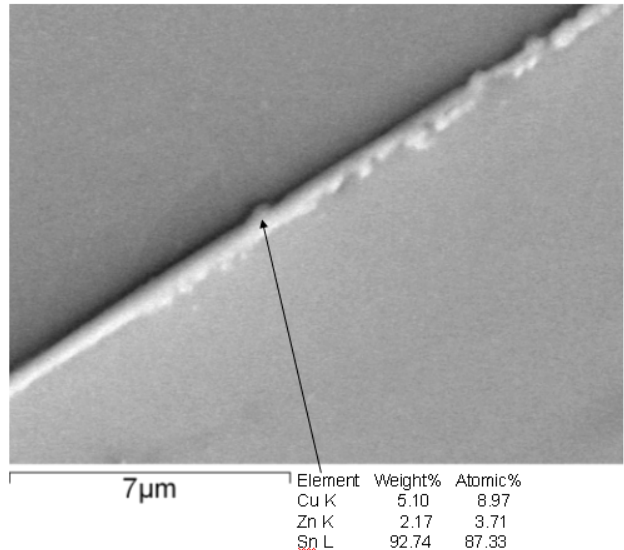
Figure 5: Partial transformation of a particle of Cu_6Sn_5 phase in the bulk of the solder, due to the quasiperitectic reaction U_1, illustrating operation of this reaction in the bulk of the solder.

Element	Weight%	Atomic%
Cu K	3.73	6.61
Zn K	2.62	4.52
Sn L	93.65	88.87

Element	Weight%	Atomic%
Cu K	31.24	32.62
Zn K	63.51	64.45
Sn L	5.25	2.93

Element	Weight%	Atomic%
Cu K	1.09	2.02
Sn L	98.91	97.98

Figure 6: Spalling formed during freezing on a copper substrate of a sample having the composition 0.5wt% Cu, 97.5wt% Sn, 2.0wt% Zn. Spalling in this case was due to quasiperitectic reaction U_2.

As seen in Figure 6, primary CuZn phase (Table 1) was formed, with the product phase Cu_5Zn_8, corresponding to reaction U_2, also present, showing operation of the quasiperitectic reaction. The sample illustrated in Figure 7 had the composition 0.5 wt% Cu, 5.0 wt% Zn, 94.5 wt% Sn, near U_3. The operation of reaction U_3 resulted in the formation of a very complex solder-substrate interface, as illustrated in Figure 7.
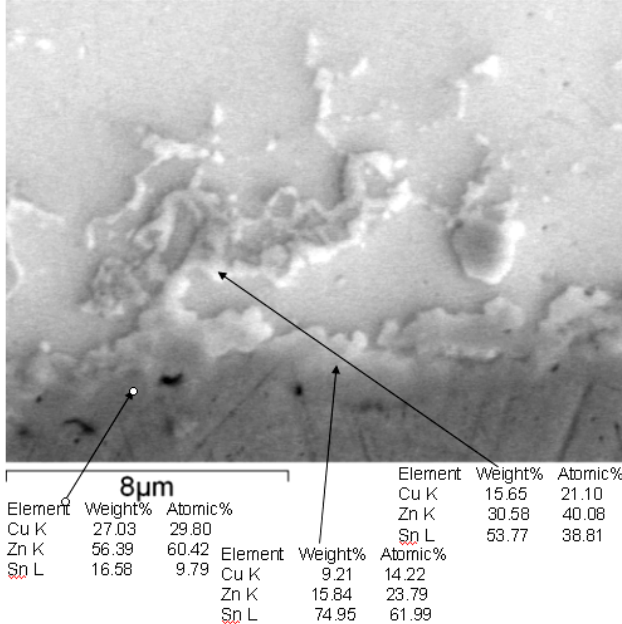

Figure 7: Extreme spalling formed during freezing on a copper substrate of a sample having the composition 0.5wt% Cu, 94.5wt% Sn, 5.0wt% Zn. Spalling due to quasiperitectic reaction U_3.

These observations confirm the conclusion that the spalling phenomenon results from the action of a quasiperitectic reaction during freezing of the ternary alloy.

DISCUSSION
In a usual soldering operation, such as the formation of a joint made with eutectic Pb-Sn solder or a Sn-Ag-Cu solder on copper, one intermetallic compound layer is formed on the substrate during freezing of the solder. In the case of Pb-Sn solder on copper the compound formed is Cu_6Sn_5: no further reaction involving the liquid takes place during freezing of the solder. However, in some cases, additional reaction can occur, as illustrated by the phenomenon of "spalling", in which multiple layers are formed on the substrate as a result of continued reaction of the compound layer with the liquid. For this to occur, after deposition of the initial layer, a change in the composition of the liquid must take place, due to segregation during freezing, in such a manner that it permits deposition of a different phase or phases on the substrate. To show the part that can be played during freezing by a ternary reaction to produce such a composition change, consider the operation of a quasiperitectic reaction.
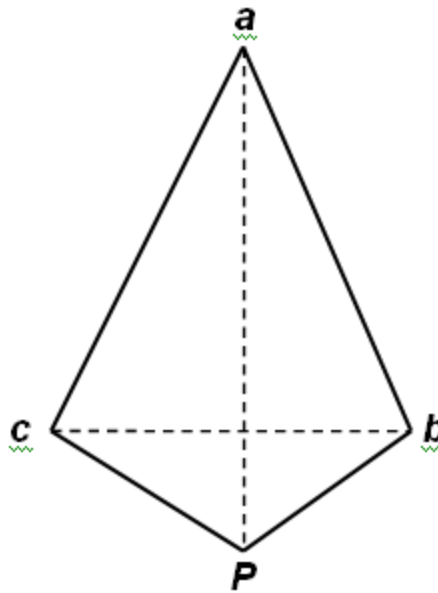
Figure 8: Form of the quasiperitectic equilibrium as seen on the four-phase isothermal reaction plane.

As illustrated in Figure 8, the quasiperitectic equilibrium is characterized by the presence of four tie triangles, representing monovariant equilibria, two of which, *abP* and *acP*, descend from higher temperatures to the invariant four-phase equilibrium plane and two of which, *abc* and *bcP*, descend from the equilibrium plane to lower temperatures (8). On cooling of a sample having a composition within the four-phase quadrilateral *abPca* from the completely liquid state the following events will occur. On intersecting the liquidus surface, the solid phase α, corresponding to the point *a* of the quadrilateral, will begin to form. As the temperature continues to fall, more α phase is formed and, owing to solute segregation, the composition of the remaining liquid moves toward point *P*. If the initial sample composition lies on the *aP* line, the composition of the primary phase, α, will reach point *a* when the composition of the remaining liquid reaches point *P*. With additional heat extraction, the quasiperitectic reaction, L+α↔β+γ will then take place, at constant temperature, forming the product phases, β and γ, corresponding to points b and c, respectively. If the sample composition lies in the region *abc*, all of the liquid will be consumed by the reaction and some α phase will remain. If the sample composition lies in the region *bPc*, all of the α phase will be consumed and some liquid will remain, to freeze by a monovariant three-phase reaction at lower temperatures. If the original sample composition lies off the *aP* line, then the final segregation of the liquid composition to the quasiperitectic point *P* is achieved by a three-phase monovariant reaction involving the liquid, the primary phase, α, and one of the two possible product phases. The quasiperitectic reaction can then occur, with the introduction of the other product phase, completing the reaction. It is seen, therefore, that the quasiperitectic reaction is preceded by the formation of a primary solid phase and then leads to the introduction of two additional solid phases. Thus, the occurrence of a quasiperitectic reaction provides the required mechanism for the

introduction of two additional phases on the solder substrate during solidification of the solder.

The amount of isothermal quasiperitectic reaction that will occur depends on the composition of the original alloy in relation to the quasiperitectic quadrilateral. If near the composition of the primary phase, much primary will be formed and little reaction will occur, because there will be much solid and little liquid remaining at the isothermal reaction temperature. If the sample composition is near that of the quasiperitectic liquid, there will be little isothermal reaction because only a small amount of primary phase will be formed, to be quickly consumed by the reaction, leaving much liquid to freeze at lower temperatures. Maximum isothermal reaction will occur for the sample composition that results in reaction of all of the primary phase with all of the liquid phase.
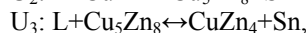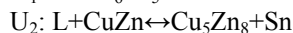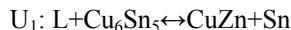
The Sn corner of the Cu-Sn-Zn system can be compared with that of the Cu-Ni-Sn system, reported previously (9). These alloy systems are similar in that both show a series of quasiperitectic reactions, involving intermetallic compound phases, lying on a reaction valley joining two binary eutectic reactions. The Cu-Sn-Zn system is the more complex of the two, due to the presence of more compound phases in that system.

When a solder of the SAC type is used on nickel, some nickel is dissolved from the substrate into the liquid solder, forming the Cu-Ni-Sn alloy system. (The Ag component of the solder is inert with respect to "spalling"). As noted in an earlier paper (4) the "spalling" phenomenon can be accounted for as due to the action of one of the quasiperitectic reactions in this system. The "spalling" phenomenon has been reported (10) to occur also when Sn-Zn solders are used on a copper substrate. In this case, during the soldering operation, Cu is dissolved into the liquid from the substrate, forming the Cu-Sn-Zn alloy system and thereby introducing the possibility of ternary phase reactions. The "spalling" phenomenon that has been reported (10) in this system results from the action of the quasiperitectic reaction U_1, as shown in the present paper. In addition, as shown in the present study, the spalling phenomenon can occur whenever there is the possibility of a quasiperitectic reaction occurring during freezing of the solder alloy, confirming the conclusion that it provides the mechanism that causes the spalling phenomenon. As shown in Figure 7, the introduction of additional phases can sometimes result in the formation of complex solder-substrate interface microstructures.
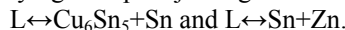
The formation of multiple layers of different phases during freezing of a solder joint in the ternary solder alloys of the present investigation forms an illustration of the fact that solidification reactions that occur in ternary and higher order systems, in addition to those that take place in binary systems, must be taken into account in considerations of the formation of microstructure during freezing in such alloys.

SUMMARY

1. The Sn corner of the Cu-Sn-Zn alloy system is characterized by the presence of three quasiperitectic reactions
U_1: $L+Cu_6Sn_5 \leftrightarrow CuZn+Sn$
U_2: $L+CuZn \leftrightarrow Cu_5Zn_8+Sn$
U_3: $L+Cu_5Zn_8 \leftrightarrow CuZn_4+Sn$,
lying on a path joining the two binary reactions
$L \leftrightarrow Cu_6Sn_5+Sn$ and $L \leftrightarrow Sn+Zn$.
2. Each of the quasiperitectic reactions is capable of producing the spalling phenomenon when used in making a solder joint on a copper substrate, provided that the solder composition lies within the appropriate quasiperitectic quadrilateral.
3. The fact that all quasiperitectic reactions of this alloy system are capable of producing spalling confirms the conclusion that this reaction is the cause of the spalling effect

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