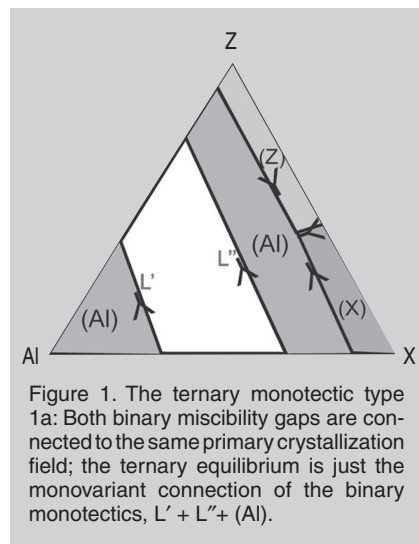# Phase Transformations in Ternary Monotectic Aluminum Alloys

Joachim Gröbner and Rainer Schmid-Fetzer

Monotectic aluminum alloys are of interest for the development of new alloys for technological applications such as self-lubricating bearings. In contrast to the well-known binary phase diagrams, many of the ternary systems are not well established. Moreover, in a ternary monotectic alloy one may encounter the four-phase equilibrium L′ + L″ + solid₁ + solid₂, whereas in a binary system only a three-phase equilibrium L′ + L″ + solid₁ is possible. This opens a window for generating entirely new monotectic microstructures. The basis for such developments is the knowledge of the ternary phase diagrams and the conditions under which such four-phase reactions or different extensions of the binary monotectic reactions may form. This work presents a systematic classification of monotectic ternary aluminum alloys, illustrated by real systems. The study employs thermodynamic calculations of the ternary phase diagrams.

INTRODUCTION

Monotectic alloys offer several possibilities for the development of new alloys for technological applications such as self-lubricating bearings.[1,2] Beyond such promising applications, these alloys are of scientific interest because of their very interesting microstructures during solidification. These microstructures comprise two different solidified liquids and, therefore, two parts differing in phase content and properties. This work focuses on ternary systems containing aluminum. This choice was made since numerous binary aluminum systems with immiscibility in liquid exist and these alloys have numerous practical applications.

In contrast to binary monotectic systems, systematic studies of ternary metallic monotectic alloys are scarce. In a classical work, Meijering[3] showed the existence of an isolated ternary miscibility gap by thermodynamic calculations if the interaction parameters of one binary system are much more negative than in the two others. Butt and Bodsworth proposed two models for predicting liquid immiscibility in ternary metallic alloys.[4] Their focus was on ternary immiscibilities occurring at complete liquid miscibility in binary subsystems. The investigation of ternary monotectic reactions was not considered by their work. This is, however, probably the most interesting aspect when extending binary to ternary alloys. The binary monotectic reaction L′ = L″ + solid may extend quite differently into a ternary system. Even nonvariant four-phase equilibria, L′ + L″ + solid₁ + solid₂, are possible in the ternary in contrast to the binary three-phase reaction. This opens a window for entirely new microstructures.

This work presents a systematic classification of monotectic ternary aluminum alloys, illustrated by real systems. This study employs thermodynamic calculations of the ternary phase diagrams, an approach that offers essential advantages not only for the relatively fast screening of a larger number of systems but also for the more detailed study of the solidification equilibria.

THERMODYNAMIC CALCULATION

The phase diagrams were calculated by the Calphad method,[5] some recent

Figure 1. The ternary monotectic type 1a: Both binary miscibility gaps are connected to the same primary crystallization field; the ternary equilibrium is just the monovariant connection of the binary monotectics, L′ + L″+ (Al).

	Table I. Systematic Overview of Ternary Monotectic Aluminum Systems					
	Binary Liquid Miscibility Gap			**Schematic Phase Diagram Given**	**Real Example**	**Ternary Monotectic Four-Phase**
Type	**Al-X**	**Al-Z**	**X-Z**	**in Figure**	**Al-X-Z**	**Reactions**
1a	Stable	Stable	None	1	Al-Bi-Pb Al-Bi-In Al-Pb-In	No
1b	Stable	Metastable	None	3	Al-Bi-Sn Al-Pb-Sn	No
2a	Stable	None	Stable	5	Al-Bi-Zn Al-Pb-Zn Al-Pb-Cu	Yes
2b	Stable	None	Metastable	8	Al-Bi-Cu Al-Bi-Ag* Al-In-Zn*	Yes
2c	Stable	None	None	8	Al-In-Cu	Yes
3a	None	None	Metastable	10	Al-Sn-Cu	Yes
3b	None	None	None	10	Al-Mg-Sc	Yes

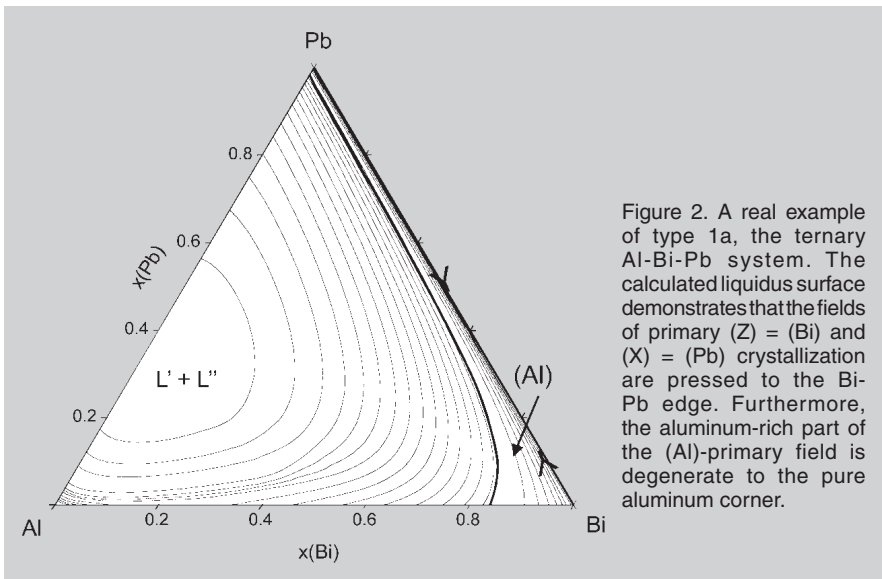* Both Al-Z and X-Z exhibit metastable binary liquid miscibility gaps.

Figure 2. A real example of type 1a, the ternary Al-Bi-Pb system. The calculated liquidus surface demonstrates that the fields of primary (Z) = (Bi) and (X) = (Pb) crystallization are pressed to the Bi-Pb edge. Furthermore, the aluminum-rich part of the (Al)-primary field is degenerate to the pure aluminum corner.

developments of which are summarized by Chang et al.[6] All calculations were performed using *Pandat* software.[7,8] A particular strength of this software is the automatic detection of miscibility gaps. The starting point of the present thermodynamic data is formed by four ternary systems taken from the Adamis database.[9] This database was expanded by the binary aluminum systems from the literature. Published parameters were used for the binary subsystems Al-Cu,[10] Al-Pb,[11] Al-In,[12] Al-Sn,[13] and Cu-Sn.[14] The thermodynamic descriptions of the ternary Al-Mg-Sc[15] and Al-Bi-Zn[16] systems are described in detail in previous

publications. The Gibbs energy of the ternary liquid phase was extrapolated in all systems using the Redlich-Kister/Muggianu-type extrapolation from the binary sets; all the equations are given in an earlier work.[17]

SYSTEMATIC CLASSIFICATION OF TERNARY MONOTECTIC ALLOYS

The following systematic classification is quite general for ternary monotectic alloys. It is presented with respect to aluminum-based systems just to enable an easier connection to the real alloy examples. Monotectic aluminum systems can be categorized into three different types according to their basic character:

- Type 1: A ternary miscibility gap (L′ + L″) starting from one or two

binary systems without generating a ternary monotectic four-phase reaction
- Type 2: A similar ternary miscibility gap (L′ + L″), but forming a ternary monotectic four-phase reaction (non-variant)
- Type 3: A miscibility gap (L′ + L″) occurring only in the ternary system

These three types can be divided into several subgroups, as given in Table I.

Type 1

In type 1a, illustrated in Figure 1, both binary miscibility gaps of the liquid phase are connected to the same field of primary crystallization, denoted as (Al). Therefore the ternary equilibrium is just the monovariant connection of the binary monotectics, L′ + L″ + (Al). The temperature range of this monovariant L′ + L″ + (Al) equilibrium is typically given by the binary monotectic temperatures. However, a maximum or minimum along this monovariant is also possible. It is most important that no invariant four-phase reaction involving the two liquids occurs.

Real ternary systems displaying this feature are Al-Bi-Pb, Al-Bi-In, and Al-Pb-In. Figure 2 shows the liquidus surface of the Al-Bi-Pb system. The miscibility gap of the liquid dominates the liquidus surface. The primary crystallization fields of (Pb) and (Bi) are degenerate to the binary Bi-Pb edge. Even the (Al) field in the aluminum-rich corner is degenerate to the one point of virtually pure aluminum.
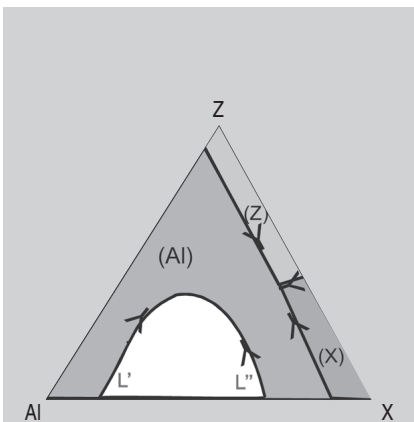
A variant of this type is depicted in

Figure 3. The ternary monotectic Type 1b: the miscibility liquid gap closes in the ternary system cutting only one primary crystallization field. The monovariant equilibrium is again L′ + L″ + (Al). Often the liquid gap in the binary Al-Z edge is metastable and hidden beneath the (Al) liquidus line.
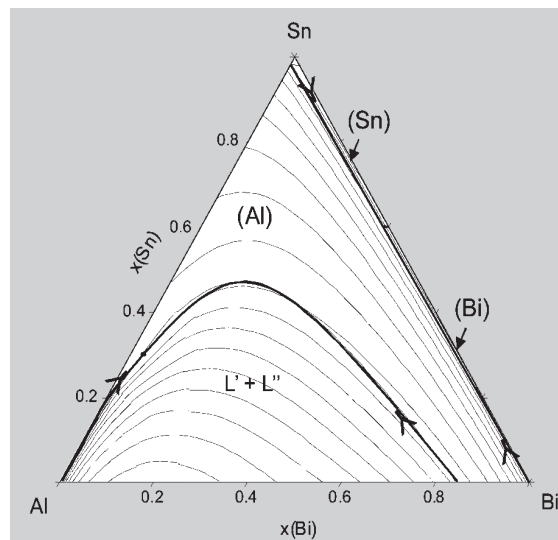

Figure 4. A real example of type 1b, the ternary Al-Bi-Sn system as displayed in the calculated liquidus surface. The monotectic reaction manifests itself only in a monovariant equilibrium, L′ + L″ + (Al) which, in contrast to Figure 2, ends in a critical point at Al66-Bi02-Sn32 (at.%) and 611°C (estimated). This closing of the ternary miscibility gap is related to the fact that the liquid gap in the binary Al-Sn edge is metastable with a critical point of the L′ + L″ equilibrium at Al78-Sn22 (at.%) and 536°C.
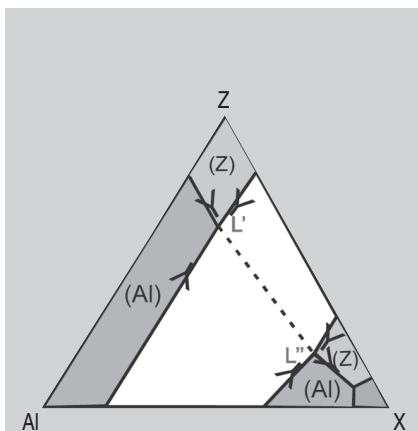
Figure 5. The ternary monotectic type 2a. The miscibility gap in the liquid phase is connected to two different fields of primary crystallization. Therefore, a monotectic four-phase equilibrium L′ + L″ + (Al) + (Z) occurs that is nonvariant. The most important tie line L′ + L″ of this invariant is shown as a dashed line. Both binary liquid gaps, Al-X and X-Z, are stable.

Figure 3, type 1b, where the liquid gap closes in the ternary system. The liquid gap on the opposite Al-Z edge may be metastable and hidden beneath the (Al) liquidus or not existing. This generates a critical point of the L′ + L″ + (Al) equilibrium in a temperature minimum where the two liquids merge. Again, no invariant four-phase reaction involving the two liquids occurs.

This behavior of type 1b is observed in the Al-Bi-Sn and Al-Pb-Sn systems. As an example, the Al-Bi-Sn liquidus surface is given in Figure 4. In this case the miscibility gap closes in the ternary, because the binary gap in the Al-Sn system is metastable. The aluminum-rich primary field of (Al) crystallization appears as shrinking to a narrow line, almost degenerate to the Al-Sn edge. In contrast to type 1a, where the primary field of (Al) is separated in two parts, it is contiguous in type 2b, which is more clearly visible in a comparison of Figures 1 and 3.

Type 2

In type 2, the liquid phase miscibility gap intersects two different fields of primary crystallization. This results in a four-phase equilibrium L′ + L″ + (Al) + (Z), as depicted in Figure 5. This nonvariant equilibrium offers most interesting possibilities for the synthesis of new

solidification microstructures that are not possible in binary monotectic systems. The nonvariant monotectic equilibrium may occur in three basically different reaction types. A eutectic type, L′ = L″ + (Al) + (Z), was assumed in the schematic shown in Figure 5. With sufficiently large solid solubilities, a transition type, L′ + (Al) = L″ + (Z), or even a peritectic type, L′ + (Al) + L″ = (Z), is in principle also possible. The eutectic type was found in the two real aluminum alloys described here and may be denoted as the monotectic ternary reaction. The transition type was actually found in real aluminum alloys, but based on intermetallic phases and not on extended solid solubilities, as detailed later in subtype 2b.

In subtype 2a, the binary system X-Z displays a stable immiscibility of the liquid phase. The resulting liquidus surface is shown in Figure 5. This type was detected in the real system Al-Bi-

Zn.[16] The ternary monotectic invariant reaction L′ = L″ + (Al) + (Zn) is calculated and measured around 376°C, 5 K below the binary Al-Zn eutectic. The decomposing liquid L′ contains about 2 at.% bismuth and therefore a measurable amount of L″ is produced in the eutectic-type reaction. Figure 6 shows the calculated liquidus surface, which is also supported by experimental data in this recent investigation.[16]

A second example of this type is found in the Al-Pb-Zn system (Figure 7). However, the liquid gap is much wider and, thus, the lead-poor primary crystallization fields of (Al) and (Zn) are almost degenerate to the Al-Zn binary edge. Therefore, even though the invariant reaction L′ = L″ + (Al) + (Zn) at 380.1°C exists, it is almost degenerate to the binary Al-Zn eutectic. The lead-rich liquid L″ is virtually not involved in the formed phase amounts, since the liquid
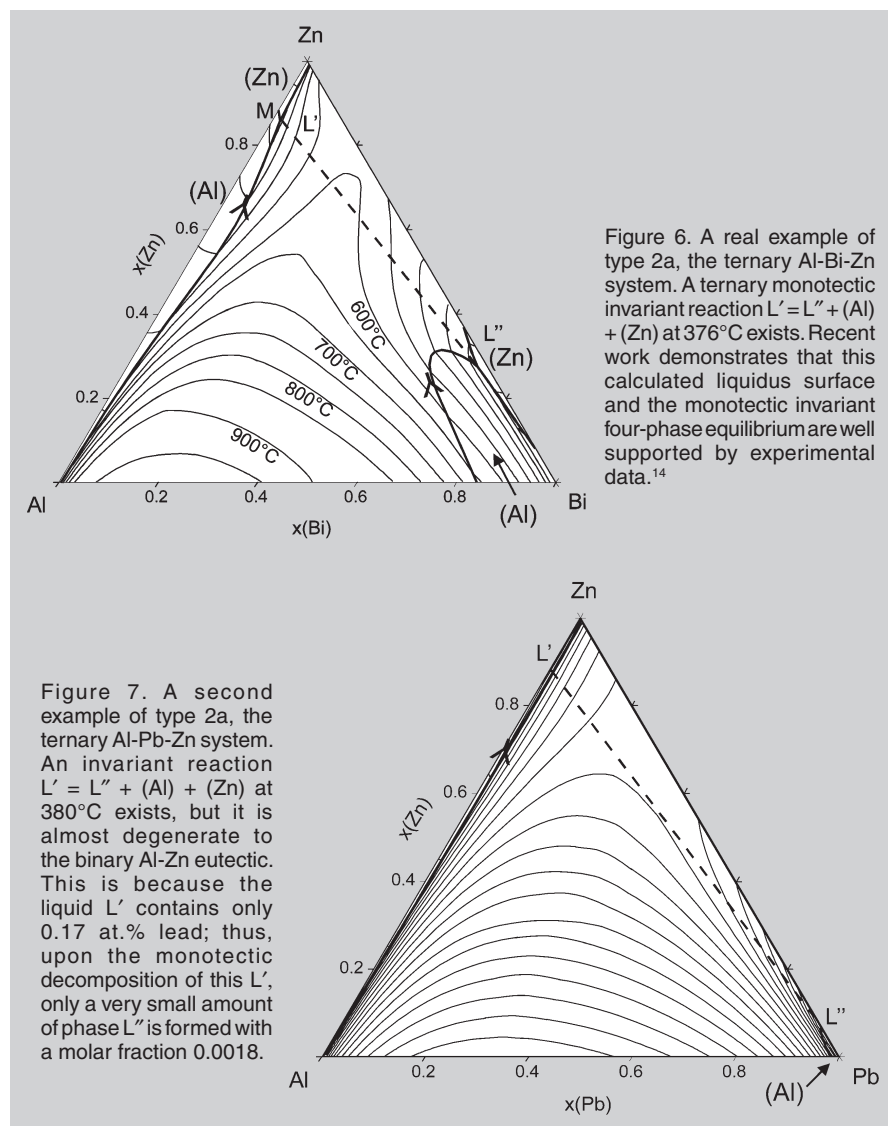

Figure 6. A real example of type 2a, the ternary Al-Bi-Zn system. A ternary monotectic invariant reaction L′ = L″ + (Al) + (Zn) at 376°C exists. Recent work demonstrates that this calculated liquidus surface and the monotectic invariant four-phase equilibrium are well supported by experimental data.[14]

Figure 7. A second example of type 2a, the ternary Al-Pb-Zn system. An invariant reaction L′ = L″ + (Al) + (Zn) at 380°C exists, but it is almost degenerate to the binary Al-Zn eutectic. This is because the liquid L′ contains only 0.17 at.% lead; thus, upon the monotectic decomposition of this L′, only a very small amount of phase L″ is formed with a molar fraction 0.0018.
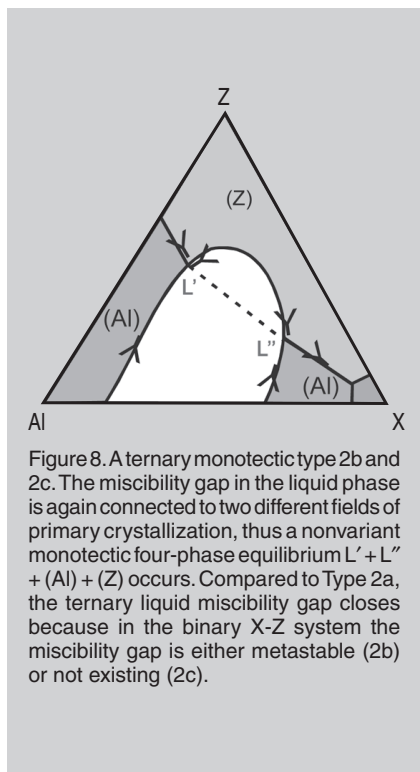
Figure 8. A ternary monotectic type 2b and 2c. The miscibility gap in the liquid phase is again connected to two different fields of primary crystallization, thus a nonvariant monotectic four-phase equilibrium L′ + L″ + (Al) + (Z) occurs. Compared to Type 2a, the ternary liquid miscibility gap closes because in the binary X-Z system the miscibility gap is either metastable (2b) or not existing (2c).

L′ contains only 0.17 at.% lead. Also, the four-phase reaction temperature is almost identical to that of the binary eutectic L′ = (Al) + (Zn) at 380.9°C.[16] As a consequence, the solidification microstructure is not expected to display the new features related to a four-phase compared to the binary three-phase reactions. It is interesting to note that such a nonvariant equilibrium L′ + L″ + (Al) + (Z) was only detected in the two examples shown in Figures 6 and 7 if the search is confined to aluminum-alloy systems containing no intermetallic phases.

In subtype 2b the binary miscibility gap in X-Z is metastable and in subtype 2c it does not exist. The separation may be difficult if the critical temperature of the metastable binary gap is extremely low. In both cases the liquid miscibility gap must close in the ternary system, as depicted in Figure 8. The key point is that the liquid gap still intersects more than one primary field, thus producing the L′ + L″ + (Al) + (Z) equilibrium. If intermetallic compounds exist in the Al-Z binary system, their primary crystallization fields may also intersect the ternary liquid gap, producing even more four-phase equilibria. This is the case for many real aluminum-alloy systems.

Examples for subtype 2b are Al-Bi-Cu, Al-Bi-Ag, and Al-In-Zn. Examples for subtype 2c are the Al-In-Cu, Al-In-Sn, Al-Pb-Ag, and Al-Pb-Sn systems. Figure 9 shows the calculated liquidus surface of the Al-In-Cu system. Six ternary invariant reactions involving two liquids can be observed. The different reaction types are also exemplified in this system and compiled in Table II. The only eutectic type, L′ = L″ + (Al) + ΘAl_2Cu, occurs adjacent to the Al-In binary edge. All five other L′ + L″ + $solid_1$ + $solid_2$ equilibria are of the transition type. Quite different solidification microstructures may be envisaged based on these different reaction types.

Type 3

A monotectic phase diagram of type 3 exists if the miscibility gap occurs in the ternary system only and in none of the binaries. Again, the intersection of the liquid gap with more than one primary crystallization field generates the nonvariant L′ + L″ + (Al) + (Z) equilibrium. A schematic liquidus surface is given in

Figure 10. The authors do not consider the trivial case where the liquid gap intersects one primary phase field.

The type 3 phase diagram may be formed in different subtypes, with or without metastable binary liquid gaps. In subtype 3a, the metastable gap in the binary X-Z (or/and Al-X) becomes stable in the ternary system. A real example for this type is the Al-Cu-Sn system where numerous invariant reactions are connected with the ternary gap.

In subtype 3b there is no metastable binary gap, not even a tendency for demixing in the binary liquid phases, even though an isolated ternary miscibility gap can be formed. Meijering[3] showed in his classical work the existence of such a ternary gap by thermodynamic calculations if the interaction parameters of one binary system are much more negative than the two others. Such a case was in fact detected in the real alloy system Al-Mg-Sc.[15] The calculated liquidus surface of this system is shown in Figure
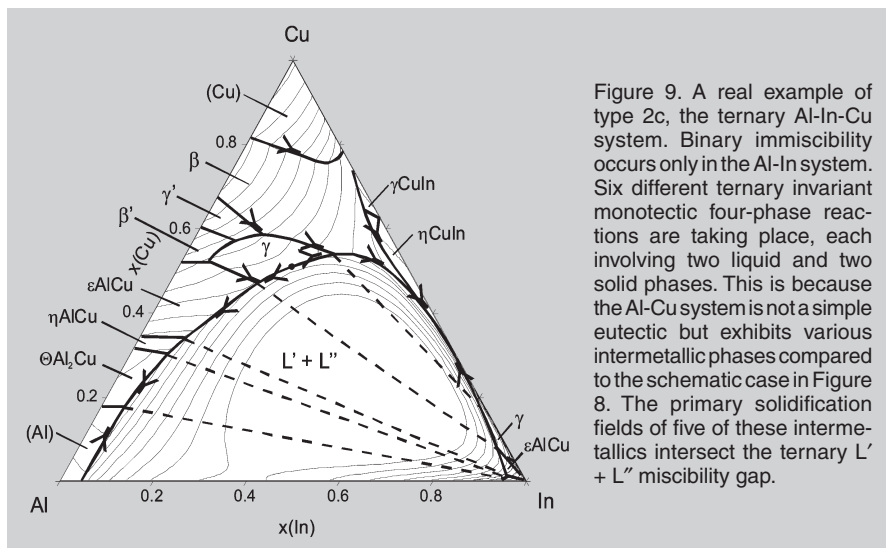

Figure 9. A real example of type 2c, the ternary Al-In-Cu system. Binary immiscibility occurs only in the Al-In system. Six different ternary invariant monotectic four-phase reactions are taking place, each involving two liquid and two solid phases. This is because the Al-Cu system is not a simple eutectic but exhibits various intermetallic phases compared to the schematic case in Figure 8. The primary solidification fields of five of these intermetallics intersect the ternary L′ + L″ miscibility gap.
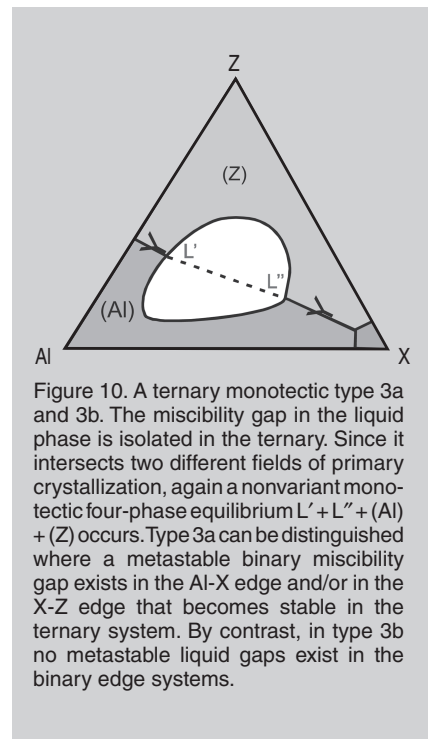

Figure 10. A ternary monotectic type 3a and 3b. The miscibility gap in the liquid phase is isolated in the ternary. Since it intersects two different fields of primary crystallization, again a nonvariant monotectic four-phase equilibrium L′ + L″ + (Al) + (Z) occurs. Type 3a can be distinguished where a metastable binary miscibility gap exists in the Al-X edge and/or in the X-Z edge that becomes stable in the ternary system. By contrast, in type 3b no metastable liquid gaps exist in the binary edge systems.
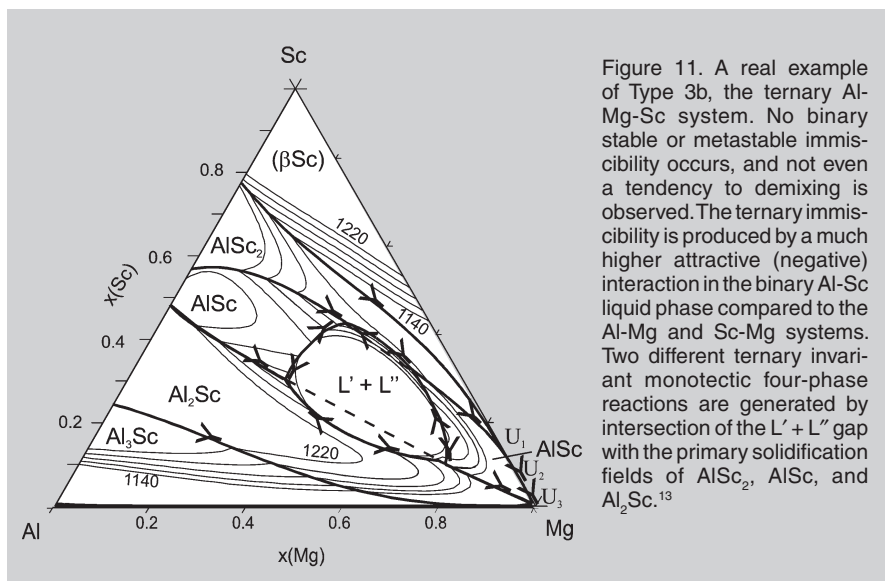
Figure 11. A real example of Type 3b, the ternary Al-Mg-Sc system. No binary stable or metastable immiscibility occurs, and not even a tendency to demixing is observed. The ternary immiscibility is produced by a much higher attractive (negative) interaction in the binary Al-Sc liquid phase compared to the Al-Mg and Sc-Mg systems. Two different ternary invariant monotectic four-phase reactions are generated by intersection of the L′ + L″ gap with the primary solidification fields of AlSc₂, AlSc, and Al₂Sc.[13]

11. The primary crystallization field of the AlSc phase is divided by the gap and two ternary monotectic reactions, $L' = L'' + AlSc + Al_2Sc$ and $L' = L'' + AlSc + AlSc_2$ occur.

CONCLUSION

In quaternary or multicomponent aluminum alloys, more complicated phase diagrams may be found. In a four-component system invariant reactions involving five phases are expected. If these are generated by intersecting a simple L′ + L″ gap with various crystallization fields, equilibria up to $L' + L'' + solid_1 + solid_2 + solid_3$ can be expected. The most interesting point is that the reaction types can be very different, from a eutectic decomposition type to a peritectic formation type or various transition types. These different reaction types are expected to produce solidification microstructures that were not seen before. Research in this direction is currently under way.

ACKNOWLEDGEMENT

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Joachim Gröbner, postdoctoral fellow, and Rainer Schmid-Fetzer, professor, are with the Institute of Metallurgy, Clausthal University of Technology.

For more information contact Rainer Schmid-Fetzer, Institute of Metallurgy, Clausthal University of Technology, D-38678 Clausthal-Zellerfeld, Germany. Fax +49-5323-723120; e-mail schmid-fetzer@tu-clausthal.de