

---

# Critical Evaluation of Ternary Phase Diagram Data

## Notes for Authors

3<sup>rd</sup> revised Edition, March 2000

Authors : MSIT<sup>®</sup> Task Force; Ringberg Meeting 1999, chaired by R. Schmid-Fetzer

Editors: G. Effenberg and R. Schmid-Fetzer

These Notes for Authors give detailed instruction to those which want to contribute to the *MSIT<sup>®</sup> Ternary Evaluation Program*.

The instructions, conventions and the terminology matured over more than 16 years of joined evaluation work within MSIT<sup>®</sup>, the Materials Science International Team. The basis for this was provided even many years before at the Max-Planck-Institut für Metallforschung, Stuttgart.

Some 3500 System Reports published in the MSIT<sup>®</sup> program have set internationally agreed standards under the auspices of APDIC, the Alloy Phase Diagram Commission.

The guide lines to meet the standards are made public here; within the *MSIT<sup>®</sup> Ternary Evaluation Program* these Notes for Authors are binding.

MSI, Materials Science International Services gives office and services to MSIT<sup>®</sup> and publishes the System Reports in the book series *Ternary Alloys* and/or electronically in the *MSI Workplace*.

Dr. G. Effenberg  
Materials Science International Services, GmbH  
Data and Knowledge Base for Materials Development  
Postfach 800749  
D-70507 Stuttgart  
Federal Republic of Germany

Prof. R. Schmid-Fetzer  
TU Clausthal  
Institut für Metallurgie  
Robert-Koch-Str. 42  
D-38678 Clausthal-Zellerfeld  
Federal Republic of Germany

This book was carefully produced. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate

Published by  
MSI, Stuttgart (Federal Republic of Germany)

**Critical Evaluation of Ternary Phase Diagram Data. Notes for Authors. 3<sup>rd</sup> revised edition.**  
ed. by G. Effenberg and R. Schmid-Fetzer – MSI, Stuttgart, 2000

ISBN 3-932120-43-4

© Materials Science International Services GmbH, D-70507 Stuttgart (Federal Republic of Germany), March 2000

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprint, or any other means – nor transmitted or translated into a machine readable format without written permission from the copyright owner. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Interested scientists are welcome to download and printout “Critical Evaluation of Ternary Phase Diagram Data. Notes for Authors” for own academic use. For current information go to:  
<http://www.msiwp.com/scienceforum/groupwork/>

In publications please refer to :

G. Effenberg and R. Schmid-Fetzer (Eds.), *Critical Evaluation of Ternary Phase Diagram Data. Notes for Authors. 3<sup>rd</sup> revised edition*, MSI, Stuttgart (2000)

## Contents

Chapter 1. The Readers' Expectations.....	4
1.1. Data Covered.....	5
1.2. General.....	5
1.3. Structure of a System Report.....	5
1.4. Literature Data.....	5
1.5. Binary Systems.....	5
1.6. Solid Phases.....	6
1.7. Pseudobinary Systems.....	6
1.8. Invariant Equilibria.....	6
1.9. Liquidus Surface.....	8
1.10. Isothermal Section.....	9
1.11. Temperature-Composition Sections.....	9
1.12. Thermodynamics.....	11
1.13. Material Properties and Applications.....	11
1.14. Miscellaneous.....	11
1.15. References.....	11
1.16. General References.....	12
Chapter 2. The Authors' Job and Proceeding.....	14
Chapter 3. The Structure of a System Report.....	16
3.1. Heading.....	17
3.2. Literature Data.....	17
3.3. Binary Systems.....	17
3.4. Solid Phases.....	18

3.5. Pseudobinary Systems.....	19
3.6. Invariant Equilibria.....	19
3.7. Liquidus, Solidus and Solvus Surfaces.....	22
3.8. Isothermal Sections.....	23
3.9. Temperature-Composition Sections.....	23
3.10. Thermodynamics.....	23
3.11. Materials Properties and Applications.....	23
3.12. Miscellaneous.....	24
3.13. References.....	24
Chapter 4. Best Technical and Editorial Practice.....	28
4.1. Diagrams.....	28
4.2. Text.....	29
4.3. Liquid Miscibility Gaps.....	31
4.4. Examples for the table "Solid Phases".....	34
4.5. Chemical Order of the Elements.....	38
Chapter 5. Examples of System Reports.....	40
5.1. As-Mo-Ru - Very Short Report.....	41
5.2. Al-Ge-Yb - Short with ternary phases.....	42
5.3. Al-Ru-Zr - More solid phases + corresponding isothermal sections.....	44
5.4. Au-Ge-Sb - Medium size with liquidus surface and vertical sections.....	50
5.5. Al-In-Sb - Medium size with liquid miscibility gap and line compound.....	60
5.6. Al-Fe-O - Large size with „Miscellaneous“ diagrams; oxide-metal equilibria.....	70

## Chapter 1

### The Readers' Expectations

The readership has been informed on what they can expect from System Reports made by MSIT<sup>®</sup>.

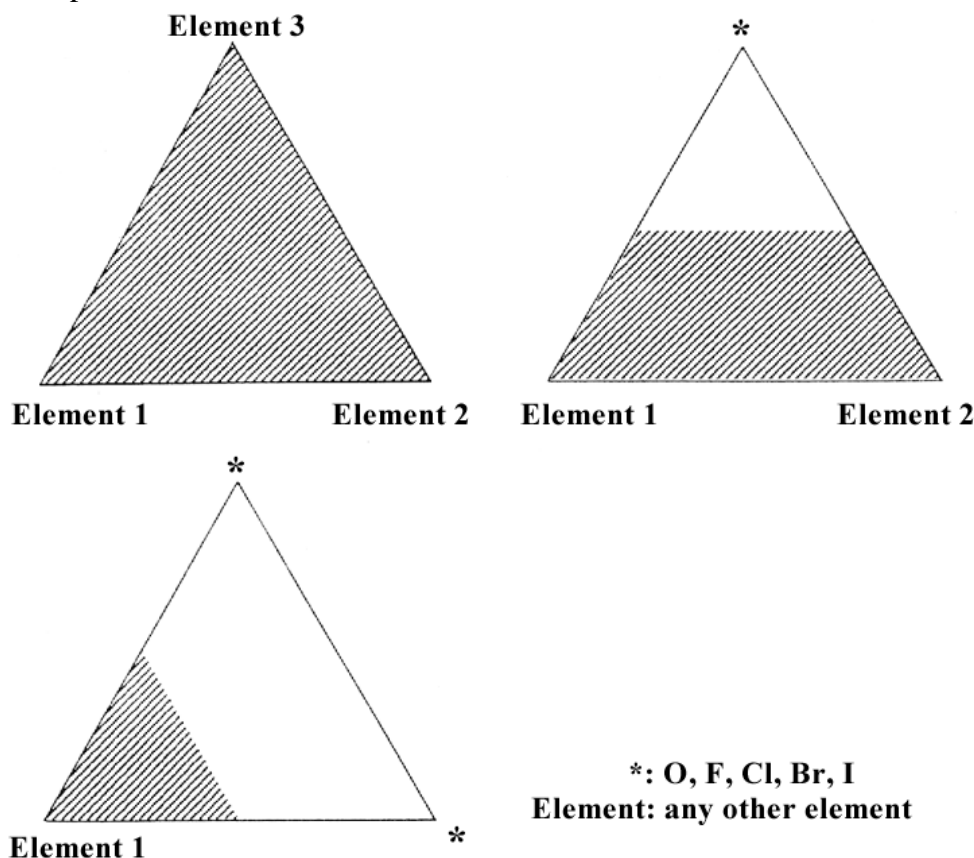
Each of the printed *Ternary Alloys* volumes has a chapter "Introduction to Ternary Alloys", which explains the contents of the individual chapters.

This "Introduction to Ternary Alloys" as it will appear in the next volume is reprinted below for your notice.

#### 1.1. Data Covered

The series *Ternary Alloys* focuses on metallic ternary systems and includes phase equilibria of importance for alloy development, processing or application. Data and equilibria of distinct ceramic nature are not included.

The shaded areas of the concentration triangles below indicate the composition ranges for which published data are compiled and assessed - if they refer to equilibria involving a "non-oxide/halide" phase.



The shaded areas broadly show the minimum coverage.

## 1.2. General

The series *Ternary Alloys* provides concise and - as far as published data allow - consistent phase diagram descriptions for individual ternary systems within complete ternary categories, such as Ag-X-Y or Al-X-Y. The representation of the equilibria of ternary systems as a function of temperature results in spacial diagrams whose sections and projections are generally published in the literature. In *Ternary Alloys* phase equilibria are described in terms of liquidus projections, isothermal and pseudobinary sections; data on invariant equilibria are generally given in the form of tables.

The world literature is thoroughly and systematically searched back to the year 1935. Then, the published data are critically evaluated by experts in materials science and reviewed under the authority of the phase diagram group of the Max-Planck-Institute for Metals Research, Stuttgart. Conflicting information is commented upon and errors and inconsistencies removed wherever possible.

In general, the approach used to discuss the phase relationships is to consider changes in state and phase reactions which occur with decreasing temperature. This has influenced the terminology employed and is reflected in the tables and the reaction schemes presented.

The system reports present concise descriptions and hence do not repeat in the text facts which can clearly be read from the diagrams. For most purposes the use of the compendium is expected to be self-sufficient. However, a detailed bibliography of all cited references is given to enable original sources of information to be studied if required.

## 1.3. Structure of a System Report

The constitutional description of an alloy system consists of text and a table diagram section which are separated by the bibliography referring to the original literature. The tables and diagrams carry the essential constitutional information and are commented on in the text if necessary.

Where published data allow, the following sections are provided in each report.

## 1.4. Literature Data

The opening text reviews briefly the status of knowledge published on the system and outlines the experimental methods that have been applied. Furthermore, attention may be drawn to questions which are still open or to cases where conclusions from the evaluation work modified the published phase diagram.

## 1.5. Binary Systems

Where binary systems are accepted from standard compilations reference is made to these compilations. In other cases the accepted binary phase diagrams are reproduced for the

convenience of the reader. The selection of the binary systems used as a basis for the evaluation of the ternary system was at the discretion of the assessor.

## 1.6. Solid Phases

The tabular listing of solid phases incorporates knowledge of the phases which is necessary or helpful for understanding the text and diagrams. Throughout a system report each phase is allocated a unique phase name and abbreviation. Phases with the same formulae but different space lattices (e.g. allotropic transformation) are distinguished by:

- small letters
  - (h), high temperature modification ( $h_2 > h_1$ )
  - (r), room temperature modification
  - (l), low temperature modification ( $l_1 > l_2$ )
- Greek letters, e.g.,  $\epsilon$ ,  $\epsilon'$
- Roman numerals, e.g., (I) and (II) for different pressure modifications.

In the table "Solid Phases" ternary phases are denoted by \* and different phases are separated by horizontal lines.

## 1.7. Pseudobinary Systems

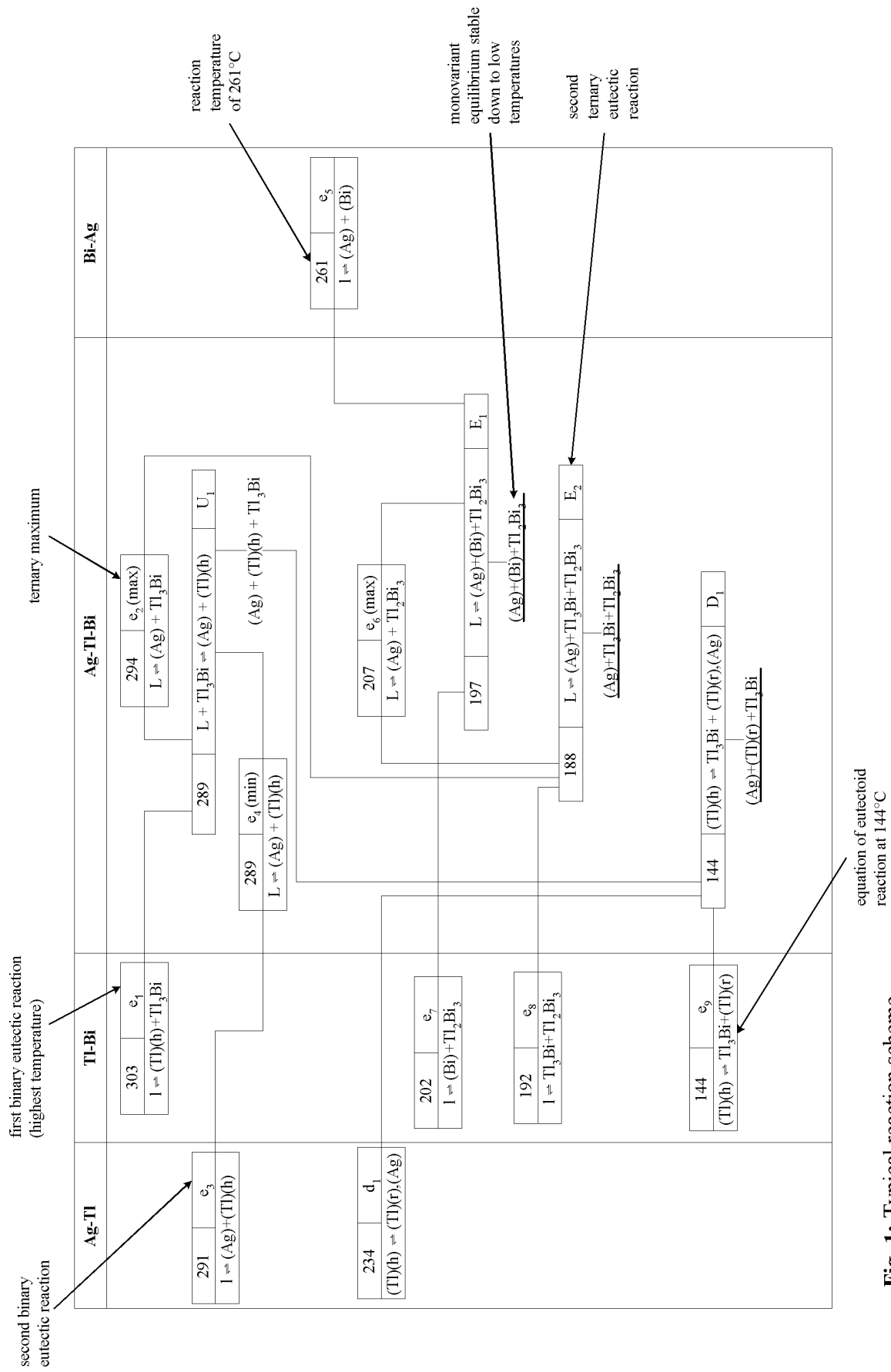
Pseudobinary sections describe equilibria and can be read in the same way as binary diagrams. The notation used in pseudobinary systems is the same as that of vertical sections, which are reported under "Temperature-Composition Sections".

## 1.8. Invariant Equilibria

The invariant equilibria of a system are listed in the table "Invariant Equilibria" and, where possible, are described by a constitutional "Reaction Scheme". While the table "Invariant Equilibria" is self-explanatory, the conventions which have been adopted for standard presentation of the "Reaction Scheme" need to be explained (see Fig. 1).

Invariant reactions are depicted in boxes reporting the reactions temperature, the type of reaction and the equation of the reaction.

The sequential numbering of invariant equilibria increases with decreasing temperature, one numbering for all binaries together and one for the ternary system.





Equilibria notations are used to indicate the reactions by which phases will be

- decomposed (e- and E-type reactions)
- formed (p- and P-type reactions)
- transformed (U-type reactions)

For transformed or transition reactions the letter U (Übergangsreaktion) is used in order to reserve the letter T to denote temperature. The letters d and D indicate degenerate equilibria which do not allow a distinction according to the above classes. Lower case letters denote three-phase equilibria and upper case letters four-phase equilibria.

## 1.9. Liquidus Surface

The phase equilibria are commonly shown in triangular coordinates which allow a reading of the concentration of the constituents in at.% from the grid. For concentration readings in mass% the binary axes of the triangles are scaled accordingly, thus allowing the user to superimpose a mass% (wt.%) screen, if required (see Figs. 2 and 3).

In the polythermal projection of the liquidus surface, monovariant liquidus grooves separate phase regions of primary crystallization and, where available, isothermal lines contour the liquidus surface (see Fig. 2).

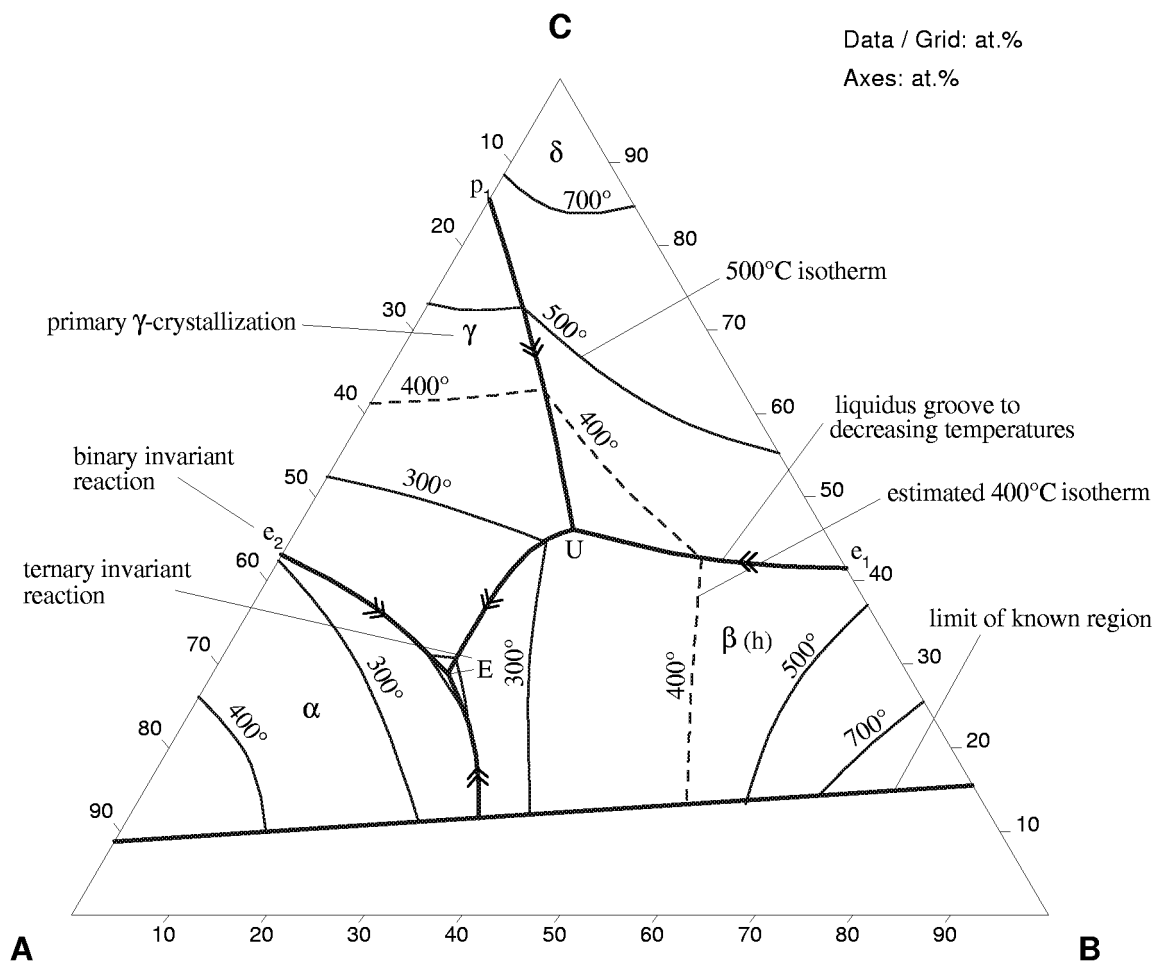


Fig. 2: Hypothetical liquidus surface showing notation employed

### 1.10. Isothermal Section

Phase equilibria at constant temperatures are plotted in the form of isothermal sections (see Fig. 3).

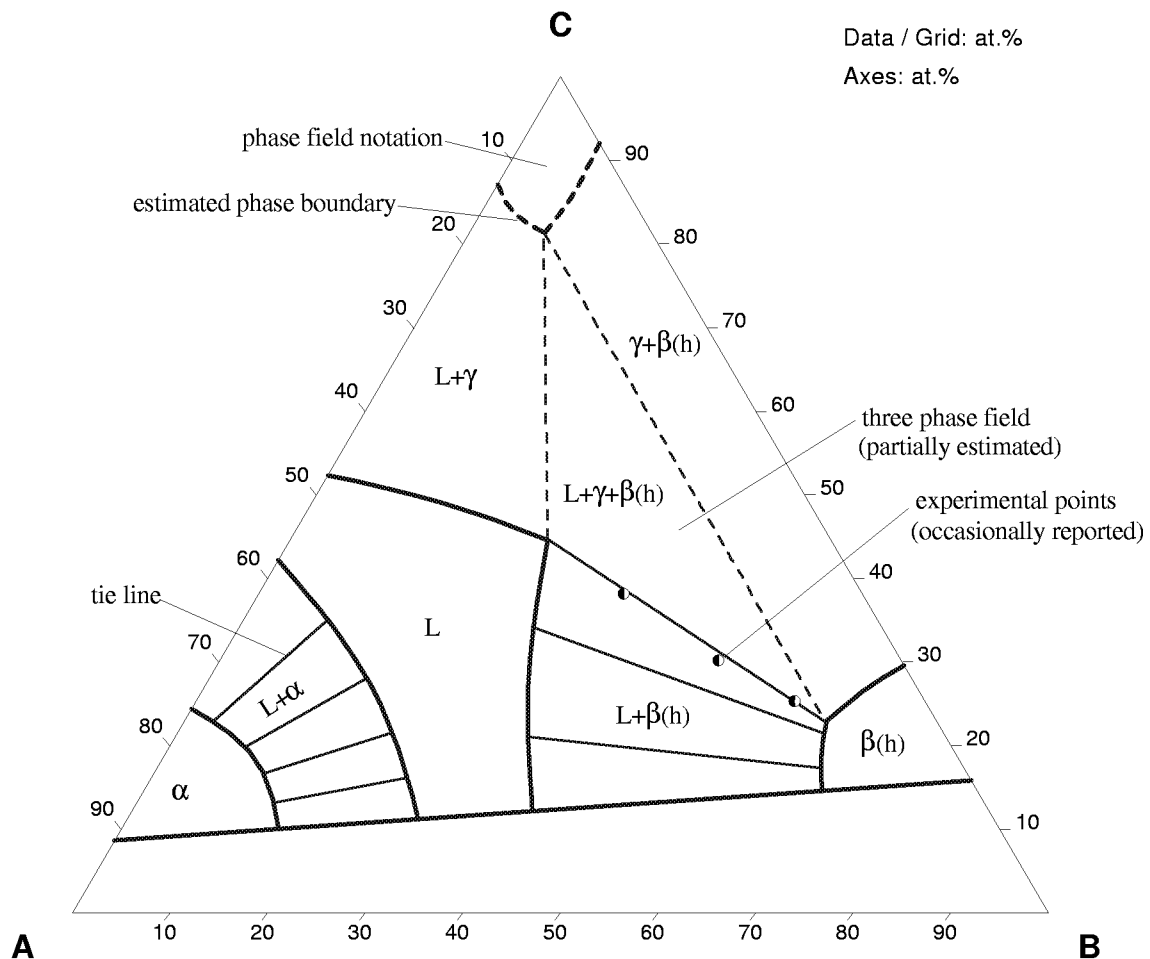


Fig. 3: Hypothetical isothermal section showing notation employed

### 1.11. Temperature-Composition Sections

Non-pseudobinary T-X sections (or vertical sections, isopleths) show the phase fields where generally the tie lines are not in the same plane as the section. The notation (see Fig. 4) is the same as that used for Pseudobinary Systems.

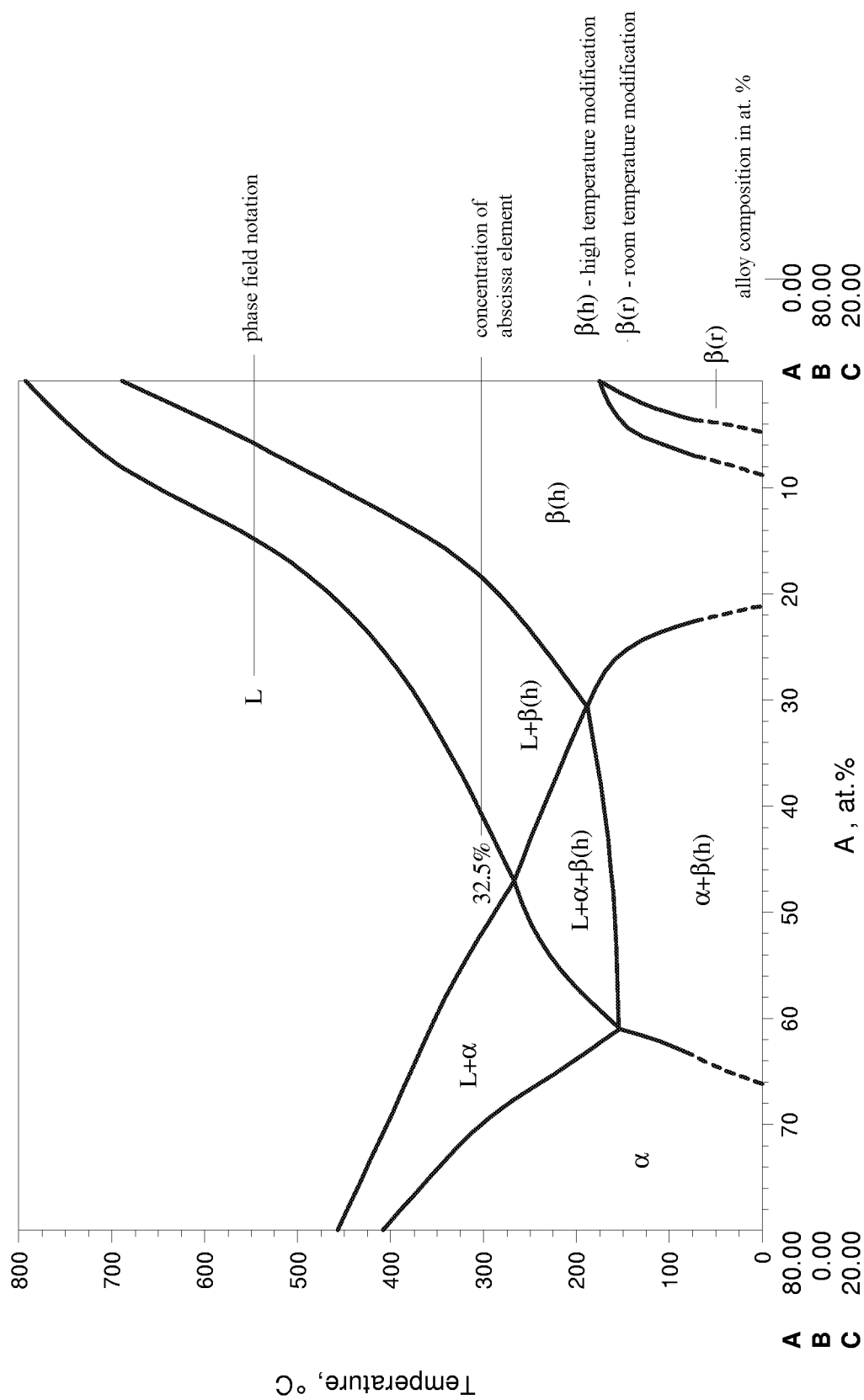


Fig. 4: Hypothetical vertical section showing notation employed

### **1.12. Thermodynamics**

Experimental ternary data are reported and reference to thermodynamic modelling is made.

### **1.13. Material Properties and Applications**

Noteworthy physical and chemical materials properties and application areas are briefly reported if they were given in the original constitutional and phase diagram literature.

### **1.14. Miscellaneous**

In this section noteworthy features are not reported which are not described in preceding paragraphs. These include graphical data not covered by the general report format, such as lattice spacing – composition data, as well as special phase diagrams (Temperature-chemical potential, ...).

### **1.15. References**

The publications which form the basis of the assessments are listed in the following manner:

[74Hay] Hayashi, M., Azakami, T. and Kamed, M., "Effects of Third Elements on the Activity of Lead in Liquid Copper Base Alloys" (in Japanese), *Nippon Kogyo Kaishi*, **90**, 51-56 (1974) (Experimental, Thermodyn., 16)

This paper, for example, whose title is given in English, is actually written in Japanese. It was published in 1974 on pages 51-56, volume 90 of *Nippon Kogyo Kaishi*, the Journal of the Mining and Metallurgical Institute of Japan. It reports on experimental work that leads to thermodynamic data and it refers to 16 cross-references.

Additional conventions used in citing are:

# to indicate the source of accepted phase diagrams

\* to indicate key papers that significantly contributed to the understanding of the system.

Standard reference works given in the list "General References" are cited using their abbreviations and are not included in the reference list of each individual system.

## 1.16. General References

- [E] Elliott, R.P., *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965)
- [Eff1] Effenberg, G., Petrova, L.A., *Red Book. Phase Diagrams of Metallic Systems (published in 1990)*, MSI, Stuttgart, Vol. 35 (1993)
- [Eff2] Effenberg, G., Petrova, L.A., *Red Book. Phase Diagrams of Metallic Systems (published in 1991)*, MSI, Stuttgart, Vol. 36 (1994)
- [Eff3] Effenberg, G., Petrova, L.A., *Red Book. Phase Diagrams of Metallic Systems (Summaries of the publication year 1992)*, MSI, Stuttgart, Vol. 37 (1997)
- [Eff4] Effenberg, G., Bodak, O.I., Petrova, L.A., *Red Book. Constitutional Data and Phase Diagrams of Metallic Systems (Summaries of the publication year 1993)*, MSI, Stuttgart, Vol. 38 (1997)
- [Eff5] Effenberg, G., Bodak, O.I., Petrova, L.A., *Red Book. Constitutional Data and Phase Diagrams of Metallic Systems (summaries of the publication year 1994)*, MSI, Stuttgart, Vol. 39 (1997)
- [Eff6] Effenberg, G., Bodak, O.I., Petrova, L.A., *Red Book. Constitutional Data and Phase Diagrams of Metallic Systems (summaries of the publication year 1995)*, MSI, Stuttgart, Vol. 40 (1998)
- [Eff7] Effenberg, G., Bodak, O.I., Yanson, T.I., *Red Book. Constitutional Data and Phase Diagrams (summaries of the publication year 1996)*, MSI, Stuttgart, Vol. 41 (1999)
- [G] Gmelin *Handbook of Inorganic Chemistry*, 8th ed., Springer-Verlag, Berlin
- [H] Hansen, M. and Anderko, K., *Constitution of Binary Alloys*, McGraw-Hill, New York (1958)
- [L-B] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology (New Series). Group 3 (Crystal and Solid State Physics)*, Vol. 6, Eckerlin, P., Kandler, H. and Stegherr, A., *Structure Data of Elements and Intermetallic Phases* (1971); Vol. 7, Pies, W. and Weiss, A., *Crystal Structure of Inorganic Compounds, Part c, Key Elements: N, P, As, Sb, Bi, C* (1979); Group 4: *Macroscopic and Technical Properties of Matter*, Vol. 5, Predel, B., *Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys*, Subvol. a Ac-Au ... Au-Zr (1991); Springer-Verlag, Berlin.
- [Mas] Massalski, T.B. (Ed.), *Binary Alloy Phase Diagrams*, ASM, Metals Park, Ohio (1986)
- [Mas2] Massalski, T.B. (Ed.), *Binary Alloy Phase Diagrams*, 2nd edition, ASM International, Metals Park, Ohio (1990)
- [P] Pearson, W.B., *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, New York, Vol. 1 (1958), Vol. 2 (1967)

[S] Shunk, F.A., *Constitution of Binary Alloys, Second Supplement*, McGraw-Hill, New York (1969)

[V-C] Villars, P. and Calvert, L.D., *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM, Metals Park, Ohio (1985)

[V-C2] Villars, P. and Calvert, L.D., *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd edition, ASM, Metals Park, Ohio (1991)

---

## Chapter 2

### The Authors' Job and Proceeding

Prepare a critical evaluation of the world literature, write it down in a System Report that meets the readers expectations and communicate with MSI and the board of reviewers to back the decisions which you make during evaluation.

Please note that different from manuscript supply to traditional journals the work within MSIT is team work.

The reviewers do not operate anonymous but discuss with you and MSI assists you in your work from the very beginning.

1. Check if literature provided by MSI is complete, check your personal literature list. Merge both lists to one comprehensive reference list.

2. Carefully read the literature. Separate non-relevant papers and mark them in the reference list. Collect all information and data for the ternary system, data which is relevant for the constitution and thermodynamics, for crystal structure, applications or properties of that system.

3. Critical evaluation of the published data, for example

- conflicts within the published data have to be pointed out and settled wherever possible (in this case, explicitly discuss reasons for rejecting published data)
- the author is expected to draw conclusions from the information extending over the different literatures, but he is not allowed to speculate, *he has to stick to what is known*. Reliably known data + the rules of heterogeneous equilibria + the competence of the author may lead to new valuable information
- wherever possible construct isothermal sections from temperature-concentration cuts
- correct published diagrams if necessary by redrawing according to theoretical rules (Gibbs phase rule, Schreinemakers rule, Gibbs-Konovalov-rule)
- draw diagrams, which are mutually consistent, e.g. intersections of the diagrams have to be checked and the temperature sequence of the diagrams has to be possible and logical. The diagrams have to be consistent with the accepted edge binary systems
- at the end re-check carefully internal consistency between text, tables and figures

4. Send the manuscript to MSI as soon as possible.
5. Each report will be thoroughly reviewed by the MSI panel of reviewers. They have at hand the same base literature for review which was used by the author for evaluation. A revision of the manuscript may have to be performed according to the guiding remarks of the reviewer.
6. The final version (galley proof) has to be confirmed by the author.



---

## Chapter 3

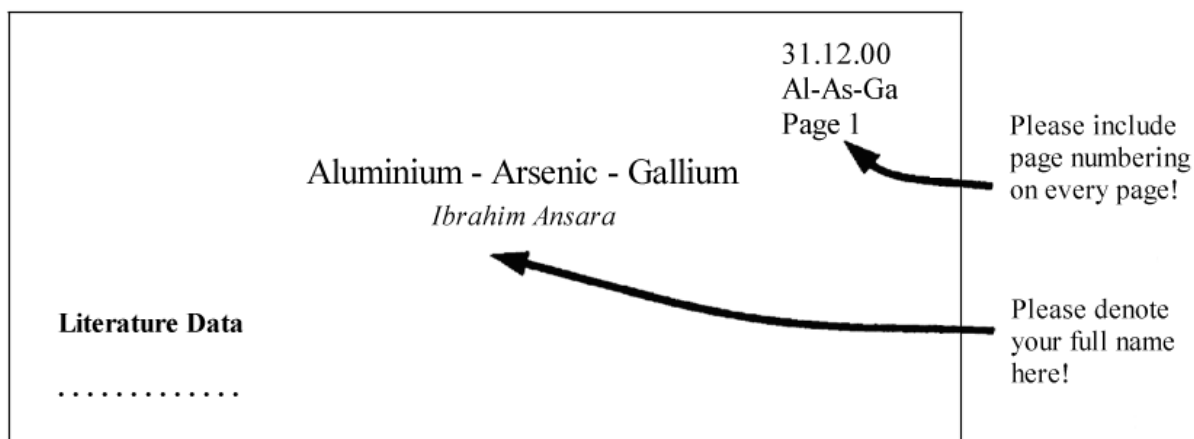
### The Structure of a System Report

- 3.1. Heading
- 3.2. Literature Data
- 3.3. Binary Systems
- 3.4. Solid Phases
- 3.5. Pseudobinary Systems
- 3.6. Invariant Equilibria
- 3.7. Liquidus, Solidus and Solvus Surfaces
- 3.8. Isothermal Sections
- 3.9. Temperature-Composition Sections
- 3.10. Thermodynamics
- 3.11. Materials Properties and Applications
- 3.12. Miscellaneous
- 3.13. References
- 3.14. Tables
- 3.15. Figures

Note: The section 3.2. “Literature Data“ summarizes the work that others have published whereas the topics 3.3 to 3.11, 3.13 and 3.14 involve your conclusions as an expert author.

Topics without sufficient data are skipped.

### 3.1. Heading



Insert the date as follows: 31.12.00. Do not use options that amend the date when the document is opened.

### 3.2. Literature Data

According to our general strategy a short overview of 'what has been done by whom' should be included.

A brief critical review of the published work on the ternary system should outline the experimental methods, the amount of work involved in studying the ternary system and state the extent of agreement between different authors.

The arguments on which the decision on final selection of data will be based is NOT given here but later in the individual chapters.

### 3.3. Binary Systems

For binary phase diagrams refer to standard compilations if the binary diagram which you accept is from one of the following compilations: [Mas2, Mas, S, E, H] (see "General References").

In all other cases reproduce and include the accepted binary diagram in the ternary evaluation report.

If ternary findings conflict with a binary subsystem, the author should mention this explicitly in the later sections.

### 3.4. Solid Phases

The assessed information is mainly presented in the Table “Solid Phases”.

The Table “Solid Phases” should incorporate all phases of the ternary system; or a specified selection (see Examples in Part IV), *starting* with unary, proceeding to binary and closing with the ternary phases. Two binary phases originating from different boundary systems and forming a continuous solid solution in the ternary are considered as *one* phase only and should be put behind the binary phases and before the ternary phases.

Each phase appears only once. Different phases are separated by horizontal lines.

Check the examples in Part IV now if you like.

1. The *first column* of the table contains the formulae (at least an approximate one) of the phases. Whenever Greek letters are used to denote phases, these symbols must also appear in the first column.

Two phases must not have the same name and one phase can not have two different names. A one to one relation between symbol and phase is necessary.

If the same Greek symbol is used for different phases, they must be distinguished by suffixes.

The sequence of the elements in the formula of a phase has to be according to the *chemical order* specified by Pettifor, see Part IV. We use SiC (instead of CSi) in the C-Si system.

Different phases with the same formulae are distinguished by:

- a. different symbols  $\epsilon$ ,  $\epsilon'$ , for allotropic transformations
- b. Roman letters (I), (II), for pressure modifications
- c. the temperature range of phase stability.

Different temperature modifications can further be indicated by lower case letters in parenthesis behind the phase designation, with

- a. (h) = high temperature modification
- b. (r) = room temperature modification
- c. (l) = low temperature modification ( $l_1 > l_2$ ).

These letters are used in the sequence  $h_2$ ,  $h_1$ , r,  $l_1$ ,  $l_2$ .

Also,  $\alpha\text{Mn}$ ,  $\beta\text{Mn}$  or  $\alpha\text{Pr}$ ,  $\beta\text{Pr}$ ,  $\alpha\text{Pr}_3\text{Al}_{11}$  and  $\beta\text{Pr}_3\text{Al}_{11}$  are possible within one system report.

All ternary phases are indicated with asterisks (\*) in front of the formula. Generally,  $\tau_1$ ,  $\tau_2$  should be used as Greek letters for ternary phases.

2. The *second column* characterizes the crystal structure by the Pearson symbol and its prototype, which also has to be given in *chemical order*. The prototype is the first phase where this structure was reported. If a sentence "is isotype to A<sub>2</sub>XY [refs.]" is given in the literature, please check for prototype of A<sub>2</sub>XY. If the structure is not known exactly (for example the locations of the atoms are unknown), the symmetry is sufficient (such as c\*\*, t\*\*, h\*\*, o\*\*, ...). No prototype may appear.

In some cases it may be helpful to give an incomplete Pearson symbol such as (o\*60).

If the structure is known completely the prototype must be reported.

3. The *third column* gives the lattice parameters in pm and if necessary the angle of inclination of the crystal lattice. For rhombohedral lattices the hexagonal setting is preferred.

4. *Column four* allows the inclusion of additional information, such as: references, comments on accuracy, concentrations, etc. The source of data has to be referenced. In the case of ternary phases, [V-C] as the reference is not enough, the original reference must be given.

**Binary phases of no relevance to ternary information should be omitted (see Examples).**

Authors should indicate whether the original work has truly proved the existence of a ternary phase or merely the presence of a metastable phase, or a solid solution based on one of the binary phases.

For solid solutions between two binary phases the formulae of the terminal binary phases should be given together with their lattice parameters.

Examples for the Table "Solid Phases" are given in Part IV Section 4 and the System Report Al-Ru-Zr.

### 3.5. Pseudobinary Systems

Pseudobinary systems should be described and the diagram presented.

### 3.6. Invariant Equilibria

Invariant equilibria and the sequential order by which they appear form a skeleton that should be illustrated by a reaction scheme.

The authors must design a layout of the reaction scheme according to

[86Luk] Lukas, H.L., Henig, E.T., Petzow, G., "50 Years Reaction Scheme after Erich Scheil", *Z. Metallkunde*, **77**, 360-367 (1986)

The basic principles are briefly outlined below.

**Glossary:**

L = ternary liquid, l = binary liquid

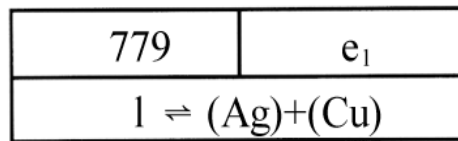
**Binary three-phase equilibria and ternary maxima and minima.**

$l' \rightleftharpoons l'' + \alpha$	monotectic reaction	e-type reactions “decomposition”
$l \rightleftharpoons \alpha + \beta$	eutectic reaction	
$\alpha \rightleftharpoons l + \beta$	metatectic reaction	
$\alpha \rightleftharpoons \beta + \gamma$	eutectoid reaction	
$\beta_1 \rightleftharpoons \alpha + \beta_2$	monotectoid reaction	
$l' + l'' \rightleftharpoons \alpha$	syntectic reaction	p-type reactions “formation”
$l + \alpha \rightleftharpoons \beta$	peritectic reaction	
$\alpha + \beta \rightleftharpoons \gamma$	peritectoid reaction	

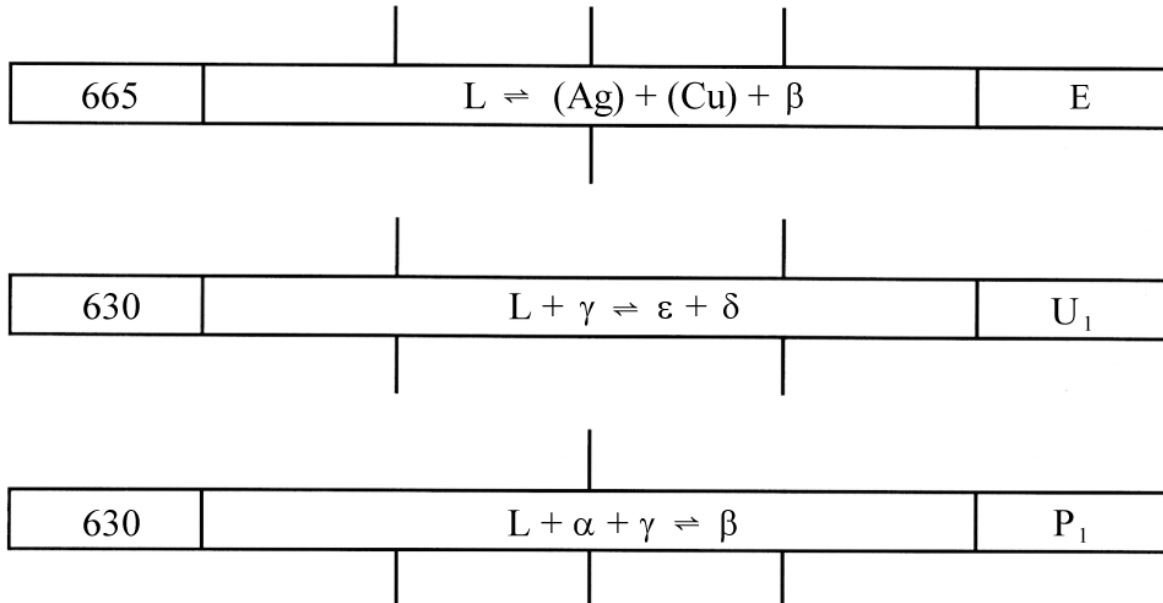
**Ternary four-phase equilibria.**

$L' \rightleftharpoons L'' + L''' + \alpha$	bitectic reaction	E-type reactions “decomposition”
$L' \rightleftharpoons L'' + \alpha + \beta$	monotectic reaction	
$L \rightleftharpoons \alpha + \beta + \gamma$	eutectic reaction	
$\alpha \rightleftharpoons \beta + \gamma + \delta$	eutectoid reaction	
$L' + \alpha \rightleftharpoons L'' + L'''$	liquid transition reactions	U-type reactions “transition” or “transformation”
$L' + \alpha \rightleftharpoons L'' + \beta$		
$L' + L'' \rightleftharpoons \alpha + \beta$		
$L + \alpha \rightleftharpoons \beta + \gamma$		
$\alpha + \beta \rightleftharpoons \gamma + \delta$	solid transition reaction	
$L' + L'' + L''' \rightleftharpoons \alpha$	syntectic reaction	P-type reactions “formation”
$L' + \alpha + \beta \rightleftharpoons L''$	—	
$L + \alpha + \beta \rightleftharpoons \gamma$	peritectic reaction	
$\alpha + \beta + \gamma \rightleftharpoons \delta$	peritectoid reaction	

**Binary reactions are represented in the following way:**



**Ternary reactions are represented as follows:**

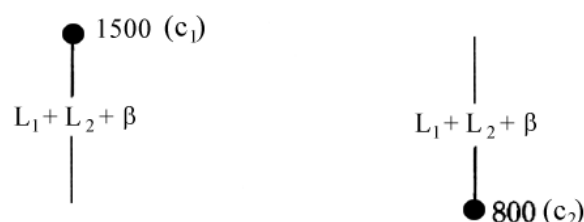


**Pseudobinary three-phase equilibria** (ternary maxima or minima) are indicated by a convention similar to that adopted for binary invariant reactions. They are numbered together with the binaries, see “Introduction” (Fig. 1) and section 4.3 (Fig. 4):



**Univariant three-phase equilibria** are not written in boxes. Those existing down to "room temperature" are underlined, those starting in one ternary and ending in another ternary reaction are indicated without underlining. Univariant three-phase equilibria starting or ending at a binary reaction are indicated by a line to this binary reaction.

Univariant three-phase equilibria starting or ending at a critical point (c) are represented as:



### Degenerate reactions:

In systems with stoichiometric phases some of the invariant equilibria may be degenerate. This means, no decision can be made between e- and p-type in a binary system respectively, between E- and U-type or between U- and P-type or even between all the 3 types in a ternary system.

For a more detailed discussion of the treatment of degenerated reactions (d-type or D-type) authors may refer to a paper

[86Luk] Lukas, H.L., Henig, E.T., Petzow, G., "50 Years Reaction Scheme after Erich Scheil", *Z. Metallkunde*, **77**, 360-367 (1986)

See examples in System Reports Au–Ge–Sb and Al–In–Sb.

### Table „Invariant Reactions“.

In addition to the reaction scheme, this section should include a table showing the details of the invariant equilibria present in the ternary system. Four columns are necessary: reaction with temperature (°C), type, phase and composition. For example, the ternary peritectic reaction in a system should be tabulated as follows:

T (°C) Reaction	Type	Phase	Composition (at.%)		
			Ag	Cu	Mg
505	P	L	9.8	15.5	74.7
$L + \beta' + \gamma \rightleftharpoons \varepsilon$		$\beta'$	36.5	6.8	56.7
		$\gamma$	2.5	30.0	67.5
		$\varepsilon$	14.0	15.2	70.8

See examples in Au–Ge–Sb, Al–In–Sb and Al–Fe–O.

### 3.7. Liquidus, Solidus and Solvus Surfaces

The projection of the *liquidus surface* should be included. All monovariant curves separating the regions of primary crystallization of individual phases are to be drawn with two closely-spaced arrows pointing to descending temperatures. Ternary invariant points are to be labeled with the appropriate letters E, U and P or the designations e and p in the case Max. and Min., defined in corresponding tables.

If more than one liquid phase is involved in an invariant reaction, the phase designations  $e'_1$ ,  $e''_1$ ,  $E'_1$ ,  $E''_1$  should be attached to the appropriate invariant points, where  $e_1$ ,  $E_1$  designate the *reaction* and the ' and '' designate the different *liquid phases/compositions* (see Part IV.3).

The regions of primary crystallization are to be labeled with the appropriate phase designation, e.g. (Ag), etc.

Isotherms should be inserted on the liquidus surface.

Comment should be made on specific features of the liquidus surface in the text.

### **3.8. Isothermal Sections**

*Isothermal sections* should be presented as needed.

All single-phase regions and all three-phase regions should be designated, e.g. L, (Ag), AgAl, etc.

Inside the three-phase fields put an asterisk (\*).

If Greek symbols are used, they must be identical with those used for the phase in the table of solid phases, and in the text.

If only vertical sections through a ternary T-composition diagram are available, the author is asked to determine the corresponding isothermal sections, but not to speculate.

### **3.9. Temperature-Composition Sections**

All non-pseudobinary *T-x sections* (vertical sections, isopleths) can be presented here.

### **3.10. Thermodynamics**

Ternary experimental data can be given,  $\Delta H$  (formation, mixing, transformation),  $c_p$ , activity, etc. Very extensive tabulated data may be just referred to. If thermodynamic modelling is performed just the reference is given, not the equations or parameters. Accepted calculated phase diagrams are given in the appropriate sections 5-9 or in section 12 for special phase diagrams ( $\log p(\text{O}_2)$  versus T etc.). To perform an own consistent thermodynamic assessment may be possible occasionally. In this case it is necessary to tabulate all parameters and equations.

### **3.11. Materials Properties and Applications**

No specific literature search is performed for this section. However all relevant and noteworthy materials properties (mechanical, magnetic, electrical, optical, etc.) and applications (functional or structural application areas, processing, etc.) found in the constitutional literature basis should be briefly reported here.



### 3.12. Miscellaneous

This paragraph should include noteworthy features not covered by the preceding form of presentation. For example, for systems containing gas as a third element (Al-Fe-O), other kinds of presentation may be chosen for the description of the system, e.g. ( $\log p(\text{O}_2)$  vs. T). In this case no instruction for the size and the form of diagrams is given for the authors.

Note: It is recommended to suggest further experiments which are crucial for a more complete understanding of the ternary system. Specify what kind of information is wanted from these experiments.

### 3.13. References

All references should be included. General references used in the text need not to be included in the reference list of each individual system. These are:

#### General References

[E] Elliott, R.P., *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965)

[Eff1] Effenberg, G., Petrova, L.A., *Red Book. Phase Diagrams of Metallic Systems (published in 1990)*, MSI, Stuttgart, Vol. 35 (1993)

[Eff2] Effenberg, G., Petrova, L.A., *Red Book. Phase Diagrams of Metallic Systems (published in 1991)*, MSI, Stuttgart, Vol. 36 (1994)

[Eff3] Effenberg, G., Petrova, L.A., *Red Book. Phase Diagrams of Metallic Systems (Summaries of the publication year 1992)*, MSI, Stuttgart, Vol. 37 (1997)

[Eff4] Effenberg, G., Bodak, O.I., Petrova, L.A., *Red Book. Constitutional Data and Phase Diagrams of Metallic Systems (Summaries of the publication year 1993)*, MSI, Stuttgart, Vol. 38 (1997)

[Eff5] Effenberg, G., Bodak, O.I., Petrova, L.A., *Red Book. Constitutional Data and Phase Diagrams of Metallic Systems (summaries of the publication year 1994)*, MSI, Stuttgart, Vol. 39 (1997)

[Eff6] Effenberg, G., Bodak, O.I., Petrova, L.A., *Red Book. Constitutional Data and Phase Diagrams of Metallic Systems (summaries of the publication year 1995)*, MSI, Stuttgart, Vol. 40 (1998)

[Eff7] Effenberg, G., Bodak, O.I., Yanson, T.I., *Red Book. Constitutional Data and Phase Diagrams (summaries of the publication year 1996)*, MSI, Stuttgart, Vol. 41 (1999)

[G] Gmelin *Handbook of Inorganic Chemistry*, 8th ed., Springer-Verlag, Berlin

[H] Hansen, M. and Anderko, K., *Constitution of Binary Alloys*, McGraw-Hill, New York (1958)

[L-B] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology (New Series). Group 3 (Crystal and Solid State Physics)*, Vol. 6, Eckerlin, P., Kandler, H. and Stegherr, A., *Structure Data of Elements and Intermetallic Phases* (1971); Vol. 7, Pies, W. and Weiss, A., *Crystal Structure of Inorganic Compounds*, Part c, Key Elements: N, P, As, Sb, Bi, C (1979); Group 4: *Macroscopic and Technical Properties of Matter*, Vol. 5, Predel, B., *Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys*, Subvol. a Ac-Au ... Au-Zr (1991); Springer-Verlag, Berlin.

[Mas] Massalski, T.B. (Ed.), *Binary Alloy Phase Diagrams*, ASM, Metals Park, Ohio (1986)

[Mas2] Massalski, T.B. (Ed.), *Binary Alloy Phase Diagrams*, 2nd edition, ASM International, Metals Park, Ohio (1990)

[P] Pearson, W.B., *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, New York, Vol. 1 (1958), Vol. 2 (1967)

[S] Shunk, F.A., *Constitution of Binary Alloys, Second Supplement*, McGraw-Hill, New York (1969)

[V-C] Villars, P. and Calvert, L.D., *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM, Metals Park, Ohio (1985)

[V-C2] Villars, P. and Calvert, L.D., *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd edition, ASM, Metals Park, Ohio (1991)

All other references are to be given by the last two figures of the year and the first three letters of the name of the first author. If two different papers would have the same abbreviation a number index is added.

Examples are:

" ... it has been shown by [68Joh1] that ... " or

" ... experiments with calcium [68Joh2], potassium [75Dal] ... "

Other abbreviations are:

Gürtler [43Gue]

El-Boragy [71ElB]

Mc Kisson [79McK]

von Unterrichter [76Unt].

Use for ä = ae, ö = oe, ü = ue and Å = A.

The reference list should be written in the following style:

[62Kir] Kirkpatric, M.E., Bailey, D.M., Smith, J.F., "The Structure of NiZr, NiZr and Their Hafnium Analogs", *Acta Crystallogr.*, **15**, 894-903 (1962) (Equi. Diagram, Crys. Structure, Experimental, 5).

For a journal article as mentioned in the example all authors are given, even when there are very many, followed by the title of the paper in quotation marks. The title is always given in English. The original language, if not English, is indicated in brackets after the title. The abbreviation of the journal is given as listed in "*Chemical Abstracts, List of Periodicals*". Names of journals or other periodical publications not listed there should be written in full. The volume number is bold and the first and last page numbers must be given. Journals with unnumbered volumes are cited as: *J. Chem. Soc.*, 2516-2522 (1965).

For journals that start the pagination of each issue with 1, the issue number must be given in parentheses following the volume number, if there is any:

[86Pay1] Paygai, I.N., Khairidinov, S.Kh., Vakhobov, A.V., "The Ba-La Phase Diagram", *Russ. Metall.*, **3**, 213-214 (1986), translated from *Izv. Akad. Nauk. SSSR, Metally*, **3**, 216-217 (1986) (Experimental, Equi. Diagram, #, \*, 4)

Where an English translation exists, this should be first referenced and followed by the data on the original publication, as shown by the example above.

For pamphlets, bulletins or any publications other than "regular" books or journals give all the information available and do not use abbreviations.

Keywords at the end of references should indicate the nature of the data available in the reference.

1. *Equi. Diagram* for Equilibrium Diagram

2. *Crys. Structure* for Crystal Structure

3. *Thermodyn.* for Thermodynamic

4. *Experimental*

5. *Review*

6. *Theory*

**Important: Only the above keywords and abbreviations may be used.**

In addition the following symbols are used:

# – indicates accepted phase diagram in the paper

\* – indicates key papers that constitute an important reference for the proposed diagram

Number – number of references in the paper

### **Examples.**

#### *Report:*

[61Eng] English, J.J., "Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum and Tungsten", *Defense Metals Information Center Report*, Battelle Memorial Institute, Columbus, OH, Report No. 152, 1-53 (1961) (Equi. Diagram, #, 7)

#### *Book:*

[82Kub] Kubaschewski, O., *Iron Binary Phase Diagrams*, Springer Verlag, Berlin, Verlag Stahleisen, Düsseldorf, 152-156 (1982) (Equi. Diagram, Review, 26)

#### *Chapter of Book:*

[61Sem] Semchysen, M., Barr, R.Q., "Molybdenum and Molybdenum-Containing Refractory Alloys", *AIME Metallurgical Society Conferences*, in "Refractory Metals and Alloys", Vol. 11, Interscience Publishers, Inc., New York, 283-317 (1961) (Crys. Structure, Review)

#### *Proceedings:*

[78San] Sankar, S.G., "Magnetic Properties of  $\text{Er}(\text{Fe}_{1-x}\text{Mn}_x)_2$ ", *The Rare Earths in Modern Science and Technology*, Proc. Conf., Wheeling, W. Virginia, 1977, 69-74 (Publ. 1978) (Experimental, 7)

If a reference is not available but quoted by a given literature, review or even Chemical Abstract, then it should be presented in the following form:

[64Tiv] Tivilivi, E.T., "The Al-Ar-He Phase Diagram", *Moldavian Chemical Congress*, **1**, 23-27 (1964) quoted by N.V. Ageev, "Phase Diagrams of Metallic Systems" (in Russian), 1965 (Publ. 1968)

**This form may only appear, if the primary source is definitely not available.**

---

## Chapter 4

### Best Technical and Editorial Practice

#### 4.1. Diagrams

#### 4.2. Text

#### 4.3. Liquid Miscibility Gaps

#### 4.4. Table Solid Phases

#### 4.5. Sequential Order of the Elements

### 4.1. Diagrams

The diagrams, which authors send to Stuttgart will be digitized. The diagrams have to be as clear and complete as possible. Any error in these diagrams will enter the database. A correction at a later date is an avoidable, time consuming work that delays publication. Several points require special attention.

1. The diagrams have to be labelled with the concentrations/temperatures of at least three points, normally the three corners of the diagram, in order to enable digitizing by computer means. *This labelling has to occur in the units of the diagram itself.*

2. On the diagrams it should be stated, which lines have to be thick and which ones have to be thin.

3. No general correction remarks should be included on the diagrams, e.g. "please change all one-phase fields to polygons": the diagram has to be redrawn by the author.

4. If it is necessary to allocate to a specific point a numerically known concentration/temperature, these should be denoted on the diagram in a non-confusing way.

5. If *by exception* copies of diagrams from the literature are used as base drawing, these copies have to include the full description of the drawing:

- a. continuous lines may not be interrupted due to low copying quality;
- b. separated lines may not intersect or overlay;

c. The phase areas has to be re-labeled by the author according to the table "Solid Phases" after removing the original designations. Refrain from this approach and redraw the diagram if the readability becomes questionable!

6. If already digitized diagrams require corrections of line curvatures or angles between lines, these corrections have to be done with a *thin* pen, denoting clearly the correct location of the line.

7. Please check that the use of solid and dashed lines is consistent with those of the Reaction Scheme.

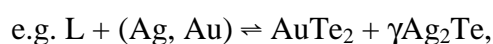
8. Does the use of "after [xxAbc]" or "from [xxAbc]" in figure legends have any significance? If not, omit "after" and "from".

9. Always place references in square brackets [ ]; do not use anything else.

## 4.2. Text

### General

- Each page should be labelled in the upper right corner with the chemical symbols of the alloy system in alphabetical order. The pages should be numbered.
- In text the binary and ternary systems are indicated as: "The Au-Pb system ...", "In the ternary Au-In-Pb system ...".
- Use American spelling, e.g. *crystallization*, *homogenization*, *behavior*, *sulfur* (but *aluminium*, since this spelling is recommended by IUPAC).
- Within a report, reference may be made to individual sections of the report (not to chapters).
- Make complete sentences (e.g. "The solid phases are given in Table 1." but not "The solid phases see Table 1.").
- Do not capitalize the names of mineral forms (e.g. sphalerite, wurtzite).
- Omit the hyphen in phrases such as "a compound of Ag<sub>2</sub>Te type" or "tie line"; do not write "Ag<sub>2</sub>Te-type" or "tie-line".
- Use only lower case letter p to denote pressure (not P).
- The temperature symbol is written italic: *T*, following the IUPAC.
- Differentiate between allotropic phases by using Greek letters only; do not use commas or dashes (e.g. αAgI neither α-AgI nor α,AgI) in Table 1.
- Capitalize all main words in the section and table headings. In figure captions capitalize only the first word.
- A statement of accuracy of the data should be given wherever it can be concluded from the published work.
- All citations should be given in "References" and all the references listed in "References" should appear in the text or tables.
- Use only  $\rightleftharpoons$  (and not  $=$ ) in equations describing equilibria (e.g.  $L \rightleftharpoons (\text{Te}) + \mu$ ; **not**  $L = (\text{Te}) + \mu$ ).
- Use only the Greek letter ρ (rho) to denote density, given in the units g · cm<sup>-3</sup>.
- Write the equation of equilibrium in one line,



and not  $L + (Ag, Au) \rightleftharpoons$

$AuTe_2 + \gamma Ag_2Te$ .

- There is a blank space before and after *equal*, *less than* and *more than* signs; e.g.  $\kappa = 10$  and  $0 \leq \kappa \leq 1$
- Do not write "isn't", "doesn't", etc. Use the unabbreviated forms "is not", "does not", etc.
- If a paper is referred to as, [71Gly], then it is singular, e.g. "[71Gly] finds", even if several authors have contributed to the paper. The plural should be used, for example, in the following manner: "The authors of [71Gly] find that ...".
- [62Mai] is to be used as a noun in sentences.
- For several references listed together the format is, e.g.: "[62Mai, 63Mai, 72Ran, 73Luk] have ...", or, where two references are used as different nouns: "... both [62Mai] and [63Sch] found by different techniques ...".
- There should be no space inside phase symbols; e.g.  $Co_2Ni(h)$  or  $Co_2Ni(r)$ .
- There is a blank between \* and the phase symbols in Table 1: e.g. \* AlCoU.

## Abbreviations

- An alloy may be abbreviated, for example, Cu-10Zn-20Cd (at.%) or Cu-Zn10-Cd20 (at.%).
- Do not use the abbreviations "Fig." or "Figs." at the beginning of a sentence, but write out "Figure" or "Figures".
- Use emf for electromotive force, not EMF.

## Numbers and Numbering

- Decimal points should be used for decimal figures, (e.g. 1.23 not 1,23).
- If a list of numbered points is presented, number them "1. 2. 3. ..." (Not 1) 2) 3) or 1.) 2.) 3.)).
- Use a, b, c as an additional label to identify figures (e.g. Fig. 11a, 11c; not Fig. 11.1, 11.2).
- Number figures according to the order in their logical sequence.
- In formulae, write e.g.  $5 \cdot 10^{10}$ , **not**  $5 \times 10^{10}$ .

## Units

- In the text all temperatures should be given in °C (not °). At very low temperatures Kelvin (K) may be used.
- All other physical and chemical properties should be expressed in SI units (see International Organization for Standardization ISO, International Standard ISO 1000, First Edition, 1973).
- Use "mass%" not "wt.%".
- Hours and days are abbreviated by h and d respectively.

- Usually leave a space between a number and its unit (e.g. 0.28 eV, 260 h, 6.5 at.%, but between number and °C leave no blank, e.g. 286°C not 286 °C).

## Table

- Footnotes are denoted in tables by superscripts in lower case letters without brackets and without full stop, e.g.  $xyz^a$  or  $xyz^b$ , (not  $xyz^a.$  nor  $xyz^b.$ ). Do not use subscripts for footnotes.
- In the 'Table Solid Phases' use "to" when giving the ranges of lattice parameters, e.g. 543.3 to 550 (not 543.3-550).
- In the Table "Solid Phases" write lattice parameters, their ranges and accuracy in one line, e.g.  $a = 1654 \pm 3$ .

## 4.3. Liquid Miscibility Gaps

Example.

$E'_1$  denotes the composition of L' at the reaction  $E_1$ .

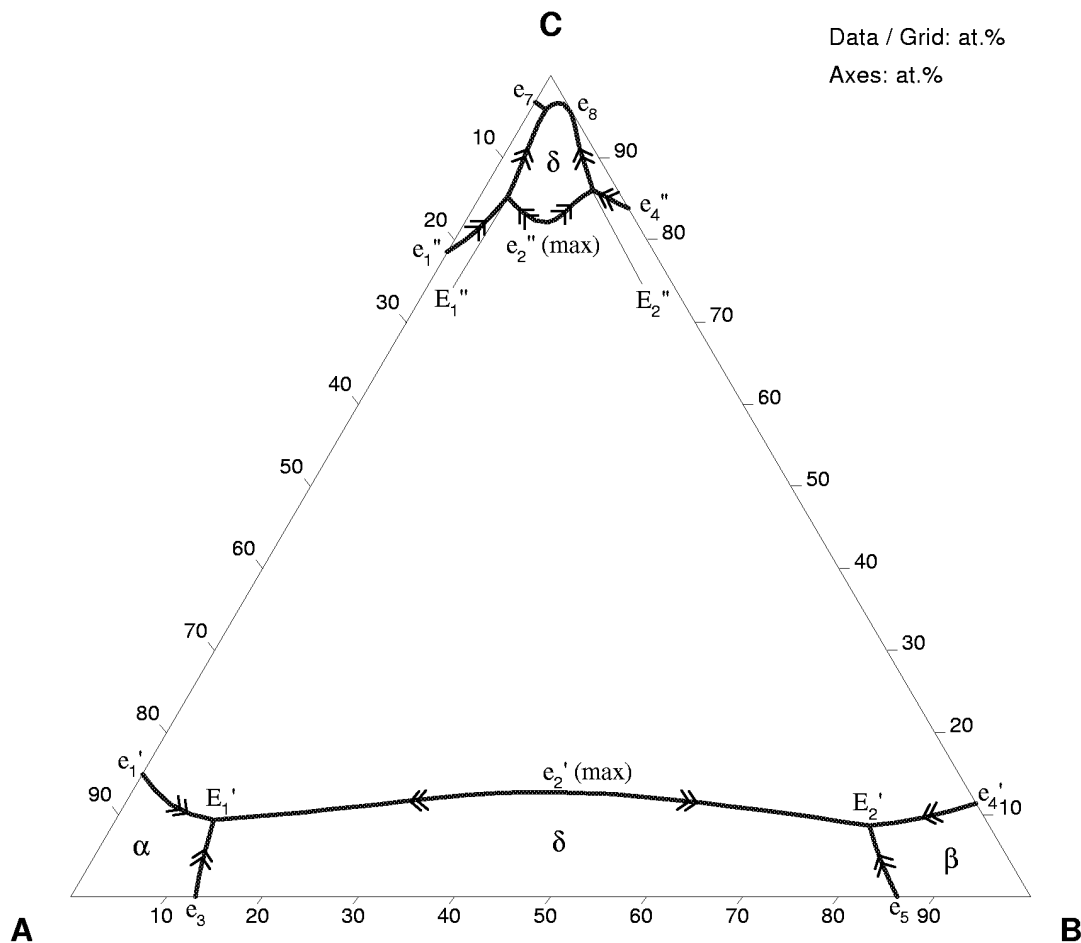
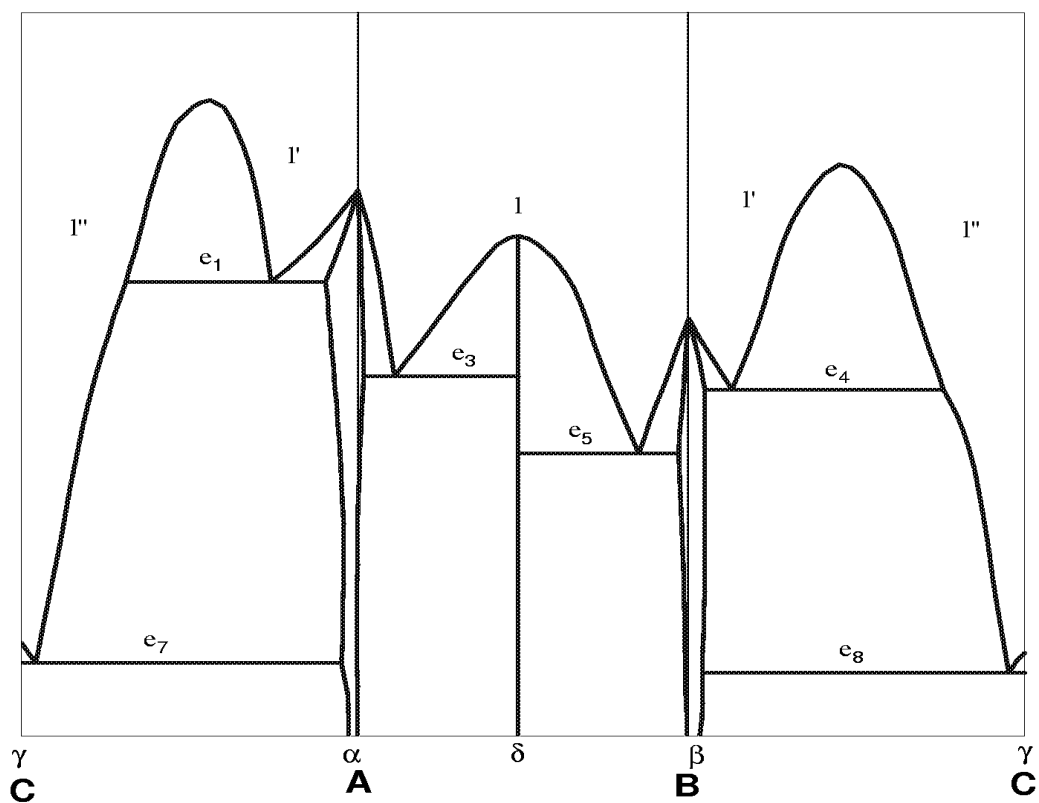
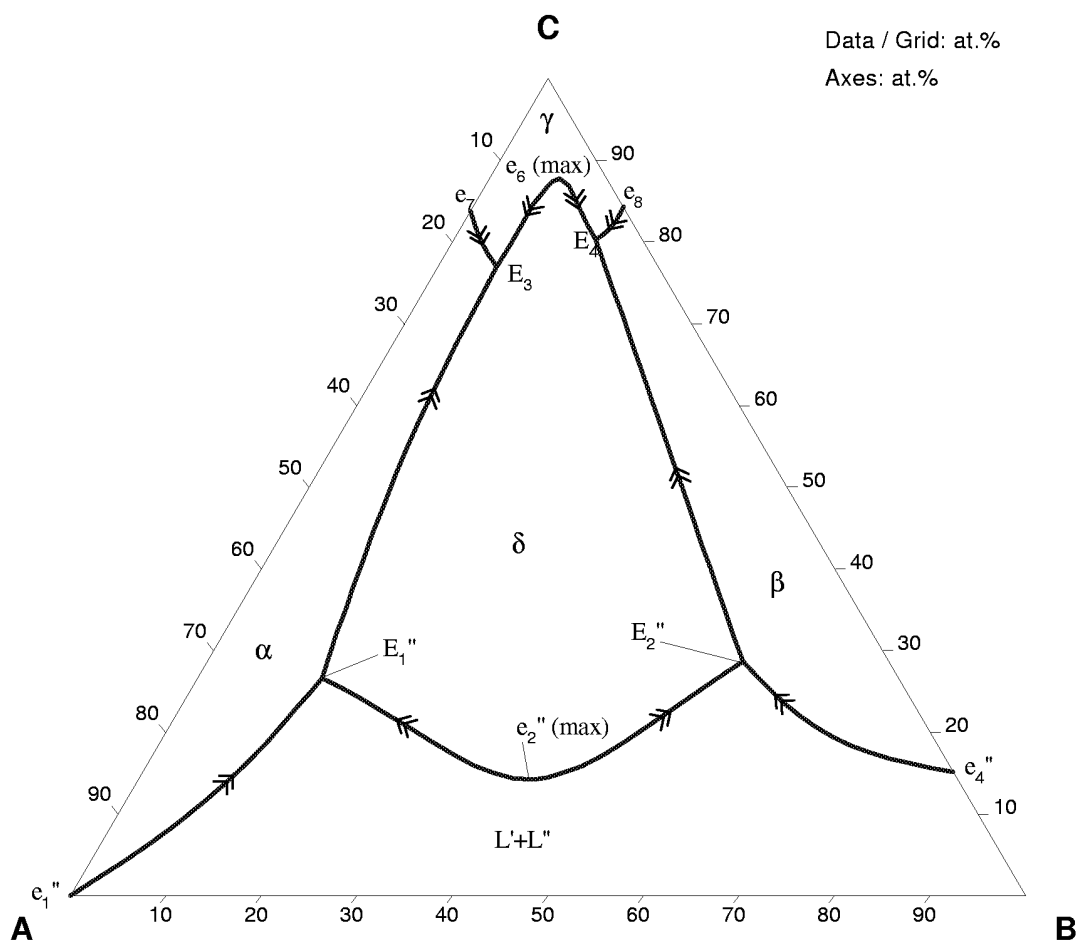


Fig. 1: Liquidus surface of A-B-C system with miscibility gap in the liquid





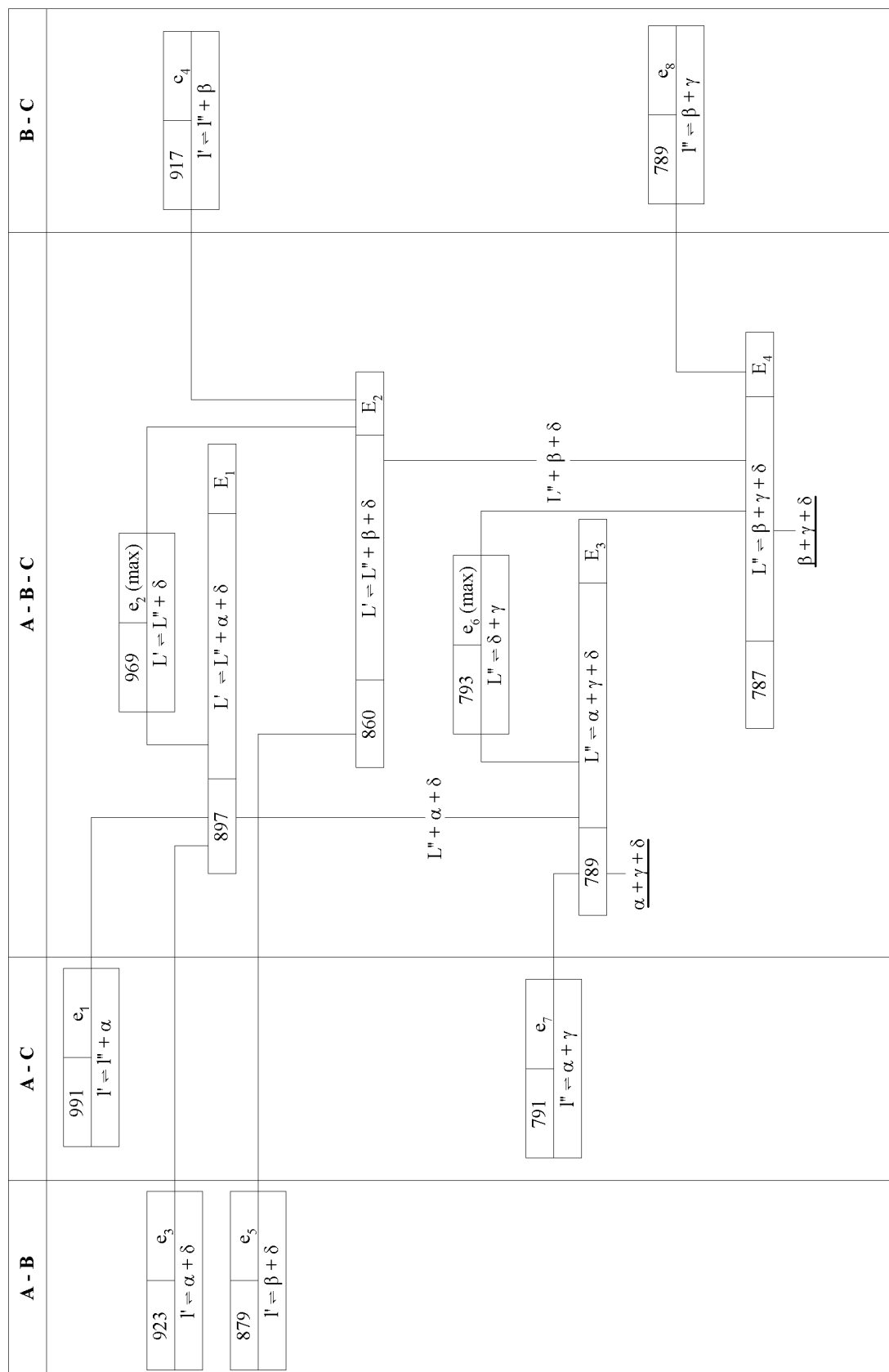


Fig. 4: Reaction scheme

#### 4.4. Examples for the table "Solid Phases"

*If not all phases are given in the table, the selection criterion should be indicated in the text.*

##### Examples for selection criteria

1. All phases are given in Table 1.
2. All ternary phases ...
3. All stable phases of the A-A<sub>2</sub>B-C partial system ...
4. The phases of the A<sub>2</sub>B-A<sub>2</sub>C pseudobinary system ...
5. All phases stable below (at, above) 900°C ...
6. All phases known to be stable ... (indicates, that there are reports on additional phases, assumed to be not stable)

but please do not give:

1. All phases shown in the diagrams ... (this describes a subjective criterion of selection and gives the impression, that some phases arbitrarily are omitted)
2. All known phases ... (that is equivalent to "all phases", because nobody can include phases detected later than the date of the evaluation)

##### Examples for the Style of the Table:

Example 1 (Figure 5): Binary, Complete Solutions and Ternary Phases - Note the sequence

Table 1: Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
(Al) < 660.5	<i>cF4</i> Cu	<i>a</i> = 404.88	24°C [Mas, V-C]
Y <sub>1-x</sub> Er <sub>x</sub> Al <sub>3</sub>	<i>hR12</i> BaPb <sub>3</sub>		0 ≤ <i>x</i> ≤ 0.4 at 800°C, [69Zal]
YAl <sub>3</sub> < 980		<i>a</i> = 620.4 <i>c</i> = 2118.4 <i>a</i> = 618.5 <i>c</i> = 2114	at <i>x</i> = 0 [V-C] at <i>x</i> = 0.09 [65Vuc]
Y <sub>x</sub> Er <sub>1-x</sub> Al <sub>3</sub>	<i>cP4</i> AuCu <sub>3</sub>		0 ≤ <i>x</i> ≤ 0.02, at 800°C, [69Zal]
ErAl <sub>3</sub> < 1070		<i>a</i> = 421.5	at <i>x</i> = 0 [65Vuc, 69Zal, V-C]
Y <sub>1-x</sub> Er <sub>x</sub> Al <sub>2</sub>	<i>cF24</i> Cu <sub>2</sub> Mg		0 ≤ <i>x</i> ≤ 1 [72Wil]
ErAl <sub>2</sub>		<i>a</i> = 779.2±0.1	at <i>x</i> = 1 and 27°C [72Wil]

< 1455			
YAl <sub>2</sub>		$a = 785 \pm 1$	at $x = 0$ and 27°C [72Wil]
< 1485			
* $\tau_1$ , Y <sub>x</sub> Er <sub>1-x</sub> Al <sub>3</sub>	<i>hP20</i>		$0.05 \leq x \leq 0.35$
	HoAl <sub>3</sub>		[69Zal]
		$a = 604.3$	at $x = 0.05$ [69Zal]
		$c = 3578$	
		$a = 604.8$	at $x = 0.35$ [69Zal]
		$c = 3578$	
* $\tau_2$ , Y <sub>x</sub> Er <sub>1-x</sub> Al <sub>3</sub>	<i>hP16</i>		$0.4 \leq x \leq 0.55$
	TiNi <sub>3</sub>		[69Zal]
		$a = 608.6$	at $x = 0.4$ [69Zal]
		$c = 953.0$	
		$a = 607.7$	at $x = 0.55$ [69Zal]
		$c = 951.9$	

Fig. 5: Isothermal section of the system Al-Er-Y at 500°C in the range 66-100 at.% Al

Example 2: Binary and Ternary Phases - note the dual statement in x and at. %

Table 1: Solid Phases

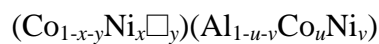
Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
$U(Ni_xAl_{1-x})_2$	<i>cF24</i> $Cu_2Mg$		$0 \leq x \leq 0.18$ [78Dre]
$UAl_2$ < 1622		$a = 776.3$ $a = 770.4$	at $x = 0$ at $x = 0.18$ (12 at. % Ni)
$U(Ni_{1-x}Al_x)_2$	<i>hP12</i> $MgZn_2$		$0 \leq x \leq 0.25$ [78Dre]
$UNi_2$ < 985		$a = 496.17$ $c = 824.16$ $a = 500.3$ $c = 826.0$ $a = 503.9$ $c = 826.4$	at $x = 0$  at $x = 0.15$ (10 at. % Al) at $x = 0.25$ (16.7 at. % Al)
* $U(Ni_{1-x}Al_x)_2$	<i>hP9</i> $Fe_2P$		$0.505 \leq x \leq 0.54$ [78Dre]
		$a = 674.4$ $c = 403.8$ $a = 666.4$ $c = 403.2$	at $x = 0.505$ (33.6 at. % Al) at $x = 0.54$ (36 at. % Al)

Example 3: Quantitative data on solubility in two directions

Table 1: Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
$\beta, (Co_{1-x}Ni_x)Al_{1-y}$	<i>cP2</i> $CsCl$		$0 \leq x \leq 1$ [09Abc]
$CoAl_{1-y}$ < 1645		$a = 286.2$	at $x = 0$ and $y = 0$ [V-C] $-0.04 \leq y \leq 0.73$ [Mas] (51 to 21 at. % Al)
$NiAl_{1-y}$ < 1638		$a = 288.7$	at $x = 1$ and $y = 0$ [V-C] $-0.30 \leq y \leq 0.55$ [Mas] (55 to 38 at. % Al)

The range of homogeneity of the phase is known to be due to vacancies on the (Co, Ni) sublattice at the Al-rich side and to Co or Ni atoms on the Al sublattice at the Al poor side, corresponding to the crystallographic formula:



Example 4: High temperature, high pressure modifications

Table 1: Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
Ag <sub>2</sub> Se(h) 897-133	<i>cI16</i> Ag <sub>2</sub> Se(h)	<i>a</i> = 498	[E]
Ag <sub>2</sub> Se(r) <133	<i>oP12</i> Ag <sub>2</sub> Se(r)	<i>a</i> = 705 <i>b</i> = 432.5 <i>c</i> = 782	[V-C]
In <sub>2</sub> Se <sub>3</sub> (h <sub>3</sub> ) 900-750	<i>m**</i>		[S]
In <sub>2</sub> Se <sub>3</sub> (h <sub>2</sub> ) 750-650	<i>c**</i>	<i>a</i> = 1010	[S, P]
In <sub>2</sub> Se <sub>3</sub> (h <sub>1</sub> ) 650-195	<i>h**</i>	<i>a</i> = 401 <i>c</i> = 1924	[E]
In <sub>2</sub> Se <sub>3</sub> (r) < 195	<i>hP160</i> -	<i>a</i> = 1600 <i>c</i> = 1924	[V-C]
* α', AgInSe <sub>2</sub> (h) 778-625			[66Pal1], [67Pal]; most probably identical to αIII, range of homogeneity
* α, AgInSe <sub>2</sub> (r) < 695	<i>tI16</i> FeCuS <sub>2</sub>	<i>a</i> = 610.4 <i>c</i> = 1171.4	chalcopyrite structure, lattice parameter [80Grz], range of homogeneity
* αIII, AgInSe <sub>2</sub> (III)	<i>hR12</i> NaFeO <sub>2</sub>	<i>a</i> = 394.7 <i>c</i> = 1988.4	High pressure - high temperature phase [77Jay, 83Sch], lattice parameter at 1 bar [77Jay]
* αII, AgInSe <sub>2</sub> (II)	<i>cF8</i> ZnS	<i>a</i> = 600 to 606	high pressure phase, sphalerite type structure [68Ran, 77Jay]
* αI, AgInSe <sub>2</sub> (I)	<i>cF8</i> NaCl	<i>a</i> = 569 <i>a</i> = 551	(1 bar) non-equilibrium high pressure phase [69Ran1] lattice parameter [77Jay] (80 kbar)
* β', AgIn <sub>5</sub> Se <sub>8</sub> (h) 811-662	<i>cF8</i> ZnS sphalerite		[66Pal3] peritectic melting point from [67Pal]
* β, AgIn <sub>5</sub> Se <sub>8</sub> (r) < 740	<i>tP14</i> AgIn <sub>5</sub> Se <sub>8</sub> (r)	<i>a</i> = 579.34 <i>c</i> = 1162.23	ordered defect structure □ <sub>2</sub> AgIn <sub>5</sub> Se <sub>8</sub> [66Pal3, 71Rob, 83Ben], lattice parameters from single crystal [83Ben]

Example 5:

Table 1: Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
$\delta$ Fe 1538-1394	<i>cI2</i> W	$a = 293.78$	at 1480°C [V-C]
$\alpha$ Fe < 912	<i>cI2</i> W	$a = 286.65$	at 20°C [V-C]
$\gamma$ Fe 1394-912	<i>cF4</i> Cu	$a = 366.0$	at 1167°C [V-C]

Comment: If the  $\alpha$ Fe and  $\delta$ Fe solution range merges in the system, the designation of  $\alpha\delta$ Fe is recommended.

#### 4.5. Sequential Order of the Elements

For system names: alphabetical order of element symbols

For compound names: chemical order according to G.D. Pettifor, *J. Phys. C*, **19**, 285-313 (1986)

Examples:

Hf(Al<sub>x</sub>Ge<sub>1-x</sub>)<sub>2</sub> in the Al–Ge–Hf system

MnCu<sub>2</sub>Al in the Al–Cu–Mn system

Ac 48	Be 77	Cm41	Fe 61	Ho 23	Md 36	No 35	Pr 31	Sb 88	Te 92	Yb 17
Ag 71	Bi 87	Co 64	Fm37	I 97	Mg 73	Np 44	Pt 68	Sc 19	Th 47	Zn 76
Al 80	Bk 40	Cr 57	Fr 7	In 79	Mn 60	O 101	Pu 43	Se 93	Ti 51	Zr 49
Am42	Br 98	Cs 8	Ga 81	Ir 66	Mo 56	Os 63	Ra 13	Si 85	Tl 78	
Ar 3	C 95	Cu 72	Gd 27	K 10	N 100	P 90	Rb 9	Sm 28	Tm 21	
As 89	Ca 16	Dy 24	Ge 84	Kr 4	Na 11	Pa 46	Re 58	Sn 83	U 45	
At 96	Cd 75	Er 22	H 103	La 33	Nb 53	Pb 82	Rh 65	Sr 15	V 54	
Au 70	Ce 32	Es 38	He 1	Li 12	Nd 30	Pd 69	Rn 6	Ta 52	W 55	
B 86	Cf 39	Eu 18	Hf 50	Lr 34	Ne 2	Pm29	Ru 62	Tb 26	Xe 5	
Ba 14	Cl 99	F 102	Hg 74	Lu 20	Ni67	Po 91	S 94	Tc 59	Y 25	

Exception: If the ionic nature of a compound is to be emphasized.

Example:

Mg(VO<sub>3</sub>)<sub>2</sub> may be used if the formation of Mg<sup>2+</sup> and (VO<sub>3</sub>)<sub>2</sub><sup>-1</sup> ions is discussed. However, the strict chemical order V<sub>2</sub>MgO<sub>6</sub> is to be used instead of MgV<sub>2</sub>O<sub>6</sub>.





---

## Chapter 5

### Examples of System Reports

Arsenic - Molybdenum – Ruthenium

Aluminium - Germanium - Ytterbium

Aluminium - Ruthenium – Zirconium

Gold – Germanium – Antimony

Aluminium - Indium – Antimony

Aluminium - Iron – Oxygen

## Arsenic - Molybdenum – Ruthenium

*Peter Rogl*

### Literature Data

Superconducting metallic glasses have been reported by [79Joh] for the ternary composition  $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{As}_x$  with  $x = 0.24, 0.28$ .

### References

[79Joh] Johnson, W.L., Williams, A.R., "Structure and Properties of Transition Metal-Metalloid Glasses Based on Refractory Metals", *Phys. Rev.*, **B20**, 1640-1655 (1979) (Experimental, 47)

## Aluminium - Germanium - Ytterbium

*Riccardo Ferro, Adriana Saccone and Stefano Delfino*

### Literature Data

Ternary alloys of the compositions  $\text{YbAl}_2\text{Ge}_2$  [70Zar, 72Mur] and  $\text{YbAlGe}$  [74Rya, 74Yan] have been studied. [70Zar] prepared the alloys starting from Al 99.98 mass%, Ge 99.999 mass% and Yb 99.96 mass%. Powder X-ray analysis was then performed.

A compilation that includes several phases containing Al, Ge and rare earths has been presented by [82Gla].

### Solid Phases

The crystal data of two ternary phases are given in Table 1.

### References

- [70Zar] Zarechnyuk, O.S., Murav'eva, A.A., Gladyshevskii, E.I., "Some New Intermetallic Compounds with a Structure Similar to that of  $\text{La}_2\text{O}_2\text{S}$ " (in Ukrainian), *Dopov. Akad. Nauk Ukr. RSR*, (A), **8**, 753-756 (1970) (Crys. Structure, Experimental, 2)
- [72Mur] Murav'eva, A.A., "Phase Equilibria and Crystal Structures of Compounds in the Ternary Systems of Al and Si (or Ge) with Rare Earth Metals" (in Russian), Thesis, Ivan Franko State University (1972) (Crys. Structure, Equi. Diagram, Experimental, 7)
- [74Rya] Ryabokov, T.I., "New Intermetallic Compounds  $\text{RAlGe}$ , where R is a Rare Earth Metal" (in Ukrainian), *Visn. L'viv Univ., Ser. Khim.*, **15**, 26-28 (1974) (Crys. Structure, Experimental, 2)
- [74Yan] Yanson, T.I., Zarechnyuk, O.S., Gladyshevskii, E.I., "New Rare Earth-Al-Ge Compounds" (in Russian), "Tezisy Dokl.-Vses. Konf. Kristallokhim. Internet. Soedin.", 2nd, Ed: R.M. Rykhal, L'vov Gos. Univ.: Lvov, USSR, 35 (1974) (Crys. Structure, Experimental, 0)
- [82Gla] Gladyshevskii, E.I., Bodak, O.I., "Crystallochemistry of Rare Earth-Metal Intermetallic Compounds" (in Russian), Ed. L'vov University (1982) (Crys. Structure, Review, 1702)

**Table 1:** Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
* YbAl <sub>2</sub> Ge <sub>2</sub>	<i>hP5</i>	$a = 418.4$	[70Zar]
	La <sub>2</sub> O <sub>3</sub>	$c = 704.7$	
		$a = 418$ $c = 705$	[72Mur]
* YbAlGe	<i>oC12</i>	$a = 430.7$	[74Rya, 82Gla]
	DyAlGe	$b = 1057$ $c = 593.5$	

## Aluminium - Ruthenium – Zirconium

*Riccardo Ferro, Adriana Saccone and Stefano Delfino*

### Literature Data

The isothermal section at 800°C in the 0 to 75 at.% Al and 0 to 67 at.% Zr region has been established by [74Spi2]. [79Rae] reported the isothermal section at 500°C in the 65 to 100 at.% Al region.

Data on ternary intermetallic phases have been reported by [66Gan, 72Spi, 74Spi1, 74Spi2].

The alloys were prepared in an arc furnace under a helium atmosphere. X-ray, micrographic and microprobe analyses were performed to determine the phase constitutions of the alloys on samples either in as-cast or in annealed conditions [74Spi1, 74Spi2].

### Binary Systems

The binary phase diagrams Al-Ru and Ru-Zr of [Mas2] have been accepted. For the Al-Zr state diagram, [74Spi2] reports in the 25 to 67 at.% Zr the following binary phases (at 800°C):  $\text{ZrAl}_3$ ,  $\text{ZrAl}_2$ ,  $\text{Zr}_2\text{Al}_3$ ,  $\text{ZrAl}$ ,  $\text{Zr}_4\text{Al}_3$ ,  $\text{Zr}_3\text{Al}_2$  and  $\text{Zr}_2\text{Al}$ . This is in agreement with the latest version of the Zr-Al phase diagram as presented by [86Sau] and modified by [92Per].

### Solid Phases

The system shows four ternary phases corresponding to the stoichiometries  $\text{ZrRuAl}_8$ ,  $\text{ZrRuAl}_4$ ,  $\text{Zr}_5\text{Ru}_2\text{Al}_3$  and  $\text{Zr}_4\text{Ru}_5\text{Al}_{11}$  (that is 20 at.% Zr, 25 at.% Ru) and a complete solid solution between the isostructural binary phases  $\text{ZrRu}$  and  $\text{RuAl}$ . For the  $\text{Zr}_4\text{Ru}_5\text{Al}_{11}$  phase [66Gan] proposed a structure corresponding to the stoichiometry  $\text{Zr}_6\text{Ru}_7\text{Al}_{16}$  (that is 20.7 at.% Zr, 24.14 at.% Ru).

Solid phase data are listed in Table 1.

### Isothermal Sections

Figure 1 presents the isothermal section at 800°C in the 0 to 75 at.% Al and 0 to 67 at.% Zr ranges [74Spi2, 79Rae]. In comparison with [74Spi2] the  $\tau_4$  composition has been slightly corrected. Figure 2 presents the isothermal section at 500°C in the 65 to 100 at.% Al range [79Rae].

## References

- [62Poe] Poetschke, M., Schubert, K., "About the Constitution of Several Homologous and Quasihomologous Systems Related to  $T^4-B^3$ " (in German), *Z. Metallkd.*, **53**, 548-561 (1962) (Crys. Structure, Experimental, 45)
- [66Gan] Ganglberger, E., Nowotny, H., Benesovsky, F., "New G-Phases" (in German), *Monatsh. Chem.*, **97**, 829-832 (1966) (Crys. Structure, Experimental, 4)
- [72Spi] Spitsyna, T.A., Gulamova, D.D., Raevskaya, M.V., Sokolovskaya, E.M., Markiv, V.Ya., "Formation and Reactions of Intermetallic Compounds in the Systems of Ru with Groups IV and III Transition Metals" (in Russian), in "Stroenie, Svojstva i Primenenie Metallovid", Kornilov and Mateveeva (Eds.), 2nd, Mater. Simp., Moscow, 53-54 (1972, publ. 1974) (Crys. Structure, Equi. Diagram, Experimental, 3)
- [74Spi1] Spitsyna, T.A., Raevskaya, M.V., Markiv, V.Ya., Sokolovskaya, E.M., "Formation and Properties of New Phases in (Zr, Ti)-Ru-Al Systems" (in Russian), in "Tezisy Dokl.-Vses. Konf. Kristallokhim. Internet. Soedin", R.M. Rykhal (Ed.), Lvov. Gos. Univ.: Lvov, USSR, 2nd, 121 (1974) (Crys. Structure, Equi. Diagram, Experimental)
- [74Spi2] Spitsyna, T.A., Raevskaya, M.V., Markiv, V.YA., Sokolovskaya, E.M., Zubchenko, V.S., "Physicochemical Study of the Interaction of Laves Phases in the Systems Zr-Ru-Al and Hf-Ru-Al" (in Russian), *Akad. Nauk Ukr. SSR, Metallofizika*, **52**, 103-105 (1974) (Crys. Structure, Equi. Diagram, Experimental, 9)
- [79Rae] Raevskaya, M.V., Sokolovskaya, E.M., "Physical Chemistry of Ruthenium and its Alloys" (in Russian), Moscow Univ., Moscow, 99-105 (1979) (Crys. Structure, Equi. Diagram, Review)
- [86Sau] Saunders, N., Rivlin, V.G., "Thermodynamic Characterization of Al-Cr, Al-Zr and Al-Cr-Zr Alloy Systems", *Mater. Sci. Technol.*, **2**, 521-527 (1986) (Review, 48)
- [92Per] Peruzzi, A., "Reinvestigation of the Zr-rich End of the Zr-Al Equilibrium Phase Diagram", *J. Nucl. Mater.*, **186**, 88-99 (1992) (Equi. Diagram, Experimental, #, 17)

**Table 1:** Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
(Al) <660.452	<i>cF4</i> Cu	$a = 404.96$	T = 25°C [Mas2]
(Ru) <2334	<i>hP2</i> Mg	$a = 270.58$ $c = 428.16$	T = 25°C [Mas2]
(βZr)(h) 1855-863	<i>cI2</i> W	$a = 360.90$	[Mas2]
(αZr)(r) <863	<i>hP12</i> Mg	$a = 323.16$ $c = 514.7$	T = 25°C [Mas2]
Ru <sub>2</sub> Al <sub>3</sub> ≈1600-1000	<i>tI10</i> Os <sub>2</sub> Al <sub>3</sub> or <i>hP5</i> Ni <sub>2</sub> Al <sub>3</sub>	$a = 307.9$ $c = 1433$ $a = 405$ $c = 519$	[Mas2, V-C]
Ru <sub>1-y</sub> (Zr <sub>x</sub> Al <sub>1-x</sub> ) <sub>1+y</sub>	<i>cP2</i> CsCl		0 ≤ x ≤ 1 [74Spi1, 74Spi2] 0 ≤ y ≤ 0.1 at ≈800°C [Mas]
RuAl ≤2050		$a = 303$	x = 0, y = 0 [Mas2, V-C]
ZrRu 2130		$a = 325.3$	x = 1, y = 0 [Mas2, V-C]
RuAl <sub>2</sub> ≤1100	<i>oF24</i> TiSi <sub>2</sub>  or <i>tI6</i> CaC <sub>2</sub> or monoclinic	$a = 801.2$ $b = 471.7$ $c = 878.5$ $a = 440$ $c = 638$ $a = 514$ $b = 800$ $c = 490$ $\beta = 115^\circ$	[V-C, Mas2]
Ru <sub>4</sub> Al <sub>13</sub> ≤1403	<i>mC102</i> Fe <sub>4</sub> Al <sub>13</sub>	$a = 1586$ $b = 818.8$ $c = 1274$ $\beta = 107.8^\circ$	[Mas2, V-C]
RuAl <sub>6</sub> <723			[Mas2]
ZrAl <sub>3</sub> <1580	<i>tI16</i> ZrAl <sub>3</sub>	$a = 401.4$ $c = 1732.0$	[86Sau, V-C]
Zr(Ru <sub>x</sub> Al <sub>1-x</sub> ) <sub>2</sub> <1645	<i>hP12</i> MgZn <sub>2</sub>		0 ≤ x ≤ 0.4, linear depending da/dx, dc/dx <sup>a</sup> [74Spi2]
ZrAl <sub>2</sub>		$a = 528.24$ $c = 874.82$ $a = 527$	x = 0 [86Sau, V-C]  x = 0 [74Spi2]

		$c = 875$	
		$a = 526$	$x = 0.1$ [74Spi2]
		$c = 865$	
		$a = 525.5$	$x = 0.25$ [74Spi2]
		$c = 549$	(33.3 at.% Zr, 50 at.% Al)
		$a = 525$	$x = 0.4$ [74Spi2]
		$c = 833$	(33.3 at.% Zr, 40 at.% Al)
Zr <sub>2</sub> Al <sub>3</sub> <1595	<i>oF</i> 40 Zr <sub>2</sub> Al <sub>3</sub>	$a = 960.1$ $b = 1390.6$ $c = 557.4$	[86Sau, V-C]
ZrAl <1250	<i>oC</i> 8 CrB	$a = 335.3$ $b = 1086.6$ $c = 426.6$	[62Poe, 86Sau]
Zr <sub>5</sub> Al <sub>4</sub> (h) 1550-1000	<i>hP</i> 18 Ti <sub>5</sub> Ga <sub>4</sub>	$a = 844.7$ $c = 581$	[62Poe, V-C]
Zr <sub>4</sub> Al <sub>3</sub> ≤1000	<i>hP</i> 7 Zr <sub>4</sub> Al <sub>3</sub>	$a = 543.3$ $c = 539.0$	[86Sau, V-C]
Zr <sub>3</sub> Al <sub>2</sub> <1480	<i>tP</i> 20 Zr <sub>3</sub> Al <sub>2</sub>	$a = 763.0$ $c = 699.8$	[86Sau, V-C]
Zr <sub>5</sub> Al <sub>3</sub> (h) 1395-1000	<i>tI</i> 32 W <sub>5</sub> Si <sub>3</sub>	$a = 1104.9$ $c = 539.6$	[86Sau, V-C]
Zr <sub>5</sub> Al <sub>3</sub> (r) <1000	<i>hP</i> 16 Mn <sub>5</sub> Si <sub>3</sub>	$a = 818.4$ $c = 570.2$	[V-C], probably an oxygen stabilized phase
Zr <sub>2</sub> Al(h) 1250-900	<i>tI</i> 12 CuAl <sub>2</sub>	$a = 685.4$ $c = 550.1$	[86Sau, V-C]
Zr <sub>2</sub> Al(r) ≤900	<i>hP</i> 6 Ni <sub>2</sub> In	$a = 489.39$ $c = 592.83$	[86Sau, V-C]
Zr <sub>3</sub> Al <1019	<i>cP</i> 4 AuCu <sub>3</sub>	$a = 437.2$	[92Per, V-C]
ZrRu <sub>2</sub> 1825-1285	<i>hP</i> 12 MgZn <sub>2</sub>	$a = 514.1$ $c = 850.9$	[Mas2, V-C]
* $\tau_1$ , ZrRuAl <sub>8</sub>	-	-	[79Rae]
* $\tau_2$ , ZrRuAl <sub>4</sub>	-	-	[72Spi, 74Spi2]
* $\tau_3$ , Zr <sub>5</sub> Ru <sub>2</sub> Al <sub>3</sub>	-	-	[72Spi, 74Spi2]
* $\tau_4$ , Zr <sub>4</sub> Ru <sub>5</sub> Al <sub>11</sub>	<i>cF</i> 116 ThMn <sub>23</sub>	$a = 1240.0$ $a = 1242$	[66Gan] [72Spi, 74Spi2]

<sup>a</sup> as scaled from diagram



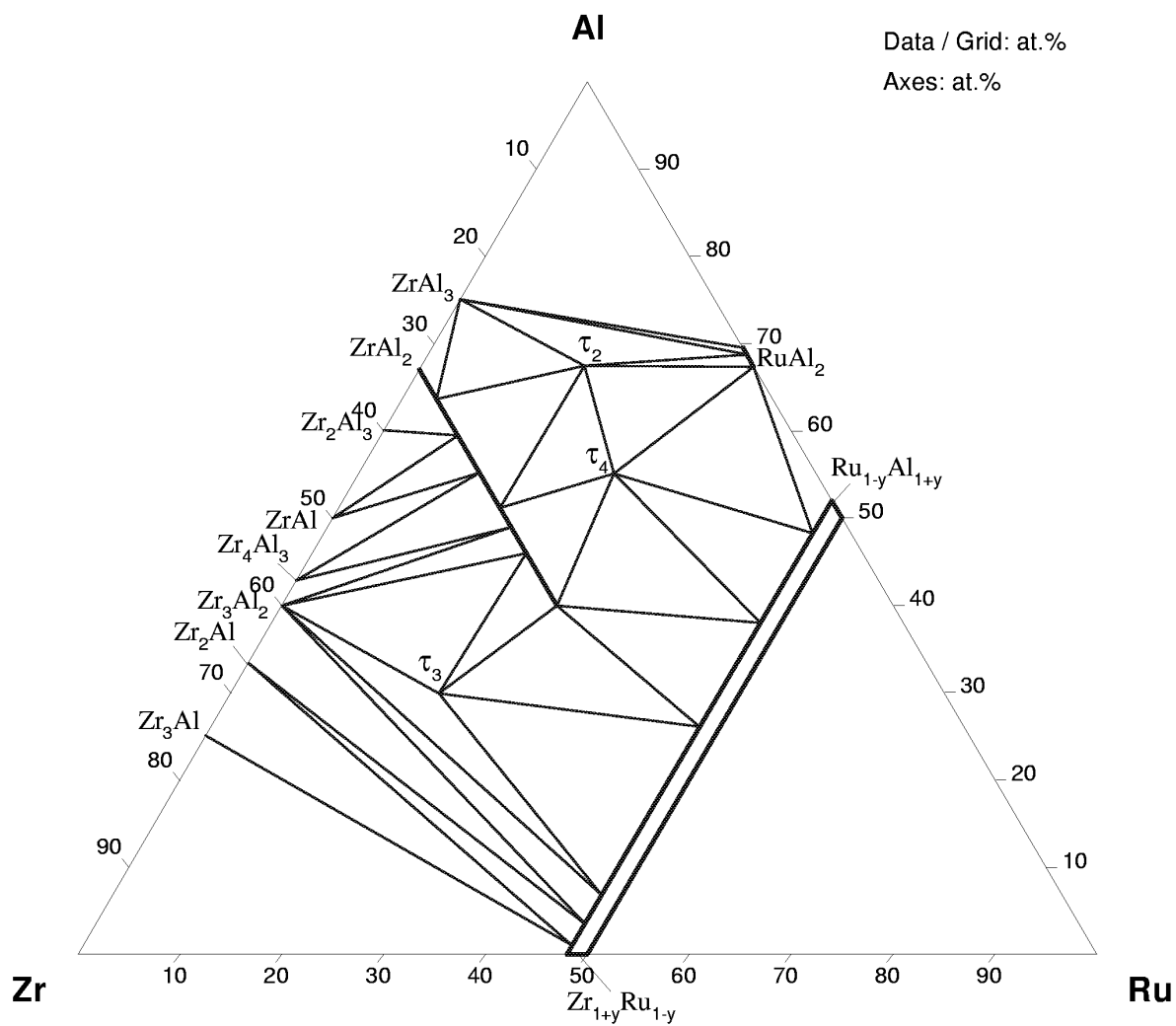


Fig. 1: Partial isothermal section at 800°C

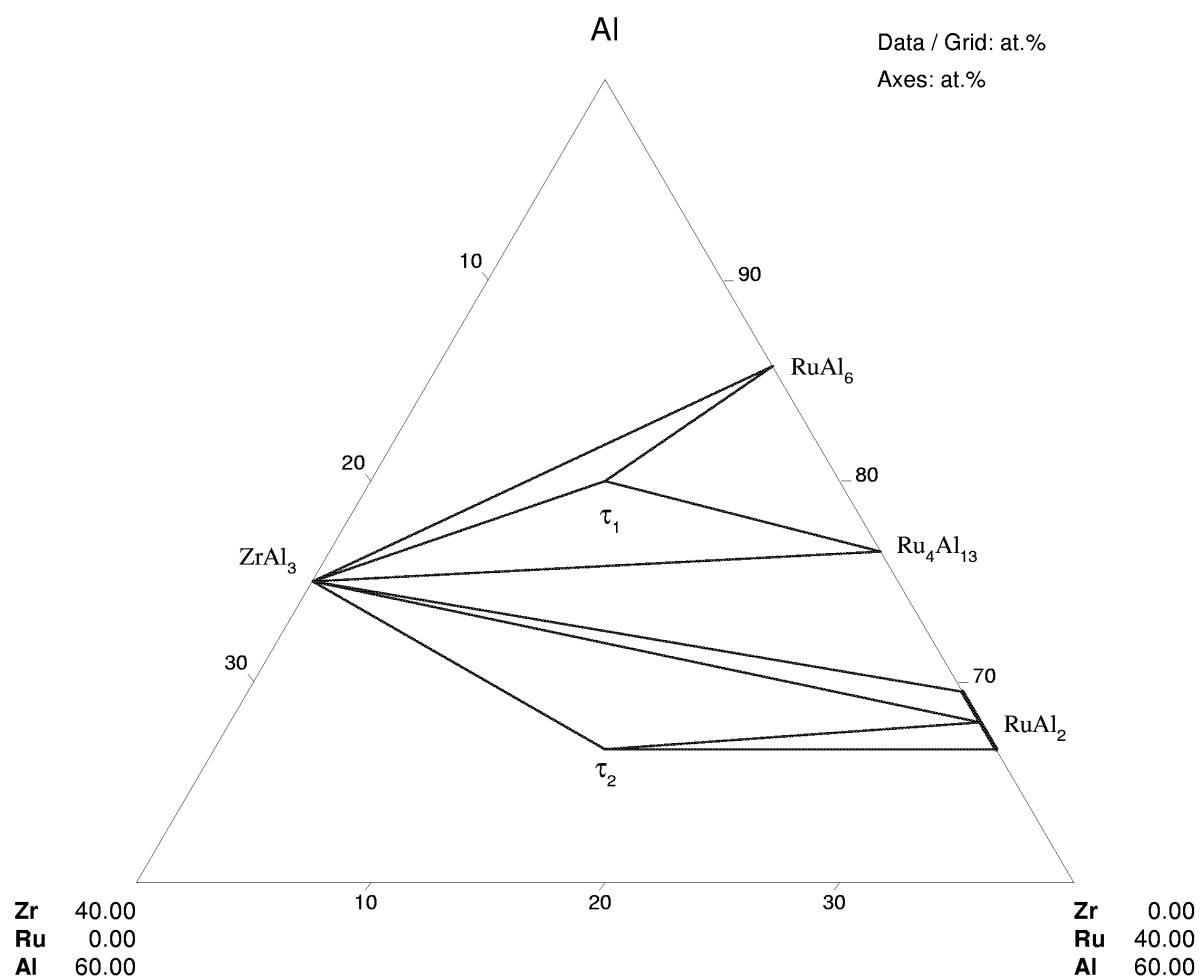


Fig. 2: Partial isothermal section at 500°C

## Gold – Germanium – Antimony

*Mireille Harmelin and Hans Leo Lukas*

### Literature Data

The ternary Au-Ge-Sb system was investigated by [64Zwi, 68Gub, 71Gub]. [64Zwi] examined 39 alloys on the sections AuSb<sub>2</sub>-Ge (Fig. 1), Au-Ge<sub>10</sub>Sb<sub>90</sub> (Fig. 2) and at 15 at.% Ge (Fig. 3). Differential thermal analyses at cooling rates of about 19 K/min at 600°C and about 8 K/min at 300°C were the primary experimental method, supplemented by metallographic examination of selected alloys. All alloys were prepared from pure elements (Au and Sb: purity 99.95; Ge: 99.9 mass%) by melting in an alumina crucible under a hydrogen atmosphere. [64Zwi] established the occurrence of two invariant reactions: a transition reaction  $L + (Sb) \rightleftharpoons (Ge) + AuSb_2$  at  $430 \pm 3^\circ C$  followed by a ternary eutectic reaction  $L \rightleftharpoons (Au) + (Ge) + AuSb_2$  at  $288 \pm 5^\circ C$  and determined the liquidus surface (Fig. 4). The liquidus curves for four alloys containing  $\geq 50$  at.% Ge on the section 98.4 at.% Au, 1.6 at.% Sb–Ge were investigated by [68Gub]. Although the isotherms due to [64Zwi] (Fig. 4) should be regarded tentatively, they are accepted in preference to the data of [68Gub] (see below "Liquidus Surface"). The work of [71Gub] on the solid solubility of Sb in Ge for the sections from Ge to a concentration of 98.4 at.% Au, 1.6 at.% Sb are not reported since [71Gub] state that under the conditions of the experiments, equilibrium was not reached.

### Binary Systems

The Au-Ge and Ge-Sb binary systems from [Mas2] are accepted. The Au-Sb system evaluated by [Mas2] indicates a peritectic liquid containing 66.6 at.% Sb, only differing slightly from the composition of the compound AuSb<sub>2</sub>. [84Pri, 90Pri] report the peritectic liquid at 65.6 at.% Sb and  $458 \pm 1^\circ C$ . The eutectic reaction occurs at  $356 \pm 1^\circ C$  and 36.1 at.% Sb. The Au-Sb phase diagram from [84Pri, 90Pri] is accepted, it is presented in Fig. 5. All the Au systems, however, disagree with Raoult's law of initial slope of liquidus at the Au melting point, if the enthalpy of melting of Au from [91Din] is accepted. This is also obvious in the calculated diagram in Fig. 10 of reference [84Oka].

### Solid Phases

Table 1 summarizes the crystal structure data for the binary phases. No ternary compounds were observed.

## Invariant Equilibria

The Au–Ge–Sb ternary system contains two invariant ternary reactions, U and E [64Zwi]. The compositions of the respective liquid phases are given in Table 2. They are considered to be within  $\pm 1\%$  for each element in terms of U and  $\pm 0.5\%$  for each element in terms of E. The reaction scheme is presented in Fig. 6.

## Liquidus Surface

The liquidus surface presented in Fig. 4 has been derived from the vertical sections determined by [64Zwi] (see Miscellaneous, Figs. 1, 2 and 3). The binary compound  $\text{AuSb}_2$  was regarded as an example of a limiting case between congruent formation from the liquid and incongruent formation. The work of [84Pri, 90Pri] has established that  $\text{AuSb}_2$  forms by peritectic reaction. The monovariant curve  $p_1U$ , (Fig. 4) has been amended to indicate this fact. In general, the isotherms drawn by [64Zwi] have been accepted. Changes have been made to the isotherms at 450, 500 and 550°C in the region of primary separation of Sb. They are not as markedly concave to the Sb corner as originally drawn [64Zwi]. The isotherms from 450 to 700°C in the primary Ge region rely mainly on data points for the Ge–Sb and Au–Ge binary systems and the  $\text{AuSb}_2$ –Ge section. The 600 and 700°C and even more the 800 and 900°C isotherms in the primary Ge field are particularly arbitrary, since they depend on an extrapolation of the liquidus of the  $\text{AuSb}_2$ –Ge section (Fig. 1).

According to [68Gub] the addition of very small amounts of Sb to Au–Ge alloys depresses the liquidus temperature significantly. This does not agree with the 600 and 700°C isotherms given by [64Zwi] (Fig. 4) on the basis of liquidus values for the  $\text{AuSb}_2$ –Ge section and the Au–Ge and Ge–Sb binary systems. The isotherms due to [64Zwi] (Fig. 4) are accepted in preference to the data of [68Gub].

## Miscellaneous

Three vertical sections were studied [64Zwi]. The  $\text{AuSb}_2$ –Ge section (Fig. 1) was determined for up to 50 at.% Ge. The Au– $\text{Ge}_{10}\text{Sb}_{90}$  section (Fig. 2) is presented on the basis of very low solubility of Ge and Sb in Au. [64Zwi] did not study alloys with more than 90 at.% Au. The 15 at.% Ge section (Fig. 3) is an exceptional case as the monovariant curve UE closely follows this line and it is impossible to decide on which side of the section it really is. In any case the two-phase fields separating the three phase fields from the field of homogeneous liquid are very narrow. In Fig. 3 the liquidus line between 17 and 85 at.% Sb is redrawn in agreement with the accepted binaries and the liquidus surface in Fig. 4. The section passes directly through the ternary eutectic point E, therefore it is degenerated at this point.

## References

- [64Zwi] Zwingmann, G., "The Ternary System Au-Sb-Ge" (in German), *Z. Metallkd.*, **55**, 192-194 (1964) (Equi. Diagram, Experimental, \*, 1)
- [68Gub] Gubenko, A. Ya., Kononykhina, N.A., " Investigation of the Ge-(Au + 1 wt.% Sb) Section", *Inorg. Mater.*, **4**, 1557-1558 (1968), translated from *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **4**, 1787-1788 (1968) (Equi. Diagram, Experimental, 7)
- [71Gub] Gubenko, A. Ya., Miller, M.B., Kononykhina, N.A., "Polythermal Cross Sections in the Systems Ge-Au-Sb and Ge-Au-Ga", *Inorg. Mater.*, **7**, 1021-1024 (1971), translated from *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **7**, 1153-1156 (1971) (Equi. Diagram, Experimental, 9)
- [84Oka] Okamoto, H., Massalski, T.B., "The Au-Sb (Gold-Antimony) System", *Bull. Alloy Phase Diagrams*, **5**, 166-171 (1984) (Equi. Diagram, Review, 38)
- [84Pri] Prince, A., Evans, D.S., in Kaufman, L., "Summary of the Proceedings of the Thirteenth CALPHAD Meeting", *CALPHAD*, **8**, 191-220 (1984), p. 212
- [90Pri] Prince, A., Raynor, G.V., Evans, D.S., "Au-Sb", in *Phase Diagrams of Ternary Gold Alloys*, The Institute of Metals, London, 483 (1990) (Equi. Diagram, # , 0)
- [91Din] Dinsdale, A.T., "SGTE Data for Pure Elements", *CALPHAD*, **15**, 319-427 (1991) (Review)

**Table 1:** Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
(Au) < 1064.43	<i>cF4</i> Cu	$a = 407.82$  $a = 408.3$	pure Au at 25°C [Mas2], dissolves up to 1.2 at.% Sb at 360°C and 3 at.% Ge at 361°C at 1 at.% Sb [V-C2]
(Sb) < 630.76	<i>hR2</i> $\alpha$ As	$a = 325.30$ $c = 495.02$	pure Sb [Mas2], practically no solubility of Au and Ge
(Ge) < 938.3	<i>cF8</i> C (diamond)	$a = 565.74$	pure Ge at 25°C [Mas2], practically no solubility of Au and Sb
AuSb <sub>2</sub> < 458	<i>cP12</i> FeS <sub>2</sub>	$a = 665.80$	at 22°C [V-C2]

**Table 2:** Invariant Equilibria

T (°C) Reaction	Type	Phase	Composition (at.%)		
			Au	Ge	Sb
430±3 $L + (Sb) \rightleftharpoons (Ge) + AuSb_2$	U	L	35	14	51
288±5 $L \rightleftharpoons (Au) + (Ge) + AuSb_2$	E	L	68	15	17

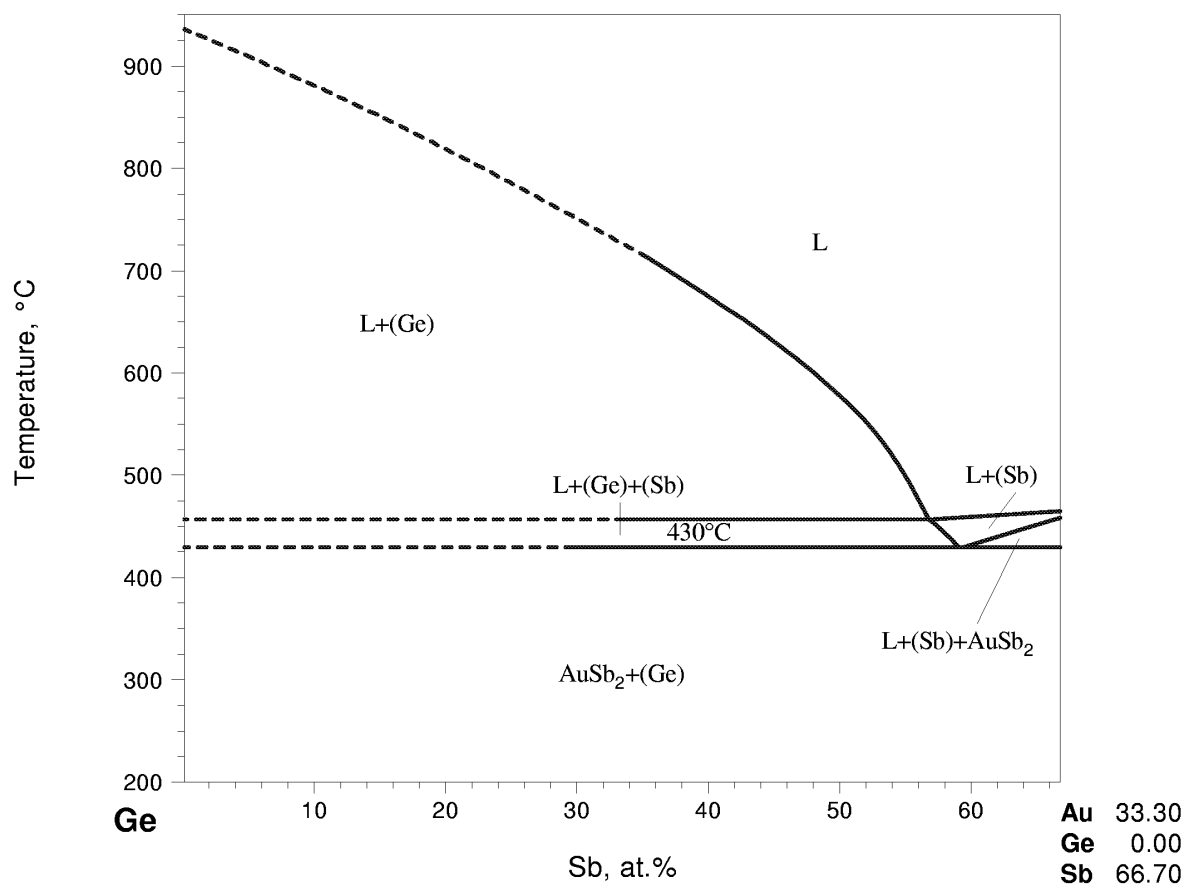


Fig. 1: The Ge-AuSb<sub>2</sub> section

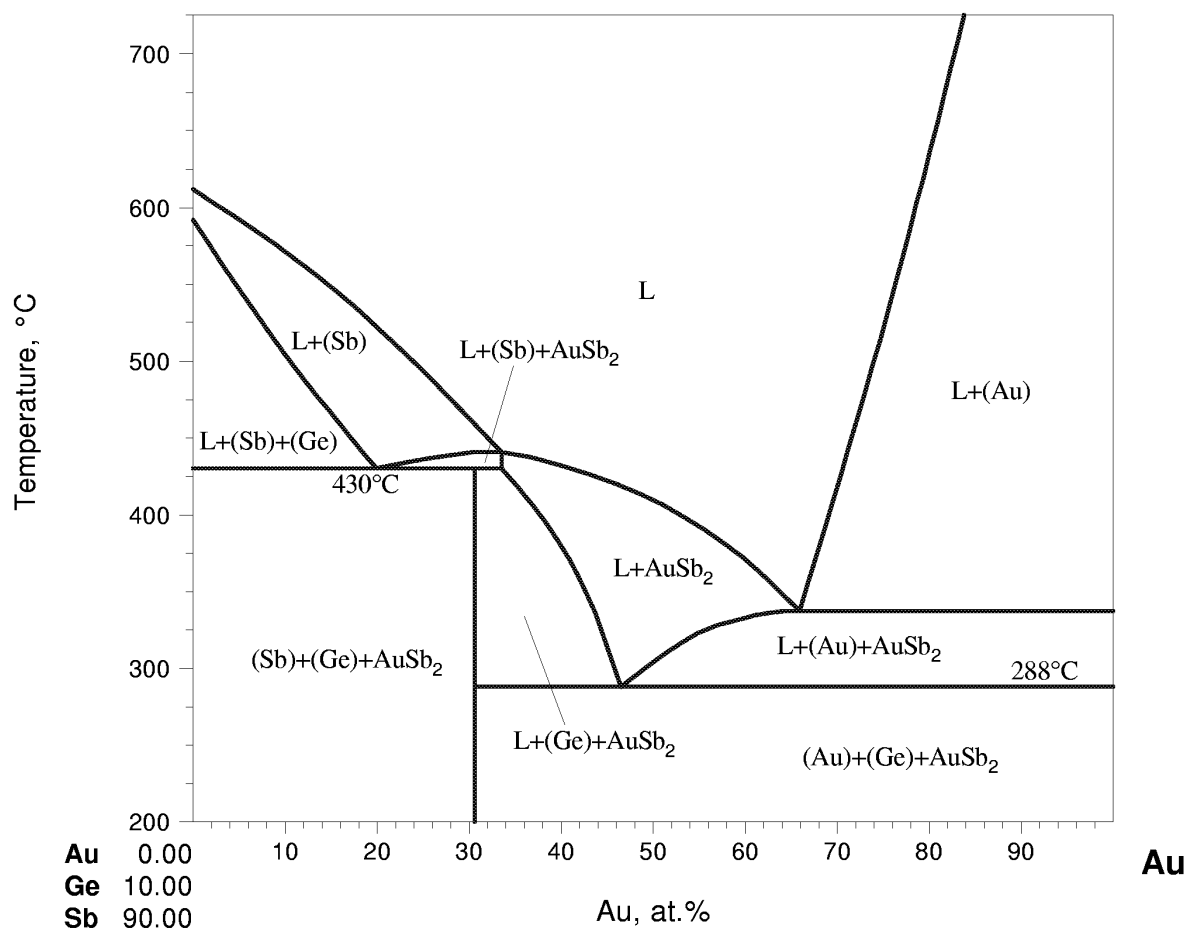


Fig. 2: The  $\text{Ge}_{10}\text{Sb}_{90}$  - Au section



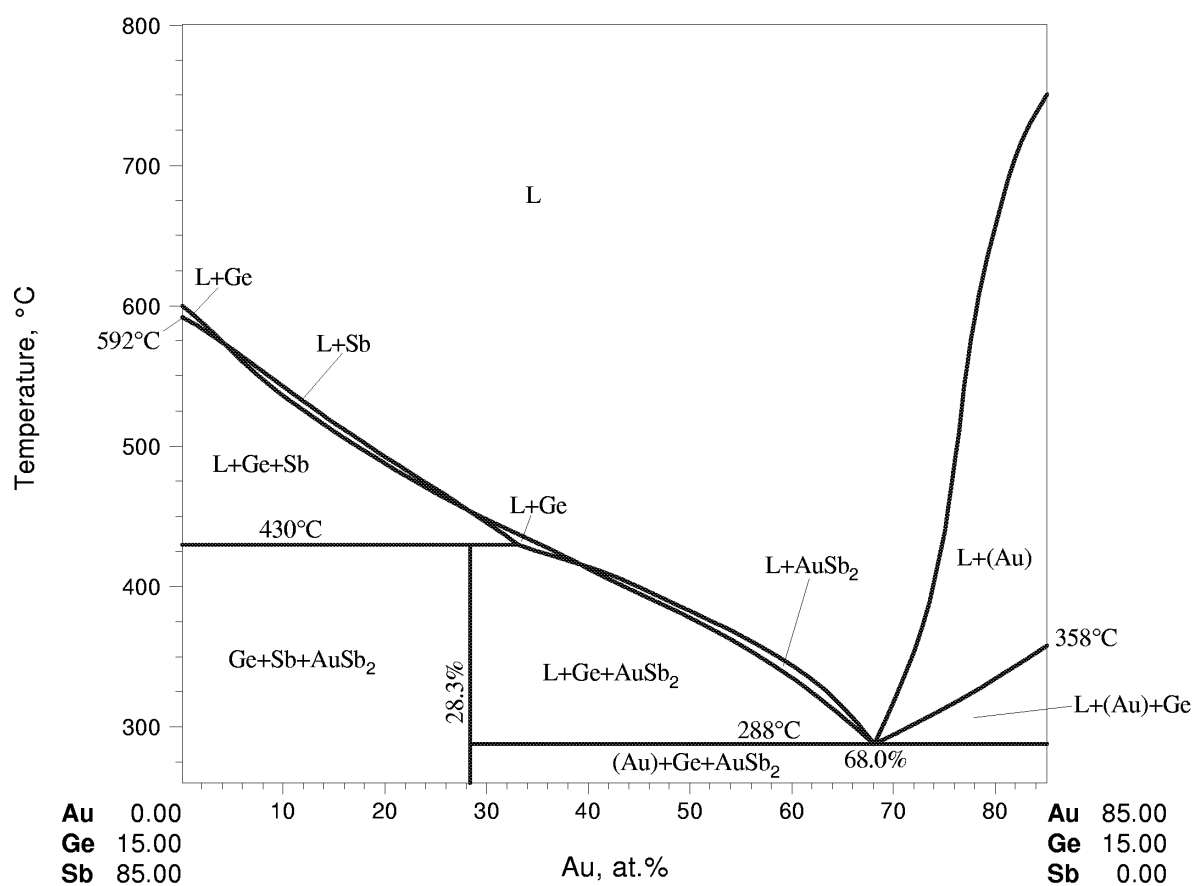


Fig. 3: The 15 at.% Ge section

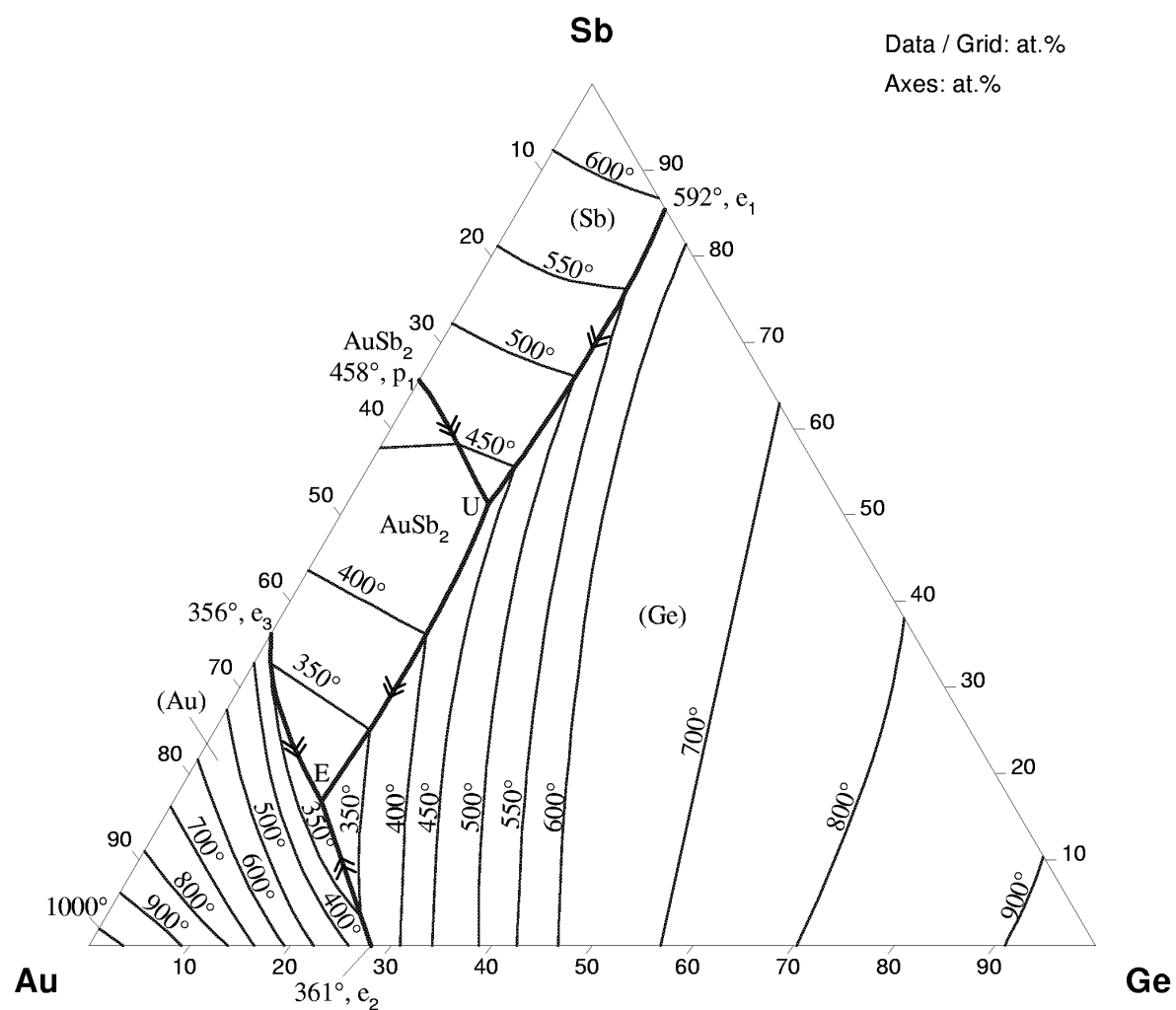


Fig. 4: The liquidus surface of the Au-Ge-Sb system

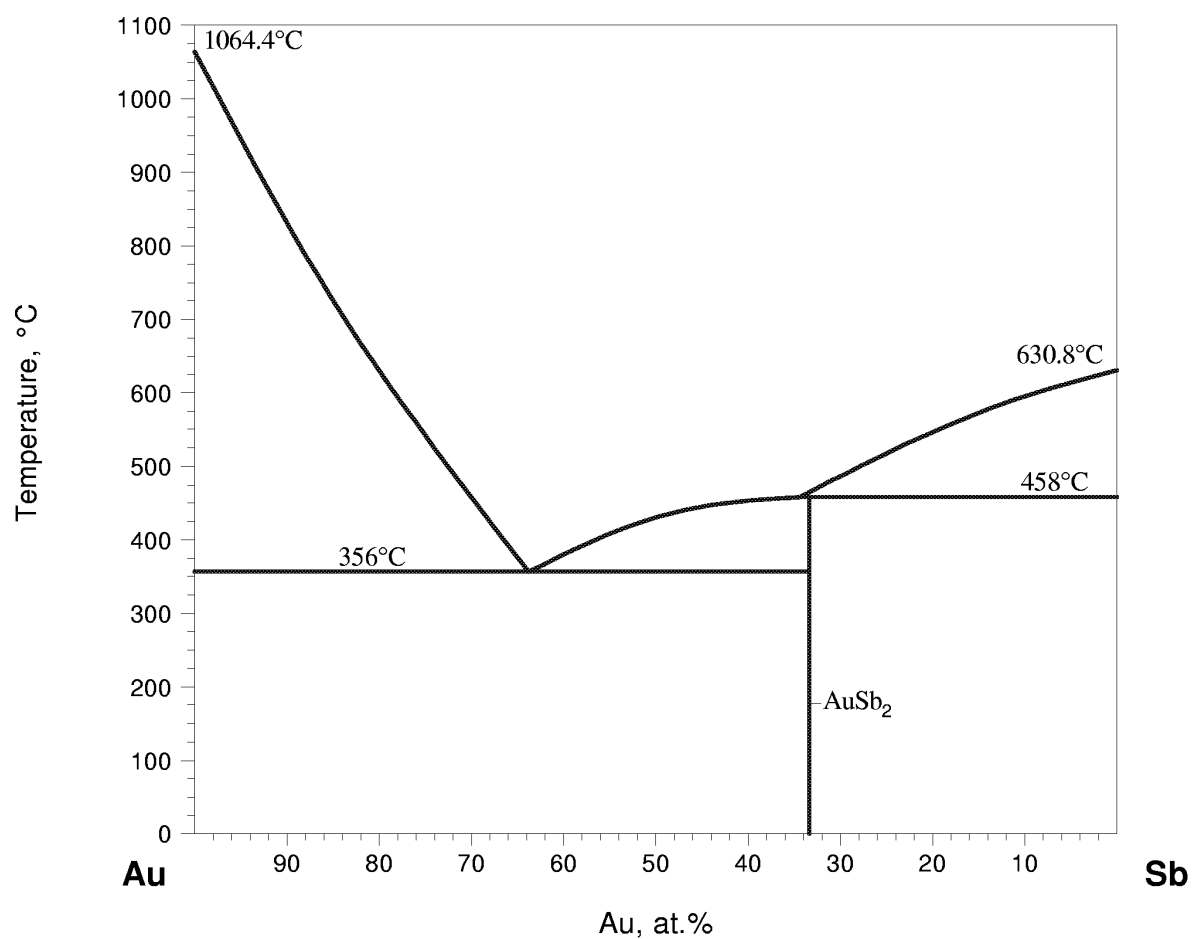


Fig. 5: The binary Au-Sb phase diagram [90Pri]

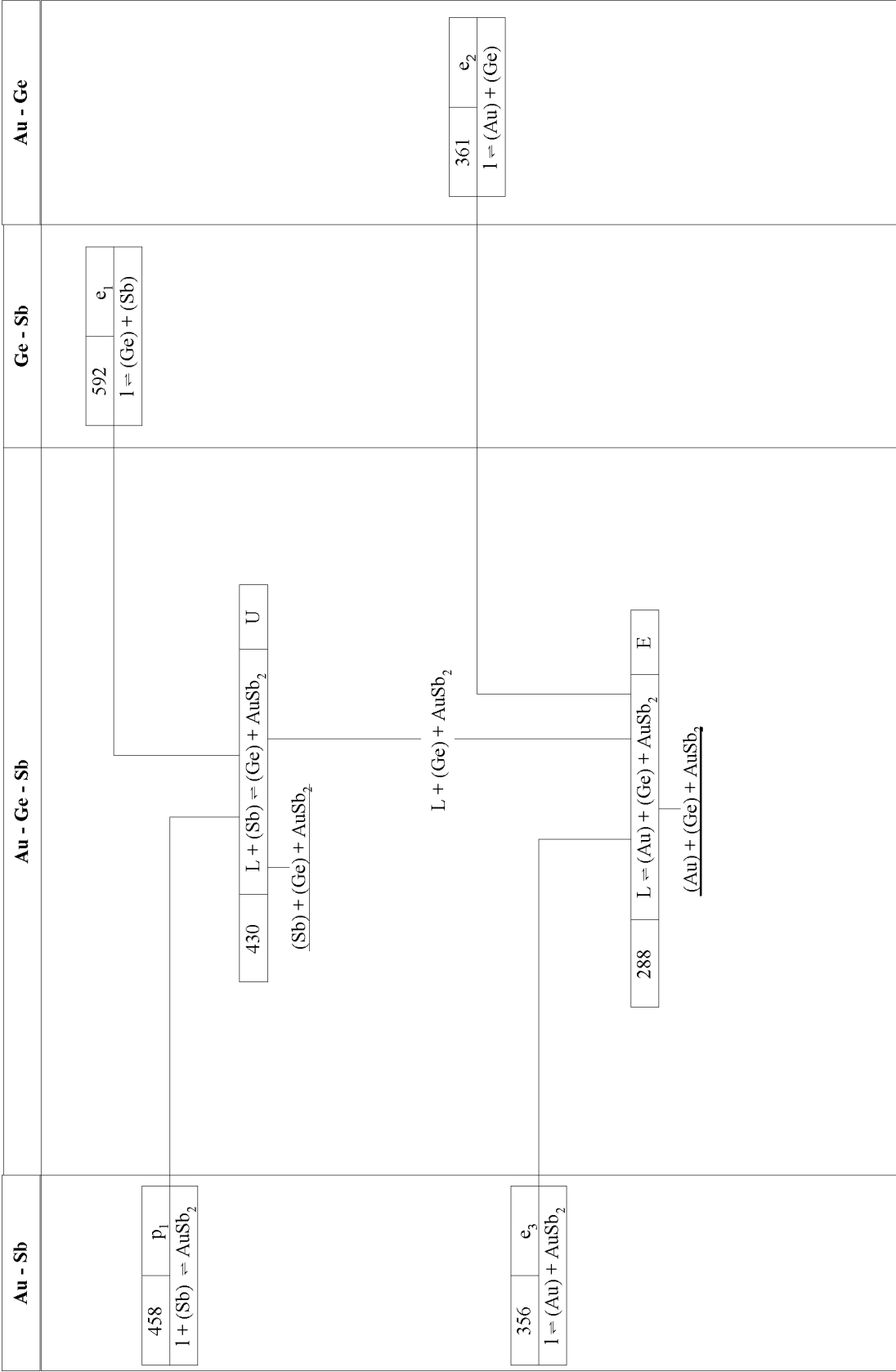


Fig. 6: Reaction scheme

## Aluminium - Indium – Antimony

*Rainer Schmid-Fetzer*

### Literature Data

Twenty-four ternary alloys mainly along the sections InSb–AlSb and Sb–Al<sub>50</sub>In<sub>50</sub> have been prepared by melting from the elements (purity 99.99%) under a LiCl protective layer and studied by thermal analysis and metallography [55Koe]. The solidus data have been misinterpreted in terms of a degenerated eutectic along the InSb–AlSb section. This misinterpretation was due to the very slow solid state diffusion in the In<sub>1-x</sub>Al<sub>x</sub>Sb ( $\alpha$ ) phase and was corrected in a follow-up work [58Koe] where the development of a homogenous  $\alpha$ -solid solution was found by X-ray diffraction on samples annealed at 500°C up to 1000 h. The solid solution was also investigated by [58Woo], who prepared 9 samples along the InSb–AlSb section by melting from the elements (purity >99.9%) in a graphite crucible enclosed by an evacuated silica capsule and quenching. Each alloy was powdered, X-rayed and then compressed and resealed in evacuated capsules and annealed at 525°C for 2200 h. It was then cooled, re-powdered and annealed at progressively higher temperatures, the approach to equilibrium being followed by X-ray methods. The solidus was determined by annealing in the (L+ $\alpha$ ) heterogeneous region, quenching and determining the composition of  $\alpha$  by its lattice parameter compared to that of single-phase samples. A linear variation of lattice parameter with the composition of  $\alpha$  was also found by [59Gor, 60Bar] and the homogeneity of  $\alpha$  was further confirmed by the changing microstructure and microhardness of annealed samples [60Bar]. Most recently, the liquidus was determined by DTA on cooling with 23 ternary samples prepared from pure ( $\geq 99.999\%$ ) elements [88Ish] and the  $\alpha$ -solidus was determined by electron microprobe analysis of quenched (L+ $\alpha$ ) samples. In addition, [88Ish] presented a thermodynamic calculation of the ternary (L+ $\alpha$ ) and (L'+L'') equilibria consistent with the experimental data. A thermal analysis of two samples on the InSb–AlSb section [65Bar] should not be interpreted in terms of solidus data. Thermodynamic calculations of the pseudobinary InSb–AlSb system have also been performed mostly using regular solution theory, and similar liquidus and solidus lines are obtained [69Nik, 70Ste, 72Pan, 72Str].

### Binary Systems

The binary systems Al–In, Al–Sb and In–Sb from [Mas] are accepted.

### Solid Phases

The solid phases observed in this system are given in Table 1.

## **Pseudobinary Systems**

The pseudobinary system InSb–AlSb, given in Fig. 1, is from the calculation of [88Ish], in good agreement with experimental data [55Koe, 58Woo, 65Bar] and a previous calculation of [72Pan].

## **Invariant Equilibria**

The reaction scheme of [58Koe] is given in revised form in Fig. 2.

## **Liquidus Surface**

The liquidus surface in Fig. 3 is from [88Ish] with the addition of the eutectic lines of the  $L+\alpha+(Sb)$  and the  $L+\alpha+(Al)$  equilibria. The location of the  $E_1'-E_1''$  four-phase liquid is estimated and  $E_2$  is almost degenerated into the melting point of Indium. The few data of [55Koe] at lower Sb content disagree with [88Ish].

## **Isothermal Sections**

The isothermal sections in Figs. 4-6 are from the thermodynamic calculation of [88Ish].

## **Miscellaneous**

The enthalpies of mixing of liquid InSb and AlSb at 1072°C have been measured by direct mixing in a calorimeter and a maximum value of 562 J/mole has been obtained [79Ger]. The enthalpies of formation of  $\alpha$ -solid solutions have been estimated from various theoretical considerations and maximum values of 630 J/mol [72Pan], 680 J/mol [78Bas], 1420 J/mol [72Str] and 1520 J/mol [84Fed] are reported. Simplified parameters for the AlSb–InSb system are also given in [80Kor]. A theoretical estimation of the chemical potentials in the  $\alpha$  phase was made by [89Ich].

## References

- [55Koe] Köster, W., Thoma, B., "Constitution of Ternary Systems Comprising Metals of Group III and V of the Periodic System" (in German), *Z. Metallkd.*, **46**, 293-297 (1955) (Equi. Diagram, Experimental, #, 7)
- [58Koe] Köster, W., Ulrich, W., "The Isomorphism of Compounds of the Type  $A^{III}B^V$ " (in German), *Z. Metallkd.*, **49**, 365-367 (1958) (Crys. Structure, Equi. Diagram, Experimental, 13)
- [58Woo] Woolley, J.C., Smith, B.A., "Solid Solutions in  $A^{III}B^V$  Compounds", *Proc. Phys. Soc.*, **72**, 214-223 (1958) (Equi. Diagram, Crys. Structure, Experimental, #, \*, 16)
- [59Gor] Goryunova, N.A., Baranov, B.V., "Solid Solutions in the AlSb-InSb System" (in Russian), *Dokl. Akad. Nauk SSSR*, **129**, 839-840 (1959) (Crys. Structure, Experimental, 2)
- [60Bar] Baranov, B.V., Goryunova, N.A., "Preparation of Homogeneous Solid Solutions in the AlSb-InSb System", *Fizika Tverd. Tela*, **2**, 262-266 (1960) (Crys. Structure, Equi. Diagram, Experimental, 9)
- [65Bar] Baranov, B.V., Prochukhan, V.D., Goryunova, N.A., "Thermal Analysis of Some Solid Solutions" (in Russian), *Latvijas PSR Zinatnu Akad. Vestis., Khim. Ser.*, **3**, 301-308 (1965) (Equi. Diagram, Experimental, #, 10)
- [69Nik] Nikitina, G.V., Romanenko, V.N., "Phase Diagrams of Semiconductor Systems in a Regular Solution Approximation" (in Russian), *Teor. Eksp. Metody Issled Diagramm Sostoyaniya Metal. Sist., Dokl. Soveshch*, Editor: N.V. Ageev, Izd. "Nauka" Moscow, 112-116 (1969) (Equi. Diagram, Theory, #, 8)
- [70Ste] Steininger, J., "Thermodynamics and Calculation of the Liquidus-Solidus-Gap in Homogeneous, Monotonic Alloy Systems", *J. Appl. Phys.*, **41**, 2713-2724 (1970) (Equi. Diagram, Theory, Review, #, 53)
- [72Pan] Panish, M.B., Ilegems, M., "Phase Equilibria in Ternary III-V Systems", *Progr. Solid State Chem.*, **7**, 39-83 (1972) (Equi. Diagram, Thermodyn., Review, Theory, #, 108)
- [72Str] Stringfellow, G.B., "Calculations of Ternary Phase Diagrams of III-V Systems", *J. Phys. Chem. Solids*, **33**, 665-677 (1972) (Equi. Diagram, Thermodyn., Review, #, 41)
- [78Bas] Bashenov, V.K., Mutal, A.M., Timofeenko, V.V., "Interaction Parameters in III-V Semiconductor Solid Solutions", *Phys. Status Solidi (b)*, **86**, (2) K139-K142 (1978) (Thermodyn., Theory, 12)
- [79Ger] Gerdes, F., Predel, B., "Thermodynamic Study of the Systems GaSb-InSb, AlSb-GaSb and AlSb-InSb", *J. Less-Common Met.*, **64**, 285-294 (1979) (Thermodyn., Experimental, 11)
- [80Kor] Korenyuk, I.M., "Investigation of Phase Equilibria in Quasibinary Systems" (in Russian), *Zh. Fiz. Khim.*, **54**, 1656-1665 (1980) (Thermodyn., Theory, 28)
- [84Fed] Fedders, P.A., Müller, M.W., "Mixing Enthalpy and Composition Fluctuations in Ternary III-V Semiconductor Alloys", *J. Phys. Chem. Solids*, **45**, (6), 685-688 (1984) (Thermodyn., Theory, 9)
- [88Ish] Ishida, K., Shumiya, T., Ohtani, H., Hasebe, M., Nishizawa, T., "Phase Diagram of the Al-In-Sb System", *J. Less-Common Met.*, **143**, 279-289 (1988) (Equi. Diagram, Thermodyn., Experimental, Theory, #, \*, 20)
- [89Ich] Ichimura, M., Wada, T., "Chemical Potentials of Constituent Compounds in III-V Alloy Semiconductors", *J. Cryst. Growth*, **97**, 542-550 (1989) (Thermodyn., Theory, 32)

**Table 1:** Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
(Al) <660.5	<i>cF4</i> Cu	$a = 404.96$	[Mas]
(In) <156.6	<i>tI2</i> In	$a = 459.90$ $c = 494.70$	[Mas]
(Sb) <630.8	<i>hR2</i> $\alpha$ As	$a = 450.68$ $\alpha = 57.11^\circ$ $a = 430.82$ $c = 1127.4$	[Mas]  hexagonal axes
$\alpha$ , In <sub>1-x</sub> Al <sub>x</sub> Sb	<i>cF8</i> ZnS		$0 \leq x \leq 1$ [58Woo, 58Koe, 59Gor, 60Bar, 88Ish]
InSb <525		$a = 647.91$	$x = 0$ [V-C, 72Pan]
AlSb <1058		$a = 613.55$	$x = 1$ [V-C, 72Pan]



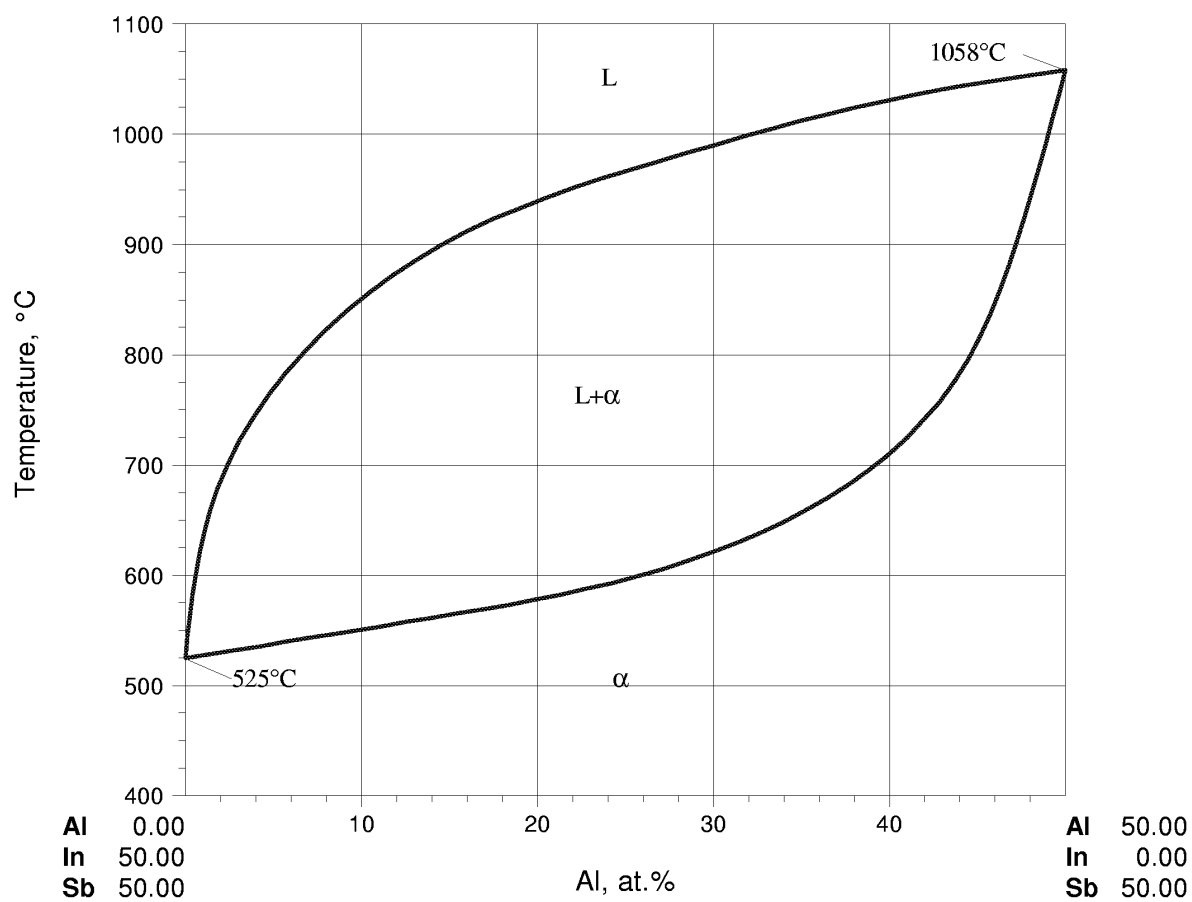
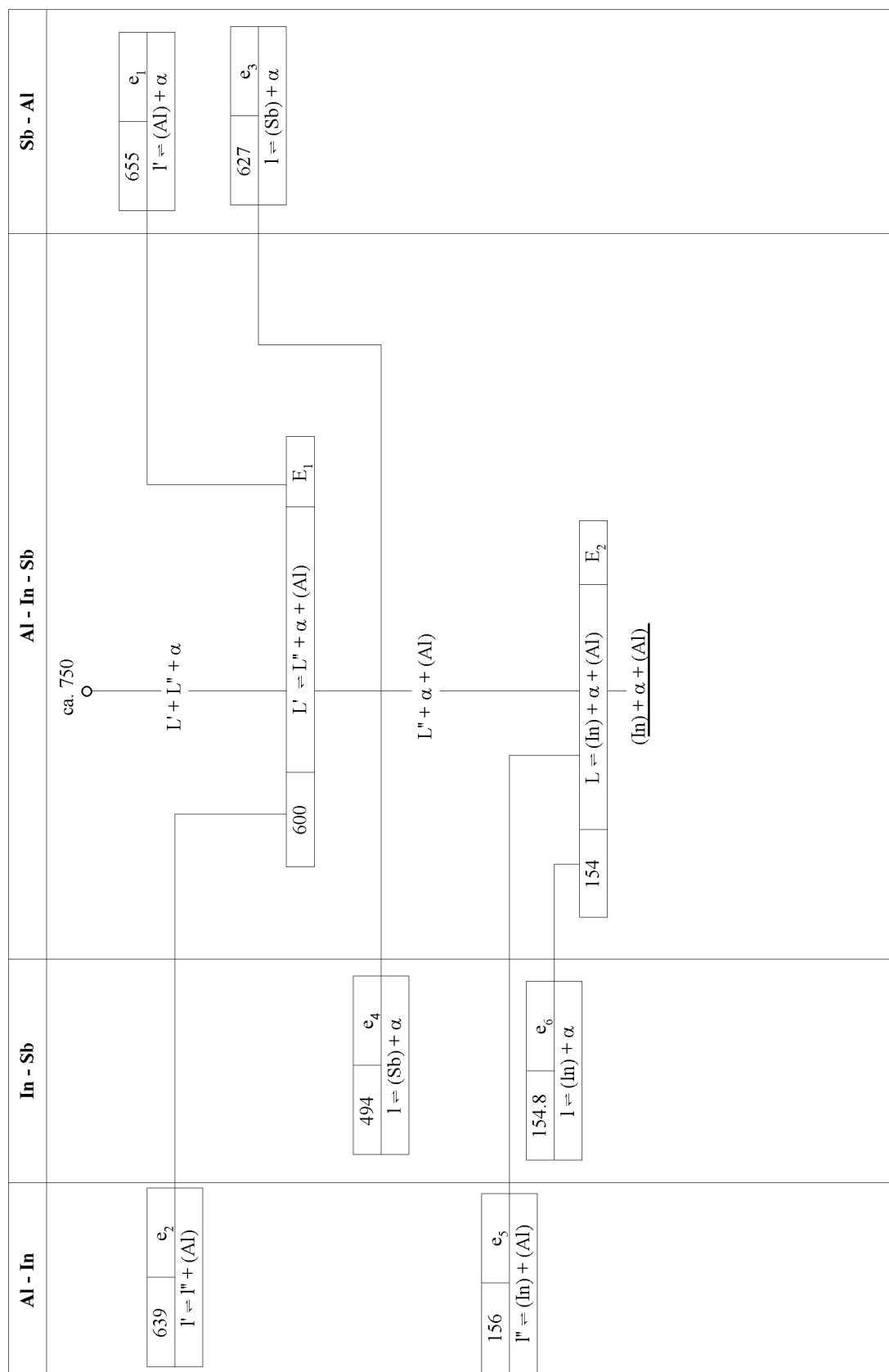


Fig. 1: The pseudobinary system InSb-AlSb



**Fig. 2:** Reaction scheme

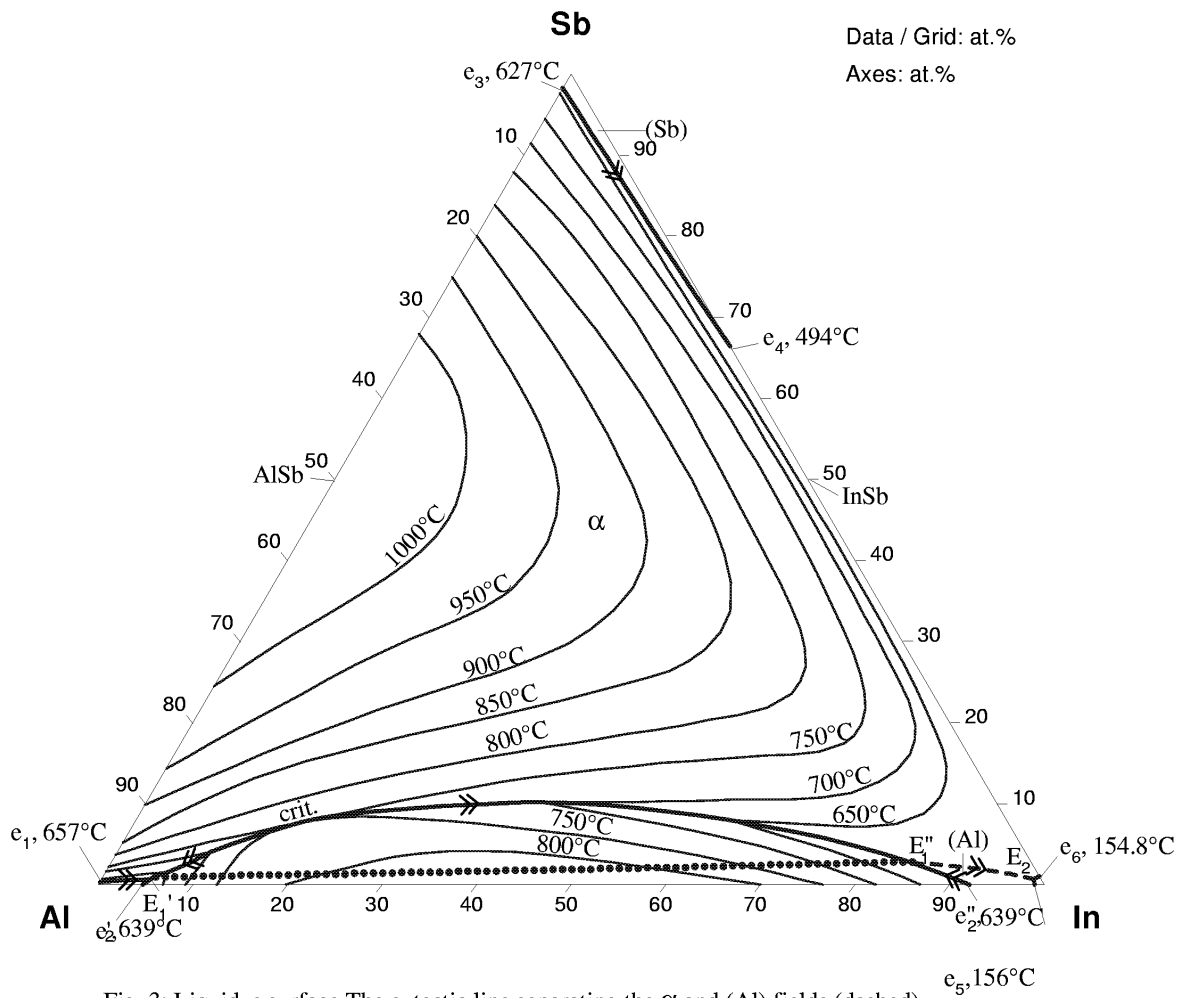


Fig. 3: Liquidus surface. The eutectic line separating the  $\alpha$  and (Al) fields (dashed) and the tie line  $E'_1$ - $E''_1$  (dotted) are estimated

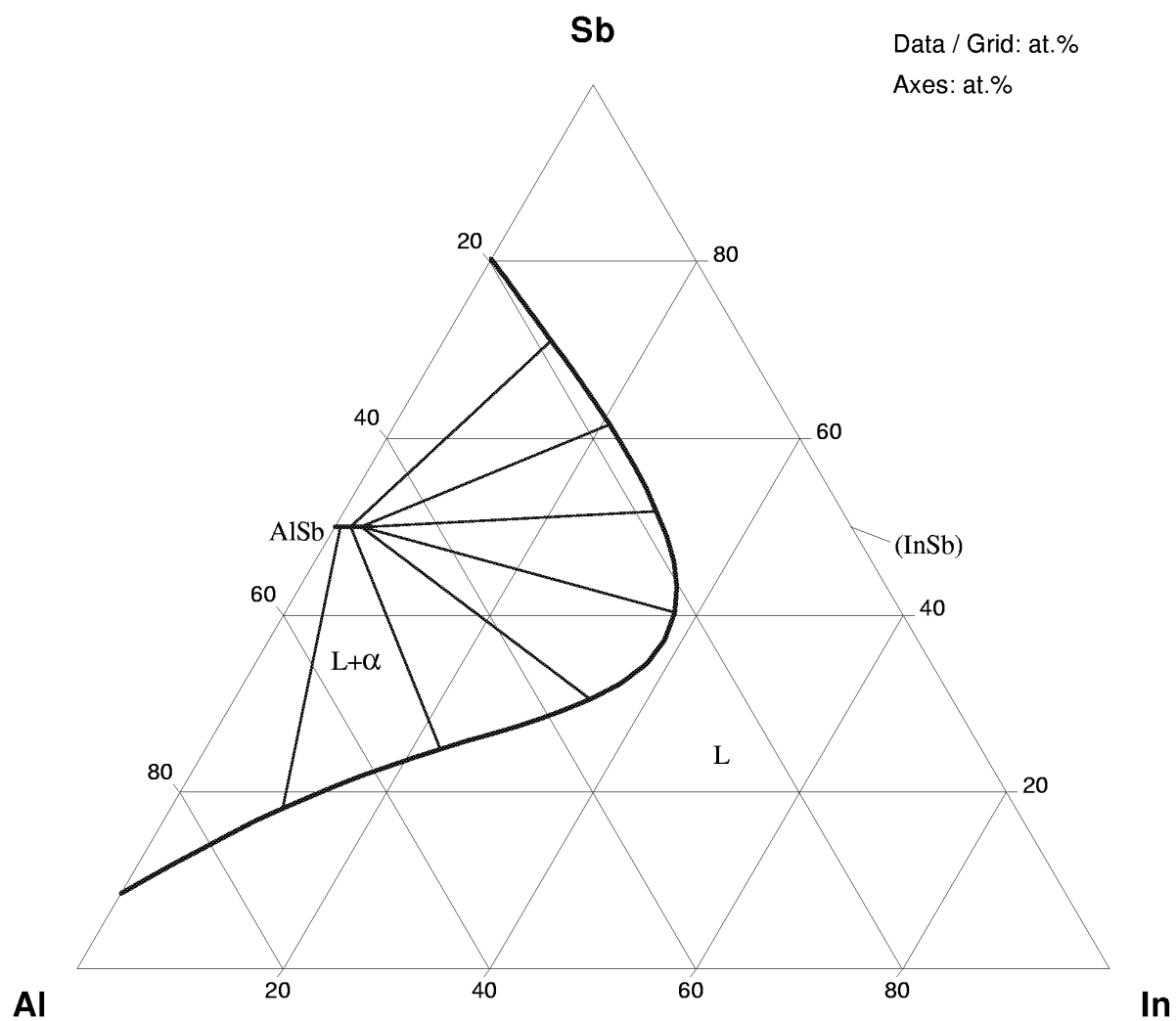


Fig. 4: Isothermal section at 900°C

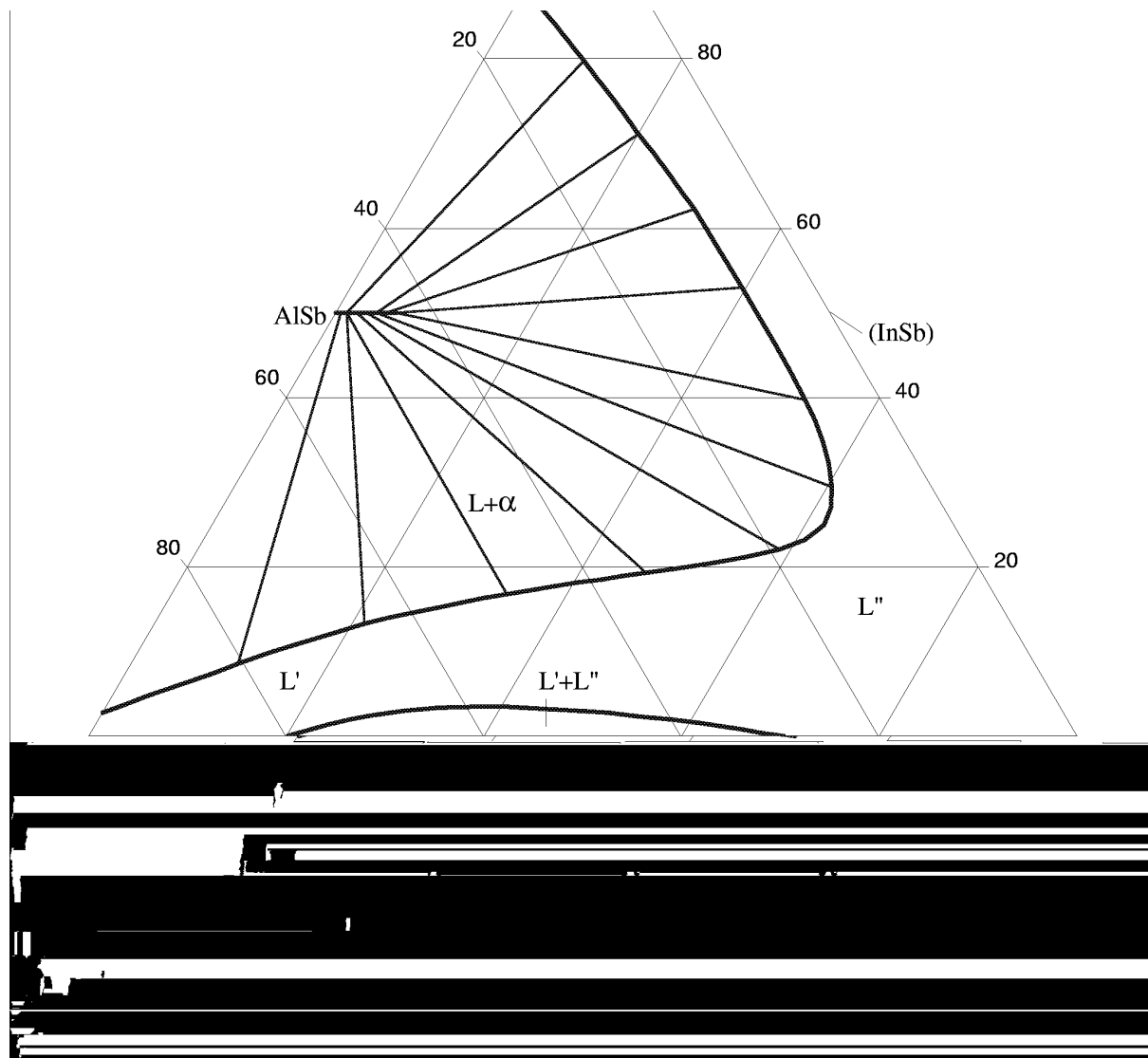


Fig. 5: Isothermal section at 800 °C

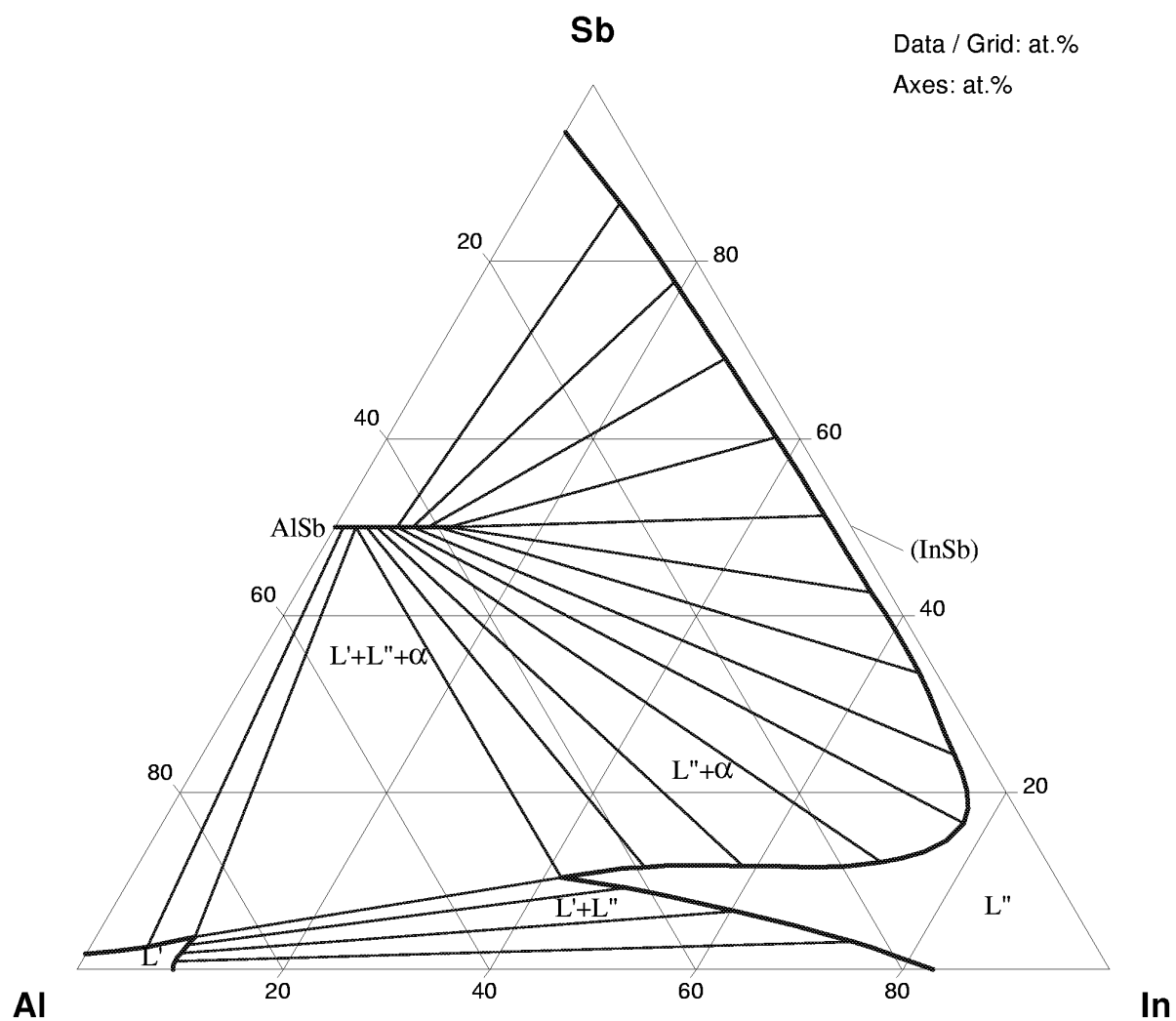


Fig. 6: Isothermal section at 700°C

## Aluminium - Iron – Oxygen

*Ortrud Kubaschewski and Rainer Schmid-Fetzer*

### Literature Data

No complete phase diagram has been reported for the system Al-Fe-O, but certain reactions of mainly industrial interest have been investigated, especially the deoxidation of steel with Al and the subsolidus reactions in the partial systems FeO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> and Al-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-Fe. The complexity of phase relationships in the Al-Fe-O system is based partly on the ratio of ferrous to ferric oxide at equilibrium, which is dependent on both temperature and oxygen pressure. This survey therefore describes the system by isothermal and polybaric projections. Among the many published contributions towards clarification and description of the phase relationships, only selected reports are given under References. The relation between deoxidation data and the phase equilibria is essential for an understanding of discrepancies and will be pointed out under Miscellaneous.

### Binary Systems

The binary phase diagrams Al-O [85Wri] Fig. 1, Al-Fe [82Kub] and Fe-O [82Kub] have been used, as well as the pseudobinary system FeO-Al<sub>2</sub>O<sub>3</sub>.

### Solid Phases

One ternary high temperature compound FeAlO<sub>3</sub> ( $\tau$ ), stable between 1318 and about 1500°C, depending on the oxygen pressure, has been found. FeAl<sub>2</sub>O<sub>4</sub> (hercynite) is actually not a ternary phase, but emerges as a solid solution from Fe<sub>3</sub>O<sub>4</sub> (magnetite) and also terminates that solution range. This solution is denoted as  $\sigma$  or spinel. Data on the solid phases are given in Table 1. The low temperature form of Fe<sub>3</sub>O<sub>4</sub> [V-C] has been omitted.

### Pseudobinary Systems

The section FeO-Al<sub>2</sub>O<sub>3</sub> is established as quasibinary using DTA, X-ray, microscopy and petrographic analysis. A new version of the pseudobinary system FeO-Al<sub>2</sub>O<sub>3</sub> was proposed by [74Ros]. It should be noted that the system is not strictly pseudobinary because Fe occurs in different states of oxidation in varying amounts even in oxide phases in contact with metallic Fe and the "melting point" of FeO corresponds to a eutectic. The results are shown in Fig. 2 which summarizes findings of [74Ros] and previous studies [55Oel, 56Fis] and [57Gal]. The congruent melting point of FeAl<sub>2</sub>O<sub>4</sub>, reported by [57Gal] as 1800°C, was accepted in Fig. 2 (1820, 1800 and 1780°C are given by [56Fis, 57Gal] and [65Nov], respectively). X-ray

diffraction and petrographic analysis of the samples from simultaneous sintering of iron aluminate and corundum at 1700°C showed that there is negligible miscibility between  $\text{FeAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  in the solid phase [65Nov], which was confirmed later by [74Ros]. According to earlier studies [56Fis, 56Mua, 58Atl and 64Roi] a measurable solution of  $\text{Al}_2\text{O}_3$  in  $\text{FeAl}_2\text{O}_4$  occurs above 1350°C.

The sections  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  are also pseudobinary at least at temperatures below solidus and high enough pressure to prevent oxide decomposition. [62Tur] carried out experiments defining the limits of the spinel solid solution of the system  $\text{Fe}_3\text{O}_4$  (magnetite) –  $\text{FeAl}_2\text{O}_4$  (hercynite). The buffered hydrothermal technique and lattice parameter measurements were used to find the course of the solvus. A method of "bracketing" was developed, i.e. approaching equilibria from both directions, the exsolution and solid solution. To induce solid solubility, samples were held 2 d at 800°C, 12 d at 700°C and 1 month at 600°C. Equilibrium at 500°C was not obtained. The total pressure was 2 kbar. The results are plotted in Fig. 3.

The section  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  below 1000°C was studied by [62Tur]. They used their own data established by the hydrothermal method and X-ray analysis, combined with results published by [56Mua] and [58Atl] to construct the diagram in Fig. 4. Measurements by [56Mua] taken into account by [62Tur] were found to contain about 5 mass% less  $\text{Al}_2\text{O}_3$  than reported by [58Atl] and extrapolated by [62Tur].

More recent investigations by [83Boj] indicate a lower solid solubility of  $\text{Al}_2\text{O}_3$  in  $\text{Fe}_2\text{O}_3$  (Fig. 4). The solubility at lower temperatures has been determined by [80Kli]. The compound  $\text{FeAlO}_3$  appears at the upper limit of Fig. 4. Some "pseudobinary" sections have also been calculated with a simple regular solution-type model as a basis for calculations in multicomponent oxide systems [78Kau].

## Invariant Equilibria

The reaction scheme for the Fe- $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ -Al partial system, constructed by [89Rag], was corrected as described in the next section and is presented in Fig. 5. It includes the invariant points of the liquidus surface and incorporates the subsolidus invariant reactions based on results published as isothermal sections. The reaction  $p_1$  at about 1700°C,  $L'' + \text{Al}_2\text{O}_3 \rightleftharpoons \text{Fe}_2\text{O}_3$ , may also be of the eutectic type,  $L'' \rightleftharpoons \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ . This reaction must not be confused with the peritectic at about 1730°C shown later in the section  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  (Fig. 21) at 0.21 bar. This peritectic cannot appear in Fig. 5 since the entire reaction scheme is given under high enough pressure to exclude the gas phase. An extrapolation of the  $\text{Fe}_2\text{O}_3$  solvus and the  $\text{Al}_2\text{O}_3$  liquidus in Fig. 21 does not lead to a clear conclusion concerning the type of the reaction  $p_1$ .

The formation and decomposition of  $\tau$  is also viewed differently compared to [89Rag]. The formation must occur above 1495°C as is obvious from the series of Figs. 22, 21 and 20, extrapolated to higher pressures. It is shown as  $P_1$  in Fig. 5, an almost degenerated reaction with  $\tau$  located almost on the tie line  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ . An alternative formation reaction in a three-phase maximum  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 \rightleftharpoons \tau$  is rather unlikely since it would require a larger O solubility range in  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  than in  $\tau$ .

Following this, the three-phase invariant reactions given in [89Rag] at 1450 and 1318°C cannot be accepted. The decomposition of  $\tau$  in  $E_3$  at 1318°C (Fig. 5) is also almost



degenerated and virtually identical to the 1318°C reactions in Figs. 20 and 21, emphasizing the non-pseudobinary character of these sections. Data on the invariant reactions at 1 bar pressure involving Fe-rich liquids are compiled in Table 2 [72Ell].

## Liquidus Surface

[89Rag] proposed a schematic liquidus surface which may be accepted in many details. However, the liquid miscibility gap of the Al-O system, had not been taken into account, leading to the conclusion that liquid Fe and liquid  $\text{Al}_2\text{O}_3$  form a continuous solution which is extremely unlikely. Another proposition, given in Fig. 6, accepts a continuous band of the miscibility gap between liquid metals (L') and liquid oxides (L"). As a consequence, the eutectic type reaction  $E_1'-E_1''$  and also a maximum  $e_2'-e_1''$  must occur. A critical point, given as  $C_1$  and mixed up with the congruent melting point of  $\text{FeAl}_2\text{O}_4$  by [89Rag], does not appear. Figure 6 incorporates the results of [72Ell, 79Ell]. The reactions  $e_3$  and  $e_9$  belong to the pseudobinary system  $\text{FeO}-\text{Al}_2\text{O}_3$  (Fig. 2). The invariant reactions  $U_6 \rightarrow E_5$  virtually coincide with the Fe-Al binary system. Quantitative data are available for liquidus surfaces in the Fe corner [72Ell, 79Ell] and Fig. 7 shows a projection. The  $\text{Al}_2\text{O}_3$  liquidus surface has been studied by [53Gok, 61Kuz, 63Ent, 65McL, 67Swi, 69Buz, 69Nov, 70Fru, 71Roh, 76Jan, 81She, 82Lia]; the early solubility data of [39Wen] are much too high and have been disregarded.

Figure 8 gives isotherms of the  $\text{Al}_2\text{O}_3$  liquidus surface from the results reported by [63Ent] 1910°C, [67Swi] 1580°C and [81She] 1600°C, respectively. The 1580 and 1600°C isotherms also reflect the scatter of the data, the actual slope of the  $\text{Al}_2\text{O}_3$  liquidus surface is considered to be smooth in the 1590 to 1910°C temperature range. [63Ent] and [67Swi] investigated the Al and O contents of liquid Fe in equilibrium with  $\text{Al}_2\text{O}_3$ . [63Ent] applied the gravimetric ( $\text{Al}_2\text{O}_3$ ) and [67Swi] the vacuum fusion method for the determination of the O concentration. As pointed out by [63Ent], the vacuum fusion method is susceptible to grave errors at high Al contents due to the absorption of gas by the Al distilled from the sample and the vaporisation of  $\text{Al}_2\text{O}$ . This would account for the low oxygen contents at high Al concentrations in the 1580°C isotherm. The findings agree that the solubility of O in Fe-Al melts decreases with increasing Al content to a minimum and then increases rapidly. The results of [67Swi] appear to be inconsistent with other data and may arise from his method of oxygen analysis. As shown in Fig. 8, 0.39 wt.% Al decreases the solubility of oxygen in liquid Fe to a minimum of 8 ppm (0.0008 mass% O) at 1600°C.

The 0.01 to 100 mass% Al range at 1600°C was studied by [81She] who also discussed earlier work by [61Kuz]. The initial materials were hydrogen-refined carbonyl-iron and high purity Al. The solubility of oxygen was examined by the phase equilibrium method [79She, 80Nov]. The curve has 2 minima and one maximum. The first minimum is in good agreement with published data [61Kuz, 63Ent, 67Swi, 71Roh]. There are no other reported data on the position of the second minimum. The maximum approaches the experimental findings by [63Ent] and [70Fru].

In a recent calculation of the liquidus isotherms, [82Lia] used the most elaborate thermodynamic model based on Wagner's solvation-shell approach which required only data from the binary edge systems. His predictions for the ternary Al-Fe-O liquid alloys are in good agreement with the experimental data and Fig. 8 up to about 3 mass% Al, while at 10 mass% the calculated solubility at 1627 to 1727°C is approximately 0.1 mass% O, about 10

times higher than the recent data of [81She] at 1600°C. In addition, [82Lia] clearly demonstrated that previous calculations using interaction parameters are not suitable above 0.3 mass% Al. At higher Al contents the first order interaction parameter calculation gives a too strong increase in O solubility. The first and second order calculation also gives a maximum qualitatively similar to the one at 1600°C in Fig. 8, but at a much lower Al content of about 1 mass% Al and then the O solubility drops to unrealistic low values with only a slight increase of Al content. It can also be concluded that the interaction parameter-type calculation must fail at higher Al contents since it is in principle restricted to "infinite" dilution of both O and Al, while the solvation-shell approach is in principle valid over the entire Fe-Al composition range. This calculation should be redone using the new experimental Al-O data of [81She].

The solubility curves of  $\text{FeAl}_2\text{O}_4$  have also been calculated by [82Lia] and from the intersection with the  $\text{Al}_2\text{O}_3$  liquidus isotherms it was concluded that  $\text{FeAl}_2\text{O}_4$  is the more stable oxidic precipitate in the liquid below  $0.2 \cdot 10^{-4}$  mass% Al at 1627°C and  $2.5 \cdot 10^{-4}$  mass% Al at 1827°C. The oxygen solubilities at this three-phase equilibria  $\text{L} + \text{Al}_2\text{O}_3 + \text{FeAl}_2\text{O}_4$  are 0.053, 0.074, 0.1 and 0.134 mass% O at 1550, 1600, 1650 and 1700°C, respectively in agreement with experimental data [66McL, 75Kim].

Oxygen solubility results obtained by [69Nov] at 1600°C by calculation and the vacuum fusion method are higher than those reported by [81She]. Values at the minimum are 0.0035 mass% O [69Nov] and 0.0008 mass% O [81She], respectively.

## Isothermal Sections

[61Tur, 62Tur] studied Fe-spinels by controlled synthesis from chemical mixtures in the temperature range 500 to 900°C and used X-ray measurements for the determination of solid solutions. Silver, not miscible with Fe at the temperature involved, was used as container material. Reaction rates are slow and experiments lasted up to 40 d. The isothermal sections displayed in Figs. 9 to 13 summarize the experimental results by [61Tur, 62Tur, 80Mey] and [83Elr] as well as findings from a review published by [89Rag] for the partial systems Fe- $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ -Al and FeO- $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ . The isothermal sections must be seen in conjunction with the oxygen pressure (stability) diagrams, given under Miscellaneous, where the techniques used by [80Mey] and [83Elr] are also described.

## Miscellaneous

[80Mey] determined the composition limits for the spinel solid solution  $\sigma = (\text{Fe}, \text{Al})_3\text{O}_4$  experimentally as a function of oxygen pressure at 1280, 1380 and 1500°C using lattice parameter measurements. The results were combined with information from the literature [46Dar, 56Fis, 56Mua, 58Atl, 58Phi, 64Roi, 76Sti, 76Pol] to develop self-consistent stability diagrams, Figs. 14 to 16, of  $p(\text{O}_2)$ , versus cation (metal) fraction at constant temperatures for the Al-Fe-O system. In these diagrams the left and right vertical axes constitute the binary Fe-O and Al-O systems, respectively. The complete spinel solid solution does not exist at any specific oxygen pressure. The spinels with higher Al content are only stable at lower oxygen pressure. The metallic Fe-Al phases would only appear below the pressure range of Figs. 14 to 16. [83Elr] determined the equilibrium oxygen pressures of the univariant ternary equilibria of  $\text{Fe}_2\text{O}_3 + \sigma + \text{Al}_2\text{O}_3$ , metal +  $\text{FeO} + \sigma$  and metal +  $\sigma + \text{Al}_2\text{O}_3$ , where the metal is essentially pure

Fe. They used data derived from solid state electrochemical cell experiments in the temperature range 850 to 1150°C in combination with published data [56Mua, 58Mua, 58Atl, 62Tur, 64Roi, 81Pet] to construct oxygen pressure diagrams at 1000, 900 and 800°C, see Figs. 17 to 19. Boundaries for the Al or Fe-rich spinel are schematic. The spinel miscibility gap ( $\sigma' + \sigma''$ ) appears at 800°C in Fig. 19, see also Fig. 3. The  $\sigma' + \sigma''$  boundaries are virtually independent of pressure. The composition of the spinel phase in equilibrium with  $\text{Al}_2\text{O}_3$  at 900°C and  $p(\text{O}_2) = 10^{-12}$ ,  $10^{-13}$  and  $10^{-14}$  bar was reported by [62Tur]. FeO dissolves up to 0.55 mol%  $\text{Al}_2\text{O}_3$ . Alumina ( $\text{Al}_2\text{O}_3$ ) was found to dissolve approximately 1.1 at.% Fe in the temperature region 1000 to 1300°C, whereas the Al content in the Al-Fe alloys was extremely small, 0.1 mass% Al above  $p(\text{O}_2) \approx 10$  to 30 bar. The data of the  $\text{Fe}_3\text{O}_4/\text{FeO}$  equilibrium were taken from [46Dar and 69Bry].

The section  $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3$  was investigated at temperatures above 1000°C and different oxygen pressures by [56Mua] and [58Mua]. They applied the "Quenching Method" and microscopy as well as lattice parameter measurements for identification of the different phases.  $\text{FeAlO}_3$  ( $\tau$ ) exists in stable equilibrium only at temperatures above 1318°C and a partial pressure of  $\text{O}_2$  above 0.03 bar. The upper decomposition temperature of  $\tau$  is pressure dependent. The phase relationships are illustrated in Figs. 20 to 22 for decreasing oxygen pressure [58Mua]. These vertical sections only look like pseudobinary diagrams which can not be true at higher temperatures. The decomposition when heating pure  $\text{Fe}_2\text{O}_3$  at 1390°C in Fig. 21 corresponds to the three-phase reaction  $6\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{O}_2$ . The resulting phase  $\text{Fe}_3\text{O}_4$  ( $\sigma$ ) is no longer located on the section  $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$  and this shift is balanced by substantial amounts of  $\text{O}_2$  (gas). This is the meaning of the designation "+ $\text{O}_2$ " in the upper phase fields. A slight inconsistency concerns the reported solubility limits of the  $\text{Fe}_2\text{O}_3 + \sigma$  equilibrium. According to [58Mua] (Figs. 20 to 22) the solubility of  $\text{Al}_2\text{O}_3$  in  $\sigma$  is larger than in  $\text{Fe}_2\text{O}_3$ . This is reverse in Figs. 15 to 19, however, where the solubility differences are small. Al is the strongest deoxidiser commonly used in steelmaking. The extent to which it removes dissolved oxygen has been the subject of many investigations. Since [53Gok] it is known that the "deoxidation constant" is extremely small. The equilibrium constant for the reaction  $\text{Al}_2\text{O}_3(\text{s}) \rightarrow 2[\text{Al}]_{\text{Fe}} + 3[\text{O}]_{\text{Fe}}$  can be calculated. However, it disagrees with the bulk of the deoxidation constants observed in practice [79Kub]. The reason for this discrepancy appears to be the following: firstly, when the Al shot is added to undeoxidized liquid steel, the reaction of the solid Al particle with  $[\text{O}]$  in the immediate surrounding, forming  $\text{Al}_2\text{O}_3$ , proceeds at a higher rate than that at which Al dissolves and diffuses through the Fe. Secondly, the resultant  $\text{Al}_2\text{O}_3$  particle in a deoxidized area is transmitted to an undeoxidized region by turbulences. Oxygen in the undeoxidized area comes out of solution to form FeO which in turn combines with the  $\text{Al}_2\text{O}_3$  particle to the spinel  $\text{FeO} \cdot \text{Al}_2\text{O}_3$  ( $\text{FeAl}_2\text{O}_4$ ). This would result in a high FeO content as well as a larger deoxidation constant [57Fit]. Careful experiments over longer periods proved that the deoxidation constant varies with time. [67Rep] and [73Iye] demonstrated that by projecting the path of reactions with the aid of the phase diagram, the metastable or nonequilibrium conditions can be anticipated in practice.

The change of Moessbauer spectra, magnetic properties and of the reduction rate of magnetite-based solid solutions was studied as function of impurity additions of Al, Ca and Mg [76Mal].

The "pseudobinary" system  $\text{FeO}_4\text{--Al}_2\text{O}_3$  has been calculated by [84Sch] in a stable and a metastable version, in which the formation of  $\text{FeAl}_2\text{O}_4$  is suppressed. The results of the calculation are in agreement with the experiments of [55Oel, 56Fis].

## References

- [39Wen] Wentrup, H., Hieber, G., "Reactions Between Al and O in Iron Melts", *Arch. Eisenhuettenwes.*, **13**, 15 (1939) (Equi. Diagram, Experimental, 10)
- [46Dar] Darken, L.S., Gurry, R.W., "The System Iron-Oxygen: II", *J. Am. Chem. Soc.*, **68**, 798-816 (1946) (Equi. Diagram, Experimental, Thermodyn., 24)
- [53Gok] Gokcen, N.A., Chipman, J., "Aluminium-Oxygen Equilibrium in Liquid Iron", *Trans. AIME, Journal of Metals*, 173-178 (1953) (Equi. Diagram, Experimental, Thermodyn., 12)
- [54Ric] Richards, R.G., White, J., "Phase Relationships of Iron-Oxide-Containing Spinel", *Trans. Brit. Ceram. Soc.*, **53**, 233-270 (1954) (Equi. Diagram, Experimental, 26)
- [55Oel] Oelsen, W., Heynert, G., "Reaction Between Iron-Manganese-Melts and the Melts of their Aluminates" (in German), *Arch. Eisenhuettenwes.*, **26**, 567-575 (1955) (Equi. Diagram, Experimental, 12)
- [56Fis] Fischer, W.A., Hoffmann, A., "FeO-Al<sub>2</sub>O<sub>3</sub> Phase Diagram" (in German), *Arch. Eisenhuettenwes.*, **27**, 343-346 (1956) (Experimental, Equi. Diagram, 15)
- [56Mua] Muan, A., Gee, C.L., "Phase Equilibrium Studies in the System Iron Oxide-Al<sub>2</sub>O<sub>3</sub> in Air and at 1 atm. O<sub>2</sub> Pressure", *J. Am. Ceram. Soc.*, **39**, 207-214 (1956) (Equi. Diagram, Experimental, 17)
- [57Fit] Fitterer, G.R., "The Physical Chemistry of Steelmaking - A Tribute to Dr. C.H. Hertz, Jr.", *The Met. Soc. AIME, Proc. Open Hearth Conf. Pittsburgh*, **40**, 281-303 (1957) (Equi. Diagram, Experimental, 40)
- [57Gal] Galakhov, F.Ya., "Alumina Regions of Ternary Aluminosilicate Systems. Communication 1. The Systems FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and MnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>", *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **5**, 539-545 (1957), translated from *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **5**, 525 (1957) (Equi. Diagram, Experimental, 16)
- [58Atl] Atlas, L.M., Sumida, W.K., "Solidus, Subsolidus and Subdissociation Phase Equilibria in the System Fe-Al-O", *J. Am. Ceram. Soc.*, **41**, 150-160 (1958) (Equi. Diagram, Experimental, 23)
- [58Mua] Muan, A., "On the Stability of the Phase Fe<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>", *Amer. J. Sci.*, **256**, 413-422 (1958) (Equi. Diagram, Experimental, #, \*, 8)
- [58Phi] Phillips, B., Muan, A., "Phase Equilibria in the System CaO-Iron Oxide in Air and 1 atm O<sub>2</sub> Pressure", *J. Am. Ceram. Soc.*, **41**, 445-454 (1958) (Equi. Diagram, Experimental, 15)
- [61Kuz] Kuznetsov, M.V., Samarin, A.M., "Deoxidation Capacity of Al in Liquid Fe" (in Russian), in "Physicochemical Fundamentals of Steelmaking", Moscow, Izd.-vo. An SSSR, 11-17 (1961) (Thermodyn., Equi. Diagram, Experimental, 2)
- [61Tur] Turnock, A.C., Lindsley, D.H., "Fe-Al and Fe-Ti Spinel and Related Oxides", *Ann. Rept. Director Geophys. Lab. 1960-61*, in *Carnegie Inst. Washington Year Book*, **60**, 152-157 (1961) (Equi. Diagram, Experimental, #, \*, 3)
- [62Tur] Turnock, A.C., Eugster, H.P., "Fe-Al Oxides: Phase Relationships Below 1000°C", *J. Petrology*, **3**, 533-565 (1962) (Equi. Diagram, Experimental, #, \*, 35)
- [63Ent] D'Entremont, J.C., Guernsey, D.L., Chipman, J., "Aluminium-Oxygen Interaction in Liquid Iron", *Trans. Metall. Soc. AIME*, **27**, 14-17 (1963) (Equi. Diagram, Experimental, 13)
- [64Roi] Roiter, B.D., "Phase Equilibria in the Spinel Region of the System FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>", *J. Am. Ceram. Soc.*, **47**, 509-511 (1964) (Equi. Diagram, Experimental, 9)

- [65McL] McLean, A., Bell, H.B., "Experimental Study of the Reaction  $\text{Al}_2\text{O}_3 + 3\text{H}_2 \rightleftharpoons 3\text{H}_2\text{O} + 2\text{Al}$ ", *J. Iron Steel Inst.*, **203**, 123-130 (1965) (Equi. Diagram, Thermodyn., Experimental, 33)
- [65Nov] Novokhatsky, I.A., Belov, B.F., Gorokh, A.V., Savinskaya, A.A., "Phase Diagram of the System Ferrous Oxide–Alumina", *Russ. J. Phys. Chem.*, **39**(11), 1489-1499 (1965) (Equi. Diagram, Experimental, 9)
- [66McL] McLean, A., Ward, R.G., "Thermodynamics of Hercynite Formation", *J. Iron Steel Inst.*, **204**, 8-11 (1966) (Experimental, Thermodyn., 36)
- [66Nov] Novokhatsky, I.A., Belov, B.F., "Phase Equilibria and Distribution of the Elements in the Fe–O–Al System" (in Russian), *Izv. Akad. Nauk SSSR, Met.*, **38**(1), (1966) (Equi. Diagram, Experimental, 2)
- [67Rep] Repetylo, O., Olette, M., Kozakevitch, P., "Deoxidation of Liquid Steel with Aluminium and Elimination of the Resulting Alumina", *J. Metals (May)*, 45-49 (1967) (Experimental, 24)
- [67Swi] Swisher, J.H., "Note on the Aluminium-Oxygen Interaction in Liquid Iron", *Trans. AIME*, **239**, 123-124 (1967) (Experimental, #, 8)
- [69Bry] Bryant, P.E.C., Smeltzer, W.W., "The Dissociation Pressure of Hematite", *J. Electrochem. Soc.*, **116**, 1409-1410 (1969) (Experimental, 4)
- [69Buz] Buzek, Z., Hutla, A., "The Influence of Aluminium, Titanium, Zirconium and Cerium Dissolved in Liquid Iron on the Activity and Solubility of Oxygen", *Freiberger Forschungshefte B*, **117**, 59-73 (1969) (Experimental, Equi. Diagram, 20)
- [69Nov] Novokhatsky, I.A., Belov, B.F., "Concentration Dependence of the Oxygen Solubility in Metals" (in Russian), *Izv. Akad. Nauk SSSR, Met.*, **15**(3) (1969) (Equi. Diagram, Experimental, Thermodyn., 3)
- [70Fru] Fruehan, R.J., "Activities in Liquid Fe–Al–O and Fe–Ti–O Alloys", *Metall. Trans.*, **1**, 3403-3410 (1970) (Equi. Diagram, Experimental, Thermodyn., 28)
- [71Roh] Rohde, L.F., "New Investigations of the Aluminium–Oxygen Equilibrium in Iron Melts" (in German), *Arch. Eisenhuettenwes.*, **B42**(3), 165-174 (1971) (Equi. Diagram, Experimental, 43)
- [72Ell] Elliott, J.F., Wright, J.K., "Equilibrium Phase Relationships During Solidification of Fe–O–C–X Alloys: System Fe–Al–O. Projected Equilibria Involving Iron Between 1500 and 1538°C at One Atmosphere", *Can. Metall. Q.*, **11**(4), 573-584 (1972) (Equi. Diagram, Experimental, #, \*, 17)
- [73Iye] Iyengar, R.K., Philbrook, W.O., "Application of Phase Diagrams to Predict Phases Formed During Deoxidation of Steel", *Metall. Trans.*, **4**(9), 2189-2193 (1973) (Equi. Diagram, Experimental, 20)
- [74Ros] Rosenbach, K., Schmitz, J.A., "Investigations in the Ternary System Iron(II)–Oxide–Chromium(III)Oxide–Alumina" (in German), *Arch. Eisenhuettenwes.*, **45**(12), 843-847 (1974) (Equi. Diagram, Experimental, #, 13)
- [75Kim] Kim, C.K., McLean, A., "Hercynite Formation in Molten Iron Alloys", Proceedings, Symp. on Metal-Slag-Gas Reactions and Processes, Eds.: Foroulis, Z.A., Smelter, W.W., Electrochemical Soc. Inc., Princeton, N.J., 275-284 (1975) (Equi. Diagram, Thermodyn., Experimental, 12)
- [76Jan] Janke, D., Fisher, W.A., "Deoxidations Equilibria of Titanicium, Aluminium and Zirconium in Liquid Iron at 1600°C", *Arch. Eisenhuettenwes.*, **47**, 195 (1976) (Equi. Diagram, Experimental, 30)

- [76Mal] Malysheva, T.YA., Lyadova, V.YA., Ostrovskaya, I.V., Model, M.S., Davidyuk, A.A., "Nature of the Ferrite Phases in the Blast-Furnace Charge" (in Russian), I.P. Bardin Razvit. Metall. SSSR, Ed.: Savitskii, E.M., Nauka, Moscow, 39-58 (1976) (Experimental, 32)
- [76Pol] Pollak, T.M., "High Temperature Electrical Conductivity and Defect Chemistry of Iron-Doped Alumina", M. Sc. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1-81 (1976) (Experimental, 29)
- [76Sti] Sticher, J., Schmalzried, H., "Geometrical Representation of Thermodynamic State Variables in the Ternary System Iron-Titanium-Oxygen in the Temperature Range Between 1300 and 1600°C", *Arch. Eisenhuettenwes.*, **47**, 261-266 (1976) (Equi. Diagram, Experimental, Thermodyn., 54)
- [78Kau] Kaufman, L., Nesor, H., "Calculation of Quasibinary and Quasiternary Oxide Systems - I.", *CALPHAD*, **2**, 35-53 (1978) (Thermodyn., Equi. Diagram, Theory, 30)
- [79Ell] Elliott, J.F., "Chemical Equilibria and Phase Equilibria", TMS/AIME 420 Commonwealth Dr., Warrendale, Pa. 15086 (1979), 185-196. Accession Number: 80(9), 72-317. Conference: Calculation of Phase Diagrams and Thermochemistry of Alloy Phases, Milwaukee, Wis., 17-18, September (1979) (Experimental, Review, Thermodyn., 19)
- [79Kub] Kubaschewski, O., Alcock, C.B., "Metallurgical Thermochemistry", 5th Edition, Internat. Series on Materials Science and Technology, Pergamon Press, Volume 24, 238-239 (1979) (Review, Theory)
- [79She] Shevtsov, V.E., "Solubility of Oxygen in High-Silicon Iron Melts", *Russ. Metall.*, **3**, 56-57 (1979), translated from *Izv. Akad. Nauk SSSR, Met.*, **3**, 62 (1979) (Experimental, 13)
- [80Kli] Klissurski, D.G., Mitov, I.G., Petrov, K.P., "A Study of the Preparation of Solid Solutions in the System  $\alpha\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ ", *Thermochim. Acta*, **41**(2), 181-186 (1980) (Experimental, 17)
- [80Mey] Meyers, C.E., Mason, T.O., Petuskey, W.T., Halloran, J.W., Bowen, H.K., "Phase Equilibria in the System Fe-Al-O", *J. Am. Ceram. Soc.*, **63**, 659-663 (1980) (Equi. Diagram, Experimental, #, \*, 20)
- [80Nov] Novokhatsky, I.A., Belov, B.F., "Method of Examining the Deoxidation of Metallic Melts" (in Russian), *Zh. Fiz. Khim.*, **44**(8), 2013-2017 (1980) (Equi. Diagram, Experimental, 18)
- [81Pet] Petric, A., Jacob, K.T., Alcock, C.B., "Thermodynamic Properties of  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$  Spinel Solid Solutions", *J. Am. Ceram. Soc.*, **64**, 632-639 (1981) (Thermodyn., Experimental, 28)
- [81She] Shevtsov, V.W., "Thermodynamics of Oxygen Solutions in the Fe-Al System" (in Russian), *Izv. Akad. Nauk SSSR, Met.*, (1), 52-57 (1981) (Equi. Diagram, Experimental, Thermodyn., #, 16)
- [82Kub] Kubaschewski, O., "Iron - Binary Phase Diagrams", Springer Verlag, Berlin; Verlag Stahl Eisen, Düsseldorf, 5-9 and 79-82 (1982) (Equi. Diagram, Review, #, 32)
- [82Lia] Liang, W.W., "Prediction of Solubility of Oxides in Liquid Fe-Al-O, Co-Al-O, Ni-Al-O and Cu-Al-O Alloys", *Z. Metallkd.*, **73**, 369-375 (1982) (Thermodyn., Equi. Diagram, Theory, #, \*, 31)
- [83Boj] Bojarski, Z., Isakov, I., "Investigations of  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  Solid Solutions in  $\alpha\text{Fe}_2\text{O}_3$  Oxide" (in Polish), *Archiv Nauki Mater.*, **4**(1), 3-20 (1983) (Experimental, #, 23)
- [83Elr] Elrefaie, F.A., Smeltzer, W.W., "Thermodynamics of the System Iron-Aluminium-Oxygen between 1073 and 1573 K", *Metall. Trans. B*, **14**(B)(1), 85-93 (1983) (Equi. Diagram, Experimental, Thermodyn., #, 31)

- [84Sch] Schürmann, E., Bannenberg, N., "Metal-Slag-Equilibria in the system Fe–Al–O as a Basis of the Aluminium-Deoxidation of Steel Melts" (in German), *Arch. Eisenhuettenwes.*, **55**(9), 409-414 (1984) (Equi. Diagram, Experimental, Thermodyn., #, 27)
- [85Wri] Wriedt, H.A., "The Al–O (Aluminium–Oxygen) System", *Bull. Alloy Phase Diagrams*, **6**(6), 548-553 (1985) (Equi. Diagram, Review, #, 46)
- [89Rag] Raghavan, V., "The Al–Fe–O System", in "Phase Diagrams of Ternary Iron Alloys, Part 5", *Indian Inst. of Metals, Calcutta*, 10-28 (1989) (Equi. Diagram, Review, #, 29)

**Table 1:** Solid Phases

Phase/ Temperature Range (°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
(Al) < 660.45	<i>cF4</i> Cu	$a = 404.96$	at 25°C [Mas2]
$\delta\text{Fe}(\text{h}_2)$ 1538-1394	<i>cI2</i> W	$a = 293.15$	[Mas2]
$\gamma\text{Fe}(\text{h}_1)$ 1394-912	<i>cF4</i> Cu	$a = 364.67$	[Mas2]
$\alpha\text{Fe}$ <912	<i>cI2</i> W	$a = 286.65$	[P, V-C]
FeO 1424-560	<i>cF8</i> NaCl	$a = 432.6$	[V-C] wustite, 51.15 to 54.6 at.% O
$\sigma$ , $\text{Fe}_{3-x}\text{Al}_x\text{O}_4(\text{r})$ $\text{Fe}_3\text{O}_4$ <1597 $\text{FeAl}_2\text{O}_4$ <1800	Spinel <i>cF56</i> $\text{MgAl}_2\text{O}_4$	$a = 839.6$ –	$0 \leq x \leq 2$ above 860°C at $x = 0$ , magnetite, 57.14 to 58.3 at.% O at $x = 2$ , hercynite, congruent melting 1800°C. Hardly measurable solub. of $\text{Al}_2\text{O}_3$ above 1400°C, spinel structure [83Elr] [55Gal, 56Fis, 65Nov, 74Ros]
$\text{Fe}_2\text{O}_3$	<i>hR10</i> $\text{Al}_2\text{O}_3$	$a = 503.4$ $c = 1374.7$	[V-C], hematite, peritectoid formation 1457°C at 1.013 bar $p(\text{O}_2)$
$\text{Fe}_2\text{O}_3$	<i>m*100</i>	$a = 1297$ $b = 1021$ $c = 844$ $\beta = 95.32^\circ$	[V-C], low-temperature or metastable
$\text{Fe}_2\text{O}_3$	<i>oI80</i> $\text{Mn}_2\text{O}_3$	$a = 939.3$	[V-C], low-temperature or metastable
$\text{Al}_2\text{O}_3$ <2054	<i>hR10</i> $\alpha\text{Al}_2\text{O}_3$	$a = 475.4$ $c = 1299$	[V-C] congruent melting 2054°C [Mas]
$\gamma\text{Al}_2\text{O}_3$	<i>cF56</i>	$a = 785.9$	[V-C], one of the metastable

	MgAl <sub>2</sub> O <sub>4</sub>		forms [Mas]
Fe <sub>3</sub> Al <552	<i>cF</i> 16 BiF <sub>3</sub>	<i>a</i> = 579.23	[V-C], (DO <sub>3</sub> )-type, 22.5 to 36.5 at.% Al
FeAl <1310	<i>cP</i> 2 CsCl	<i>a</i> = 290.9	22 to 54.5 at.% Al ordered (B2)-type, [V-C], transforms to disordered αFe (A2-type) at lower Al content
ε, Fe <sub>2</sub> Al <sub>3</sub> 1215-1092	<i>cI</i> 16		54.5 to 62.5 at.% Al [82Kub]
FeAl <sub>2</sub> ~<1154	<i>hP</i> – –	<i>a</i> = 1461.3 <i>c</i> = 1401.3	65.5 to 67 at.% Al [82Kub] [V-C], [V-C] also giving <i>aP</i> 18
Fe <sub>2</sub> Al <sub>5</sub> <1171	<i>oC</i> * or hex. Co <sub>2</sub> Al <sub>5</sub> ?	<i>a</i> = 767.5 <i>b</i> = 640.3 <i>c</i> = 420.3	[V-C] 71 to 72.5 at.% Al [82Kub]
FeAl <sub>3</sub> <1157	<i>mC</i> 102 FeAl <sub>3</sub>	<i>a</i> = 1548.9 <i>b</i> = 808.31 <i>c</i> = 1247.6 <i>β</i> = 107.72°	[V-C] 74.5 to 75.5 at.% Al [82Kub]
* τ, FeAlO <sub>3</sub> 1410-1318	Orthorhom.	<i>a</i> = 860 <i>b</i> = 925 <i>c</i> = 497	stab. range at 0.2 bar oxygen pressure, at 1 bar: 1495 to 1318°C [58Mua, 80Mey]

**Table 2:** Invariant Equilibria

T (°C) Reaction	Type	Phase	Composition (at.%)		
			Al	Fe	O
1537.6 L' ⇌ α + Al <sub>2</sub> O <sub>3</sub>	e <sub>5</sub>	L'	1.03·10 <sup>-2</sup>	99.98 <sub>8</sub>	1.12·10 <sup>-3</sup>
1535.5 L' + Al <sub>2</sub> O <sub>3</sub> ⇌ α + σ	U <sub>1</sub>	L'	8.48·10 <sup>-6</sup>	99.87 <sub>4</sub>	0.1255
1528.5 L' + σ ⇌ L'' + α	U <sub>2</sub>	L'	8.05·10 <sup>-7</sup>	99.52	0.48



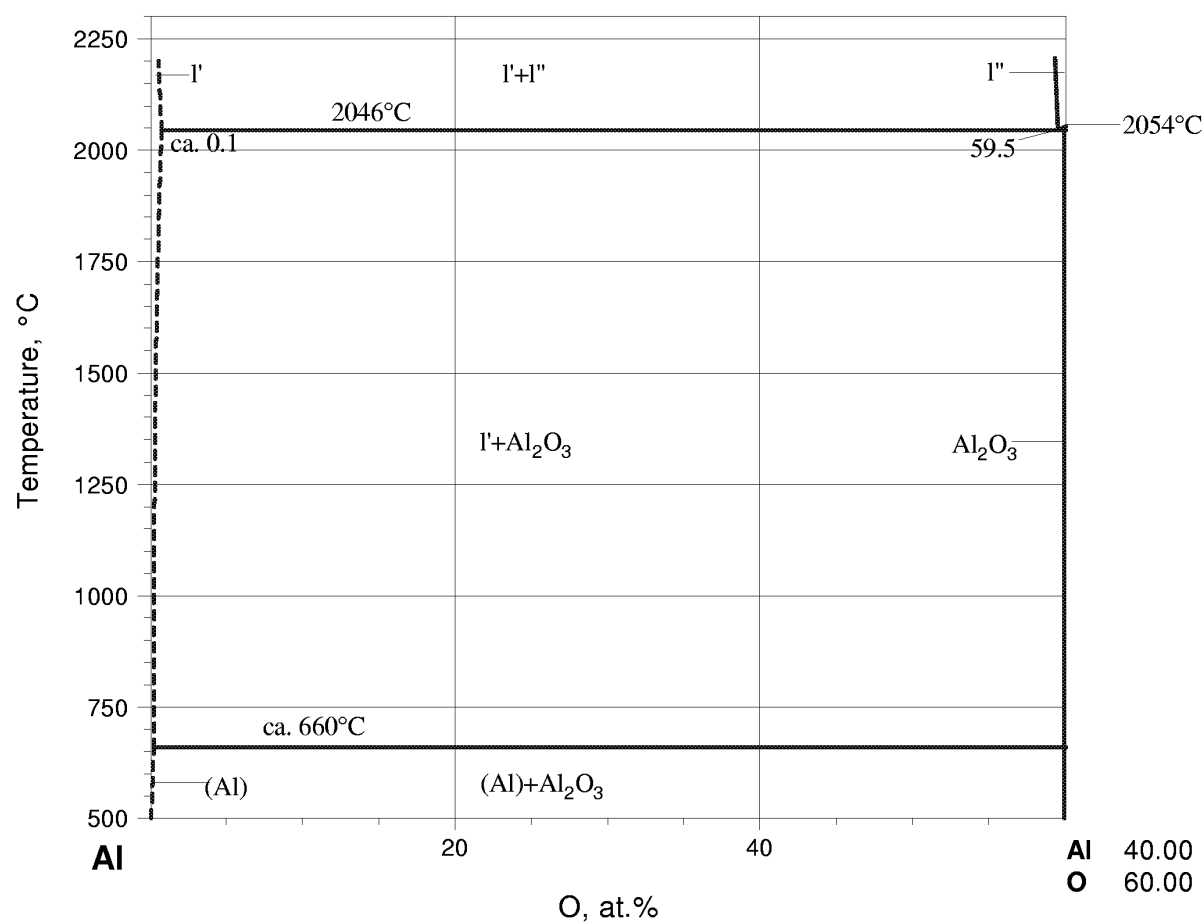


Fig. 1: The binary system Al-O [85Wri]

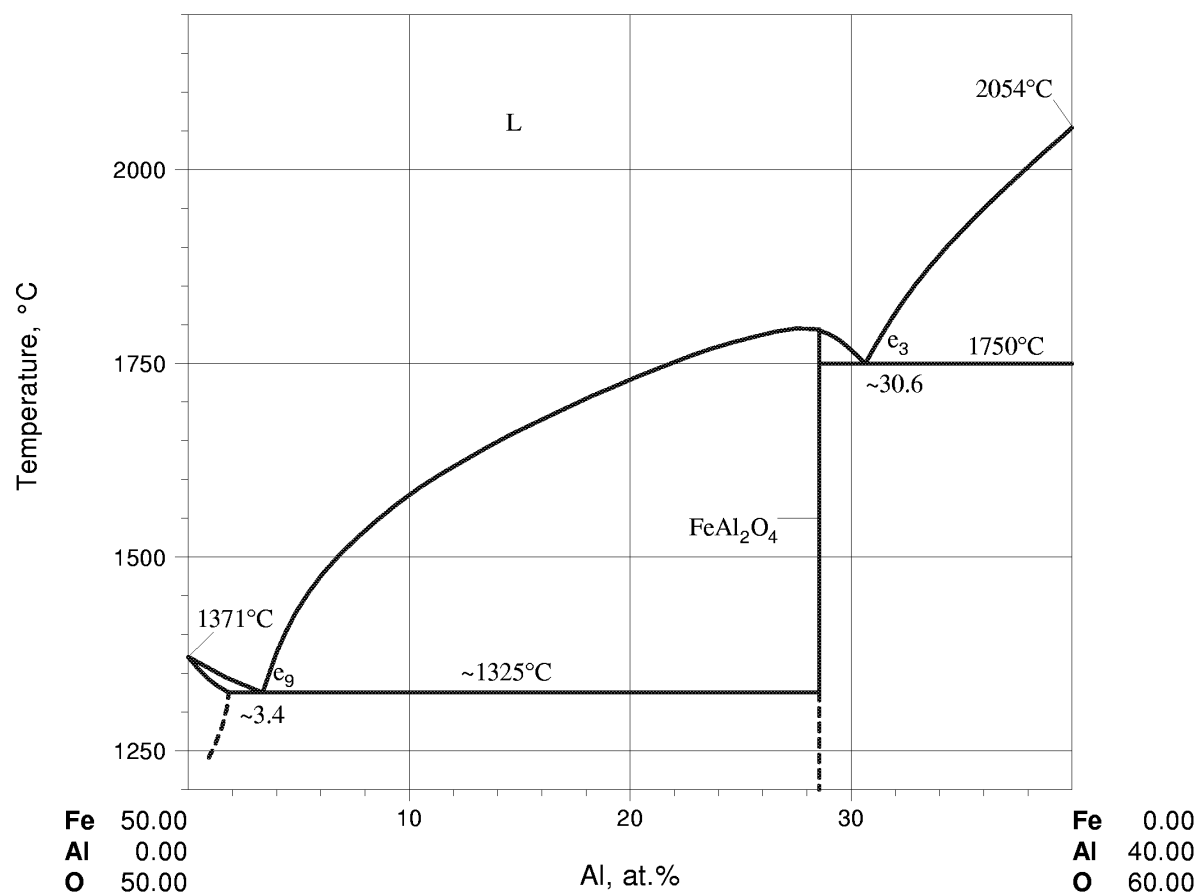


Fig. 2: Pseudobinary system FeO-Al<sub>2</sub>O<sub>3</sub>

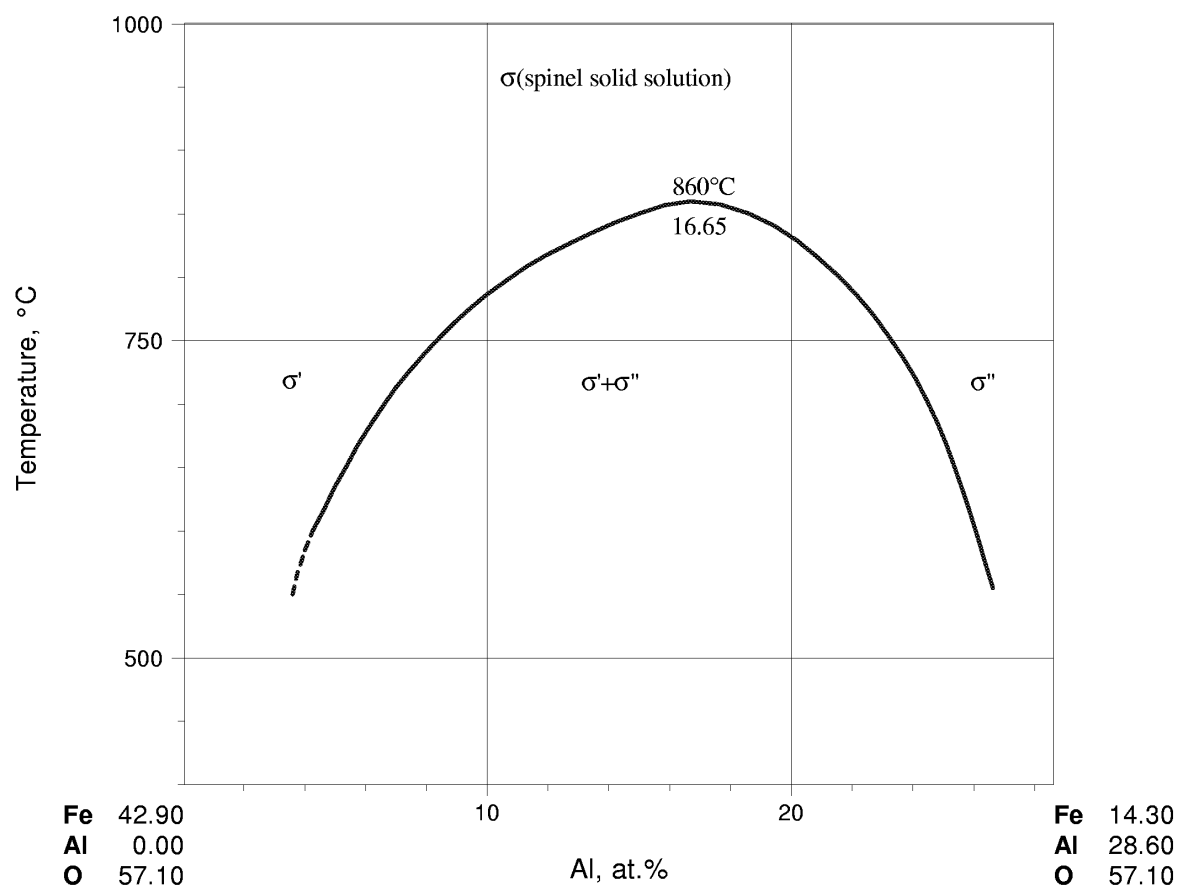


Fig. 3: Subsolidus pseudobinary section  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  under pressure (2kbar)  
[62Tur]

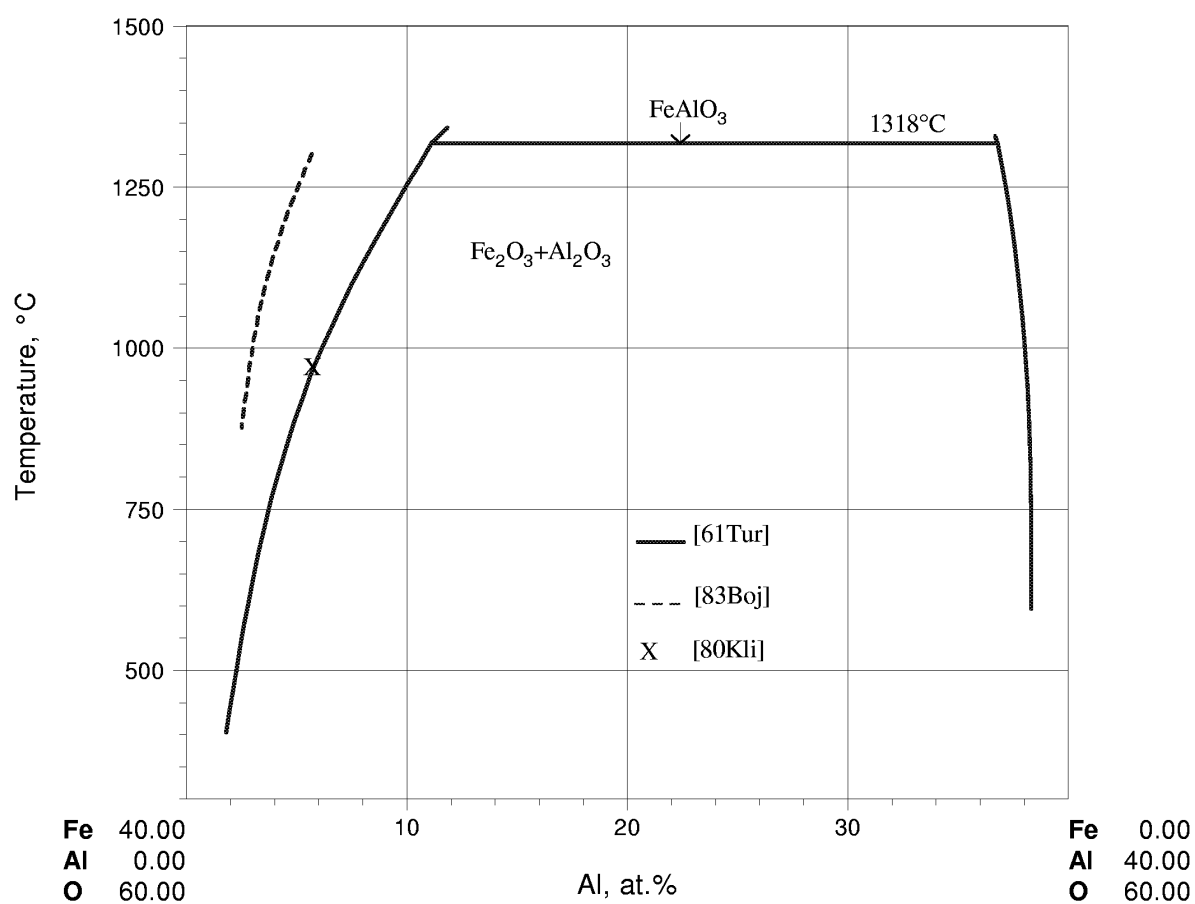


Fig. 4: Subsolidus pseudobinary part of the section Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> below 1350°C  
(1.013 bar)

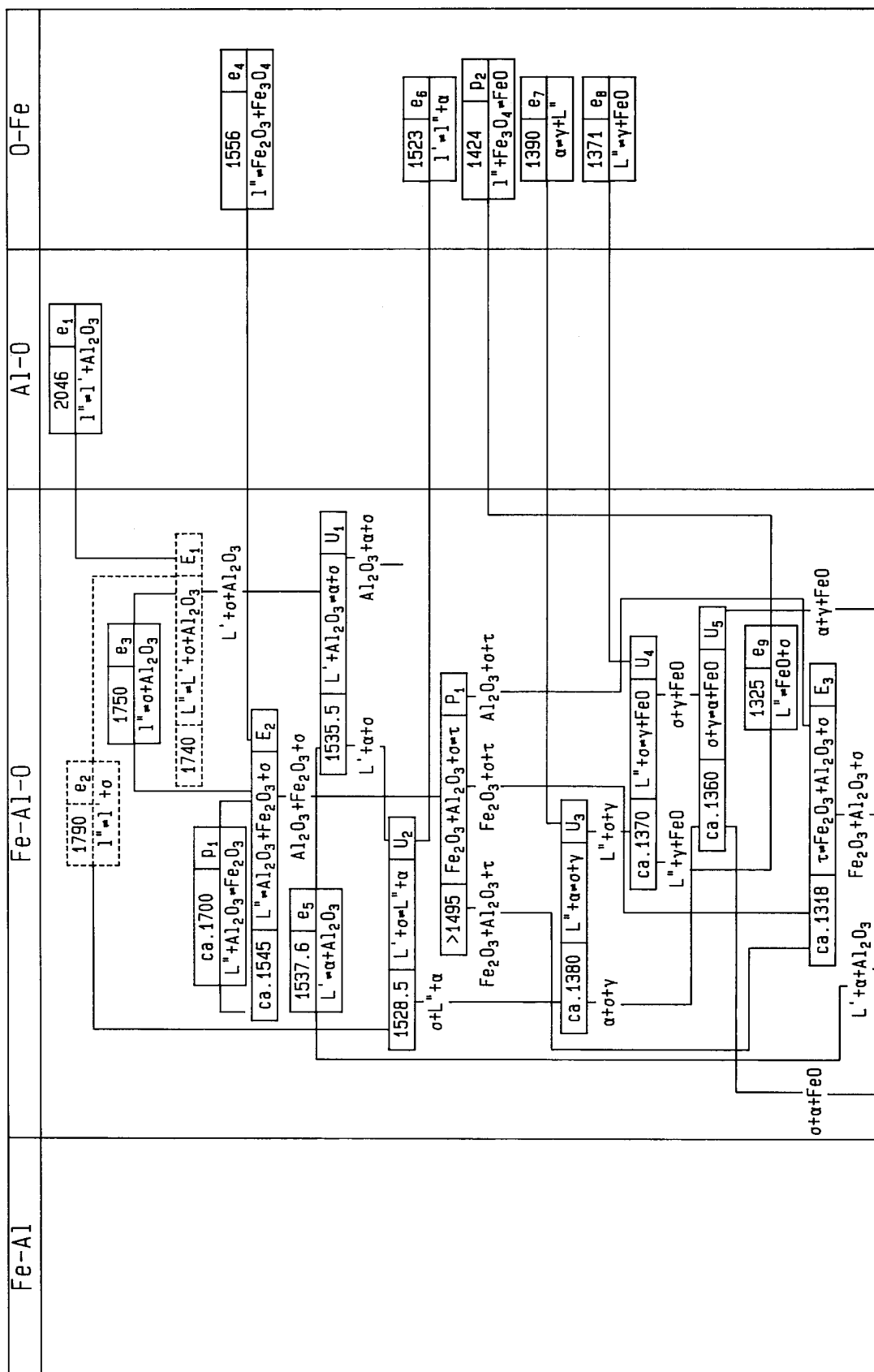


Fig. 5a: Reaction scheme

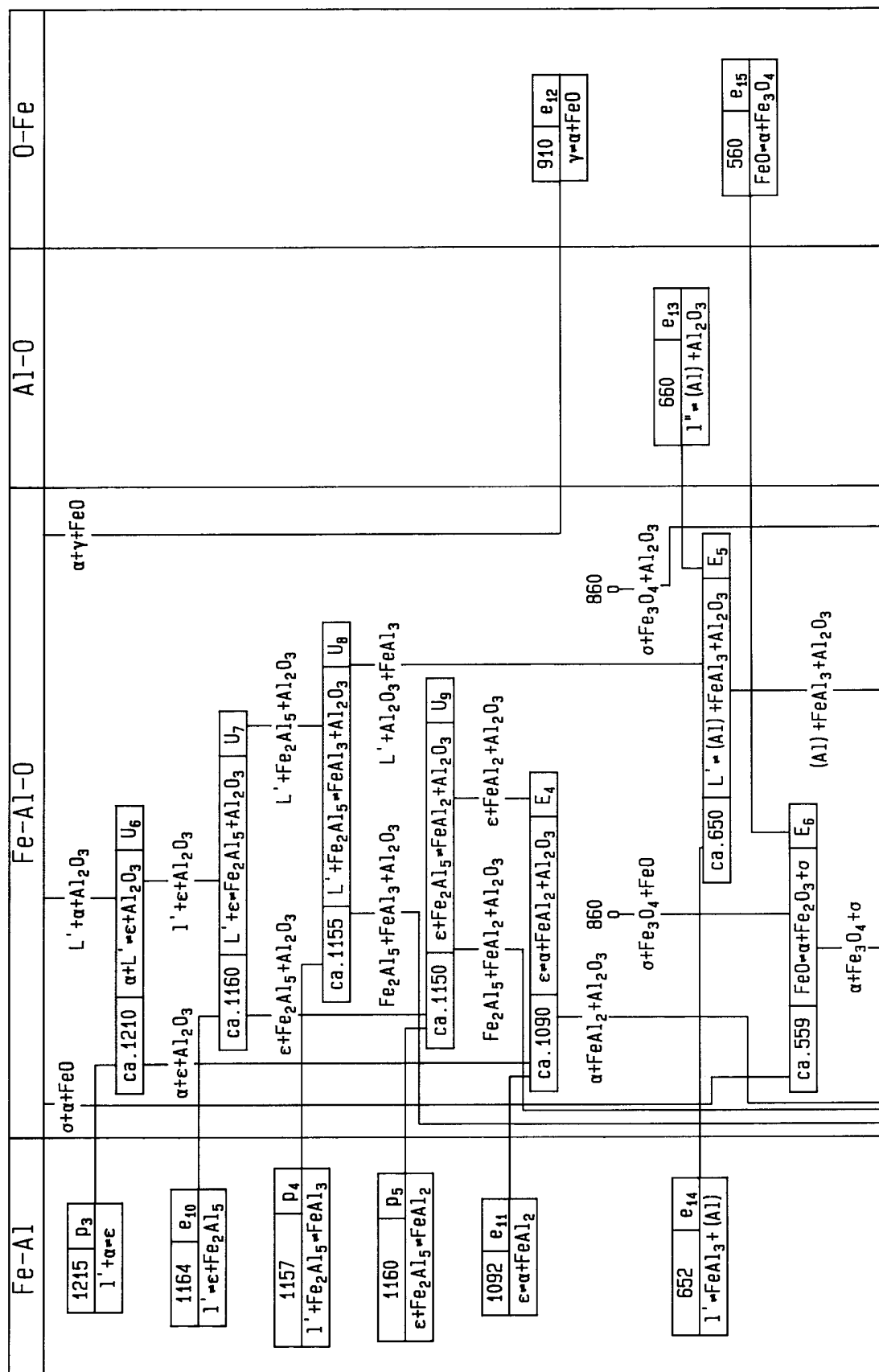


Fig. 5b: Reaction scheme

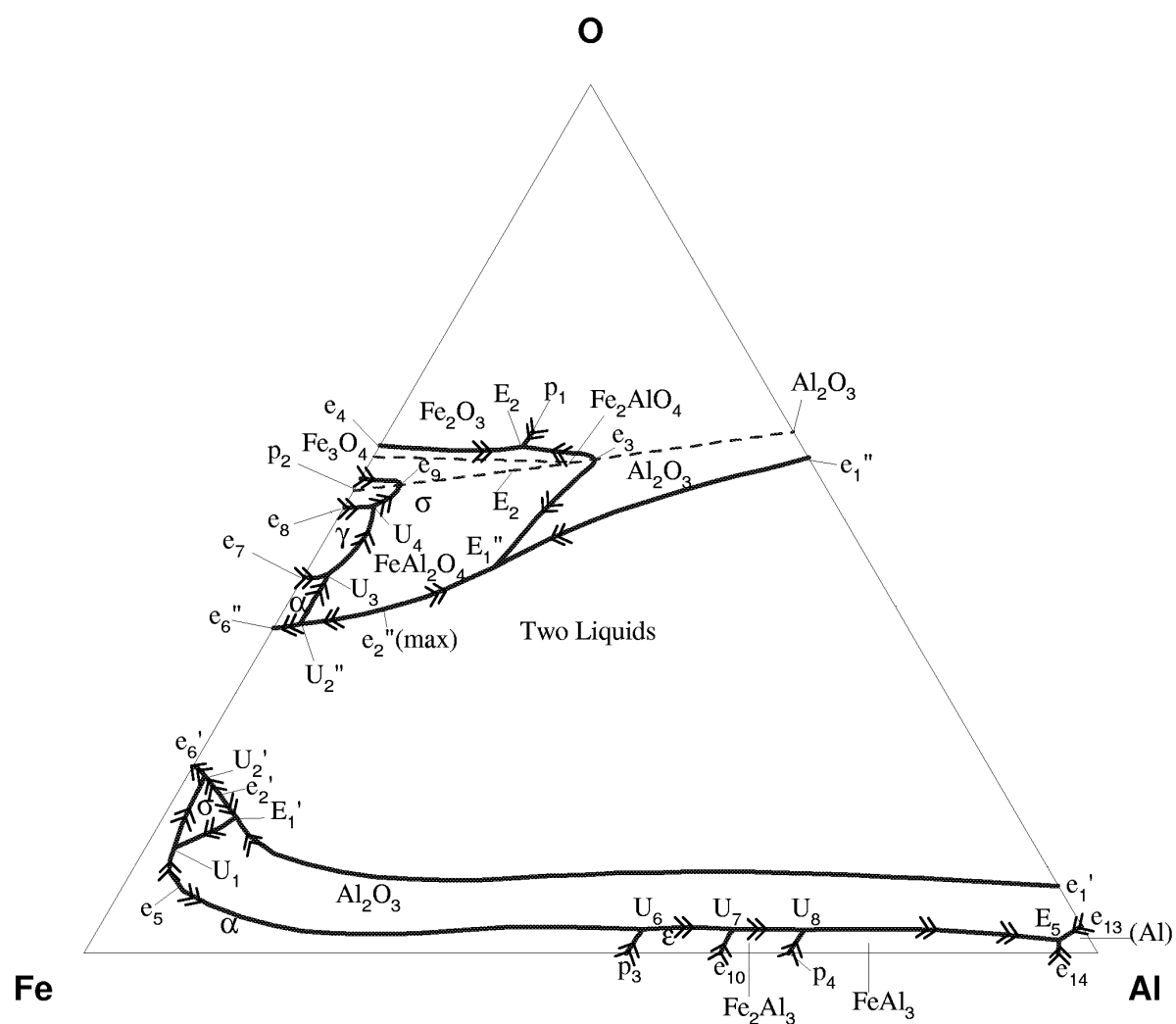
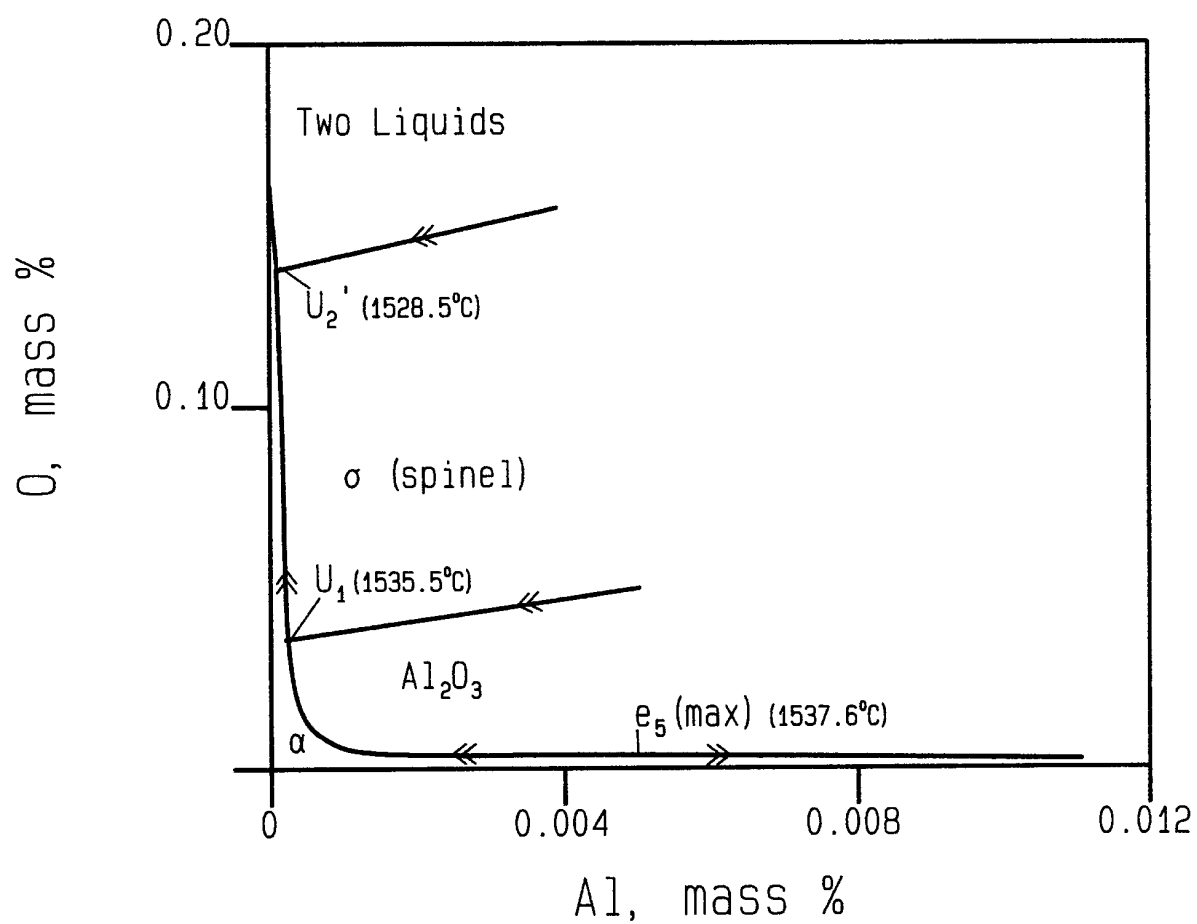
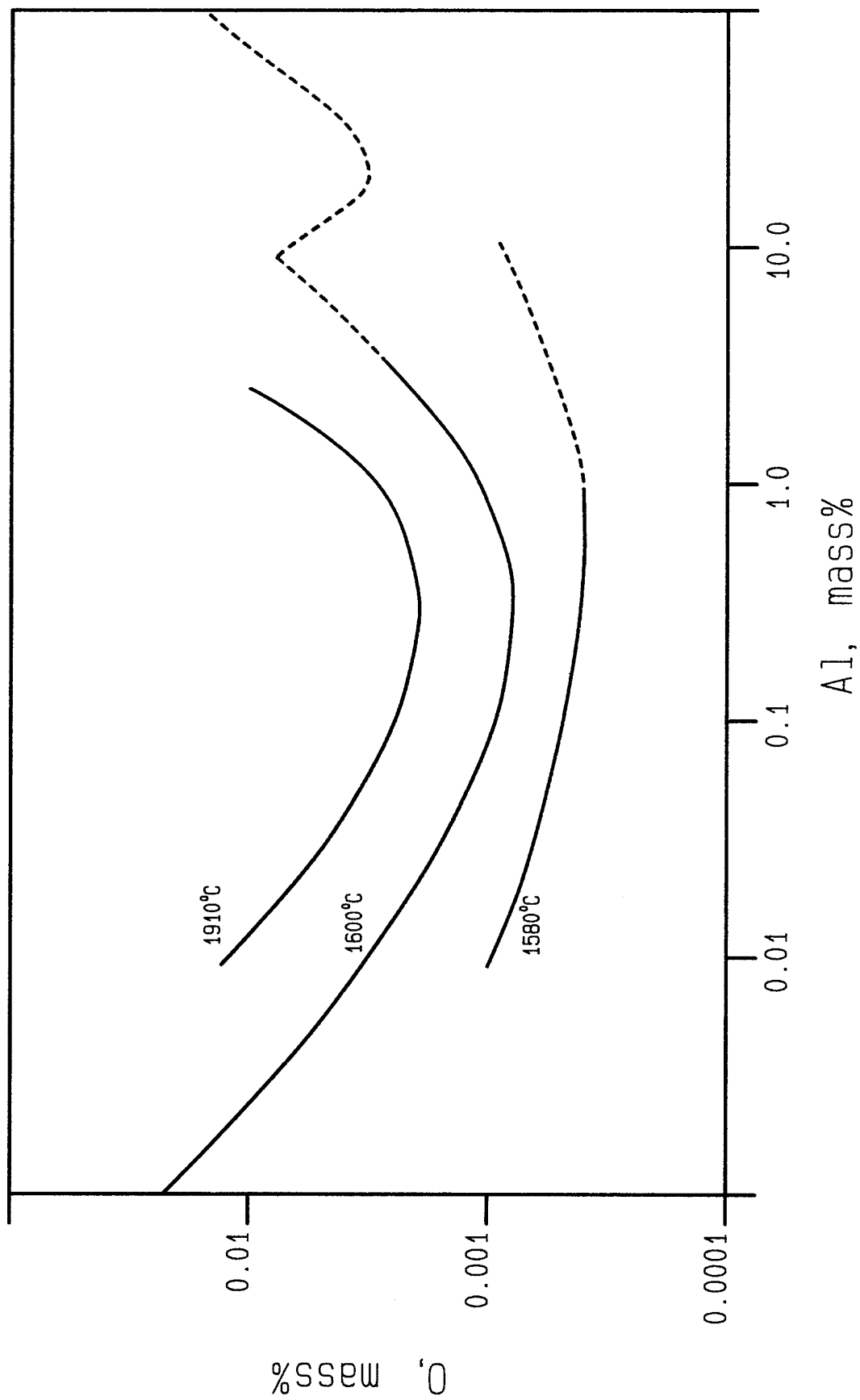


Fig. 6: Liquidus surface of the Fe-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Al region under pressure, no gas phase equilibria



**Fig. 7:** Liquidus surface of the Fe corner [72Ell]





**Fig. 8:** Isotherms of the liquidus surface of  $\text{Al}_2\text{O}_3$  in the Fe corner (deoxidation equilibrium, log scale); 1910°C [63Ent], 1600°C [81She], 1580°C [67Swi]

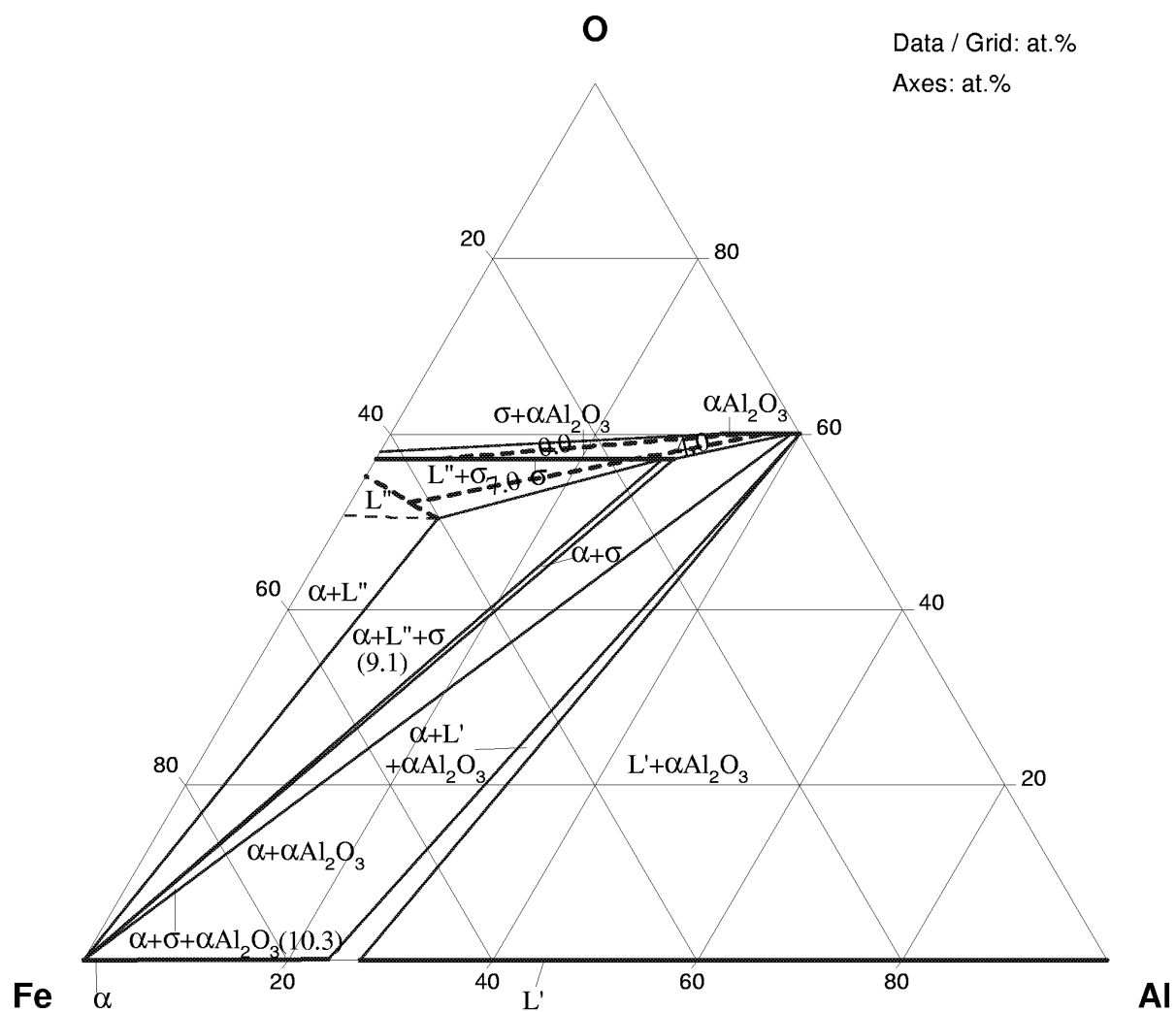


Fig. 9: Isothermal section at 1500°C (Numbers in tie-triangles and on tie lines are values of  $-\log p(\text{O}_2)$  (bar)), [89Rag]

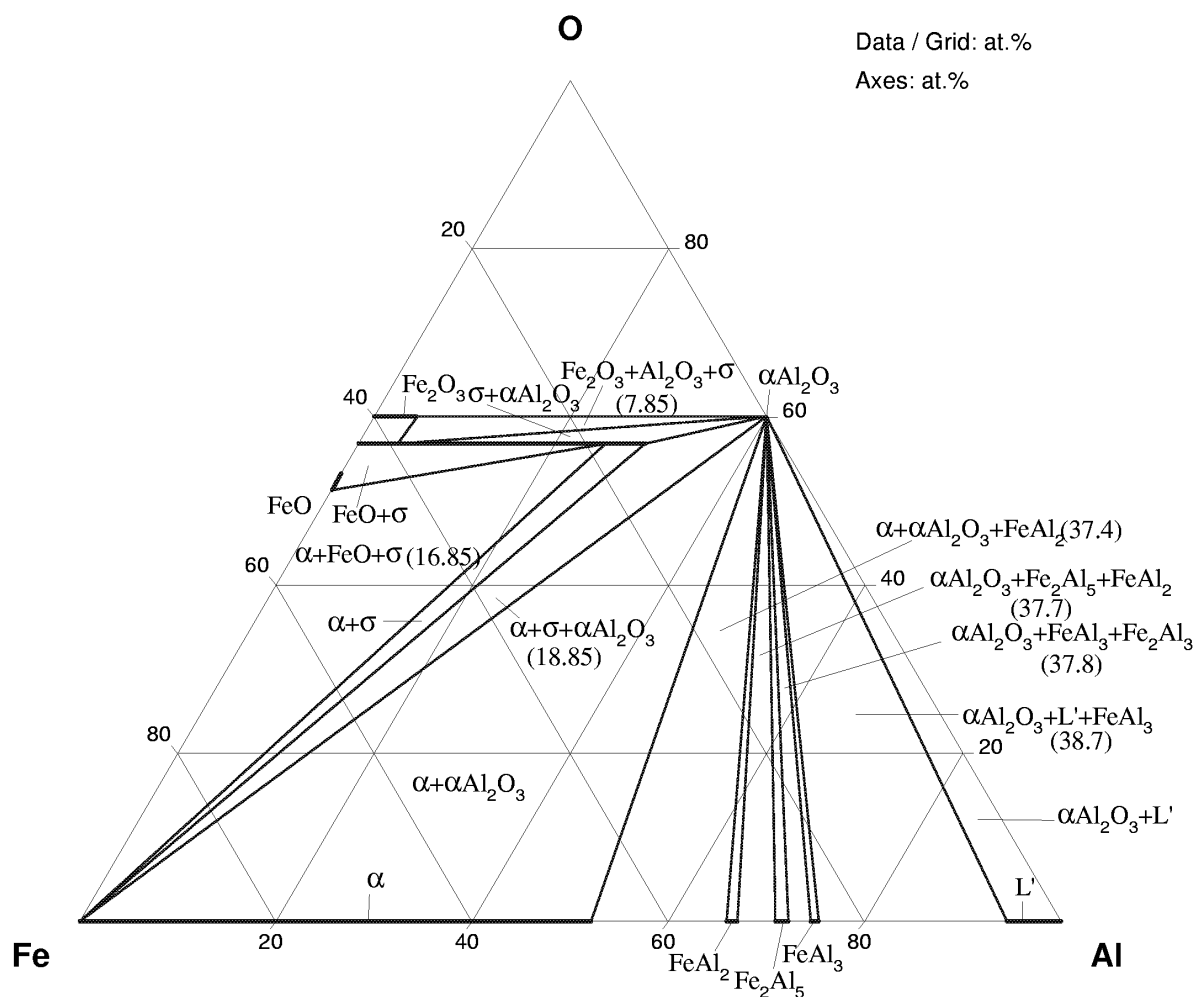


Fig. 10: Isothermal section at 900°C (Numbers in tie triangles are of  $-\log p(\text{O}_2)$  (bar)), [89Rag]

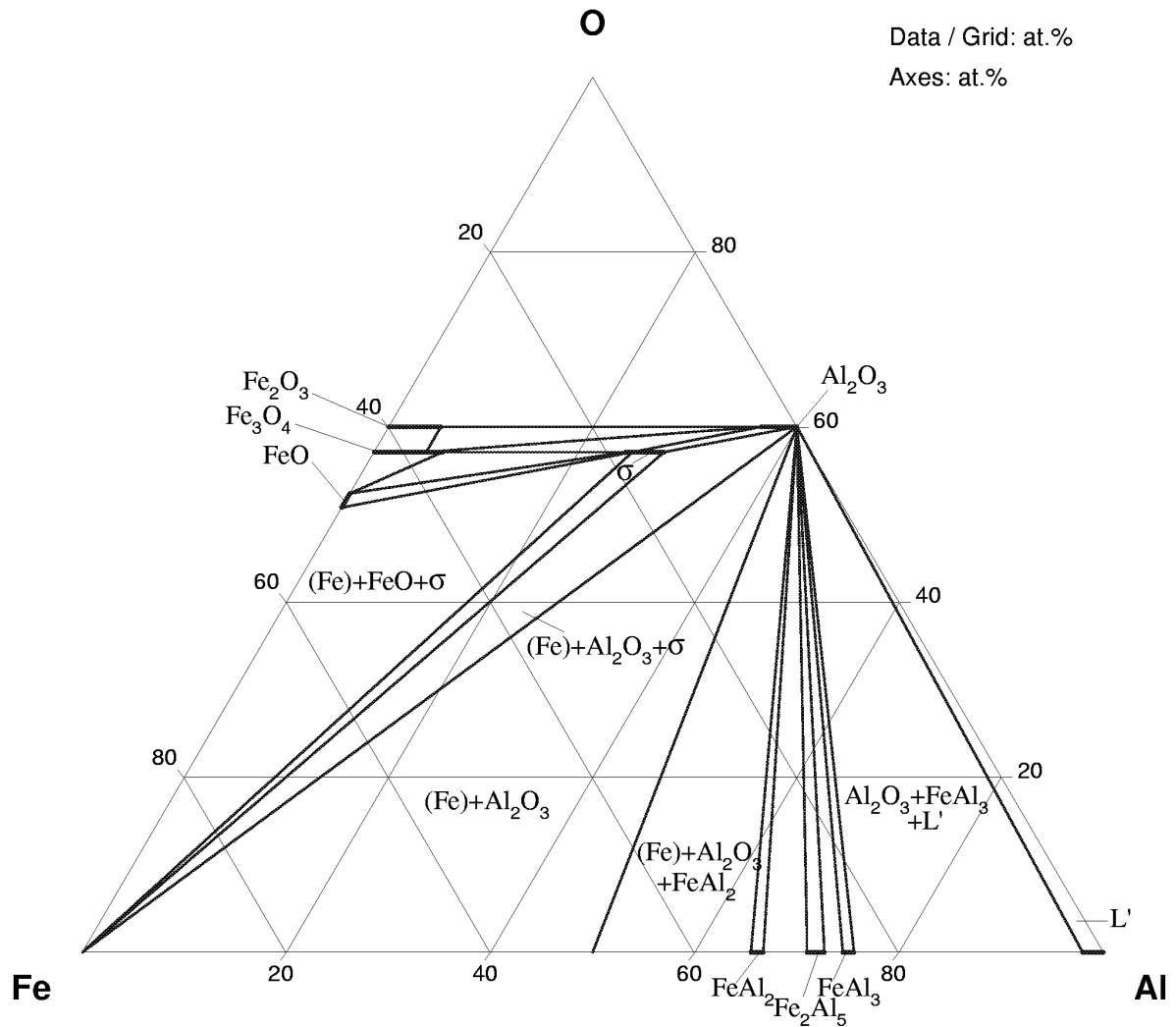


Fig. 11a: Isothermal section of the system Fe-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Al at 700°C

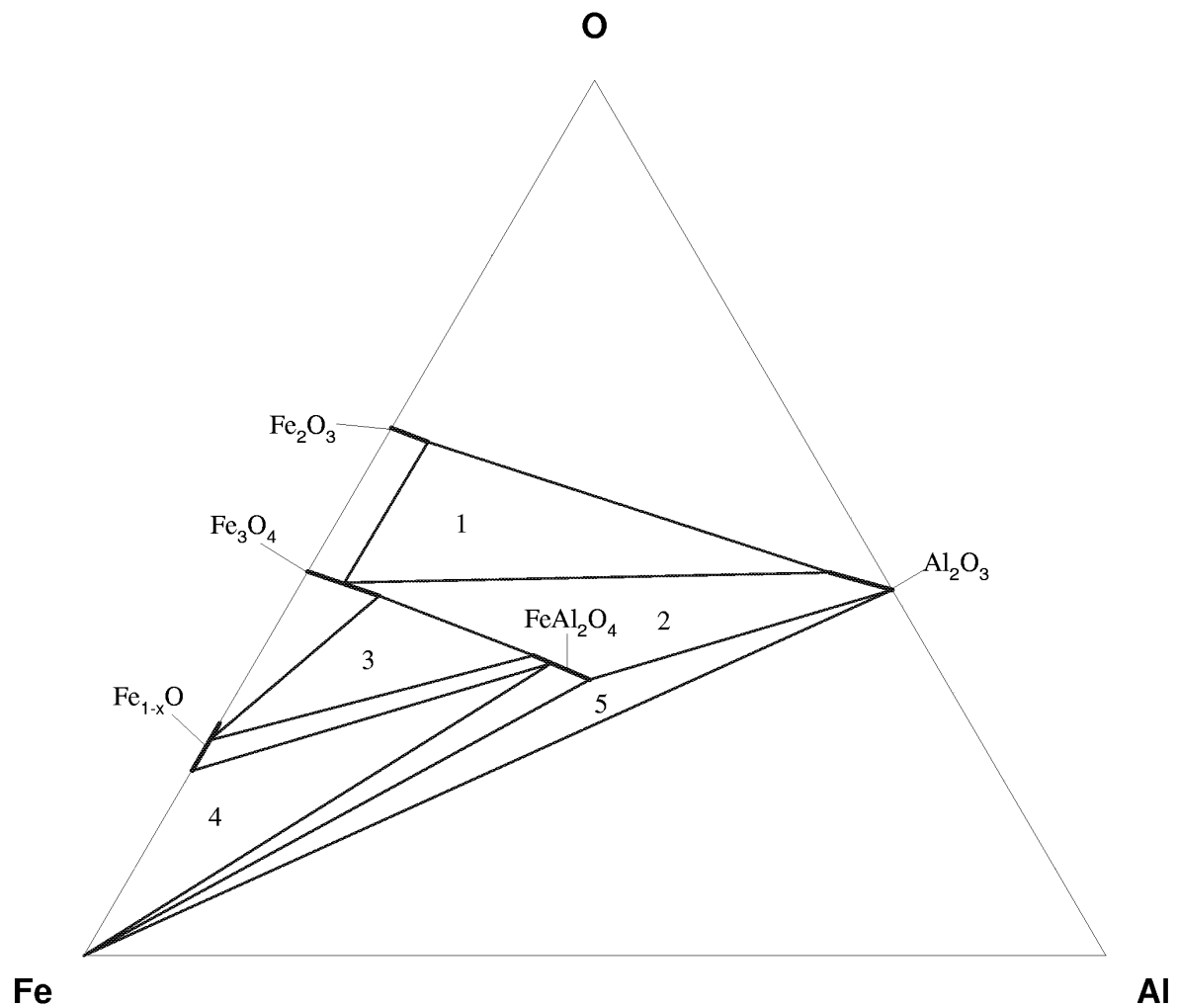


Fig. 11b: Schematic sketch at 700°C, the five three-phase solid state fields of the Fe-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> region are numbered 1 to 5 [62Tur]

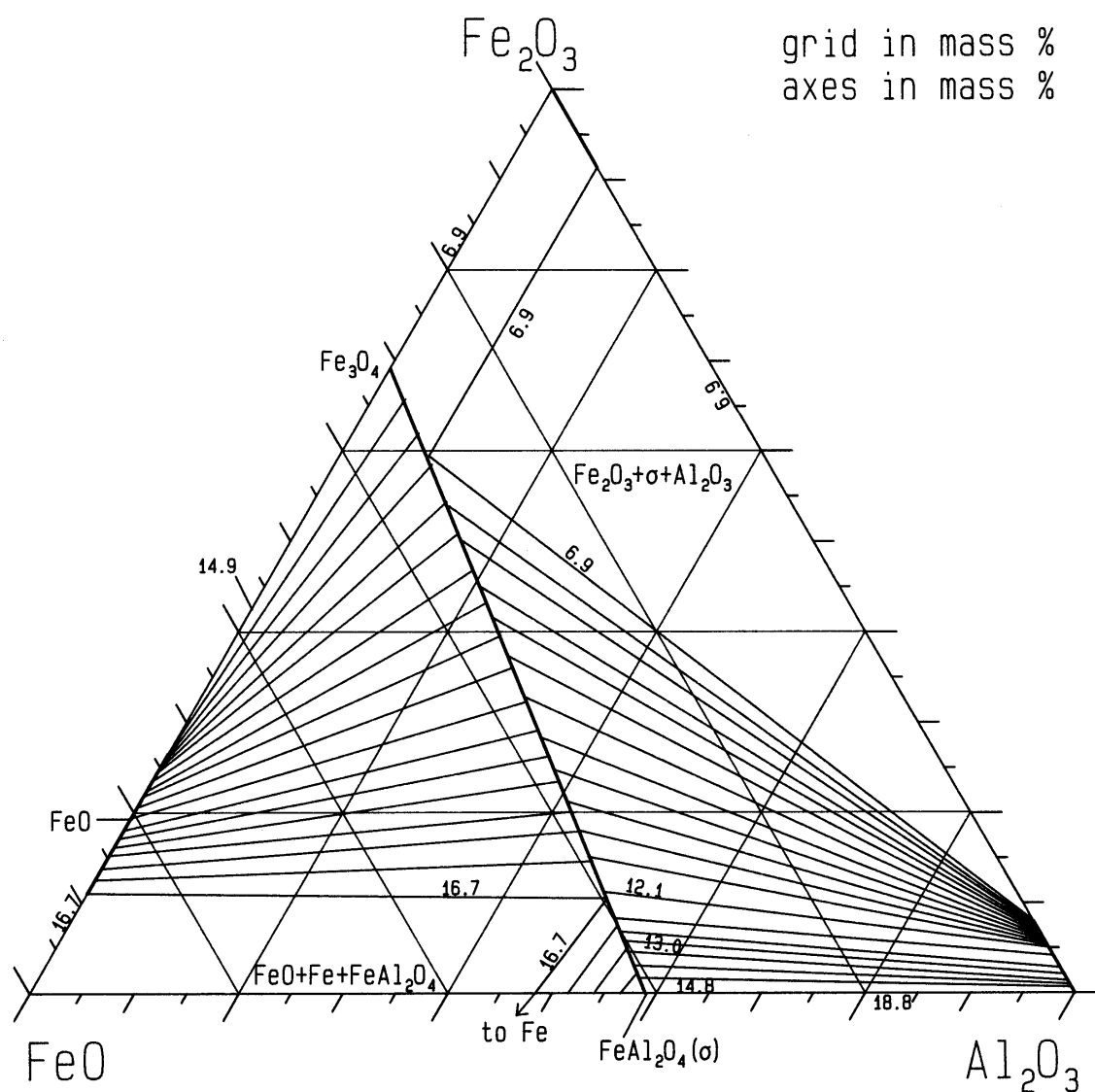
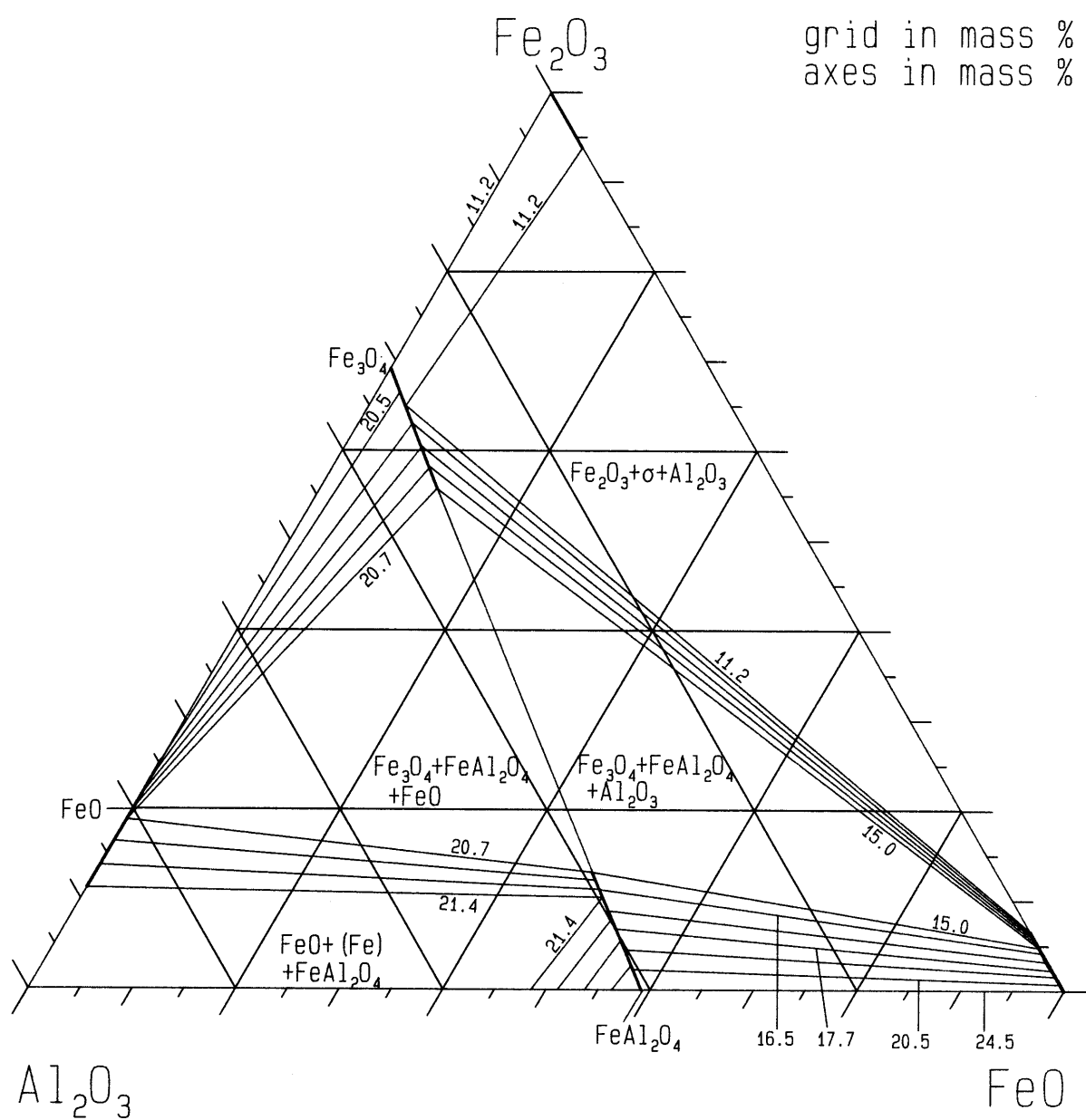


Fig. 12: Isothermal section of the partial system FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> at 900°C [61Tur], oxygen gas is in equilibrium with the condensed phases at given numbers = -log p(O<sub>2</sub>)



**Fig. 13:** Isothermal section of the partial system FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> at 700°C [61Tur], data on tie lines = -log p(O<sub>2</sub>)

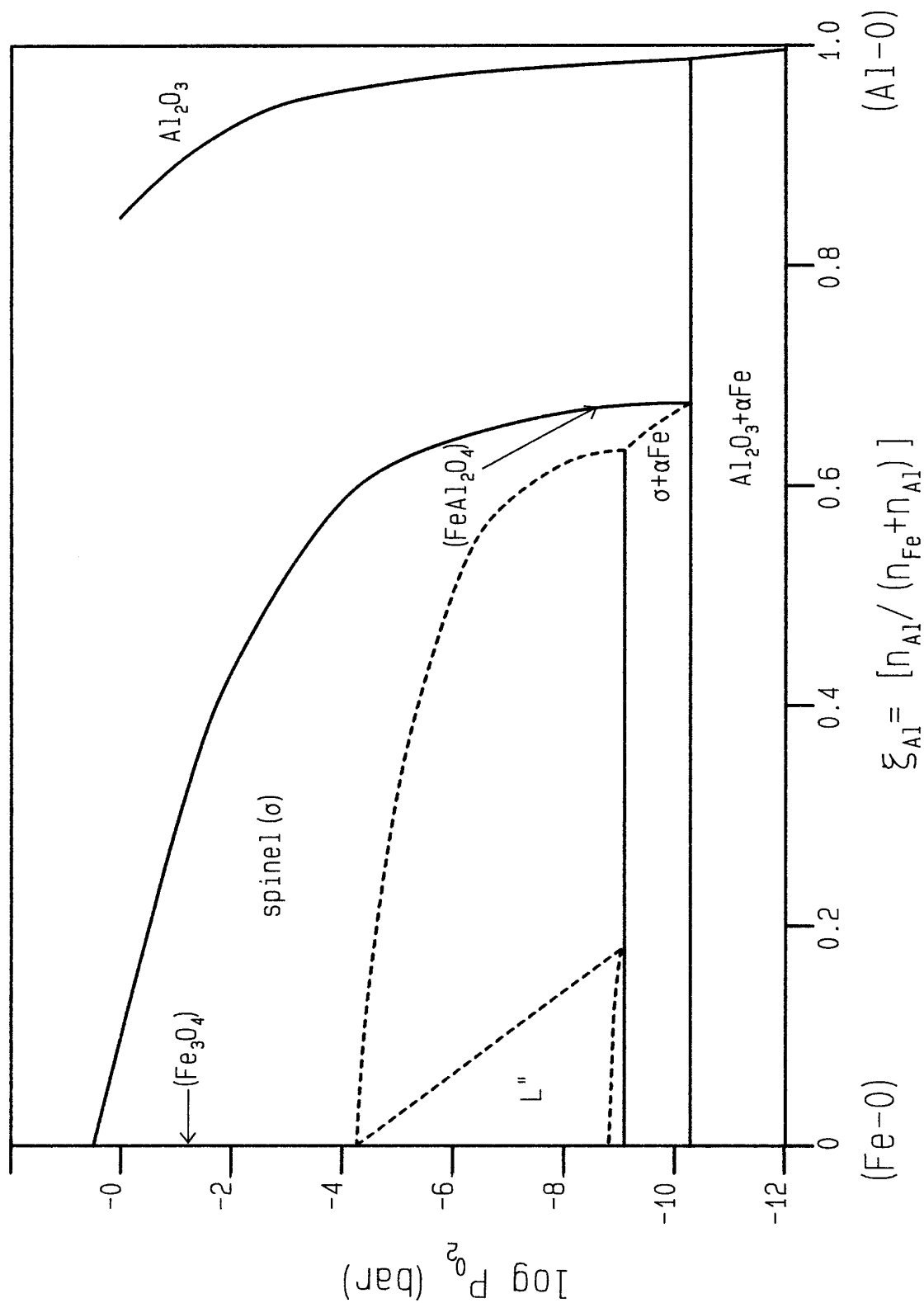


Fig. 14: Fe-Al-O equilibrium oxygen pressure diagram at 1500°C [80Mey]



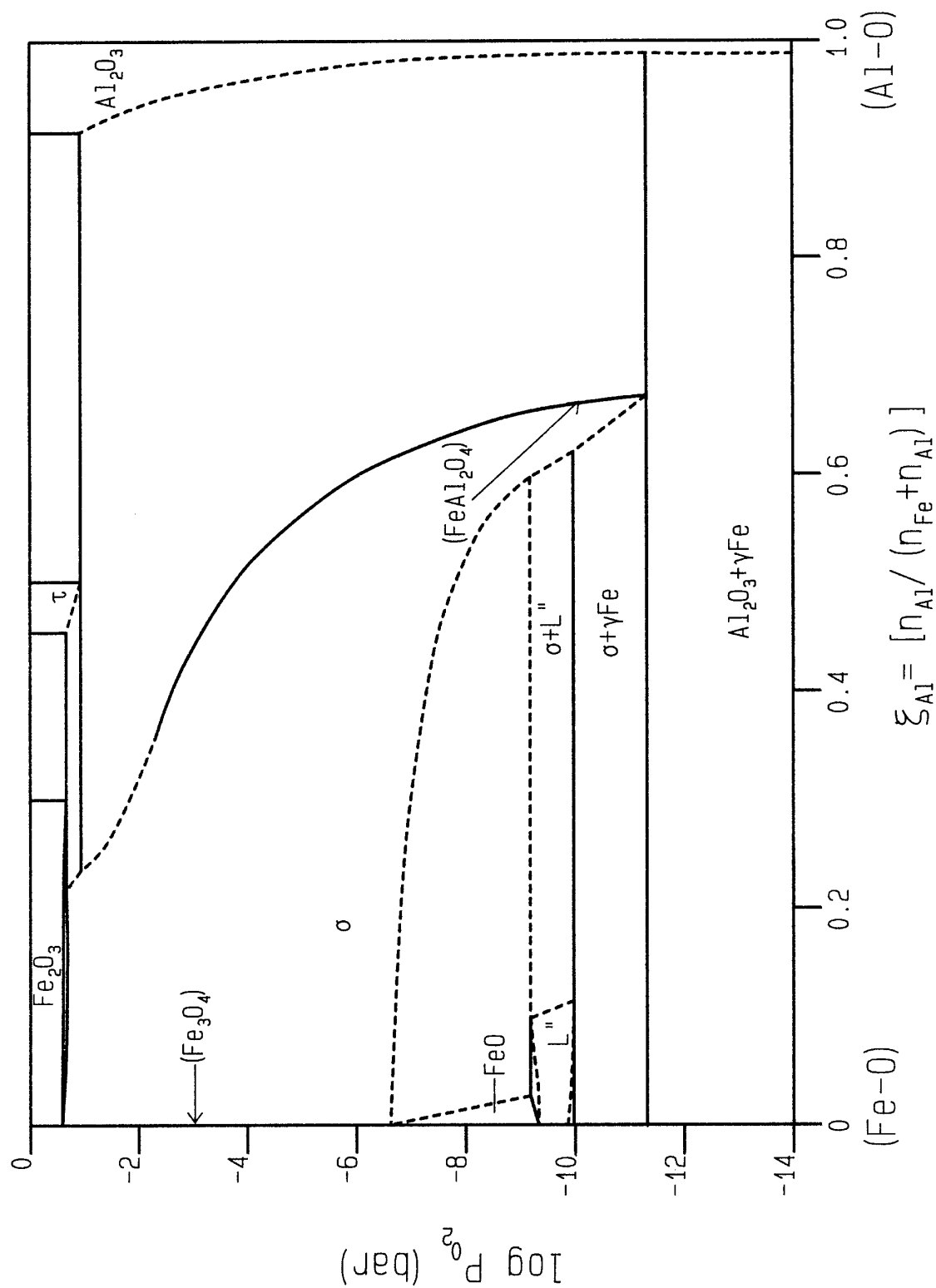


Fig. 15: Fe-Al-O equilibrium oxygen pressure diagram at 1380°C

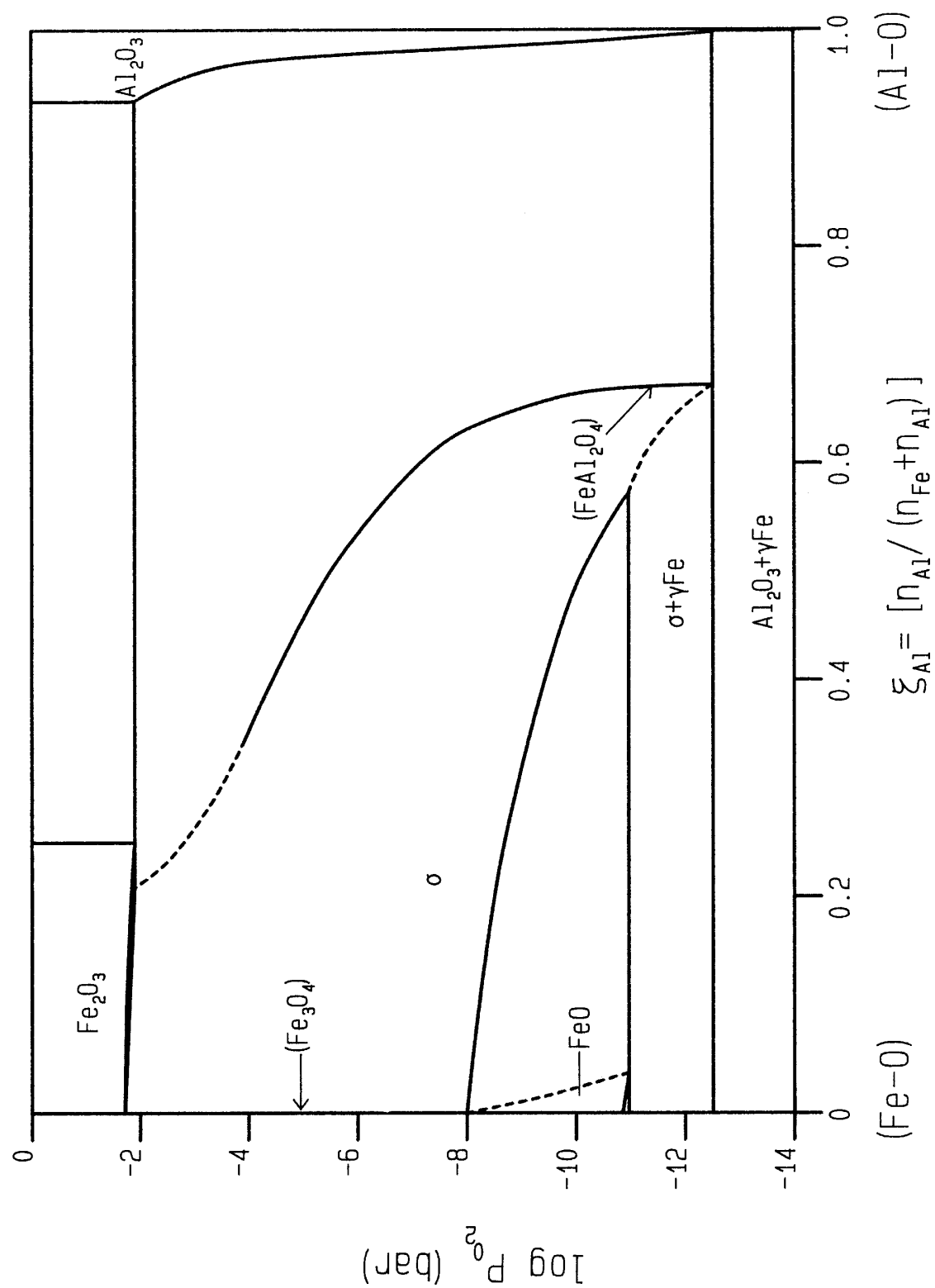


Fig. 16: Fe-Al-O equilibrium oxygen pressure diagram at 1280°C

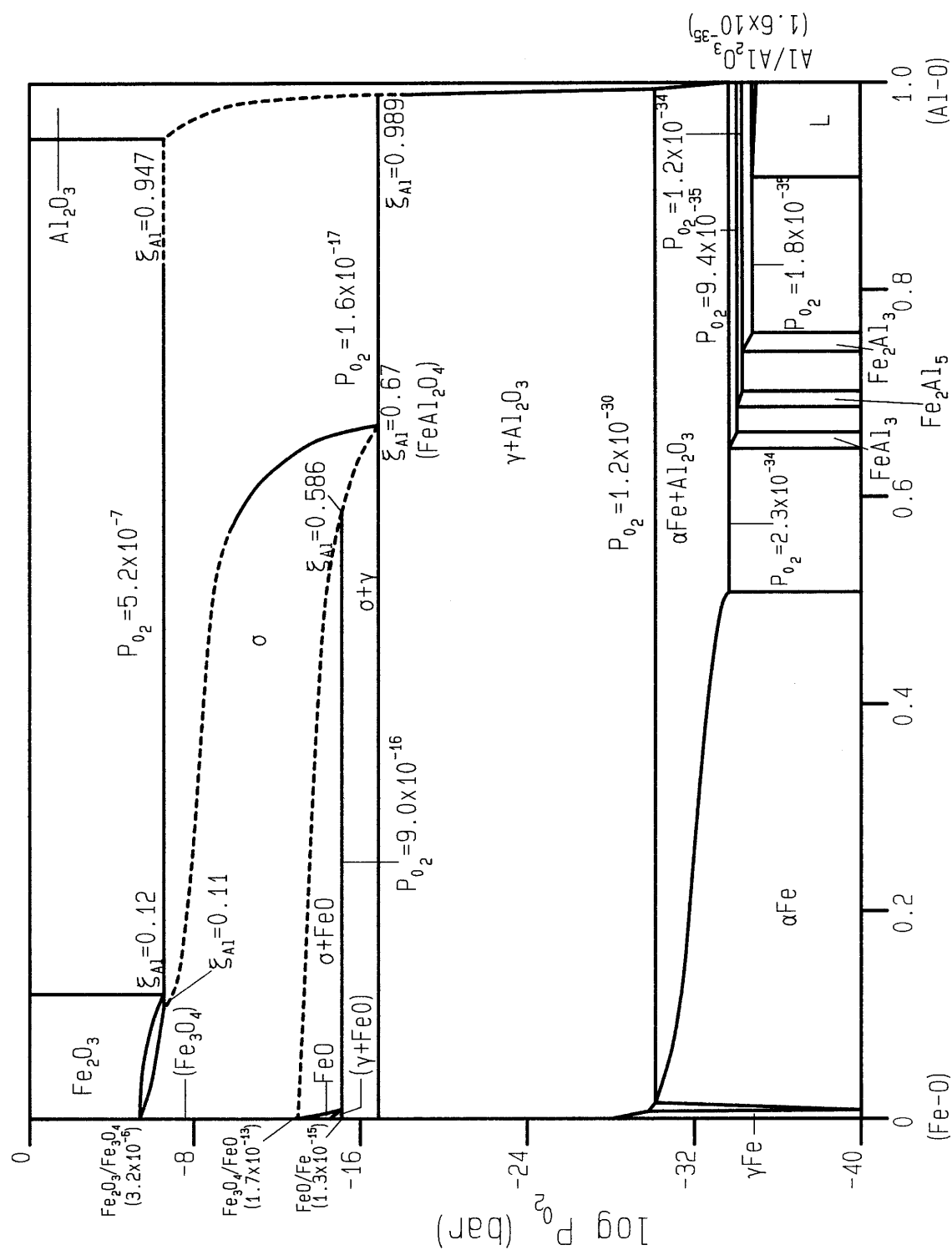


Fig. 17: Al-Fe-O equilibrium oxygen pressure diagram at 1000°C  $\xi_{Al} = [n_{Al} / (n_{Fe} + n_{Al})]$

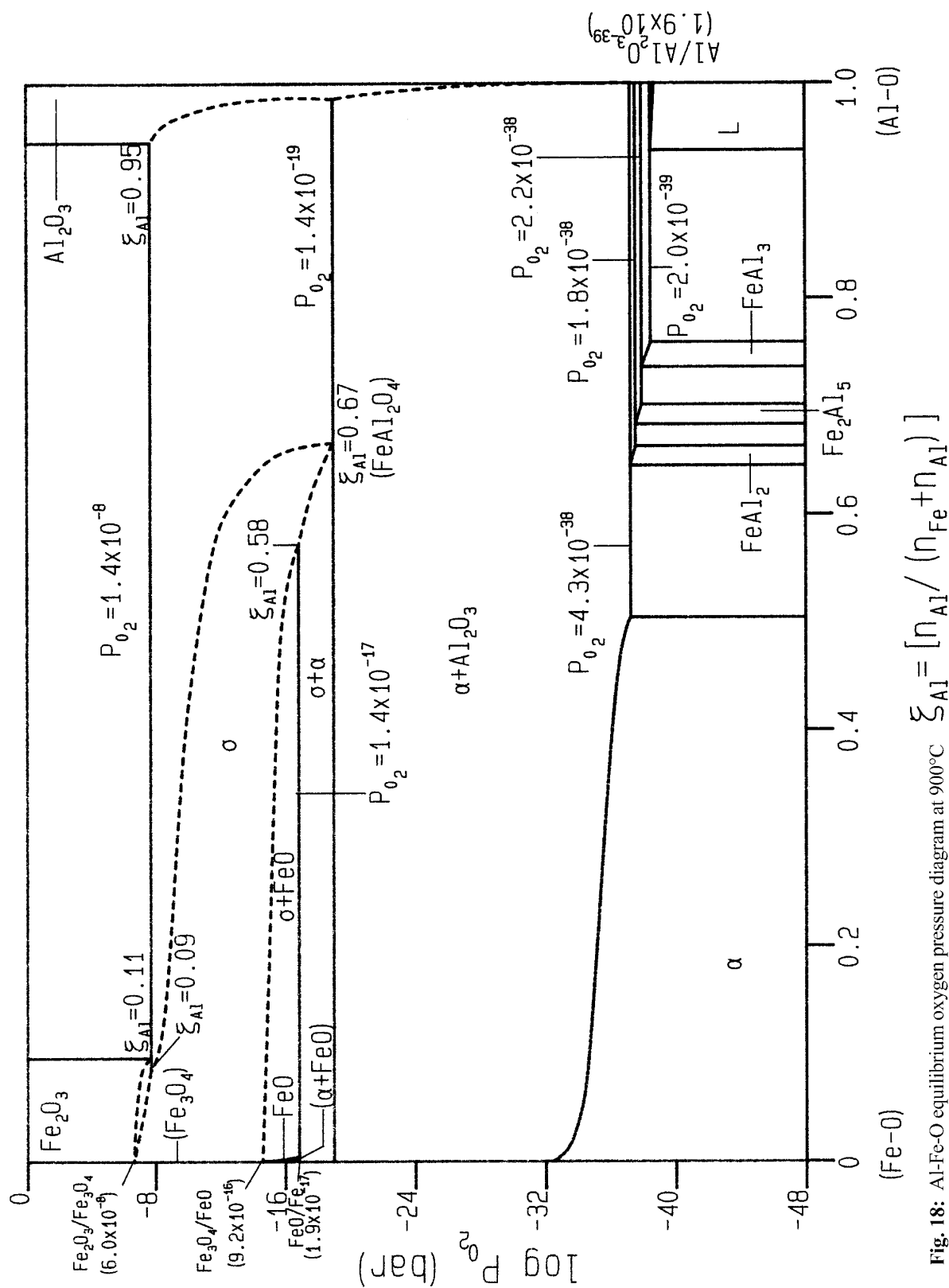


Fig. 18: Al-Fe-O equilibrium oxygen pressure diagram at 900°C  $X_{Al} = [n_{Al} / (n_{Fe} + n_{Al})]$

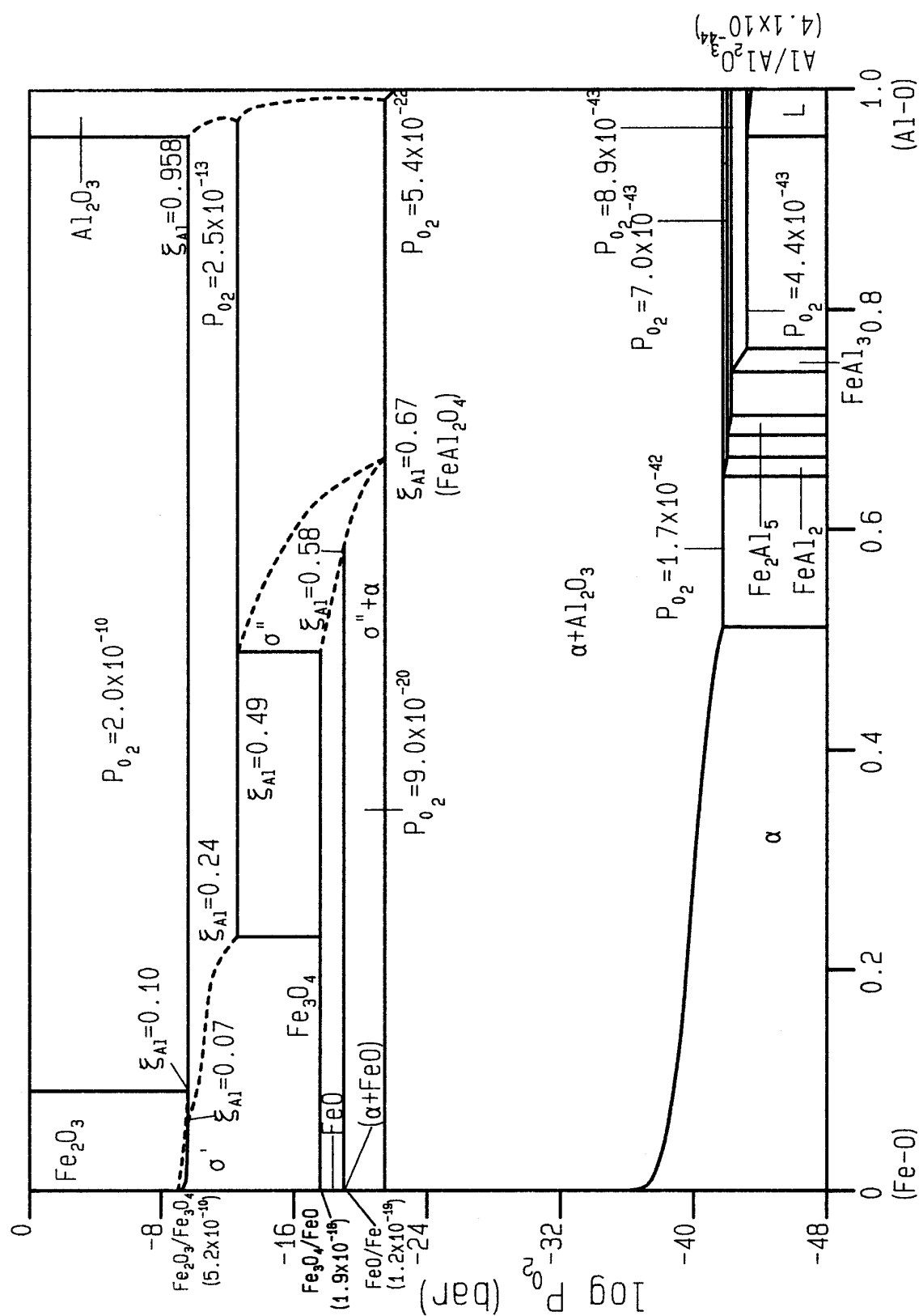


Fig. 19: Al-Fe-O equilibrium oxygen pressure diagram at 800°C  $\xi_{Al} = [n_{Al} / (n_{Fe} + n_{Al})]$

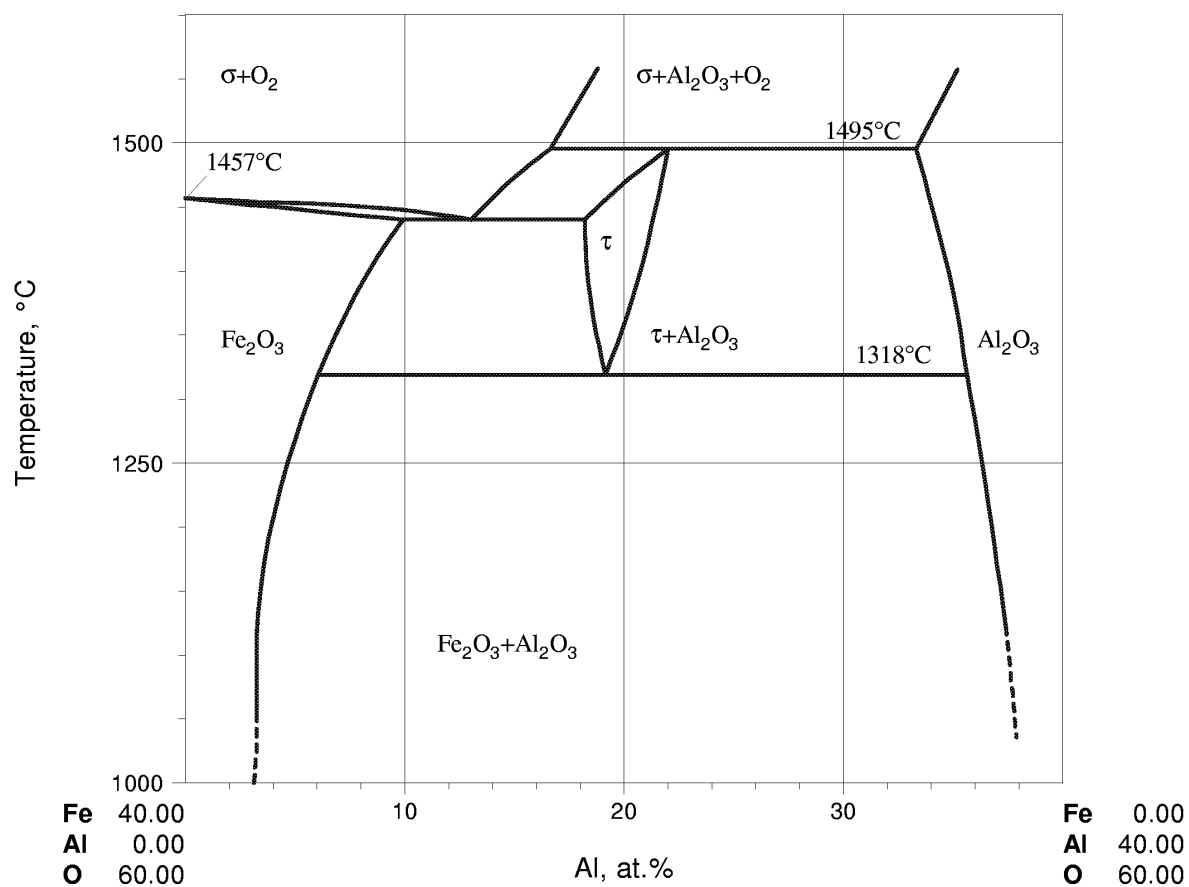


Fig. 20: Section  $Fe_2O_3$ - $Al_2O_3$  at  $p(O_2) = 1$  bar [58Mua]

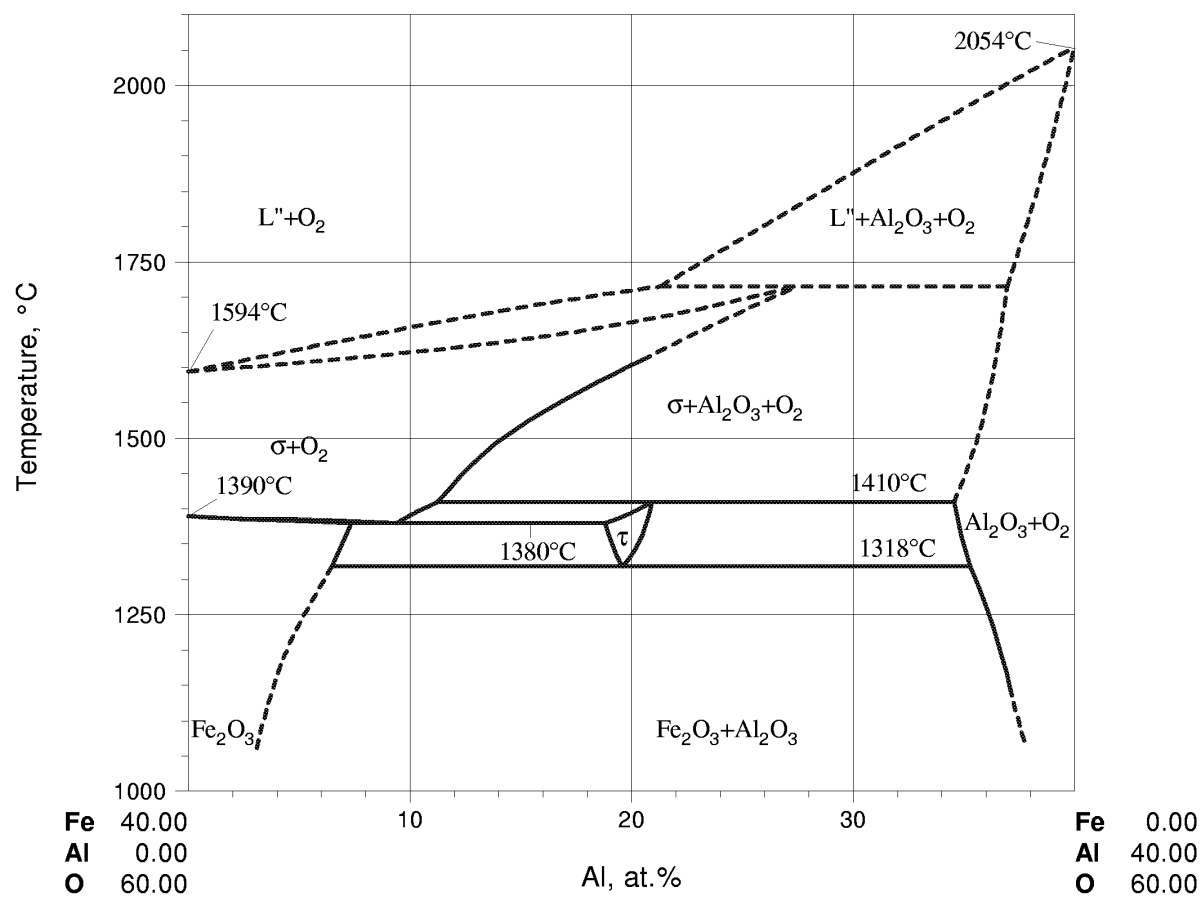


Fig. 21: Section  $Fe_2O_3$ - $Al_2O_3$  at  $p(O_2) = 0.21$  bar [58Mua]

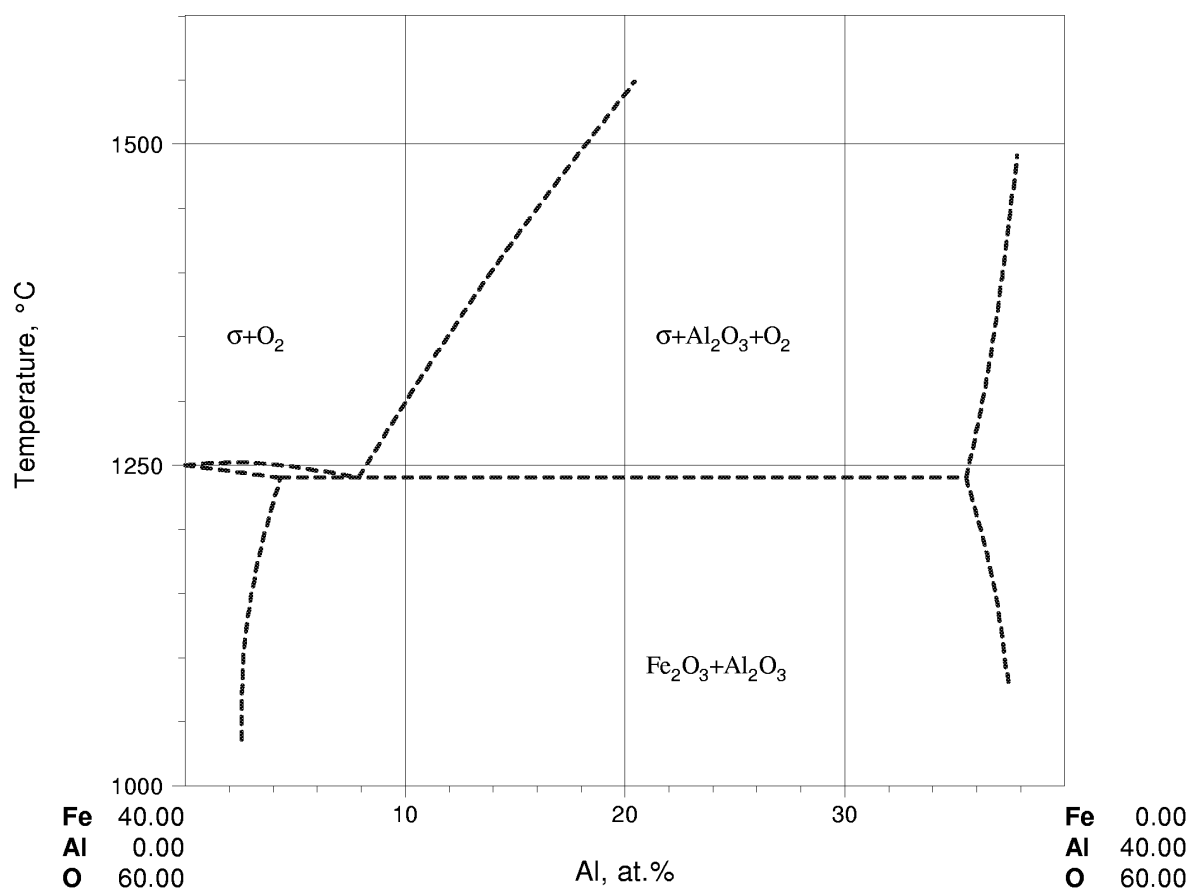


Fig. 22: Section  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  at  $p(\text{O}_2) < 0.03$  bar [58Mua].