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Phase Diagram Investigations in the Ternary
Systems Al-Co-Si and Al-Si-V

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1. Introduction

The use of metals and alloys can be traced back chiliads of human's history. The application of copper and the development of its alloys started in the Chalcolithic and the oldest archeological discoveries in this respect were dated eight thousand years B.C. Based on the use of genuine copper, gold and silver, in the Bronze age from 2200 to 1200 B.C. the usage of bronze as an alloy started. The development and utilization of tools and weapons of iron and steel characterize the Iron Age from 1200 to 450 B.C. During the centuries of course the demands and the application range of metals and alloys changed and increased a lot. Nearly no field in our modern society can get along without metals: they are of essential use in industries, transport industries, household, medicine and other areas. In the last decades the discussion about sustainable and renewable energy production was getting more and more important and the finding and processing of applicative new materials is essential in this respect. The usage of metals and alloys not only as catalysts, coating materials and energy storage materials play an important role in these developments. Intermetallic alloys are receiving extensive research activities at the present time in view of the possibilities for their application, particularly at high temperatures, as high strength materials in oxidizing or corrosive environments [1]. They offer the advantage of ceramics and certain of the beneficial mechanical characteristics of metals. The advantage of intermetallics over ceramic materials is their behaviour at high temperatures since they show yielding and stress-relieving characteristics [2].

The research of the present work is dedicated to phase diagram investigations in the ternary systems Al-Co-Si and Al-Si-V. Co and V are 3d transition metals and the ternary systems of these metals with aluminum and silicon are of significant importance for many technical applications. In metallurgical grade aluminum-silicon alloys are used to produce cast parts mainly for automotive industry. High performance light metals are required to increase fuel efficiency of transport systems and to reduce environmental pollution which is being considered seriously in modern society. Hypereutectic Al-Si alloys have been regarded to be a potential substitute for cast iron, which has been used widely for wear resistant components in the automotive industry [3]. Because of their excellent castability, it is possible to produce reliable castings, even in complex shapes.

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Additives of other metals like copper, manganese, chromium, molybdenum, cobalt, zirconium, iron or nickel enhance the characteristics of the work pieces like toughness and machinability. Copper for example is added to increase the strength and fatigue resistance and titanium additives refine the grain size. Adding iron also strengthens the work pieces but the ductility decreases drastically and additives of cobalt, nickel and molybdenum maintain the ductility. Aluminum-silicon alloys with iron and nickel have particularly good resistance to high-temperature water or steam [4-6]. Vanadium-additives to $\text{Al}_{99}\text{Si}_1$ films improve their corrosion- and electromigration-resistance, as well as their plasma etchability [7]. Vanadium and its alloys have received moderate attention during the past 30 years, primarily due to their potential for high-temperature applications such as nuclear-fusion reactors, coal-gasification units, and gas turbines. Vanadium melts at 1910 °C and can be alloyed readily with aluminum, chromium, and titanium to achieve low densities without severely depressing the melting temperature. Of additional interest are the promising mechanical properties of these alloys at elevated temperatures [8]. Because of its superconductivity the binary phase SiV_3 was subject of several investigations [9-11]. Cobalt-silicon-aluminum alloys have been investigated as cathode material of the lithium ion battery and the charging and discharging capacity is about two times of the common graphite electrode [12]. γ -TiAl based alloys show good corrosion resistance and due to their high temperature strength in combination with low density they are promising materials for aerospace and automotive applications [13]. TiAl/Ti₅Si₃ alloys are used as composite materials [14]. Ni-Al based superalloys show good oxidation and corrosion resistance, as well as excellent high temperature and creep strengths. For the development of an analogous material the Fe_3Al intermetallic is under investigation [1]. Iron disilicide (β -FeSi₂) is one of the most promising thermoelectric candidates, due to its high Seebeck coefficient, low cost, high oxidation resistance, non-toxicity, and high working temperatures. It is also promising as an important candidate for silicon-compatible devices in optoelectronic technology. Beside other elements aluminium-additives improve the thermoelectric properties of the β -FeSi₂ [15]. Alloying additions of vanadium to Ti₃Al–Si eutectic alloys, which have promising high-temperature mechanical properties, improve their ductility at room temperature. Similar research was done with Al-Fe-Si alloys adding vanadium to improve the mechanical properties at elevated temperatures [16].

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There is a great interest coming from very different fields of applied science and the role of the respective systems as key systems for the development of different highly developed alloys and materials is obvious. A full and consistent description of ternary alloys of aluminium and silicon with the 3d transition metals forms an important basis for future work in these fields.

Alloy phase diagrams describe the state of a metal system in order to characterize compounds and phases dependent of temperature, pressure and composition. In metallurgy they are important to comprehend solidification processes and to understand the microstructure of a sample, which influences the property of a material. Phase diagrams are crucial in industries to develop new alloys for specific applications, to improve fabrication of alloys into useful shapes and design. They are necessary to control heat treatment schedules for the production of desired mechanical, physical and chemical properties, and to improve product predictability [17]. Various aspects of phase equilibria are employed in the industrial processing of materials. They are intended to function in useful applications like welding, soldering, contacting of semiconductors and surface layers.

The very first binary phase diagram was the Fe-Fe₃C diagram and was published by Robert-Austen in 1897 [18]. This diagram was not an equilibrium diagram since it lacked compatibility with the equilibrium reversibility inherent in the thermodynamic constraints codified by Gibbs. Three years later in 1900 the thermodynamically valid equilibrium Fe-Fe₃C diagram was published [18]. Since this time numerous research activities have been done to determine binary, ternary and multi component phase diagrams. Because of the large number of relevant phase diagrams (~4000 binary systems and ~100000 ternary systems, etc.), one can imagine the efforts which have to be done in this field [18].

Another important method beside the experimental process in phase diagram determination is the thermodynamic modeling and calculation of phase diagrams. This method is especially important for higher order systems when experimental results are difficult and complex to gain. The CALPHAD method (Calculation of Phase Diagrams) is a critical assessment and thermodynamic optimization of binary and higher order systems. Knowledge of the equilibrium state is the basis for any successful simulation

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of processes and transformations [19]. For each relevant phase in a respective system the Gibbs energy G as a function of the intensive variables p , T , and x_i is needed. The minimum of G for the system, and thus the phase equilibria, can be calculated by minimization procedures. Starting point of all calculations and simulations of course must be an assessment of reliable experimental data concerning phase diagram determination as well as thermodynamic data. Attempts to develop high-quality databases are in progress but concerning the increased number of compounds that become of interest each year, far from completeness. To improve the application of thermodynamics and phase diagrams to solve modern materials problems, experimental research activities are extremely important [20].

2. Phase Diagram Determination

Phase diagrams are visual representations of the state of a material as a function of temperature, pressure and composition of the constituent components. Generally two-component (i.e. binary) phase diagrams are presented at constant pressure and their graphical representations are quite clearly arranged by only one figure. The precise construction of a ternary phase diagram requires three types of graphical representations: isothermal sections, vertical sections and the liquidus surface projection. Additionally a reaction scheme, called Scheil-diagram, including all binary and ternary invariant reactions can be designed for better understanding of the partially quite complicated circumstances.

The most common and traditional method for phase diagram determination is the usage of equilibrated alloys. This method was used in this work for determining the Al-Co-Si and the Al-Si-V phase diagrams. In the Al-Co-Si system the diffusion couple technique was applied additionally.

Working with equilibrated alloys, a phase diagram is constructed by preparing alloys of the required constituents, heat treating at the requested temperatures to reach equilibrium states, and then identifying the phases. After quenching the microstructure and the composition of the present phases are measured and the solubility of other elements in a phase is detected. Dynamic methods are used to determine liquidus temperatures, solidus temperatures, solubility lines, and other phase transition lines. When a phase transition occurs in an alloy, its physical and chemical properties, phase composition, and/or structure will vary. Based on this fact several techniques were utilized in this work to determine the ternary phase diagrams. They included metallographic investigations, X-ray powder diffraction (XRD), electron probe microanalysis (EPMA) and differential thermal analysis (DTA). Metallographic investigations were carried out by means of optical microscopy as well as using scanning electron microscopy (SEM). By analyzing the temperature, composition, and property changes associated with phase transitions, one can construct phase boundaries according to the phase rule [21]. The phase rule of Gibbs relates the physical state of a mixture with the number of substances of which it is composed and with the environmental conditions imposed upon it.

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For the isothermal sections one intersects the ternary phase diagram at a certain, fixed temperature horizontally. This temperature is reached by an equilibrium annealing procedure after preparing an alloy by melting the components together or by using other reaction routes like pressing a powder pellet of the components. To ensure that the samples reach the equilibrium state the alloys are kept at a definite temperature for a certain time and homogenization is achieved through diffusion. Since the diffusion coefficient increases greatly with temperature, the heat treatment temperature should be raised as high as possible to assure good homogenization. However the temperature must be at least 50 °C below the solidus temperature. By the subsequent quenching process the alloys are cooled to room temperature very fast and it can be assumed that the equilibrium state is frozen due to the very slow diffusion time at this low temperature. By means of light optical microscopy, XRD- and EPMA- measurements the present phases in each sample can be determined. Not all phases are quenchable and in this case in situ methods like high temperature XRD can be applied.

Light optical microscopy is a very useful method to examine whether an alloy is well homogenized and it is recommended to check this first before carrying on the work. Optical microscopy indicates how many phases a sample contains and the polarization mode gives first information about the crystal structure of the phases. The microstructure of a sample provides the researcher with information on the melting behaviour of the alloys. In fact optical microscopy was a very important tool in former times and many phase diagrams were determined putting large impact on this method. Excellent knowledge and good experience of course is essential for the correct conclusions and interpretation, since the information getting from optical microscopy are quite limited.

In this work a Zeiss Axiotech 100 microscope was used for optical microscopy. The microscope is equipped for four different modes: a bright field (BF) image is an ordinary magnification of the sample and gives information about the number of present phases and about the grain size. For primary crystallization studies the BF mode is essential. In the dark field (DF) mode the light beam irradiates the surface at low angle and only non horizontal surfaces are reflected. The contrast is caused by surface structures like cracks, holes, grain boundaries and rough surfaces. On polarization imaging (PI) the beam is polarized by the polarizer. At the sample surface the beam is

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modified according to the optical properties of the material. Polarizing surfaces can be identified by rotating the sample relative to the incident beam. Phases with low symmetry usually polarize strongly while phases with high symmetry do not show polarization. In this way some limited information about the crystal structure of the phases can be gained. In the differential interference contrast (DIC) the incident polarized beam is separated into two parts. According to the height difference at the samples surface they have different optical path length. After passing the analyzer they interfere according to the difference in height. During the grinding and polishing process soft phases are removed stronger than hard phases which can be displayed by the DIC mode. A Sony DSC-S75 digital still camera switched to full zoom was employed to take pictures.

In *X-ray diffraction (XRD)-measurements* one can identify the present phases due to their different crystal structure. Since the cell parameter of a phase changes when atoms are substituted at certain positions in the crystal structure one can get information about the solubility of the other elements in the respective phase. The software TOPAS [22], which was used for refining the X-ray patterns is a program based on the Rietveld-refinement-method. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile [23, 24]. The height, width and position of the reflections of the X-ray pattern can be used to determine different aspects of the materials structure like cell parameter, domain size or site occupation. With structure information given in literature (e.g. Pearson's Handbook of Crystallographic Data [25]) the program calculates a theoretical pattern and phase identification is accomplished by comparing the peaks and relative intensities from the investigated specimen with those calculated by the program. In case of the presence of several phases relative amounts can be estimated by comparing the refined area of the respective patterns. The other essential application of XRD is the determination of the crystal structures of new phases. This was the case in the ternary Al-Si-V system where a new ternary phase was discovered. The powder pattern of this phase was indexed and the comparison with structural models allowed the proposal of the crystal structure which could be confirmed by Rietveld refinement. Additionally and to affirm this suggestion single crystal measurements for structure determination were performed.

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For powder-XRD a Bruker D8 Advance Diffractometer with Cu K α radiation was used. The majority of the measurements were carried out with a Lynxeye silicon strip detector, but for the Co-rich samples an energy dispersive Solx detector was used because of fluorescence. The measurement mode follows the Bragg-Brentano geometry. The instrument works in $\theta/2\theta$ reflection mode where the autosampler rotates by the angle θ , while the detector simultaneously rotates by 2θ . Single crystal diffraction data were collected on a NONIUS four circle diffractometer equipped with a CCD detector and a 300 μm capillary optics collimator (Mo tube, graphite monochromator).

The characteristic spectrum of X-rays emitted by the different elements in the specimen after excitation by high energy-electrons is used to obtain quantitative or qualitative compositional information about the samples in *electron probe micro analysis (EPMA)*. The exact compositions of the present phases can be measured precisely and phase boundaries which terminate single-, two- and three-phase fields are constructed on the basis of these measurements. In EPMA measurements wavelength dispersive spectroscopy (WDS) is used for quantitative analysis. Energy dispersive spectroscopy (EDS) is also possible for measuring the phase composition but the accuracy is not as good as in WDS. Similar to light optical microscopy additional information concerning the microstructure is provided by this method. The back scattered electron images come from the difference in the average atomic number at each point in the sample, thus they carry compositional information. Contrast mechanism for secondary electron imaging is predominately the surface topology of the sample.

In this study the majority of the EPMA measurements were carried out on a Cameca SX electron probe 1000 (Cameca, Courbevoie, France) using WDS for quantitative analysis at 15 kV using a beam current of 20 nA. Conventional ZAF matrix correction was used to calculate the final composition from the measured X-ray intensities. Some of the samples were measured on a Jeol JXA 8600 Superprobe using EDS for quantitative analysis. The measurements were carried out at 15 kV and 20 nA. Conventional PRX matrix correction was applied. To examine as cast samples for studies concerning primary crystallization and for the characterization of the diffusion couples, SEM (scanning electron microscopy) measurements were carried out on a Zeiss Supra 55 VP equipped with an EDX detector. For all EPMA and SEM measurements pure aluminum, cobalt, silicon and vanadium were employed as standard materials.

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The isothermal sections provide a basis for the vertical sections or isopleths, where the phase diagram is cut at a constant composition. In the present research the amount of the transition metal, i.e. vanadium or cobalt was kept constant. To gain information on the ternary invariant reactions, phase stability and melting behaviour of intermetallic compounds the sample and a reference are subjected to a temperature program in the *differential thermal analysis (DTA)*. All phase transitions or reactions taking place when heating or cooling an alloy, are connected with a heat exchange, which is recorded by the DTA-instrument. When a phase transition takes place in the sample that involves release of heat, the sample temperature raises temporally above that of the reference resulting in an exothermic peak. Conversely, a transition accompanied by adsorption of heat reduces the temperature of the sample compared to that of the reference, leading to endothermic peaks. At invariant thermal effects the temperature of the sample stays constant until the reaction is completed. In this kind of reactions the extrapolated onset temperature is evaluated. In ternary phase diagrams mainly three different invariant reactions involving the liquid phase occur: the ternary eutectic, peritectic and transition reactions. Furthermore monotectic and metatectic invariant reaction can occur in ternary systems. Ternary eutectoid and peritectoid reactions are solid-state reactions and no liquid phase is involved. Because of the small amount of heat which is exchanged in solid-state reactions they are hard to detect in DTA measurements. In equilibrium reactions $\Delta G=0$ which means that $\Delta H=T\Delta S$ and the change of enthalpy which affects the heat effect in the DTA is connected with the change of the entropy. In general liquid/solid reactions show higher ΔS and therefore higher ΔH than pure solid state reactions. Another reason for the difficulty to detect solid-state reactions in DTA-determination is that the reaction is sluggish because of the slow diffusion in the solid. On the one hand a higher heating rate has positive impact on the sensitivity and as a consequence on the height of the signals. On the other hand it influences the resolution in time and the separation of the effects, negatively. In this study DTA-measurements were carried out with a heating rate of 5 Kmin^{-1} .

Beside invariant reactions non invariant reactions take place when a phase boundary is crossed during heating and cooling, respectively. In non invariant reactions the temperature at the end of the effect is appraised. An important non invariant effect is the liquidus temperature after which the alloy has melted completely. In Figure 1 an invariant, a non invariant and a liquidus effect is shown in a schematic DTA-curve.

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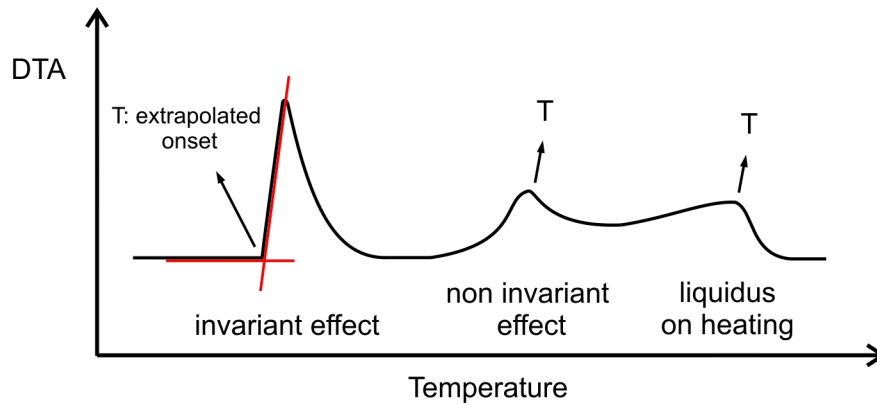


Figure 1: Schematic DTA-curve

For the interpretation of the DTA-measurements it is essential to know which phases are present before heating. The first effect observed in a three phase field gives most significant information at which temperature the liquid is formed first and an invariant four phase reaction takes place in the respective three phase field.

In another step these invariant reactions are constructed graphically to gain information on the occurrence of the respective reaction within the ternary phase diagram. The reaction is projected to an isothermal section at the reaction temperature and the vertical and isothermal occurrence of the reaction is adjusted. For this projection the composition of all reacting phases must be defined. The composition of solid phases which don't show nameable solubility dependence with temperature is fixed by their solubility measured by EPMA. In case of the liquid phase and for phases with changing solubility, the composition must be estimated to gain a reasonable sequence of reactions. The amount of material which is converted during a reaction, of course influences the heat exchange and consequently the area of the peak. This fact, in turn depends on the sample composition. In a ternary peritectic reaction for example one phase decomposes completely while heating. In a sample which contains a huge amount of this phase lots of energy is necessary to melt it and the difference in temperature of the sample and the standard will be observed. On the other hand, only small effects are detected at the edge of a reaction.

It can be assumed that a sample after the annealing procedure is in equilibrium and the effects observed in the DTA curve reflect equilibrium effects. After first heating this situation changes and often metastable thermal effects are observed in the second

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heating cycles. Therefore, mainly thermal effects on first heating of the annealed samples are used for the evaluation of the DTA data. Another important fact is that supercooling can occur when cooling an alloy, especially when the crystal structure is complex and the formation of the crystal seed is kinetically hindered. For this reason, the same effects occur at lower temperatures when cooling a sample. During the evaluation of DTA data to construct a phase diagram these considerations must be kept in mind.

In this study DTA measurements up to a maximum temperature of 1490 °C were performed on a DTA 404 S or on a DTA 404 PC (Netzsch, Selb, Germany) using open alumina crucibles and employing a slow permanent argon flow. The Pt/Pt10%Rh thermocouples (type S) of the DTA instrument were calibrated at the melting points of pure Al, Au and Ni. High temperature DTA measurements (above 1490 °C) were carried out on a Setaram Setsys Evolution 2400 using covered alumina crucibles within a slow permanent argon flow. The W5%Re/W26%Re thermocouple (type W5) was calibrated at the melting points of pure Au, Ni and Pt.

The liquidus projection is a top view of the phase diagram, similar to a topographic map where the temperature replaces the elevation. The compositions of the liquid phase of all binary and ternary invariant reactions are plotted and connected by liquidus valleys. These valleys separate the different fields of primary crystallization: cooling an alloy with a definite composition after total melting one certain phase will solidify first. The investigation of as cast samples without annealing step gives evidence on primary crystallization. From this information conclusions about the run of the liquidus valleys can be drawn. Not all as cast samples give unambiguous information but efforts in this respect complete the information needed to construct and to interpret a three component phase diagram.

A *diffusion couple* is an assembly of two materials in such intimate contact that each diffuses into the other. The couple is subjected to high temperature to promote thermal interdiffusion to form solid solutions and intermetallic compounds. If two solid materials are in contact at a sufficiently high temperature, interdiffusion will occur. Depending on the nature of the starting materials, temperature and annealing time, a new concentration distribution of the elements is set up. If the materials are completely

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miscible at that temperature, the concentration profiles are more or less smooth without any discontinuity. If, however, they are only partially miscible or if they react to form new phases, discontinuities in the concentration profiles occur which are closely related to the phase diagram of the system [26]. In almost all structural applications containing heterogeneous materials system diffusion is ubiquitous at elevated and even in many cases at ambient temperature, depending on the material systems. An understanding of this process is crucial in a wide variety of research fields, ranging from bulk applications as in composite materials or coatings to very thin metallization film in microelectronics [27]. In metallurgy many physical processes are controlled by diffusion, e.g. homogenisation, non-martensitic transformation, precipitation, oxidation and sintering. In coating and finishing techniques the interaction between base metal and applied metal at elevated temperatures must be known. This knowledge is important in respect to corrosion and in various brazing and welding processes. The diffusion coefficient may supply much information on fundamental physical and thermodynamic phenomena, like point defects in crystals and thermodynamic activities of the components [26]. In this study however, diffusion coefficients were not investigated but information concerning the phase diagram was gained from the diffusion couple experiments.

The use of diffusion couples in phase diagram studies is based on the assumption of local equilibria at the phase interfaces in the diffusion zone. This implies that an infinitesimally thick layer adjacent to the interface in such a diffusion zone is effectively in thermodynamic equilibrium with its neighbouring layer on the other side of the interface. In other words, the chemical potential (activity) of species varies continuously through the product layers of the reaction zone and has the same value at both sides of an interphase interface and the total system in which diffusion occurs cannot be at equilibrium. During the annealing time, equilibrium between the endmembers is established and in the diffusion zone layers of different phases according to the phase diagram are formed. The thickness of the layer is proportional to the square root of the reaction time. In binary diffusion couples, provided that thermodynamic equilibrium was reached completely during the reaction time, every intermetallic compound according to the phase diagram at a respective temperature must be formed. The diffusion zone morphology, which develops during solid-state interaction in a ternary couple, cannot be predicted so easily and is defined by type, structure, number, shape

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and topological arrangement of the newly formed phases. The resulting microstructure of the reaction zone can be visualized with the aid of the so-called diffusion path. This is a line on the ternary isotherm, representing the locus of the average composition in planes parallel to the original interface throughout the diffusion zone. Naturally, the diffusion path in a ternary system must fulfil the law of conservation of mass. If no material is lost or created during the interaction, then the diffusion path is impelled to cross the straight line between the end-members of the reaction couple (so-called mass balance line) at least once [28].

3. Literature Review

Since a ternary phase diagram is inevitably connected to its binary subsystems, good knowledge of the binary phase diagrams is essential and literature studies in this respect are significant. Therefore the following literature survey will start with the binary systems Al-Co, Al-Si, Al-V, Co-Si and Si-V. Afterwards the existing literature data concerning the ternary phase diagrams Al-Co-Si and Al-Si-V will be discussed.

3.1. The binary Al-Co system

Phase equilibria in the Al-rich part of the Al-Co system are complex and were discussed controversially in the past decade [29-31]. The differences in these studies refer to the Al-rich part of the phase diagram. In total, seven different phases have been found to exist in the Al-Co system: Co_2Al_9 [32], a bundle of three different phases at $\text{Co}_4\text{Al}_{13}$ stoichiometry designated o- $\text{Co}_4\text{Al}_{13}$ [33], m- $\text{Co}_4\text{Al}_{13}$ [34, 35] and h- $\text{Co}_4\text{Al}_{13}$ [30], CoAl_3 (decagonal quasicrystalline) [36, 37], Co_2Al_5 [38] and finally the extended phase field of (CoAl) with B2 structure [39]. Gödecke and Ellner [30] reported the phase m- $\text{Co}_4\text{Al}_{13}$ to be formed in the peritectoid reaction $\text{h-Al}_{13}\text{Co} + \text{Al}_3\text{Co} = \text{m-Al}_{13}\text{Co}$ at 1090 °C. Grushko et al. [29, 31] suggest the peritectic reaction $\text{h-Al}_{13}\text{Co}_4 + \text{L} = \text{m-Al}_{13}\text{Co}_4$ at 1093 °C. In [30] the o- $\text{Al}_{13}\text{Co}_4$ phase is the Al-richest and m- $\text{Al}_{13}\text{Co}_4$ the Al-poorest of the three different $\text{Al}_{13}\text{Co}_4$ phases. In Grushkos work h- $\text{Al}_{13}\text{Co}_4$ is the Al-richest and o- $\text{Al}_{13}\text{Co}_4$ the Al-poorest phase. The differences in these two studies are only small and in this study we refer to the work of Gödecke and Ellner. In Figure 2 the entire binary phase diagram is shown as a combination of data of Goedecke and Ellner [30] for the Al-rich part and data of Massalski [40] from 45 at.% cobalt. The partial phase diagram given by Gödecke and Ellner [30] was used as reference in the Al-rich part of the system and the enlargement between 22 and 28.5 at.% Co is shown in Figure 3.

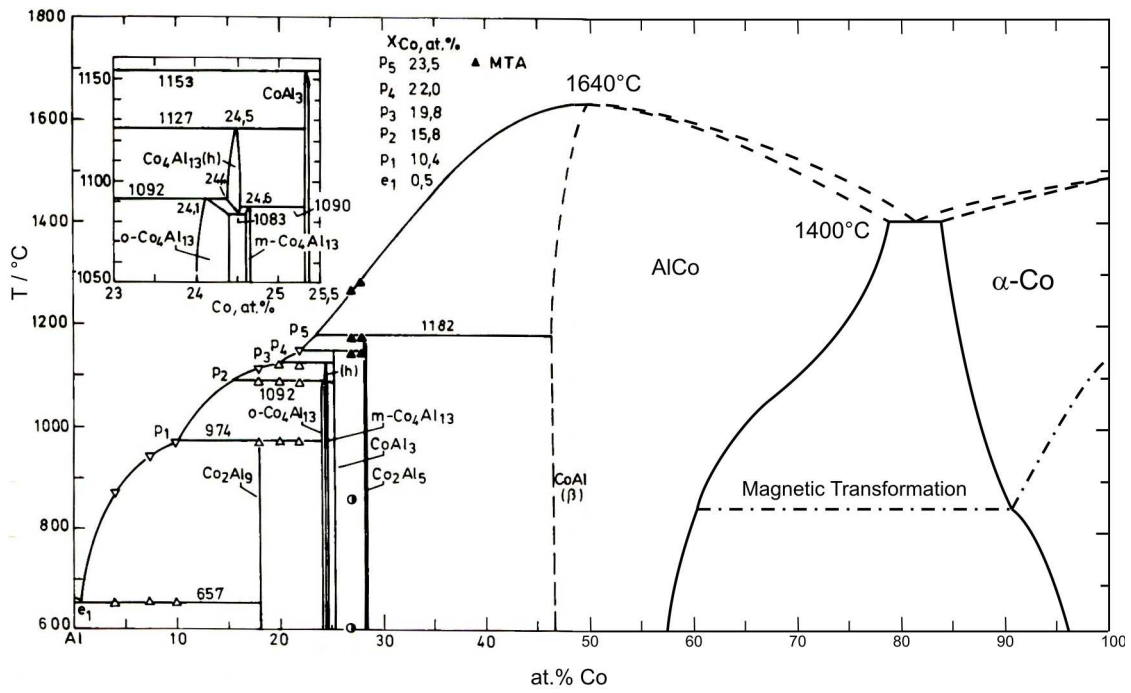


Figure 2: Binary Al-Co phase diagram according to [30, 40].

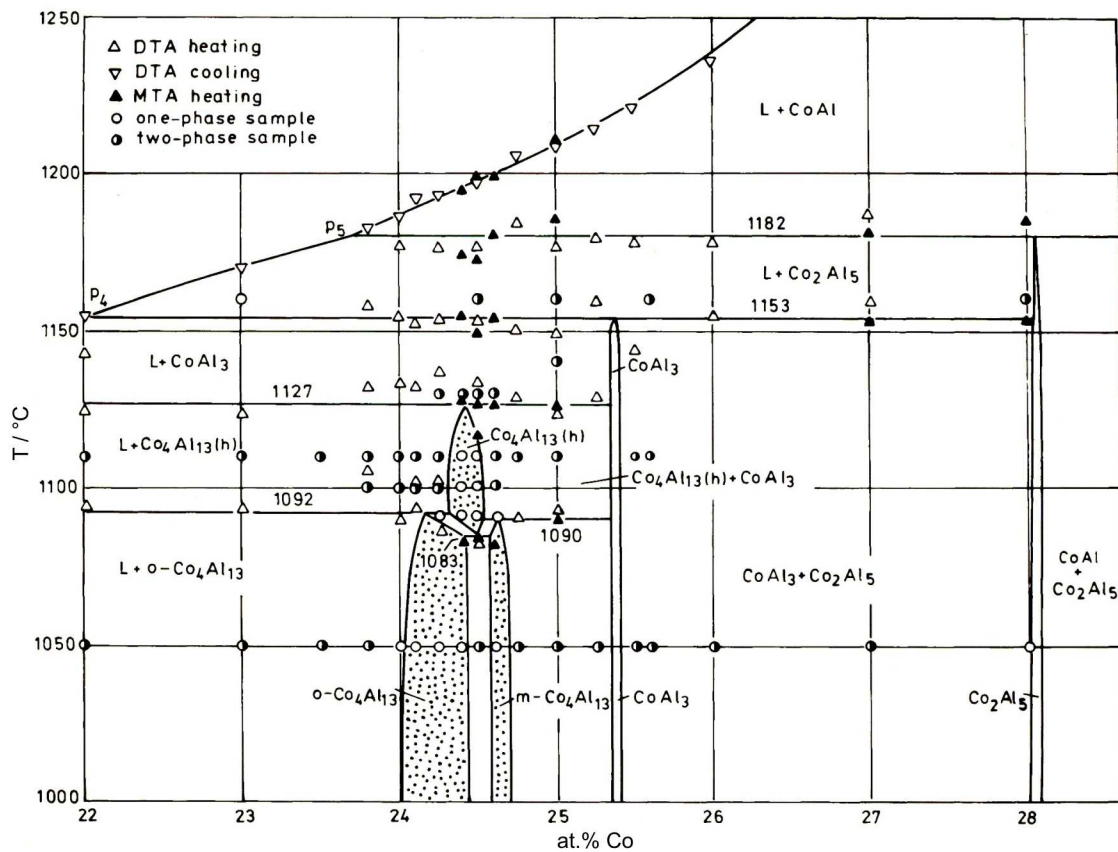


Figure 3: Enlargement of the Al-rich part of the Al-Co phase diagram according to [30].

The crystal structure data of the phases are shown in Table 1. The shape of the large phase field of (AlCo) is noticeable since it is stable from 47 to 58 at.% Co at 600 °C, but reaches its highest expansion at 1400 °C between 46.5 and 78.5 at.% Co. Invariant phase reactions of the Al-Co system are listed in Table 2 together with the composition of the involved phases.

Table 1: Structural information on binary phases in the Al-Co subsystem.

Phase	Composition / at. %	Structure type	Pearson symbol	Space group	Ref.
Al	~0 Co	Cu	<i>cF4</i>	<i>Fm-3m</i>	[40]
Al ₉ Co ₃	18.1 Co	own	<i>mP22</i>	<i>P2₁/a</i>	[32]
h-Al ₁₃ Co ₄	24.3-24.5 Co	Os ₄ Al ₁₃	<i>mC34</i>	<i>C2/m</i>	[30]
m-Al ₁₃ Co ₄	24.6-24.7 Co	own	<i>mC102-7.2</i>	<i>Cm</i>	[34, 35]
o-Al ₁₃ Co ₄	24-24.4 Co	own	<i>oP102</i>	<i>Pmn2₁</i>	[33]
Al ₃ Co	25.6 Co	--	<i>decagonal, quasicrystalline</i>		[36, 37]
Al ₅ Co ₂	28.6 Co	own	<i>hP28</i>	<i>P6₃/mmc</i>	[38]
AlCo	~48-78.5 Co	CsCl	<i>cP2</i>	<i>Pm-3m</i>	[39]
ε-Co	84-100 Co	Mg	<i>hP2</i>	<i>P6₃/mmc</i>	[40]
α-Co	~97-100 Co	Cu	<i>cF4</i>	<i>Fm-3m</i>	[40]

Table 2: Invariant phase equilibria in the binary subsystem Al-Co.

Phase reaction	Composition of the involved Phases / at.%			T / °C	Ref.
$L = Al + Al_9Co_2$	0.5 Co	0 Co	18 Co	657	[30]
$L + o-Al_{13}Co_4 = Al_9Co_2$	10.4 Co	24 Co	18 Co	974	[30]
$h-Al_{13}Co = o-Al_{13}Co + m-Al_{13}Co$	~24.45 Co	~24.4 Co	~24.6 Co	1083	[30]
$h-Al_{13}Co + Al_3Co = m-Al_{13}Co$	~24.5 Co	~25.4 Co	~24.65 Co	1090	[30]
$L + h-Al_{13}Co = o-Al_{13}Co_4$	15.8 Co	24.4 Co	24.1 Co	1092	[30]
$L + Al_3Co = h-Al_{13}Co_4$	19.8 Co	25.3 Co	24.5 Co	1127	[30]
$L + Al_5Co_2 = Al_3Co$	22 Co	28.05 Co	25.4 Co	1153	[30]
$L + (AlCo) = Al_5Co_2$	23.5 Co	47 Co	28.1 Co	1183	[30]
$L = (AlCo) + (\alpha-Co)$	81 Co	78.5 Co	84.4 Co	1400	[40]
$L = (AlCo)$		50 Co		1640	[40]

3.2. The binary Al-Si system

The binary Al-Si phase diagram, which can be seen in Figure 4, is a simple eutectic system. The eutectic reaction $L = \text{Al} + \text{Si}$ takes place at $577 \pm 1^\circ\text{C}$, the eutectic composition is 12.2 at.% Si. There is a very limited solubility of Si in Al and nearly no solubility on Al in Si. The crystal structure data of the phases are shown in Table 3.

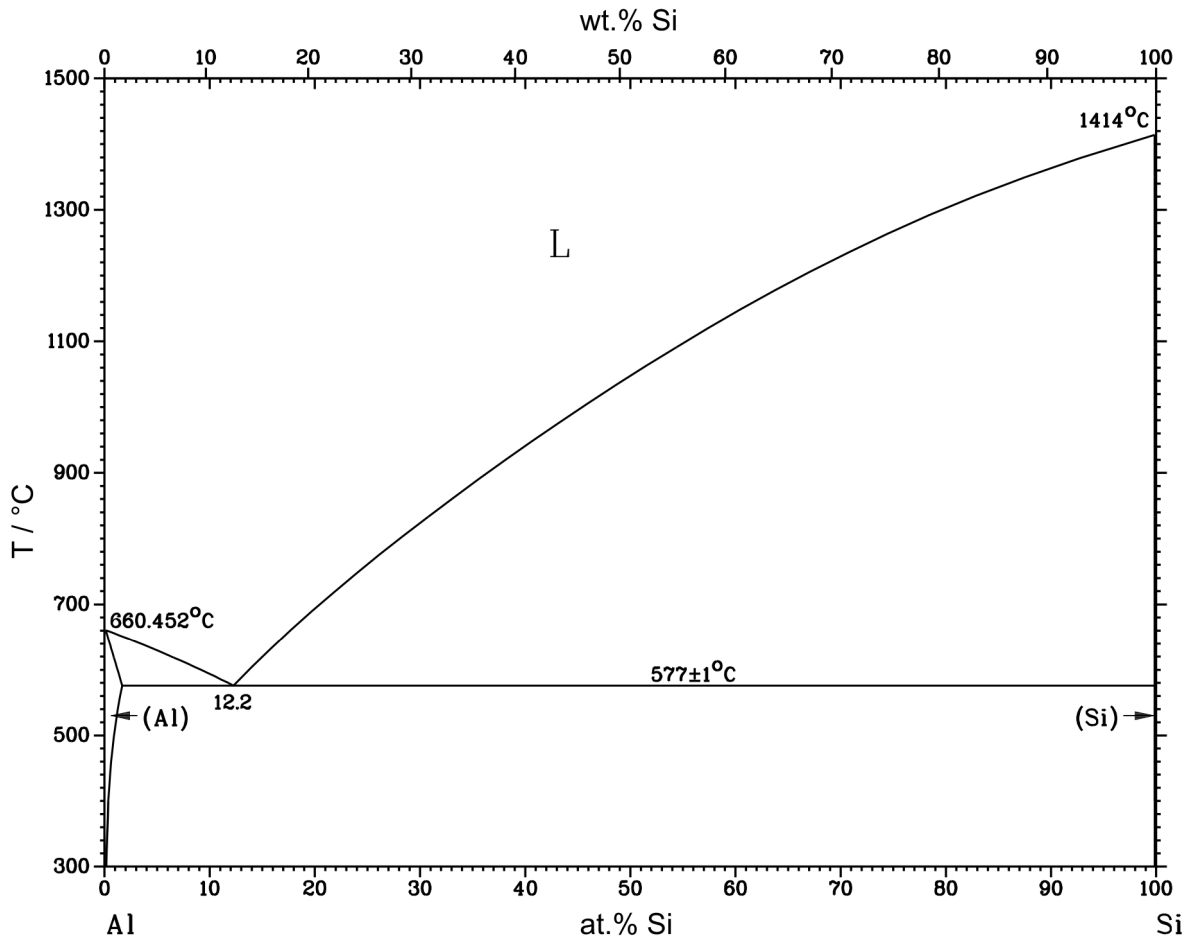


Figure 4: Binary Al-Si phase diagram according to [40].

Table 3: Structural information on binary phases in the Al-Si subsystem.

Phase	Composition / at. %	Structure type	Pearson symbol	Space group	Ref.
Al	~0 Si	Cu	<i>cF4</i>	<i>Fm-3m</i>	[40]
Si	~0 Al	C (diamond)	<i>cF8</i>	<i>Fd-3m</i>	[40]

3.3. The binary Al-V system

The binary sub system Al-V was investigated repeatedly and, amongst others, it is given in Massalski's Handbook of Binary Alloy Phase Diagrams [40]. A detailed review of the Al-V system was given by Murray [41]. In the binary Al-V system five different phases have been found to exist: Al_{21}V_2 , Al_{45}V_7 , Al_{23}V_4 , Al_3V and Al_8V_5 . The crystal structure data of the phases are listed in Table 4. On the basis of microstructure observation, XRD and thermal analysis Carlson et al. [42] determined the phase diagram for the whole composition range. They investigated the system at temperatures of 600 °C and above. Considering the change of the cell parameter of bcc-(V) they determined the phase boundary of the solid solution of Al in V. They found 42.0 at.% Al at 600 °C, 43.5 at.% Al at 800 °C, 45.0 at.% Al at 900 °C and 46.0 at.% Al at 1000 °C, respectively. Furthermore they suggested a noticeable homogeneity range for the phase Al_8V_5 although precise data are missing in this respect. Richter and Ipser [43] investigated the system at 630 °C and 1050 °C and measured significant differences concerning the invariant reaction temperatures. All five compounds were found to melt peritectically. Only two of the phases, Al_3V and Al_8V_5 , show a small homogeneity range. According to their measurements the solid solution of Al in V reaches 48.5 at.% Al at 1050 °C. Recently, Gong et al. [44] performed a thermodynamic reassessment of the system including the results of [42] and [43] to their optimization. The assessed phase diagram is shown in Figure 5. According to their calculations, in comparison to Richter and Ipser the Al content in (V) decreases slightly to 46.5 at.% Al at 1050 and 39.0 at.% Al at 500°C, respectively. The maximum solubility of Al in bcc-V is reached at the temperature of the peritectic decomposition of Al_8V_5 and was found to be between ~54 [42] and ~50 [43] at.% Al. The Al-V phase diagram, which is shown in Figure 6 is a combination of the data of Richter and Ipser [43] for the Al-rich part and of Massalski [40] and Gong [44] for the V-rich part. Table 5 gives a summary of the invariant phase reactions together with the composition of the involved phases.

Table 4: Structural information on binary phases in the Al-V subsystem.

Phase	Composition / at. %	Structure type	Pearson symbol	Space group	Ref.
Al	~0-0.3 V	Cu	<i>cF4</i>	<i>Fm-3m</i>	[40]
Al ₂₁ V ₂	8.7-8.9 V	own	<i>cF184</i>	<i>Fd-3m</i>	[32, 43]
Al ₄₅ V ₇	13.4 V	own	<i>mC104</i>	<i>C2/m</i>	[30, 43]
Al ₂₃ V ₄	14.7 V	own	<i>hP54</i>	<i>P6₃/mmc</i>	[34, 35, 43]
Al ₃ V	25.0-26.1 V	Al ₃ Ti	<i>tI8</i>	<i>I4/mmm</i>	[33, 43]
Al ₈ V ₅	36.5-39.4 V	Cu ₅ Zn ₈	<i>cI52</i>	<i>I4-3m</i>	[36, 37, 43]
V	51.5-100 V	W	<i>cI2</i>	<i>Im-3m</i>	[38, 43]

Table 5: Invariant phase equilibria in the binary subsystem Al-V.

Phase reaction	Composition of the involved Phases / at. %			T / °C	Ref.
L+Al ₂₁ V ₂ =(Al)	0.09 V	8.7 V	0.3 V	665	[41, 43]
L+Al ₄₅ V ₇ =Al ₂₁ V ₂	0.1 V	13.5 V	8.7 V	690	[41, 43]
L+Al ₂₃ V ₄ =Al ₄₅ V ₇	0.13 V	14.8 V	13.5 V	730	[41, 43]
L+Al ₃ V=Al ₂₃ V ₄	0.22 V	25 V	14.8 V	736	[41, 43]
L+Al ₈ V ₅ =Al ₃ V	~20 V	~34 V	~25 V	1270	[43]
L+(V)=Al ₈ V ₅	~33 V	~50 V	~38.5 V	1408	[43]

^a Phase composition^b Reaction temperature

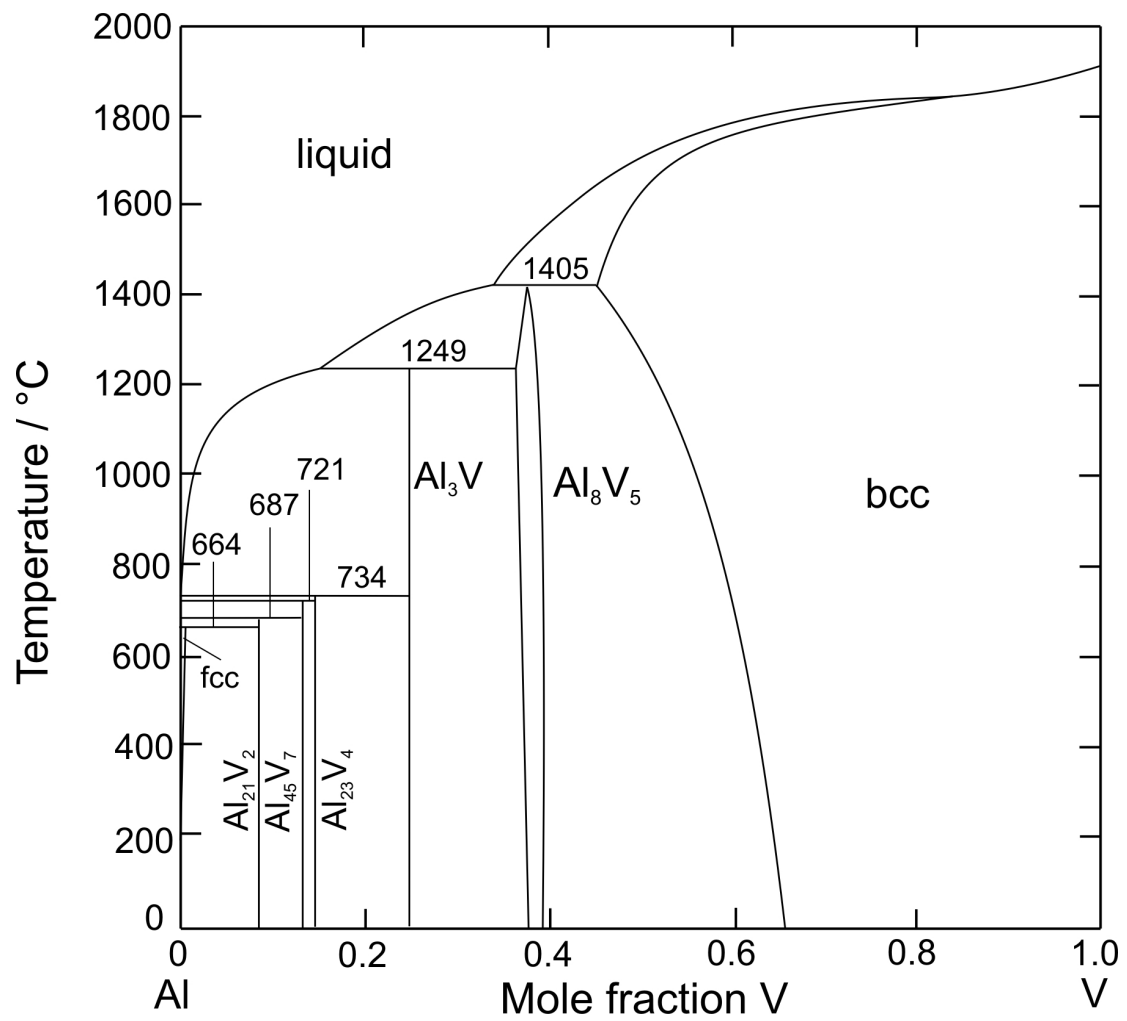


Figure 5: Assessed Al-V phase diagram according to [44].

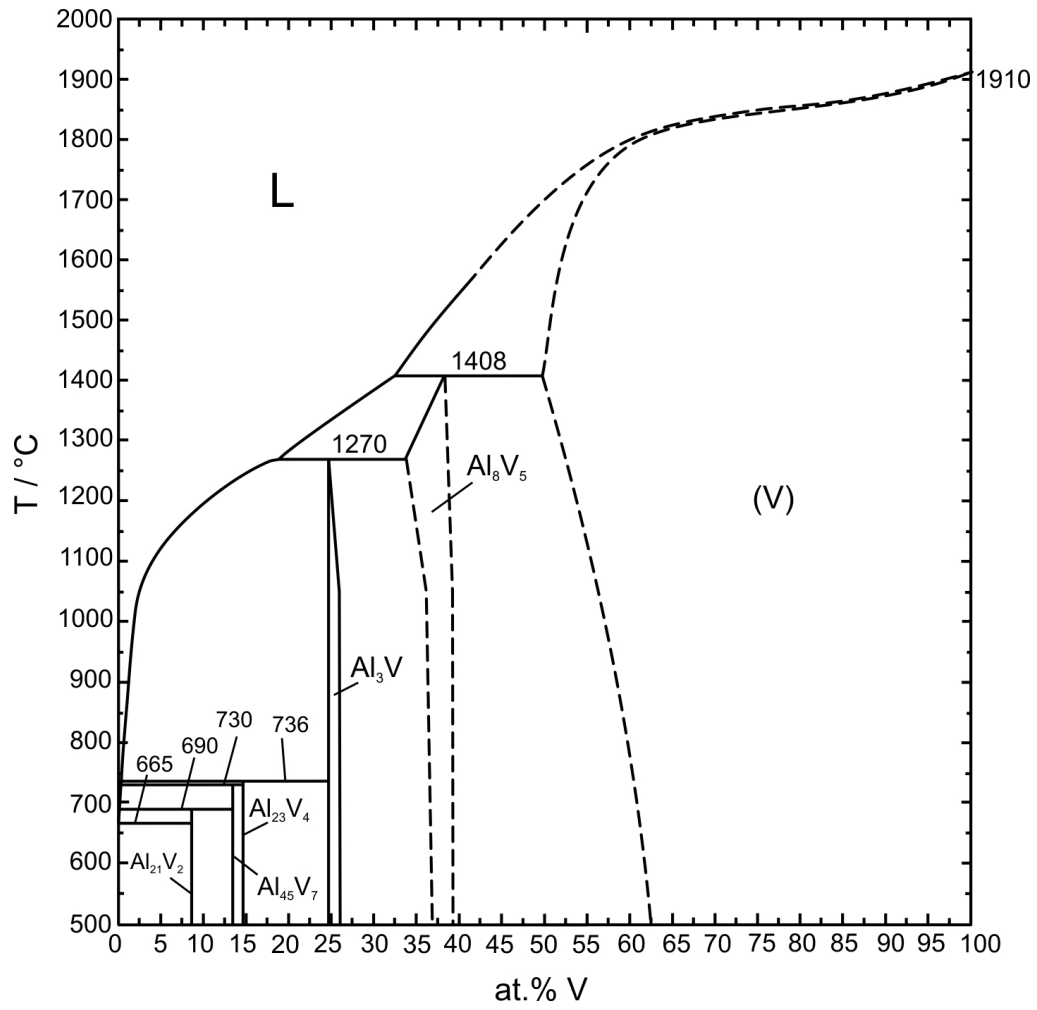


Figure 6: Binary Al-V phase diagram according to [40, 43, 44].

3.4. The binary Co-Si system

The binary Co-Si phase diagram shown in Figure 7 exhibits five intermediate compounds [40]: CoSi_2 , CoSi and $\alpha\text{-Co}_2\text{Si}$ are stable to room temperature. $\alpha\text{-Co}_2\text{Si}$ and CoSi show a small homogeneity range but CoSi_2 was found to be a line compound. Two additional high temperature phases, $\beta\text{-Co}_2\text{Si}$ and Co_3Si were reported in the system. The existence of $\beta\text{-Co}_2\text{Si}$ was recently confirmed by Baldan et. al [45], but its crystal structure was not determined up to now, neither was the crystal structure of Co_3Si . The structures of all other compounds are given in Pearson's Handbook of Crystallographic Data [25]. Crystal structure data and references are given in Table 6 and the binary invariant reactions are listed in Table 7. The phases CoSi , $\beta\text{-Co}_2\text{Si}$ and CoSi_2 melt congruently at 1640, 1334 and 1326 °C, respectively.

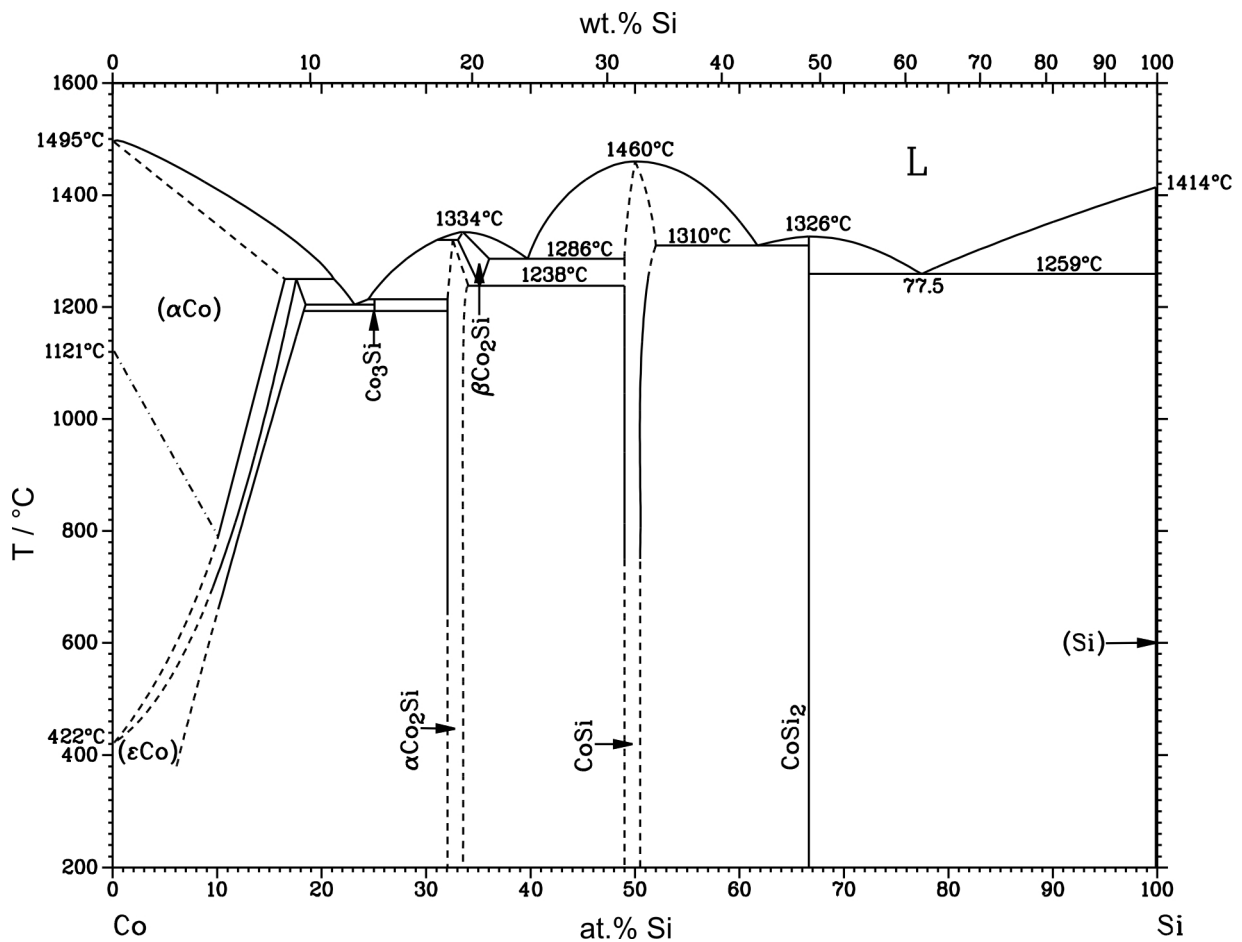


Figure 7: Binary Co-Si phase diagram according to [40].

Table 6: Structural information on binary phases in the Co-Si subsystem.

Phase	Composition / at.%	Structure type	Pearson symbol	Space group	Ref.
α -Co	0-16.4 Si	Cu	<i>cF4</i>	<i>Fm-3m</i>	[40]
ε -Co	0-18.4 Si	Mg	<i>hP2</i>	<i>P6₃/mmc</i>	[40]
Co ₃ Si	25 Si	--	--	--	[40]
α -Co ₂ Si	~32-34 Si	own	<i>oP12</i>	<i>Pnma</i>	[40]
β -Co ₂ Si	32-35.8 Si	--	--	--	[45]
CoSi	49~52 Si	FeSi	<i>cP8</i>	<i>P2₁3</i>	[40]
CoSi ₂	66.7 Si	CaF ₂	<i>cF12</i>	<i>Fm-3m</i>	[40]
Si	~100 Si	C (diamond)	<i>cF8</i>	<i>Fd-3m</i>	[40]

Table 7: Invariant phase equilibria in the binary subsystem Co-Si.

Phase reaction	Composition of the involved Phases / at. %			T / °C	Ref.
$\text{Co}_3\text{Si}=\varepsilon\text{-Co}+\alpha\text{-Co}_2\text{Si}$	25.0 Si	18.1 Si	~32.6 Si	1193	[40]
$\text{L}+\varepsilon\text{-Co}=\text{Co}_3\text{Si}$	23.1 Si	18.4 Si	25.0 Si	1204	[40]
$\text{L}+\alpha\text{-Co}_2\text{Si}=\text{Co}_3\text{Si}$	24.4 Si	~32.6 Si	25.0 Si	1214	[40]
$\beta\text{-Co}_2\text{Si}=\alpha\text{-Co}_2\text{Si}+(\text{CoSi})$	35.1 Si	~34 Si	49.0 Si	1238	[40]
$\text{L}+(\alpha\text{-Co})=\varepsilon\text{-Co}$	16.5 Si	21.4 Si	17.5 Si	1250	[40]
$\text{L}=\text{CoSi}_2+\text{Si}$	78 Si	66.7 Si	~100 Si	1259	[40]
$\text{L}=(\text{CoSi})+\beta\text{-Co}_2\text{Si}$	39.7 Si	35.8 Si	49 Si	1286	[40]
$\text{L}=(\text{CoSi})+\text{CoSi}_2$	61.8 Si	~52 Si	66.7 Si	1310	[40]
$\text{L}+\beta\text{-Co}_2\text{Si}=\alpha\text{-Co}_2\text{Si}$	~31 Si	~32.6 Si	~33 Si	~1320	[40]
$\text{L}=\text{CoSi}_2$		33.3 Si		1326	[40]
$\text{L}=\beta\text{-Co}_2\text{Si}$		66.7 Si		1334	[40]
$\text{L}=(\text{CoSi})$		50 Si		1460	[40]

3.5. The binary Si-V system

The binary Si-V system shows four intermediate compounds [40]. These phases are SiV_3 , Si_3V_5 , Si_5V_6 (high temperature phase) and Si_2V . Beside tetragonal Si_3V_5 , also hexagonal Si_3V_5 was found to exist but this phase is considered to be carbon stabilized [46, 47] and therefore it does not belong to the binary phase diagram [40]. Crystal structure data and references are given in Table 8, the phase diagram is shown in Figure 8. According to Jorda and Muller [48] SiV_3 has a noticeable homogeneity range from 21.5 to 24.8 at.% Si at 1800 °C and melts congruently at 1925 °C [48]. Savickij et al. [10] measured the solubility of SiV_3 to be 24.3-24.7 at.% Si at 800°C. Recently Zhang et al. [49] gave a thermodynamic reassessment of the entire Si-V system and calculated the maximum solubility of SiV_3 to be 20-25 at.% Si at 1837 °C. At a temperature of 900°C the solubility decreases completely. The assessed phase diagram is shown in Figure 9. Zhang et al. [49, 50] investigated the thermodynamic stability of Si_5V_6 which was still in question. In addition, they combined experiments and thermodynamic calculations to determine the eutectoidic decomposition temperature of Si_5V_6 to be 460 °C rather than 887 °C as reported earlier by Milanese et al. [51]. Milanese et al. [51] studied the diffusion-controlled growth of vanadium silicides by means of diffusion couples and they calculated the activation energies for these silicides; they scale well with the melting points of the compounds. Si_2V and Si_3V_5 which were found to be line compounds melt congruently at 1677 and 2010 °C, respectively [40, 52]. The invariant binary reactions from literature are listed in Table 9 together with the respective references.

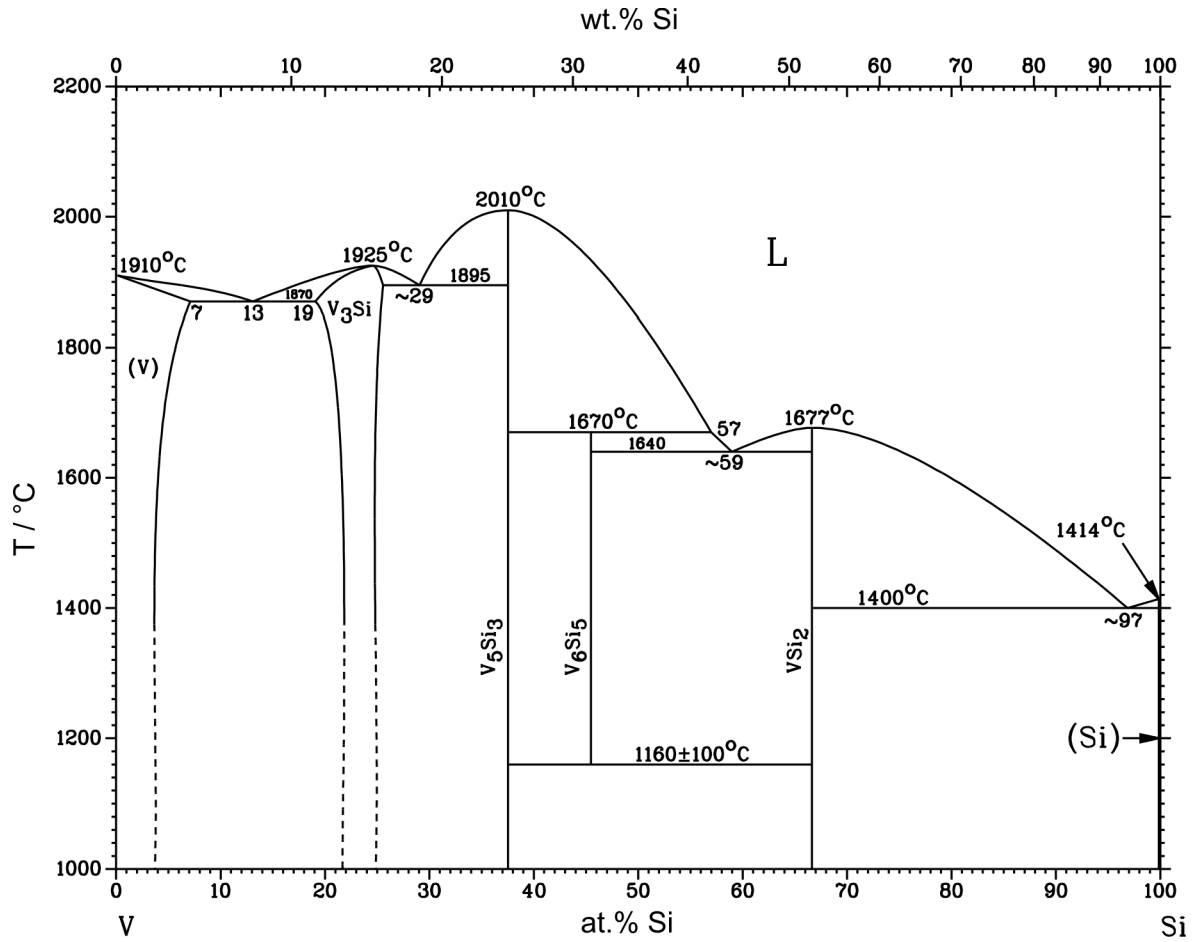


Figure 8: Binary Si-V phase diagram according to [40].

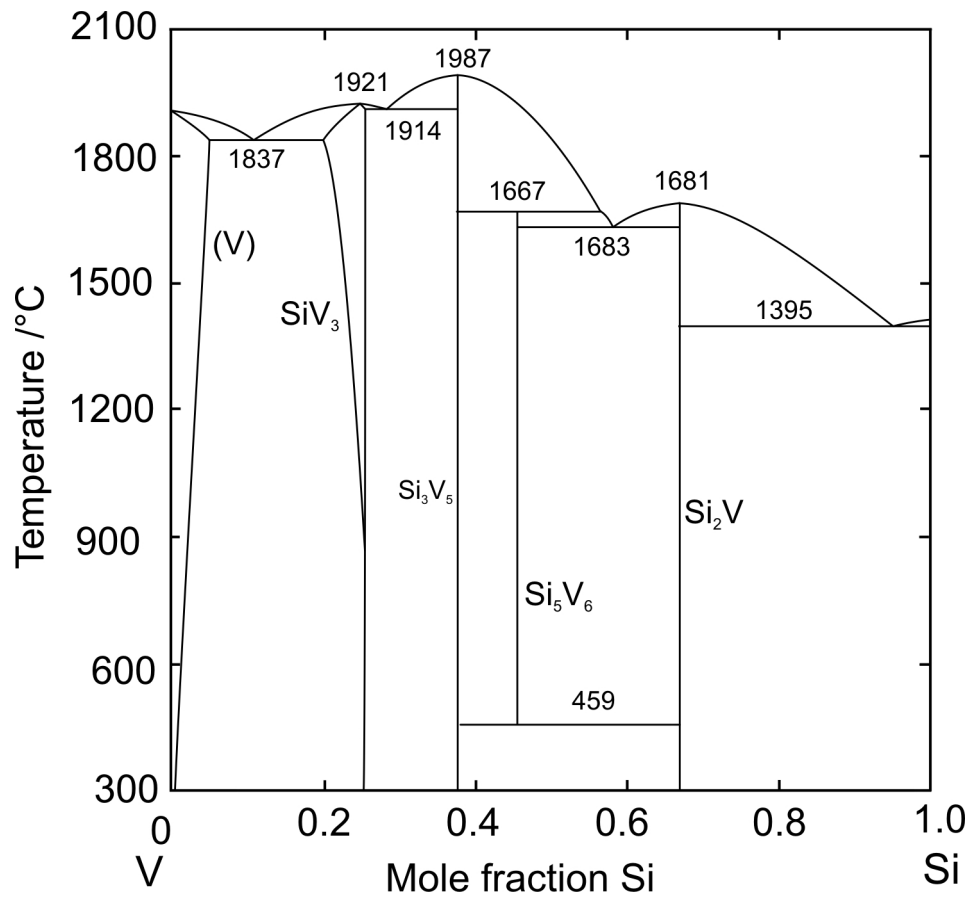


Figure 9: Assessed Si-V phase diagram according to [49]

Table 8: Structural information on binary phases in the Si-V subsystem.

Phase	Composition / at. %	Structure type	Pearson symbol	Space group	Ref.
SiV ₃	0-7 Si	Cr ₃ Si	<i>cP</i> 8	<i>Pm-3n</i>	[40]
Si ₃ V ₅	37.5 Si	Si ₃ W ₅	<i>tI</i> 32	<i>I4/mcm</i>	[40]
Si ₅ V ₆	~45 Si	Ti ₆ Ge ₅	<i>oI</i> 44	<i>Ibam</i>	[40]
Si ₂ V	66.7 Si	CrSi ₂	<i>hP</i> 9	<i>P6₂22</i>	[40]
Si ₃ V ₅	stabilized by heteroatoms	Mn ₅ Si ₃	<i>hP</i> 16	<i>P6₃/mcm</i>	[45]

Table 9: Invariant phase equilibria in the binary subsystem Si-V.

Phase reaction	Composition of the involved Phases / at. %			T / °C	Ref.
L=Si ₂ V+(Si)	~ 95 Si	66.7 Si	~ 100 Si	1393	[52]
L=Si ₅ V ₆ +Si ₂ V	~ 59 Si	45.4 Si	66.7 Si	1640	[47]
L+Si ₃ V ₅ =Si ₅ V ₆	~ 57 Si	~ 37.5 Si	~ 45.4 Si	1670	[47]
L=SiV ₃ +(V)	~ 13 Si	~ 7 Si	~ 19 Si	1870	[46]
L=SiV ₃ +Si ₃ V ₅	~ 29 Si	~ 25.5 Si	~ 37.5 Si	1895	[46]
L=SiV ₃	~ 25 Si	~ 25 Si	--	1925	[46]
L=Si ₃ V ₅	~ 37.5 Si	~ 37. Si5	--	2010	[47]
L=Si ₂ V	66.7 Si	66.7 Si	--	1677	[40]
Si ₅ V ₆ =Si ₂ V+Si ₃ V ₅	--	--	--	~ 460	[51]

3.6. The ternary Al-Co-Si system

Phase equilibria in the ternary system Al-Co-Si are quite complex. A large number of structurally complex compounds were found in the Al-rich corner while the Co-rich part of the system is dominated by extended solid solution phases. An early assessment of the Al-Co-Si system was given by Schmidt-Fetzer [53] and is based primarily on the experimental investigation of German [54]. According to this report, five ternary compounds have been found to exist in an isothermal section at 600°C. Two of the phases, α ($\text{Co}_3\text{Al}_{3-x}\text{Si}_{4+x}$) and β ($\text{Co}_2\text{Al}_{1+x}\text{Si}_{2-x}$) adopt simple crystal structures. The structures of the other three compounds γ ($\text{Co}_{28}\text{Al}_{55}\text{Si}_{17}$), δ ($\text{Co}_{33}\text{Al}_{44}\text{Si}_{23}$) and ϵ ($\text{Co}_{30}\text{Al}_{42}\text{Si}_{28}$) were not investigated by German [54]. Later, the system Al-Co-Si was studied by Richter and Tordesillas Gutierrez [55] for three isothermal sections at 600 °C (equilibria with Si), 800 °C (for alloys up to 50 at.% Co) and 900 °C (for alloys with more than 50 at.% Co). The isotherms of their studies are shown in Figure 10. In their investigation the previously reported compounds were confirmed (but with noticeable deviations in composition) and two additional compounds designated as χ and ϕ were found to exist in the Al-rich part of the system. The crystal structures of χ ($\text{Co}_4\text{Al}_{2-x}\text{Si}_{7+x}$) [56], γ ($\text{Co}_{19+x}\text{Al}_{43+y}\text{Si}_{12-y}$) [57], ϕ ($\text{Co}_{10+x}\text{Al}_{23}\text{Si}_{9-2x}$) [58] and ϵ ($\text{Co}_6\text{Al}_{11-x}\text{Si}_{6+x}$) [59] were reported in the following years, while the structure of δ ($\text{Co}_{32}\text{Al}_{45}\text{Si}_{23}$) is incommensurably modulated [55] and has not been reported up to now. Information on the crystal structure of the ternary compounds is compiled in Table 10.

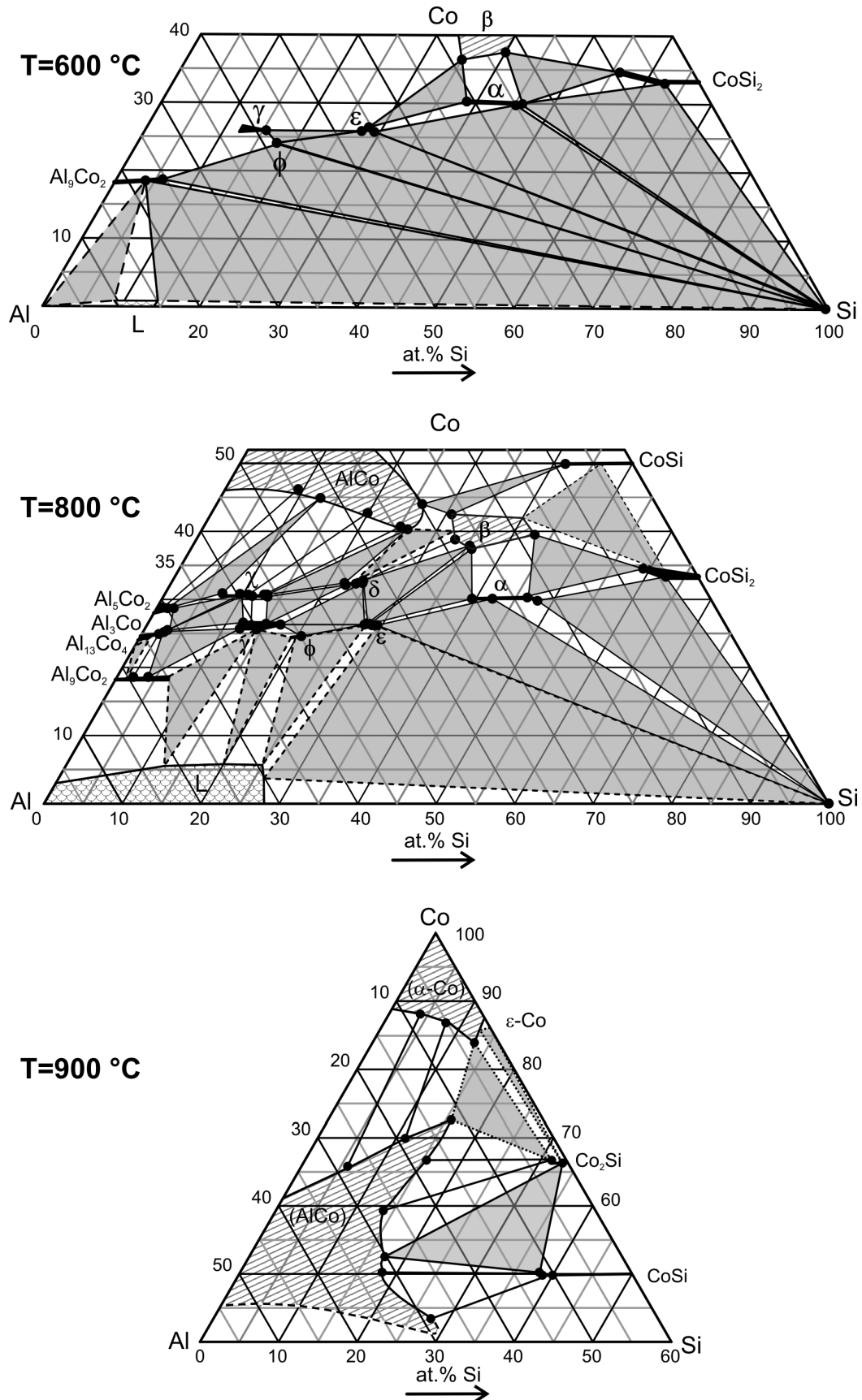


Figure 10: Ternary Al-Co-Si phase diagram according to [55].

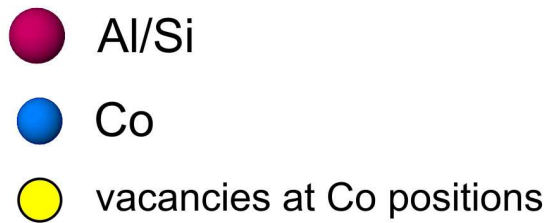
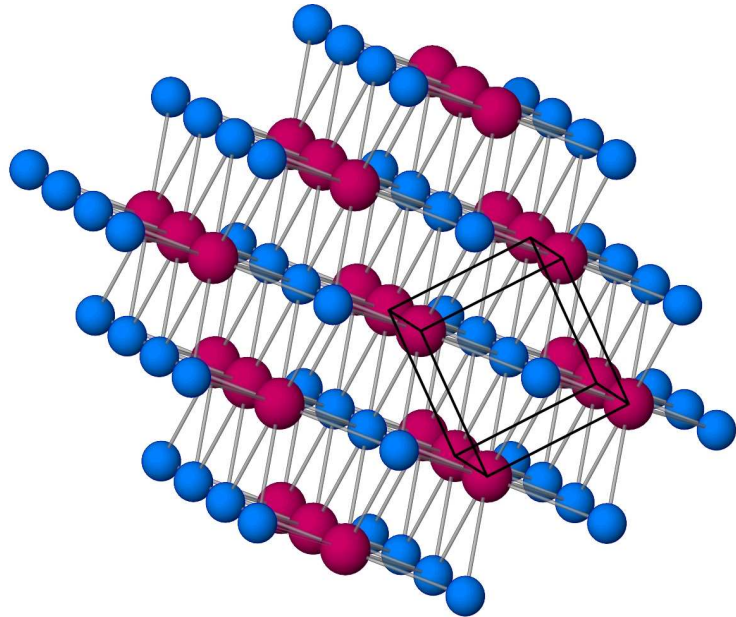
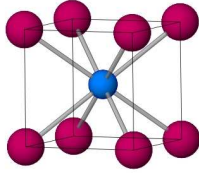
Table 10: Structural information on the ternary phases in the Al-Co-Si system.

Phase	Composition	Structure type	Pearson symbol	Space group	Ref.
α , $\tau 1$	$\text{Al}_{3-x}\text{Co}_3\text{Si}_{4+x}$	Ge_7Ir_3	<i>cI40</i>	<i>Im-3m</i>	[53]
β , $\tau 2$	$\text{Al}_{1+x}\text{Co}_2\text{Si}_{2-x}$	Al_3Ni_2	<i>hP5</i>	<i>P-3m1</i>	[53]
γ , $\tau 3$	$\text{Al}_{43+y}\text{Co}_{19+x}\text{Si}_{12-y}$	own	<i>mC296+</i>	<i>C2/c</i>	[57]
δ , $\tau 4$	$\text{Al}_{40.5-43}\text{Co}_{32.5}\text{Si}_{22-24.5}$	own	<i>mC*</i> , modulated		[55]
ϵ , $\tau 5$	$\text{Al}_{11}\text{Co}_6\text{Si}_6$	own	<i>mP92</i>	<i>P2_1/c</i>	[59]
χ , $\tau 6$	$\text{Al}_{7+x}\text{Co}_4\text{Si}_{2-x}$	own	<i>mC26</i>	<i>C2/m</i>	[56]
ϕ , $\tau 7$	$\text{Al}_{25-x}\text{Co}_{10+x}\text{Si}_7$	own	<i>oP168</i>	<i>Pnma</i>	[58]

The β -phase crystallizes in hexagonal Al_3Ni_2 structure, which is a vacancy ordering variant of the cubic CsCl structure of AlCo. This relation is visualized in Figure 11. The magenta dots stand for the mixed position of Al and Si and the occupation depends on the composition. In comparison to the cubic structure in the hexagonal Al_3Ni_2 structure every third Co-position is missing which is symbolized by yellow dots. Although a continuous transition between the two structure types is not known up to now, it is possible that such a transition exists in certain cases. The two-phase field between AlCo and the beta-phase is rather small at 800 °C (Fig. 10), so it appears to be possible that this gap is closing completely at higher temperatures.

In a recent phase diagram compilation by Raghavan [60] considering the new data of Richter and Tordesillas Gutierrez [55], the phase designation $\tau 1$ - $\tau 7$, instead of α - ϕ is suggested, so both designations are given in Table 10.

cubic CsCl
structure of AlCo



hexagonal Al_3Ni_2
structure of β

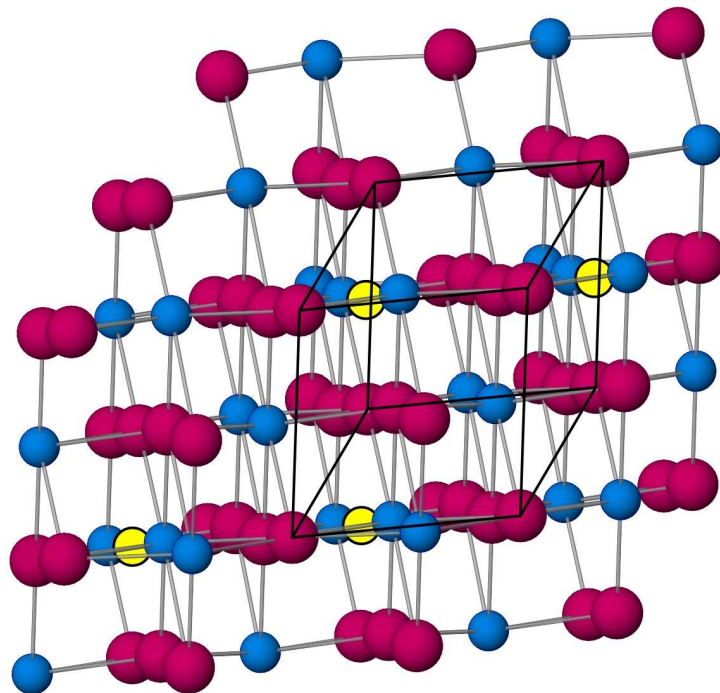
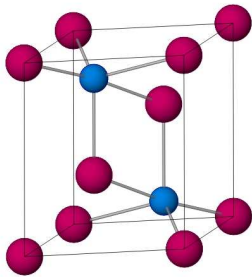


Figure 11: Comparison between the cubic AlCo structure and the hexagonal β structure.

3.7. The ternary Al-Si-V system

Literature information concerning the ternary Al-Si-V system is rather scarce. An assessment of available data is given in [61]; it is based primarily on the experimental investigation of Gebhardt and Josef [62] and Müller [63]. Gebhardt and Josef [62] investigated the Al-Si-V system up to 6.7 at.% V by means of optical microscopy, X-ray powder diffraction (XRD) and differential thermal analysis (DTA). They proposed a partial liquidus surface projection, vertical sections and a partial Scheil diagram. The schematic partial liquidus surface projection is shown in Figure 12 [62]. In Table 11 the invariant ternary reactions reported by Gebhardt and Josef [62] are listed together with the composition of the reacting phases. According to their investigations Al_{21}V_2 and Al_{23}V_4 solve about 0.3 and 1.5 at.% Si, respectively, whereas Al_{45}V_7 does not show any solubility of Si. Müller's [63] investigations in the V-rich part of the ternary system concern the superconducting binary phase SiV_3 and its ternary solid solution $\text{Al}_{1-x}\text{Si}_x\text{V}_3$. The partial isothermal section at 1000 °C presented in Figure 12 shows the solubility of Al in SiV_3 to be 3.5 at.%. No ternary Al-Si-V phases were found so far.

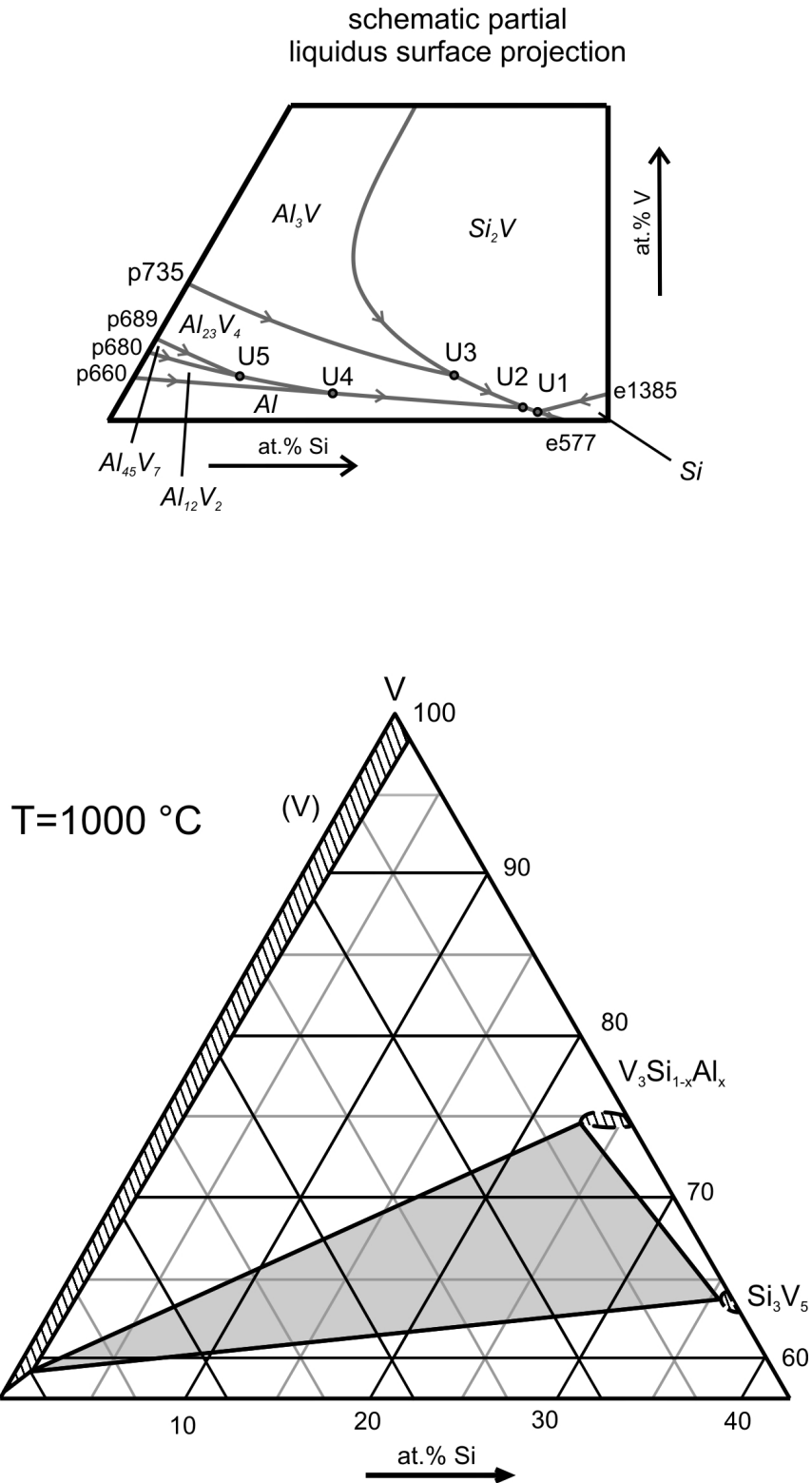


Figure 12: Ternary Al-Si-V phase diagram according to [62, 63].

Table 11: Ternary invariant phase reactions in Al-Si-V according to [62].

Reaction	T / °C	Phase	Composition / at.%		
			Al	V	Si
U1: L+Si ₂ V=(Al)+(Si)	583	L	88.6	0.1	11.3
		Si ₂ V	3.1	47.0	49.9
		(Al)	98.3	0.2	1.5
		(Si)	0.5	0.5	99.0
U2: L+Al ₂₃ V ₄ =(Al)+Si ₂ V	624	L	89.2	0.2	10.6
		Al ₂₃ V ₄	76.1	23.9	--
		(Al)	98.2	0.2	1.6
		Si ₂ V	3.1	47.0	49.9
U3: L+Al ₂₁ V ₂ =(Al)+Al ₂₃ V ₄	640	L	95.3	0.2	4.5
		Al ₂₁ V ₂	84.0	16.0	--
		(Al)	98.0	0.3	1.7
		Al ₂₃ V ₄	76.1	23.9	--
U4: L+Al ₃ V=Al ₂₃ V ₄ +Si ₂ V	643	L	89.7	0.3	10.0
		Al ₃ V	61.1	38.9	--
		Al ₂₃ V ₄	76.1	23.9	--
		Si ₂ V	3.1	47.0	49.9
U5: L+Al ₄₅ V ₇ =Al ₂₁ V ₂ +Al ₂₃ V ₄	656	L	96.05	0.35	3.6
		Al ₄₅ V ₇	77.8	22.2	--
		Al ₂₁ V ₂	84.0	16.0	--
		Al ₂₃ V ₄	76.1	23.9	--

The aim of the thesis presented here is a contribution of experimental data in the ternary Al-Co-Si and Al-Si-V systems and the determination of the ternary phase diagrams.

In the Al-Co-Si system two isothermal sections at 1050 and 1200 °C in the Co rich part were studied. Diffusion couple experiments were performed in the system. On the one hand common solid-solid diffusion couples were carried out, on the other hand couples were tried where the contact formation was done by a solid-liquid interface. Amongst other findings, these studies brought information on the relation between AlCo and the β -phase. Besides, based on DTA-measurements of a series of samples prepared in the study of Richter and Tordesillas Gutierrez [55], several vertical sections have been derived which led to a reaction scheme of the entire ternary system and a liquidus surface projection.

The Al-Si-V system was investigated at four different isothermal sections at 500, 620, 850 and 1300 °C. The ternary phase τ ($\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$) was discovered and the crystal structure of this phase was determined by means of powder XRD and additionally by single crystal XRD. Based on DTA-measurements four vertical sections were constructed, revealing a reaction scheme as well as a liquidus surface projection of the entire ternary system.

In the course of this study in the binary Al-V system a new compound was found to exist, but until now it is not clear if the phase is a low temperature phase or a metastable one. So far it was not possible to determine the crystal structure.

The results of this thesis were published in four research papers [64-67].

4. Experimental

4.1. Preparation of Ternary Al-Co-Si Alloys

The ternary Al-Co-Si alloys were prepared from aluminum rod (99.999%, Alfa Aesar, Karlsruhe, Germany), silicon lump (99.9999%, Alfa Aesar, Karlsruhe, Germany) and cobalt pieces (99.9% Alfa Aesar, Karlsruhe, Germany). The surface of the cobalt pieces was cleaned mechanically with a steel brush. Calculated amounts of the elements were weighed to an accuracy of 0.05 mg and arc melted on a water-cooled copper plate under an argon atmosphere. Zirconium was used as a getter material within the arc chamber. The ingots with a total mass of 1000 mg were re-melted one to three times for good homogenization. Subsequently all alloys were weighted back in order to check for possible mass losses. The total mass losses were less than 1 % and can be considered to be negligible. For the investigation of the isothermal section at 1050 °C a series of seven samples were placed into alumina crucibles, which were sealed into evacuated quartz glass ampoules and then annealed at 1050 °C for two weeks. Putting the samples into alumina crucibles was necessary to avoid reaction of the Al containing samples with the quartz glass during annealing. After the annealing time the samples were quenched in cold water. The microstructure of very Co-rich sample was very fine, which prevent accurate EPMA-measurements. Therefore, to enhance the microstructure nine samples for the isothermal section at 1200 °C were heated up to 1400 °C and cooled slowly to 1200 °C in the induction furnace before equilibrium annealing. These samples were sealed into evacuated Ta-crucibles, annealed at 1200 °C for one week and then quenched in a water cooled container. After the equilibrium annealing process all samples were separated into several pieces, which were investigated by optical microscopy, EPMA, SEM and XRD.

4.2. Preparation of the Diffusion Couples AlCo/Si, AlCo/Co₂Si, Al/CoSi₂ and Al/CoSi

For the diffusion couple end-members AlCo, CoSi, CoSi₂ and Co₂Si the same metals were used as described before. The ingots with a total mass of 3 g were prepared in the arc furnace. Since AlCo, CoSi and CoSi₂ melt congruently they were melted only once in the arc furnace. The Co₂Si alloy was re-melted four times and subsequently annealed at 1000 °C for one week, since it does not melt congruently. XRD-analysis proved that

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all end-members were homogeneous. The alloys as well as the pure silicon were cut to plan parallel pieces, ground and polished.

For the diffusion couples AlCo/Si and AlCo/Co₂Si the polished end-members were stacked and the required pressure was applied with weights between 2.5 and 3 kg. The couple AlCo/Co₂Si was annealed at 1050 °C for 100 hours, the couple AlCo/Si at 900 °C for 200 hours. To avoid oxidation the annealing was carried out under dynamic vacuum. The cooling after the respective reaction time was done by a cooling rate of 600°C per hour.

In the common diffusion couple technique both endmembers are solid during the whole experiment and due to the weight adjusted to the polished endmembers the contact is established. In this study we also tried diffusion couples where the contact was formed by a solid-liquid interface. The relatively low melting temperature of Al was utilized in this respect: for the diffusion couple Al/CoSi₂ a flat piece of pure aluminium was put into an alumina crucible and a CoSi₂-piece was put on it. This ensemble was sealed into a quartz glass ampoule under vacuum. To connect the Al and the CoSi₂-piece the ampoule was put into the furnace at 680 °C (i.e. above the melting point of Al) for 20 minutes and then quenched with cold water. For the Al/CoSi couple the alloy was embedded into Al-powder ($\geq 98\%$, Neu-Ulm, Germany). For contact formation the pellet was heated in the arc furnace for a second which made the aluminium melt. The couples were annealed at 550 °C for five weeks, quenched and prepared for further investigation. In this respect one has to keep in mind that the contact formation was done via a solid-liquid interface, which makes the interpretation of the results difficult and they deviate from the normal principles of solid-solid diffusion.

4.3. Preparation of Ternary Al-Si-V Alloys

The preparation of the Al-Si-V alloys followed in principle the method of the Al-Co-Si samples described in the previous chapter. The majority of samples was prepared from aluminum slug (99.999%, Alfa Aesar, Karlsruhe, Germany), silicon lump (99.9999%, Alfa Aesar, Karlsruhe, Germany) and vanadium pieces (99.7%). For some samples vanadium slug (99.8%, Alfa Aesar, Karlsruhe, Germany) was used. To remove oxides at the vanadium surface it was treated with diluted hydrochloric acid for some minutes in the ultrasonic bath. After rinsing it with water and acetone it was dried for some

Experimental

minutes at 120 °C. A series of samples at 10 and 20 at.% V was prepared and annealed at 500 °C. Subsequent investigations showed that not all of these samples were well equilibrated, as they contained unsolved pieces of pure vanadium. Therefore a different annealing procedure was applied for selected samples to improve the equilibration. These samples were heated up to 750 °C after arc melting and then cooled down slowly to the respective annealing temperature of 620 °C employing a cooling rate of 7 K h⁻¹. An additional sample series at 35, 50 and 65 at.% V was annealed at 850 °C. For investigations at higher temperatures another series of samples were sealed into evacuated Ta-crucibles, annealed at 1300 °C for one week in a permanent Ar-flow and then quenched in a water cooled container. After the equilibrium annealing all samples were prepared for further investigation by means of optical microscopy, EPMA, SEM, XRD and DTA.

5. Results and Discussion

5.1. The Al-Co-Si system

The results in the Al-Co-Si system include isothermal sections at 1050 and 1200 °C in the Co-rich part, diffusion couple experiments and the results of DTA-measurements. The latter led to fourteen vertical sections, a reaction scheme and a liquidus surface projection of the entire ternary system.

5.2.1. Isothermal sections at 1050 and 1200 °C

The results of our experimental investigation of the sample series annealed at 1050 and 1200 °C are shown graphically in Figure 13 and the phase compositions determined by EPMA in the various two- and three-phase fields are listed in Table 12. The large, Y-shaped ternary homogeneity range of (AlCo) described by Richter and Tordesillas Gutierrez [55] at 900 °C extends to a more trapezoid-shaped phase field at higher temperatures. Similar to the isothermal section at 900 °C [55] the solubility of Al in CoSi is considerable (11.6 at.%) while the solubility in α -Co₂Si is rather small (1.9 at.%). The phase Co₃Si was not found in the investigated samples and is considered to have nearly no solubility in the ternary system. The high temperature phase β -Co₂Si is not stable at 1050 and 1200 °C. In the following text and in all Figures the phase α -Co₂Si is denoted as Co₂Si.

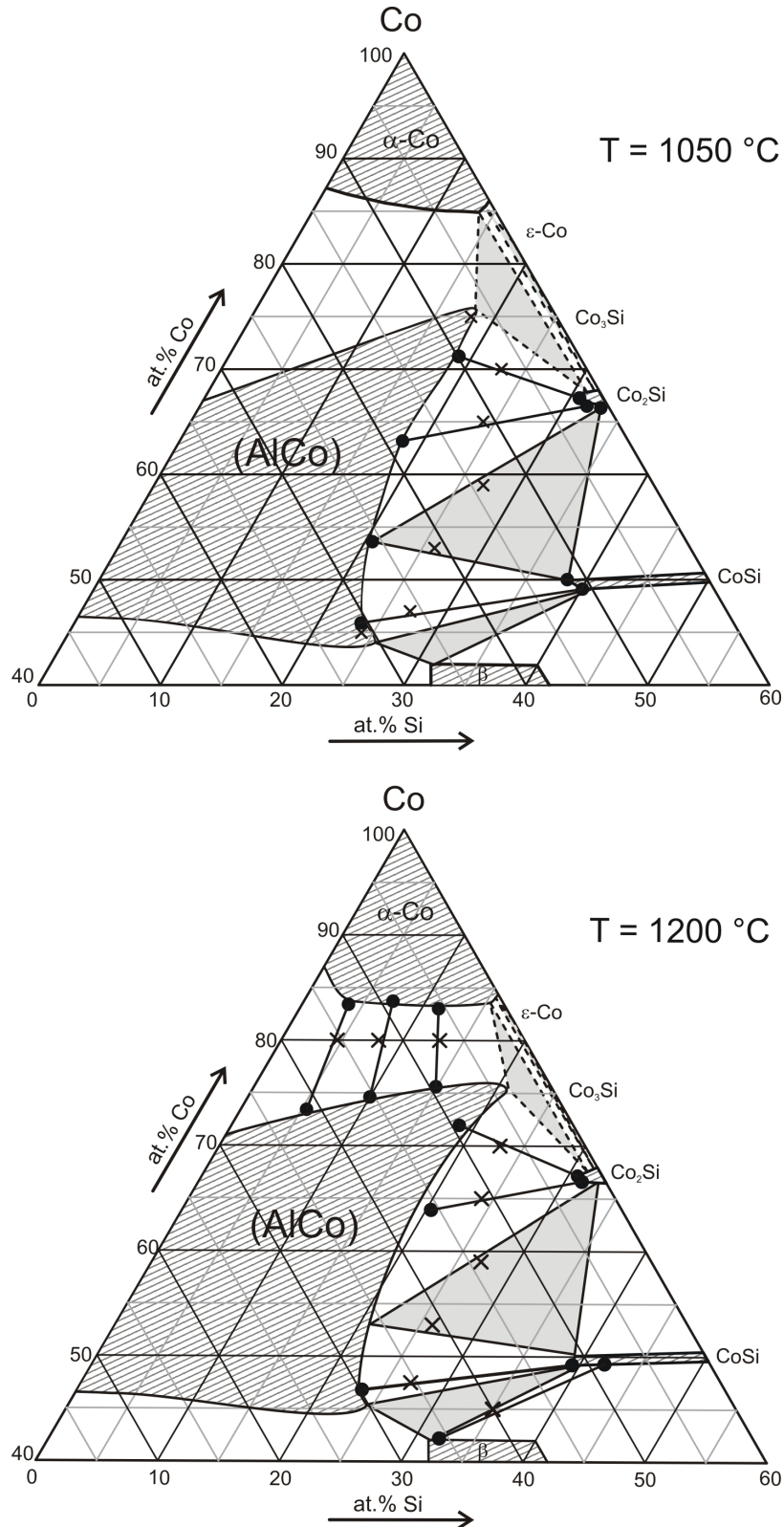


Figure 13: Cobalt-rich part of the isothermal sections through the ternary Al-Co-Si phase diagram at 1050 and 1200 °C. Phase compositions determined by EPMA are depicted as black dots and nominal compositions of the samples are shown as crosses.

Table 12: Phase composition in various samples annealed at 1050 and 1200 °C determined by EPMA.

Nominal sample composition	T/°C of annealing	Phase field by XRD	Phase composition by EPMA/at.%			
				Al	Co	Si
Al ₇ Co ₇₀ Si ₂₃	1050	[(AlCo)+Co ₂ Si]	(AlCo)	9.9(1)	71.2(5)	19.9(5)
			Co ₂ Si	1.7(3)	67.2(5)	31.1(4)
Al ₁₁ Co ₆₅ Si ₂₄	1050	[(AlCo)+Co ₂ Si]	(AlCo)	18.7(3)	63.2(2)	18.1(2)
			Co ₂ Si	1.8(3)	66.4(4)	31.8(4)
Al ₂₁ Co ₅₃ Si ₂₆	1050	[(AlCo)+(CoSi)+Co ₂ Si]	(AlCo)	26.0(1)	53.5(1)	20.5(1)
			(CoSi)	11.6(4)	50.0(4)	38.4(7)
			Co ₂ Si	0.7(1)	66.3(1)	33.0(2)
Al ₂₆ Co ₄₇ Si ₂₇	1050	[(AlCo)+(CoSi)]	(AlCo)	30.8(1)	45.7(2)	23.5(2)
			(CoSi)	10.5(3)	49.3(1)	40.2(2)
Al ₇ Co ₇₅ Si ₁₈	1050	[(AlCo)+(α-Co)+Co ₂ Si]	(AlCo)	--	--	--
			(α-Co)	--	--	--
			Co ₂ Si	--	--	--
Al ₁₄ Co ₅₉ Si ₂₇	1050	[(AlCo)+(CoSi)+Co ₂ Si]	(AlCo)	--	--	--
			(CoSi)	--	--	--
			Co ₂ Si	--	--	--
Al ₃₁ Co ₄₅ Si ₂₄	1050	[(AlCo)+(CoSi)]	(AlCo)	--	--	--
			(CoSi)	--	--	--
Al ₁₂ Co ₈₀ Si ₈	1200	[(AlCo)+(α-Co)]	(AlCo)	15.5(1)	74.5(1)	10.0(1)
			(α-Co)	9.0(1)	83.7(1)	7.3(1)

Results and Discussion

Nominal sample composition	T/°C of annealing	Phase field by XRD	Phase composition by EPMA/at. %			
				Al	Co	Si
Al ₁₂ Co ₈₀ Si ₈	1200	[(AlCo)+(α-Co)]	(AlCo)	21.0(1)	73.1(1)	5.5(1)
			(α-Co)	12.8(1)	83.4(1)	3.8(1)
Al ₇ Co ₈₀ Si ₁₃	1200	[(AlCo)+(α-Co)]	(AlCo)	9.5(1)	75.5(2)	15.0(2)
			(α-Co)	5.6(1)	83.1(1)	11.4(1)
Al ₇ Co ₇₀ Si ₂₃	1200	[(AlCo)+Co ₂ Si]	(AlCo)	9.2(9)	72.2(8)	18.6(9)
			Co ₂ Si	1.8(4)	66.9(6)	31.3(3)
Al ₁₁ Co ₆₅ Si ₂₄	1200	[(AlCo)+Co ₂ Si]	(AlCo)	15.7(6)	63.9(3)	20.4(5)
			Co ₂ Si	1.9(2)	66.4(3)	31.7(6)
Al _{25.5} Co _{47.5} Si ₂₇	1200	[(AlCo)+(CoSi)]	(AlCo)	29.9(3)	46.8(3)	29.9(3)
			(CoSi)	11.4(2)	49.2(4)	39.4(3)
Al ₂₀ Co ₄₅ Si ₃₅	1200	[(CoSi)+β]	(CoSi)	8.8(1)	49.3(1)	41.9(1)
			β	25.8(1)	42.2(2)	32.0(2)
Al ₁₄ Co ₅₉ Si ₂₇	1200	[(AlCo)+(CoSi)+Co ₂ Si]	(AlCo)	--	--	--
			(CoSi)	--	--	--
			Co ₂ Si	--	--	--
Al ₂₁ Co ₅₃ Si ₂₆	1200	[(AlCo)+ (CoSi)+Co ₂ Si]	(AlCo)	--	--	
			(CoSi)	--	--	
			Co ₂ Si	--	--	--

-- not measured due to fine microstructure

Not all of the samples prepared in the two isothermal sections could be properly measured by EPMA due to the very fine microstructure (precipitation) in some of the alloys. Powder XRD measurements of these samples confirmed their phase composition to be consistent with Figure 13. The three-phase field [(AlCo)+(CoSi)+ β] was not found in any of the investigated samples, but its position could be established quite well considering the measured data at the surrounding two-phase fields. The three-phase field [(AlCo)+(CoSi)+Co₂Si] was determined by EPMA by a sample with the nominal composition Al₂₁Co₅₃Si₂₆ annealed at 1050 °C. At 1200 °C we were not able to measure the exact phase compositions by means of EPMA, but we could fix the position of the three-phase field by means of the two samples with the nominal compositions Al₁₄Co₅₉Si₂₇ and Al₂₁Co₅₃Si₂₆, both show the presence of the three phases in their XRD pattern (compare Figure 13).

The most serious problem encountered in these sections is the exact position of the three-phase field [(AlCo)+(α -Co)+Co₂Si]. In samples with the nominal composition Al₇Co₇₅Si₁₈ and Al₄Co₈₀Si₁₆ we found (AlCo), (α -Co) and Co₂Si by means of XRD-analysis. However, considering the results of DTA-investigations discussed in section 5.2.3, we believe that the true position of the three-phase field [(AlCo)+(α -Co)+Co₂Si] is shifted towards Al-poor compositions as shown in Figure 13. According to this interpretation the observation of α -Co and Co₂Si in these samples is a consequence of precipitations upon cooling connected to the strong change of the solubility limit of Si in (AlCo) with temperature. On the basis of our DTA measurements we estimate that the solubility of Si in (AlCo) reaches its maximum extension at the ternary transition reaction $L + (AlCo) = (\alpha-Co) + Co_2Si$ between 1200 and 1230 °C. We estimate the maximum solubility of Al and Si in (AlCo) to be Al_{6.5}Co₇₆Si_{17.5} at 1050 and Al_{3.5}Co₇₆Si_{20.5} at 1200 °C, respectively. Keeping the results of our DTA-measurements and our interpretation in mind, the attempt to enhance the microstructure of the samples at 1200 °C by cooling them slowly from 1400 to 1200 before annealing was counterproductive. In fact we found the samples annealed at 1050 without previous temperature-treatment better crystallized than the sample series at 1200 °C. This is visualized in Figure 14. These two BSE images of samples with the nominal composition Al₁₁Co₆₅Si₂₄ were annealed at 1050 and 1200 °C, respectively. According to XRD-measurements both samples contain similar amounts of AlCo and Co₂Si. The sample annealed at 1050 °C exhibits well separated crystals of the two phases and the

composition could be measured by EPMA. The sample annealed at 1200 °C in contrast shows very fine microstructure between larger crystals of Co_2Si .

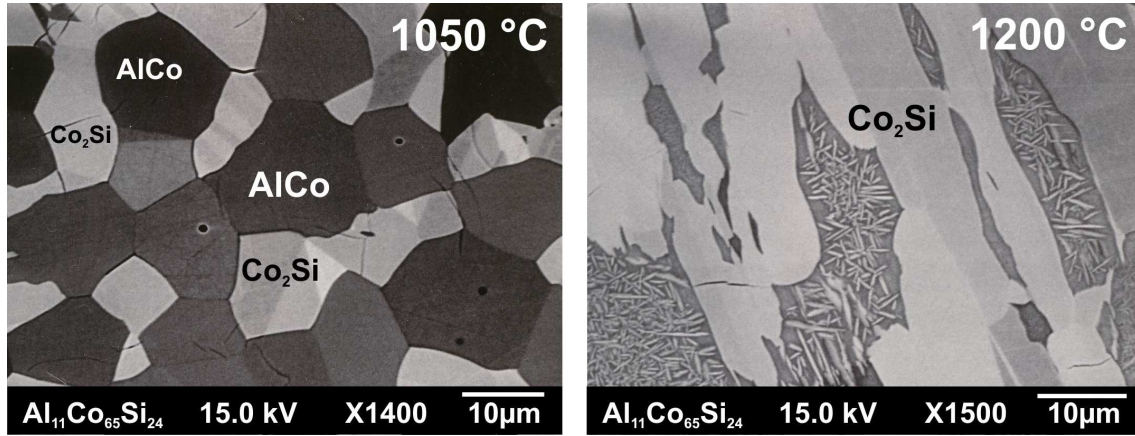


Figure 14: Comparison of BSE images of samples annealed at 1050 and 1200 °C.

5.2.2. Diffusion Couples

The results of the diffusion couple AlCo/Si annealed at 900 °C are shown in Figure 15 and Figure 16. The micrograph of the cross section in Figure 15 exhibits well separated phases which were formed during the reaction time. According to the results the diffusion path is: Si-CoSi₂- α - β -(AlCo)- χ -(AlCo)-AlCo. The composition of the measurement points are listed in Table 13. On the first glance it was not clear whether there is a continuous change in composition between the β -phase and the solid solution of (AlCo). In a second attempt we tried to enhance the resolution to differentiate the very similar composition of these two phases. In the enlarged section in Figure 15 the phases β and (AlCo) show different contrast in the BSE image. Also the measurements of the compositions prove that there is a definite difference between the phases β and (AlCo). The insular formation of the phase χ is in agreement with the fact that the diffusion path leaves (AlCo), proceeds to χ and returns back to (AlCo). In this very region the mass balance line is crossed by the diffusion path which is a basic necessity in this method. In Figure 16 the measured compositions are plotted onto the isothermal section at 900 °C based on data listed in [55] and using the liquid-solid equilibria which will be discussed in section 5.2.3. In comparison to [55] the composition of the liquid phase was changed according to our new results. The phase equilibria determined by the diffusion couple technique are in perfect agreement with the phase diagram determined from bulk samples.

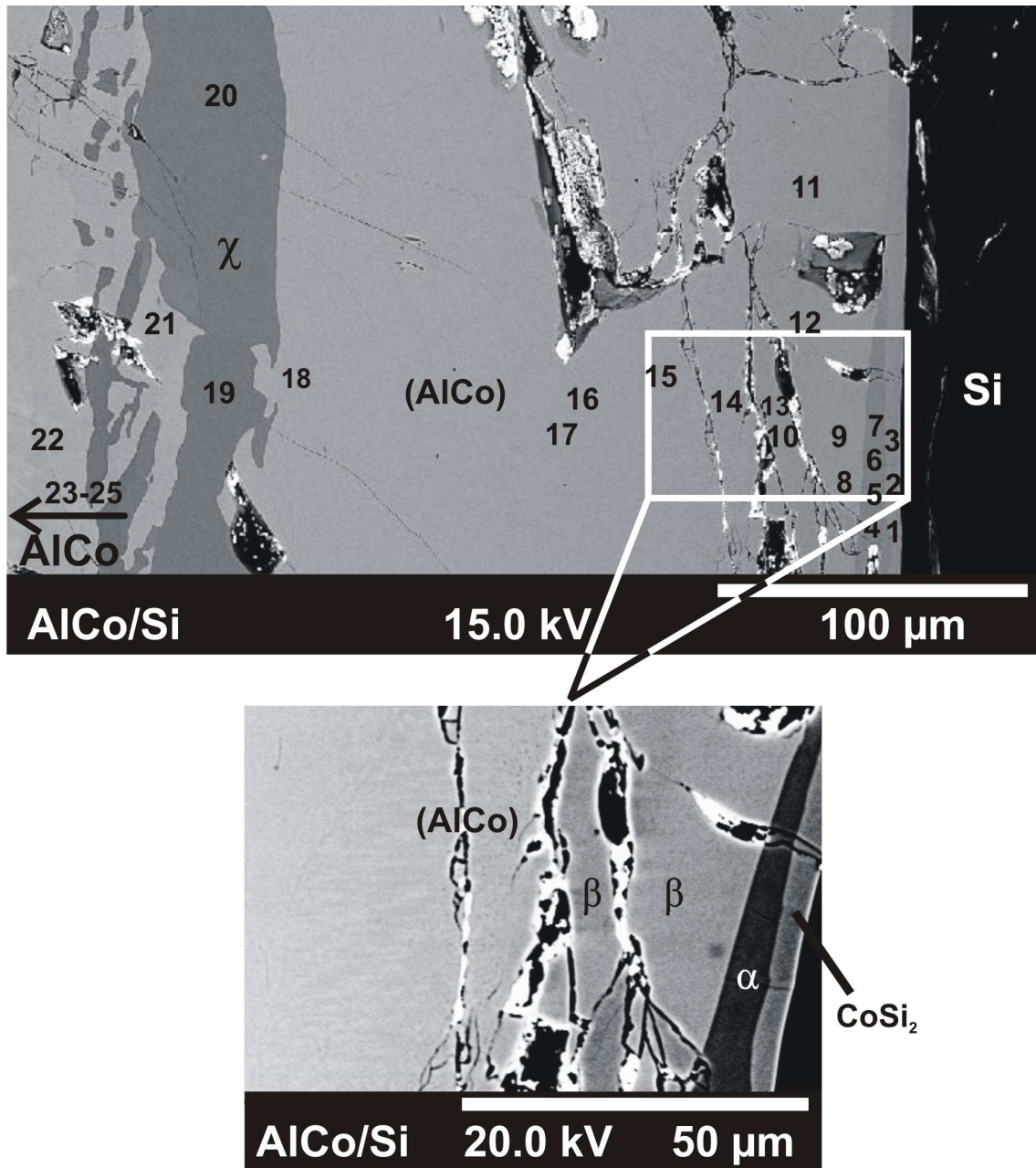


Figure 15: Back-scattered electron image of the reaction zone of the AlCo/Si diffusion couple annealed at 900 °C for 200 hours. The data points correspond to the measured compositions listed in Table 13.

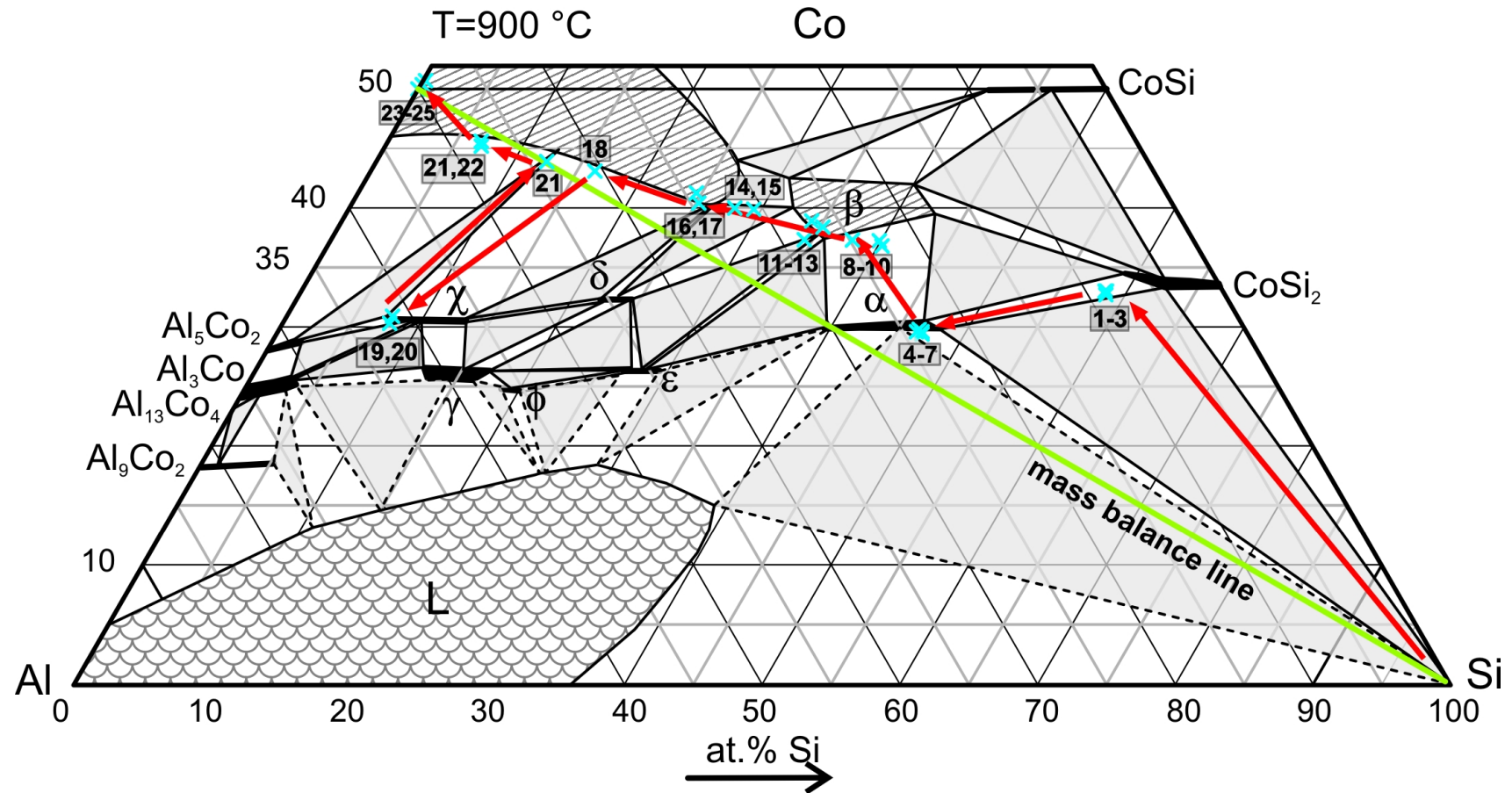


Figure 16: Measured compositions (blue crosses) for the diffusion couple AlCo/Si. The data points correspond to the measured compositions listed in Table 13 and the diffusion path is marked by red arrows.

Table 13: Composition of the measurement points in the diffusion couple AlCo/Si annealed at 900 °C determined by EPMA.

Point	Phase	Phase composition by EPMA/at.%		
		Al	Co	Si
1	CoSi ₂	8.6	33.0	58.4
2		8.5	33.0	58.5
3		8.7	32.7	58.6
4	α	23.7	29.4	46.9
5		23.6	29.6	46.8
6		23.7	29.8	46.5
7		24.0	29.6	46.4
8	β	22.9	37.3	39.8
9		22.9	36.8	40.3
10		24.8	37.3	37.9
11		28.3	37.3	34.4
12		26.4	38.4	35.2
13		27.0	38.9	34.2
14	(AlCo)	30.7	39.9	29.5
15		32.0	40.0	28.0
16		34.1	41.3	24.6
17		34.4	40.4	25.2
18		40.6	43.1	16.3
19	χ	61.4	30.9	7.7
20		61.5	30.5	7.7
21	(AlCo)	43.7	43.9	12.4
22		47.8	45.2	7.0
23		47.6	45.6	6.8
24	AlCo	49.1	50.7	0.2
25		49.6	50.4	0.0

Results and Discussion

On the basis of the diffusion couple at 1050 °C we found out that the diffusion path between the two end-members AlCo and Co₂Si is quite easy to interpret. From Co₂Si it leads to the solid solution of Si in (AlCo) and ends in pure AlCo. In Figure 17 a micrograph of the respective couple can be seen and the compositions of the measurement points are listed in Table 14. The contact equilibrium (AlCo)/Co₂Si corresponds well to a tie-line in our isothermal section shown in Figure 13.

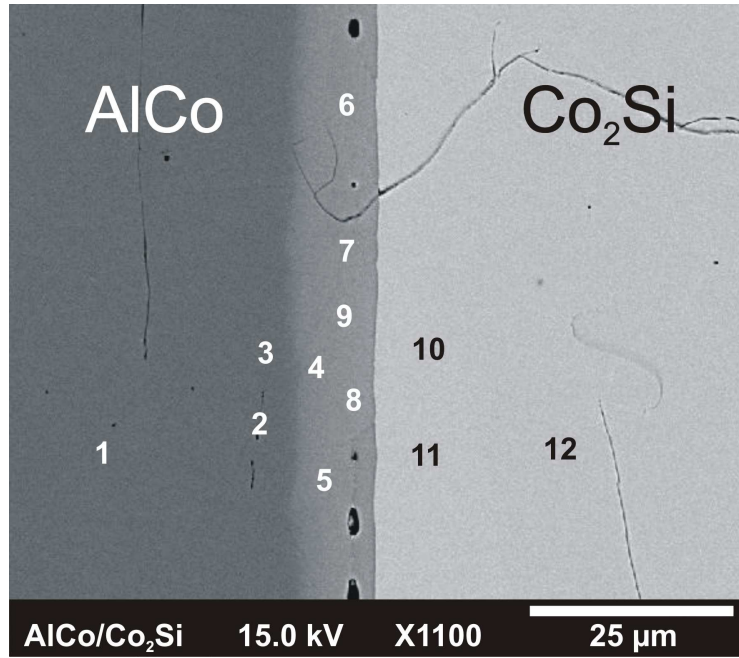


Figure 17: Back-scattered electron image of the reaction zone developed in the AlCo/Co₂Si diffusion couple annealed at 1050 °C for 100 hours. The data points correspond to the measured compositions listed in Table 14.

Table 14: Composition of the measurement points in the diffusion couple AlCo/Co₂Si, annealed at 1050 °C determined by EPMA.

Point	Phase	Phase composition by EPMA/at.%		
		Al	Co	Si
1	AlCo (AlCo)	50.5	49.4	0.1
2		50.9	49.1	0.0
3		50.7	49.1	0.2
4		28.7	54.5	16.8
5		30.8	53.6	15.6
6		26.2	56.0	17.8
7		26.4	55.7	17.9
8		26.1	55.8	18.1
9		27.8	55.0	17.2
10	Co ₂ Si	0.8	65.8	33.4
11		1.3	65.8	32.9
12		0.3	65.4	34.3

In Figure 18 cross sections of the diffusion couple Al/CoSi₂ annealed at 550 °C are shown. The micrographs illustrate three different areas along the reaction zone. The detected phases and the measured phase compositions are in quite good agreement with the isothermal section at 600 °C reported earlier [55]. However, as contact formation in this diffusion couple was done at a liquid-solid interface, it is somewhat ambiguous to talk about local equilibria in the diffusion zone and also solubility effects cannot be ruled out. In Figure 18 (a) the endmember CoSi₂ is separated by a very fine, not measurable dark layer from the ϵ phase. This layer can be seen better in Figure 18 (b) and (c) and it was measured to be Si there. Nevertheless, the Si layer was not formed over the whole area continuously to a sufficient quantity but Si precipitates are found over a wide range in the diffusion zone. Si grains are spread in the ϕ -matrix adjacent to the ϵ -layer, as well as in the Al₉Co₂-matrix adjacent to the ϕ -layer. The respective areas marked in Figure 18 (b) indicate the existence of the three phase fields [Al₉Co₂+Si+ ϕ] and [Si+ ϵ + ϕ] which is in good accordance to the phase diagram. The overall composition Al_{48.2}Co_{17.8}Si₃₄ of the very fine spotted area in Figure 18 (a) corresponds to a mixture of Si, Al₉Co₂ and ϕ located in the particular three phase field.

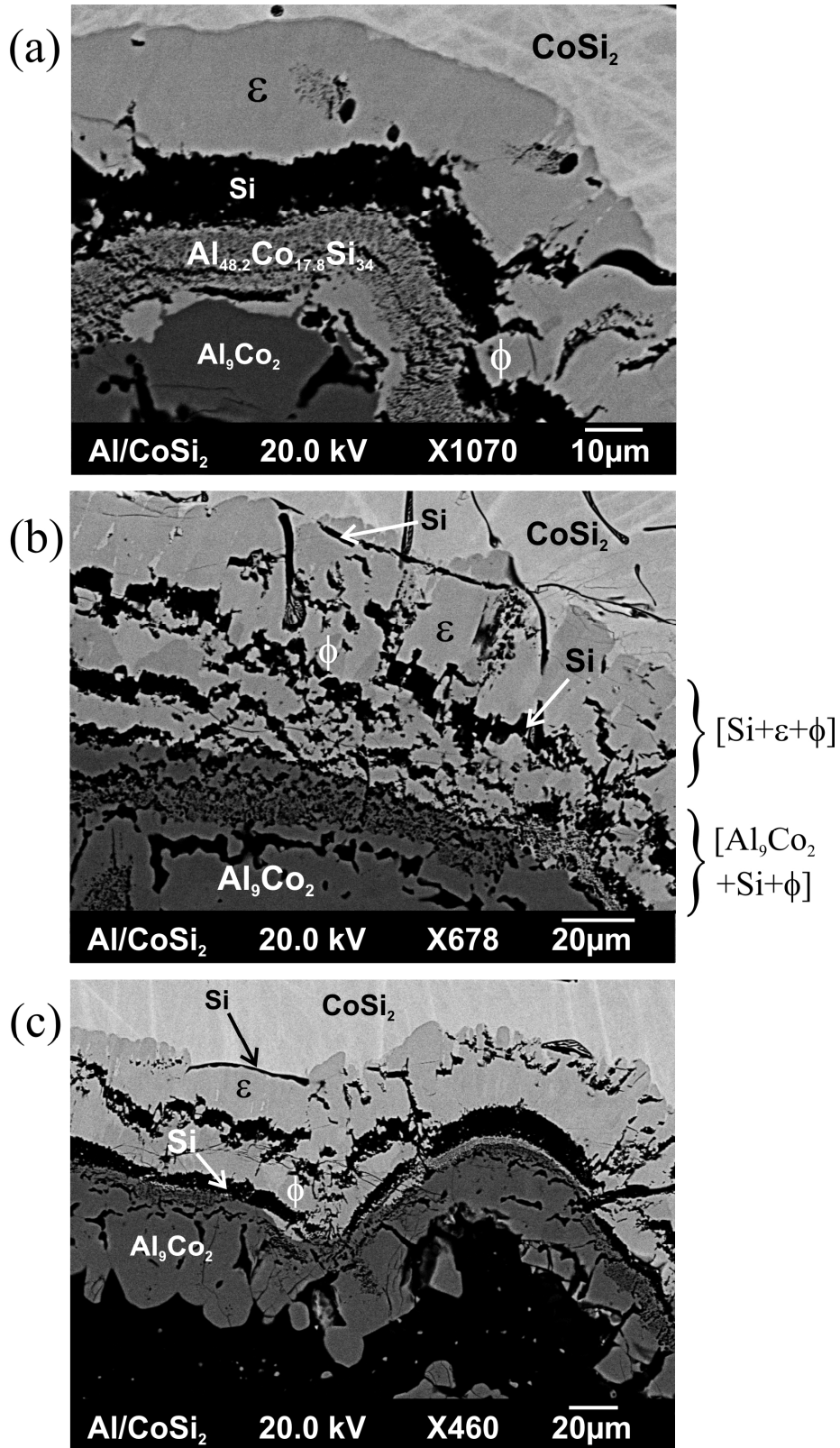


Figure 18: Three different areas of the reaction zone of the diffusion couple Al/CoSi₂ annealed at 550 °C for five weeks (back-scattered electron images).

According to our experimental observation we can interpret the diffusion path to be: CoSi_2 -Si- ϵ - ϕ -Si- Al_9Co_2 -Al. In Figure 19 the measured compositions of the formed diffusion zones together with the diffusion path are shown in the isothermal section. In Table 15 the respective compositions are listed. However, the fact that contact formation in this diffusion couple was done at a liquid-solid interface allows just a preliminary interpretation of the data and the diffusion path as shown in Figure 19 is only tentative.

Table 15: Composition of the measurement points in the diffusion couple Al/CoSi₂, annealed at 550 °C determined by SEM.

Point	Phase	Phase composition by EPMA/at. %		
		Al	Co	Si
1	CoSi ₂	0.2	32.5	67.3
2	Si	1.6	0.8	97.6
3	ϵ	47.8	24.6	27.6
4	ϕ	60.8	22.4	16.8
5	mixture	48.2	17.8	34.0
6	Al ₉ Co ₂	79.7	17.2	3.1

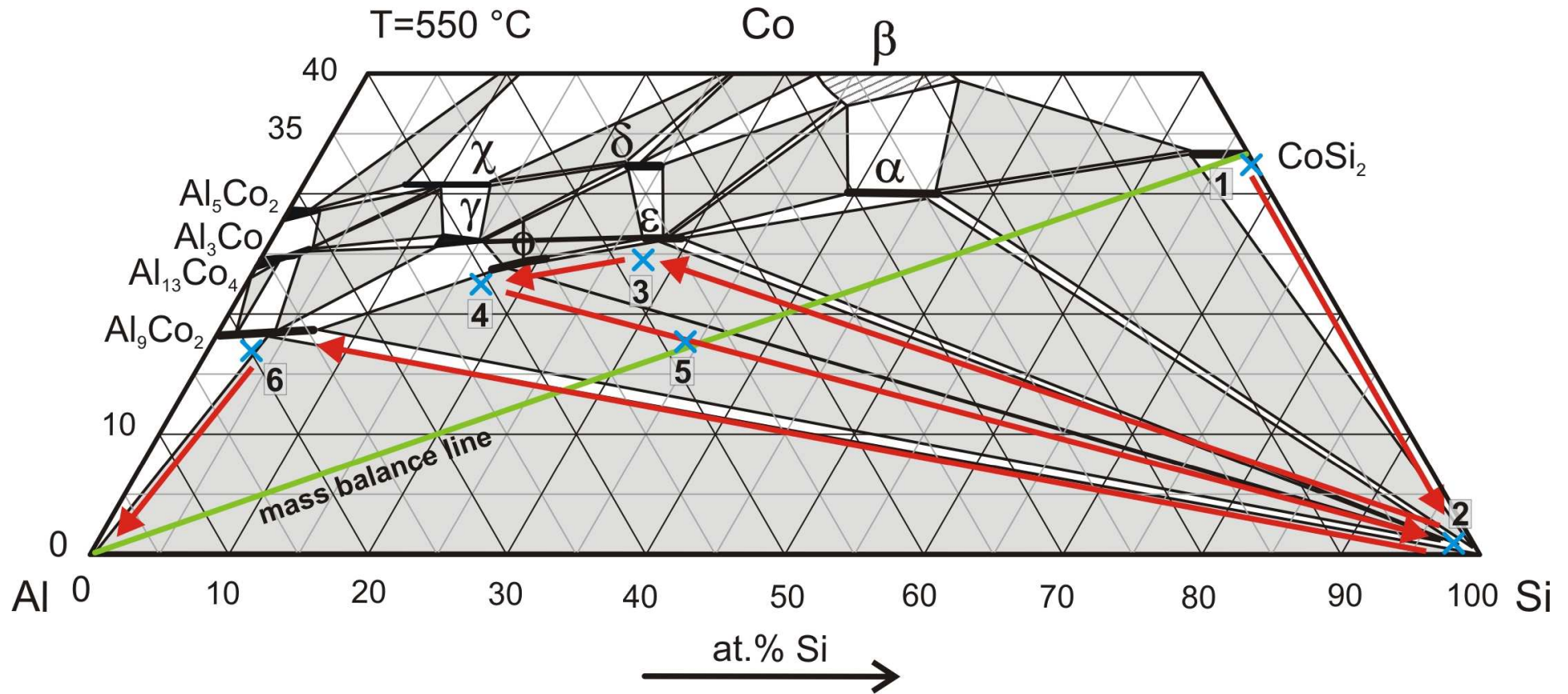


Figure 19: Measured compositions (blue crosses) and proposed diffusion path (red arrows) for the diffusion couple Al/CoSi₂. The data points correspond to the measured compositions listed in Table 15.

Results and Discussion

The analysis of the diffusion couple Al/CoSi yield indistinct results. Three different cross sections of this couple are shown in Figure 20 and it is striking that no exact layers were formed, but widespread grains of the different phases. As mentioned already in the experimental section the alloy was pressed into Al-powder and the whole assembly was heated very short in the arc furnace. This procedure had impact at least on the composition of the outer endmember and we found a mixture of Al+Al₉Co₂ instead of pure Al on the edge of the couple. Similar to the couple Al/CoSi₂ the contact formation was done by a solid-liquid interface, which makes the interpretation difficult and ambiguous. Adjacent to CoSi, over the major part of the couple, β was formed. The β -layer I followed by layers formed by ϵ and γ . This would suggest the diffusion path to be CoSi- β - ϵ - γ -Al₉Co₂. On the other hand in Figure 20 (c) one can see that the ϵ phase is in direct contact to CoSi, which is contradictory to the isothermal section at 600 °C, where CoSi was measured to be in equilibrium with AlCo, CoSi₂ and β , but there is no three phase field of [CoSi+ β + ϵ]. In other areas of the diffusion zone δ was formed adjacent to the CoSi endmember. Especially in Figure 20 (b) one can see that CoSi, δ , ϵ and γ were formed in layers quite nicely and that there is a direct contact between CoSi, δ and ϵ , indicating the existence of the three phase field [CoSi+ ϵ + δ]. The microstructure we gained from the diffusion couple Al/CoSi does not match to the isothermal section at 600 °C and we think that no local equilibrium was formed. Longer annealing time might support the formation of an equilibrium situation according to the phase diagram.

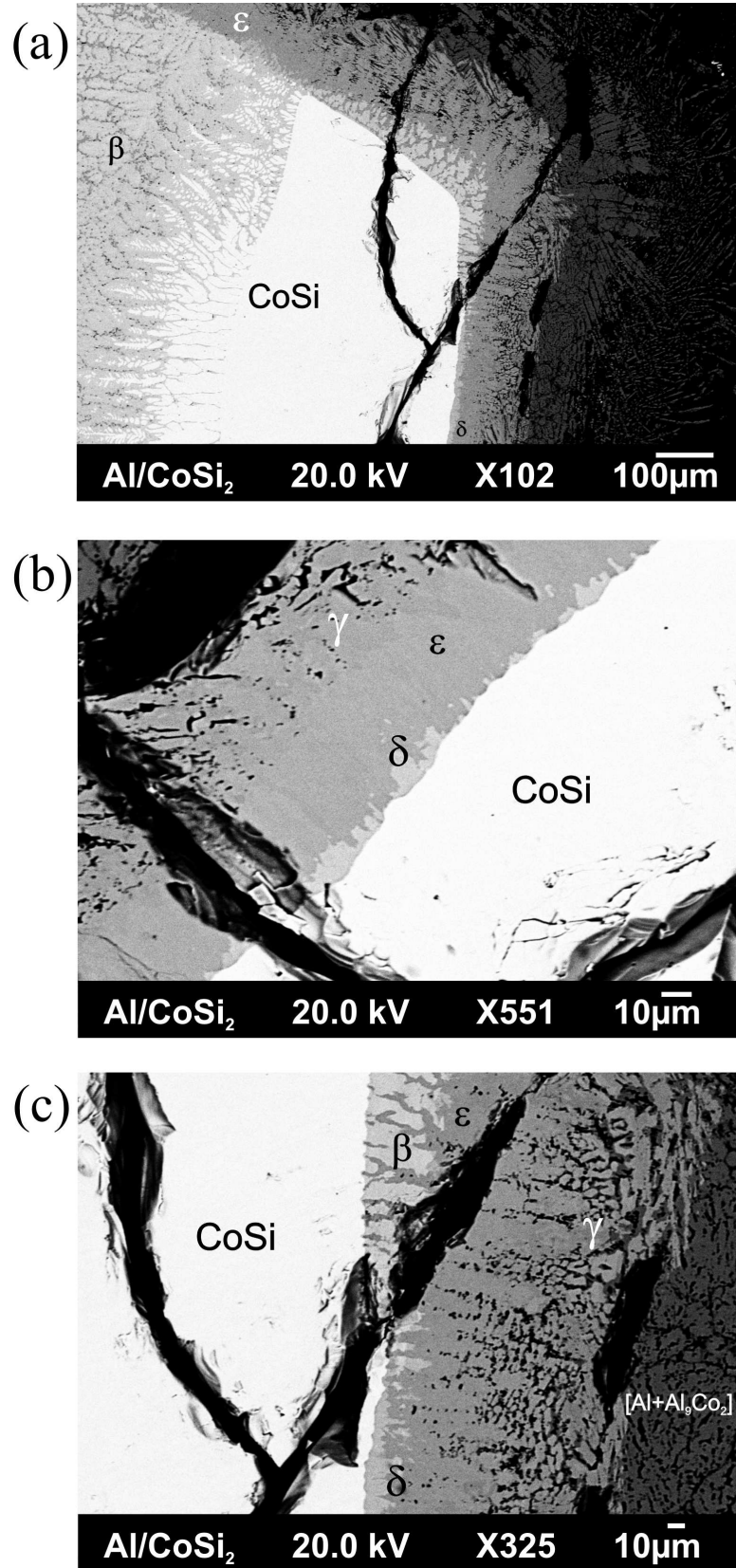


Figure 20: Three different areas of the reaction zone of the diffusion couple Al/CoSi annealed at 550 °C for five weeks (back-scattered electron images).

5.2.3. Ternary phase reactions and liquidus surface projection

The ternary phase reactions in the system Al-Co-Si were studied by DTA analysis. These measurements as well as sample preparation were not done in the course of this study, but only the evaluation of the data. To clarify the very complex ternary system, samples situated in fourteen different vertical sections at constant Co contents of 5, 15, 22, 24, 25, 26, 28, 30, 35, 40, 50, 60, 66.7 and 75 at.% Co were investigated and the corresponding samples are shown in Figure 21.

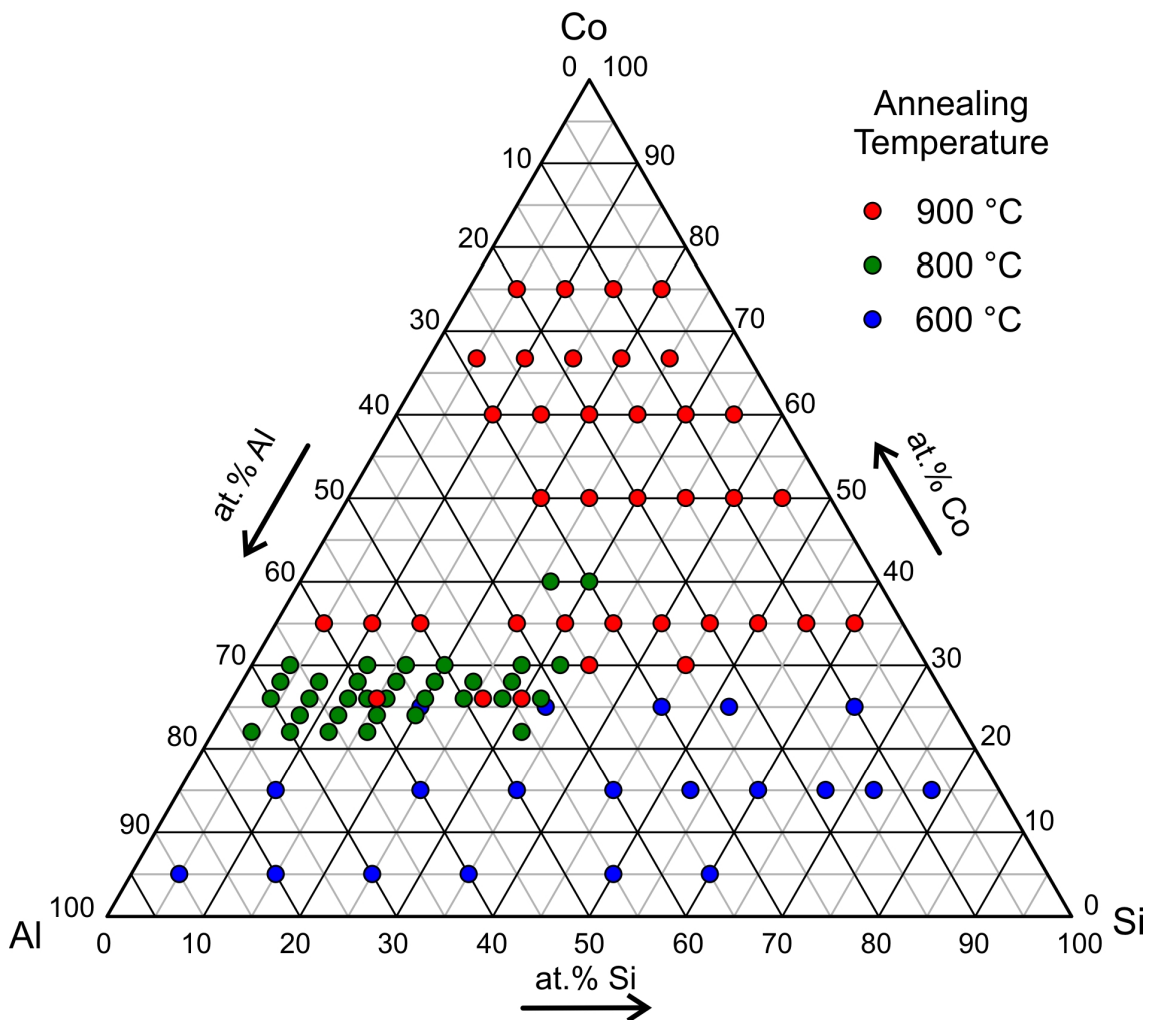


Figure 21: Samples in the Al-Co-Si system measured by means of DTA.

Results and Discussion

Two heating- and cooling- cycles were performed in each measurement in order to test if equilibrium conditions can be reestablished within the samples at the selected heating/cooling rate of 5 K min^{-1} . Starting temperature was 600, 800 and 900 °C i.e. the respective annealing temperature. The maximum temperature reached in these experiments was 1500 °C. Metastable thermal effects were observed in many samples in the second heating cycles. The experimental data points for thermal effects shown in Figures 22-27 (circles and crosses) thus represent mainly DTA results obtained on first heating of the annealed samples. The liquidus values (triangles) were evaluated from the heating- and cooling-curves, respectively. The results of our DTA-experiments are given in Table 16. Although most of the sections are not completely covered with experimental data points, the full sections are given in Figures 22-27 for the sake of clarity. Altogether, twenty-seven invariant four-phase equilibria were derived from these data. In addition the two maxima $L=(\text{AlCo})+\beta$ and $L=(\text{AlCo})+(\text{CoSi})$ and the congruent melting point of β were identified. Twenty-one different invariant reaction temperatures could be determined directly in DTA-measurements. The other reactions were proposed and the respective temperatures were estimated. A summary of these invariant phase equilibria including the reaction temperatures and the approximate compositions of the involved phases which were assessed based on a combination of all available experimental data (XRD, EPMA and DTA) is given in Table 17. A ternary reaction scheme consistent with our experimental results as well as with the rules of equilibrium thermodynamics is proposed in the Scheil diagram shown in Figure 28. We found one ternary eutectic reaction, nineteen transition reactions and seven ternary peritectic reactions.

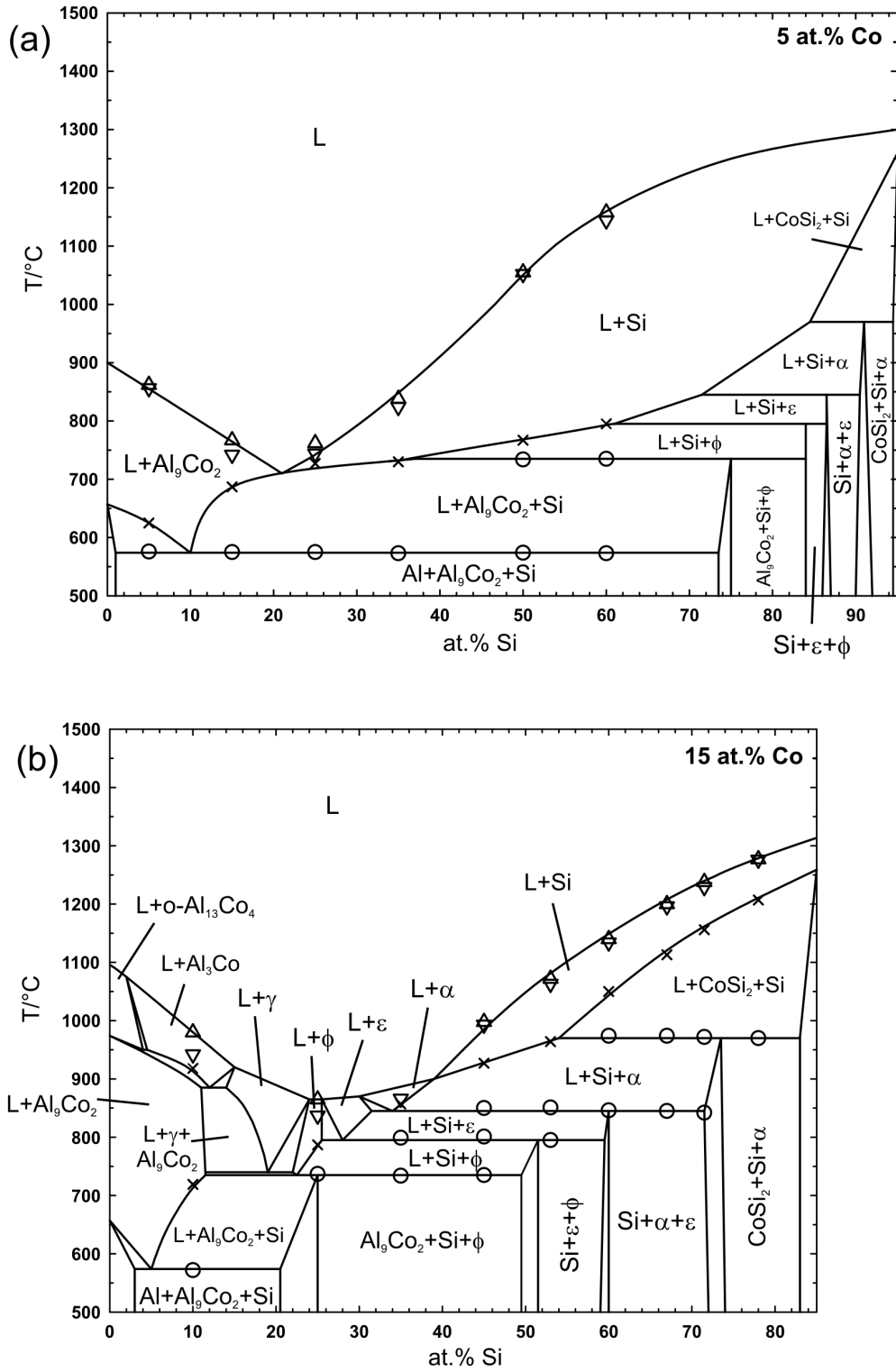


Figure 22: Vertical sections through the Al-Co-Si system at (a) 5 and (b) 15 at.% Co. Circles: invariant effects, crosses: non invariant effects; triangles up: liquidus on heating, triangles down: liquidus on cooling.

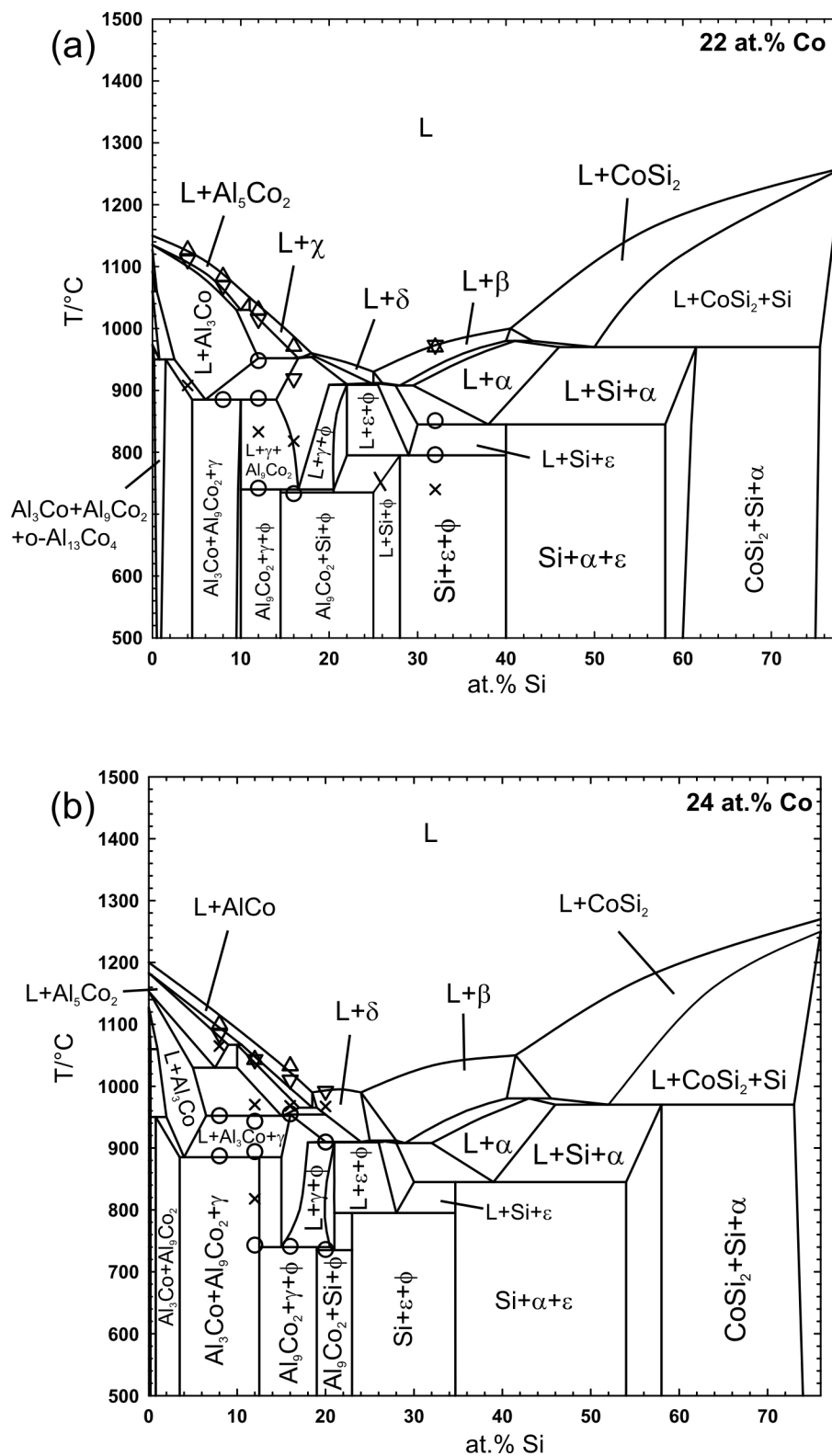


Figure 23: Vertical sections through the Al-Co-Si system at (a) 22 and (b) 24 at.% Co. Circles: invariant effects, crosses: non invariant effects; triangles up: liquidus on heating, triangles down: liquidus on cooling.

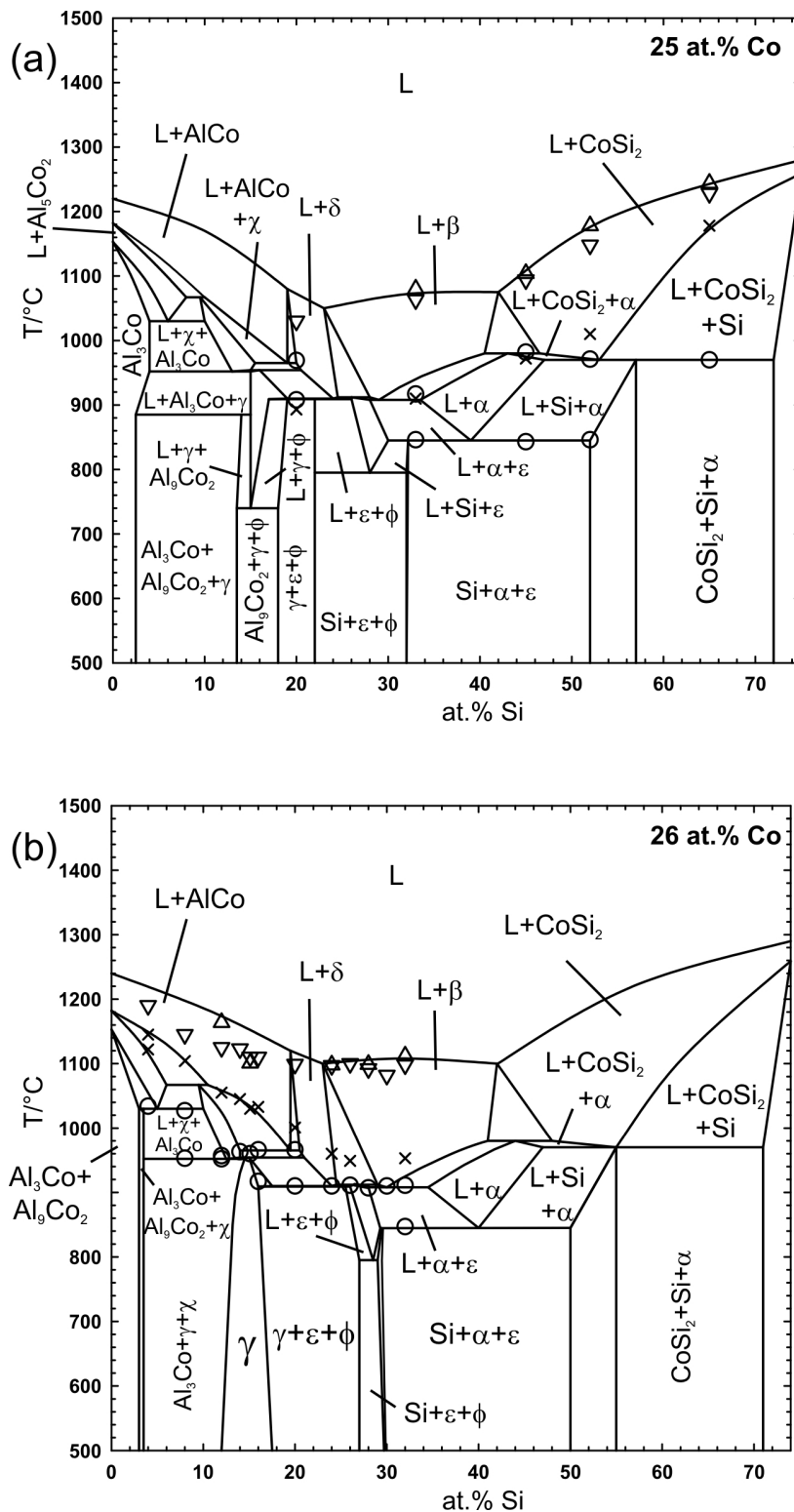


Figure 24: Vertical sections through the Al-Co-Si system at (a) 25 and (b) 26 at.% Co. Circles: invariant effects, crosses: non invariant effects; triangles up: liquidus on heating, triangles down: liquidus on cooling.

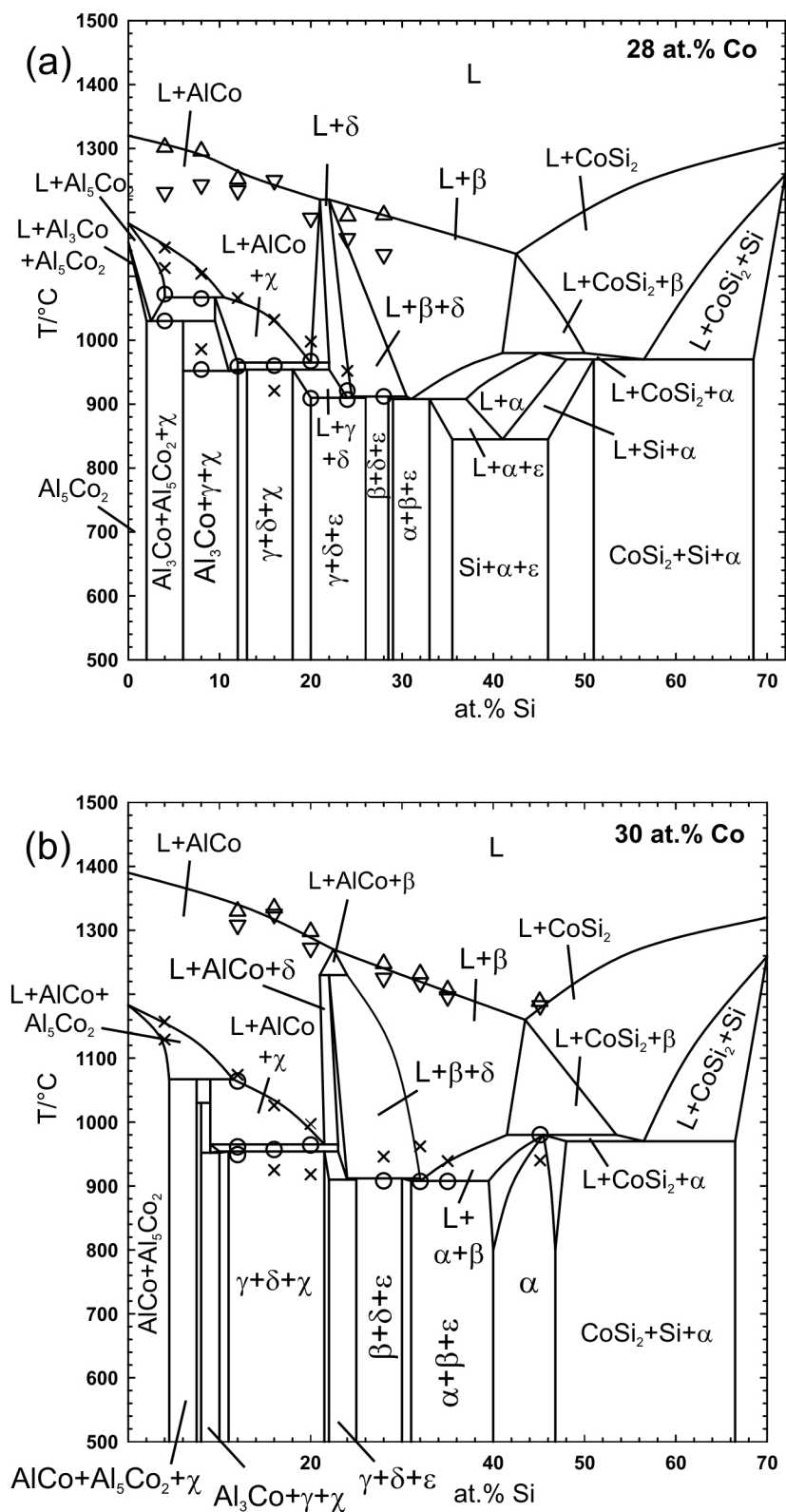


Figure 25: Vertical sections through the Al-Co-Si system at (a) 28 and (b) 30 at.% Co. Circles: invariant effects, crosses: non invariant effects; triangles up: liquidus on heating, triangles down: liquidus on cooling.

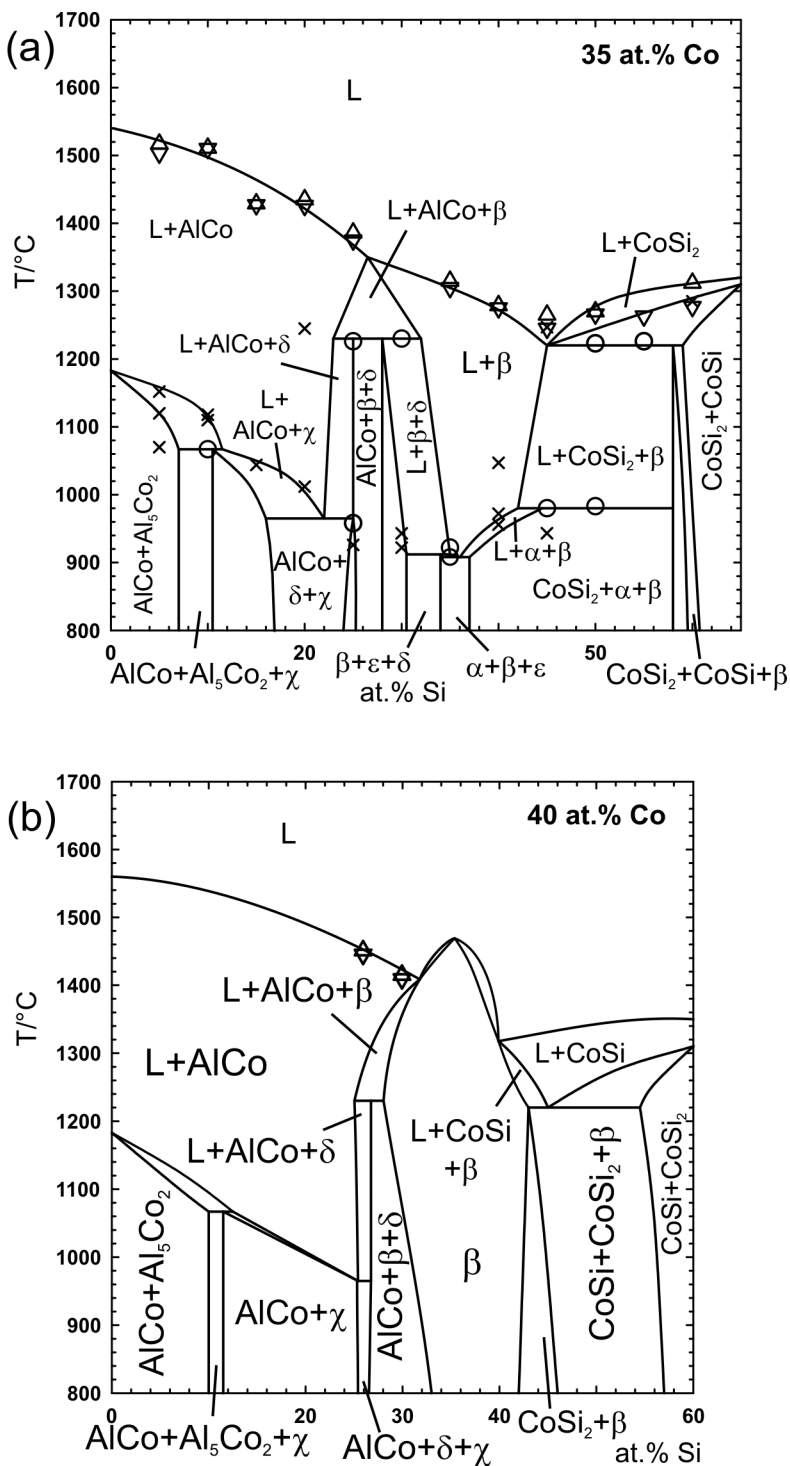


Figure 26: Vertical sections through the Al-Co-Si system at (a) 35 and (b) 40 at.% Co. Circles: invariant effects, crosses: non invariant effects; triangles up: liquidus on heating, triangles down: liquidus on cooling.

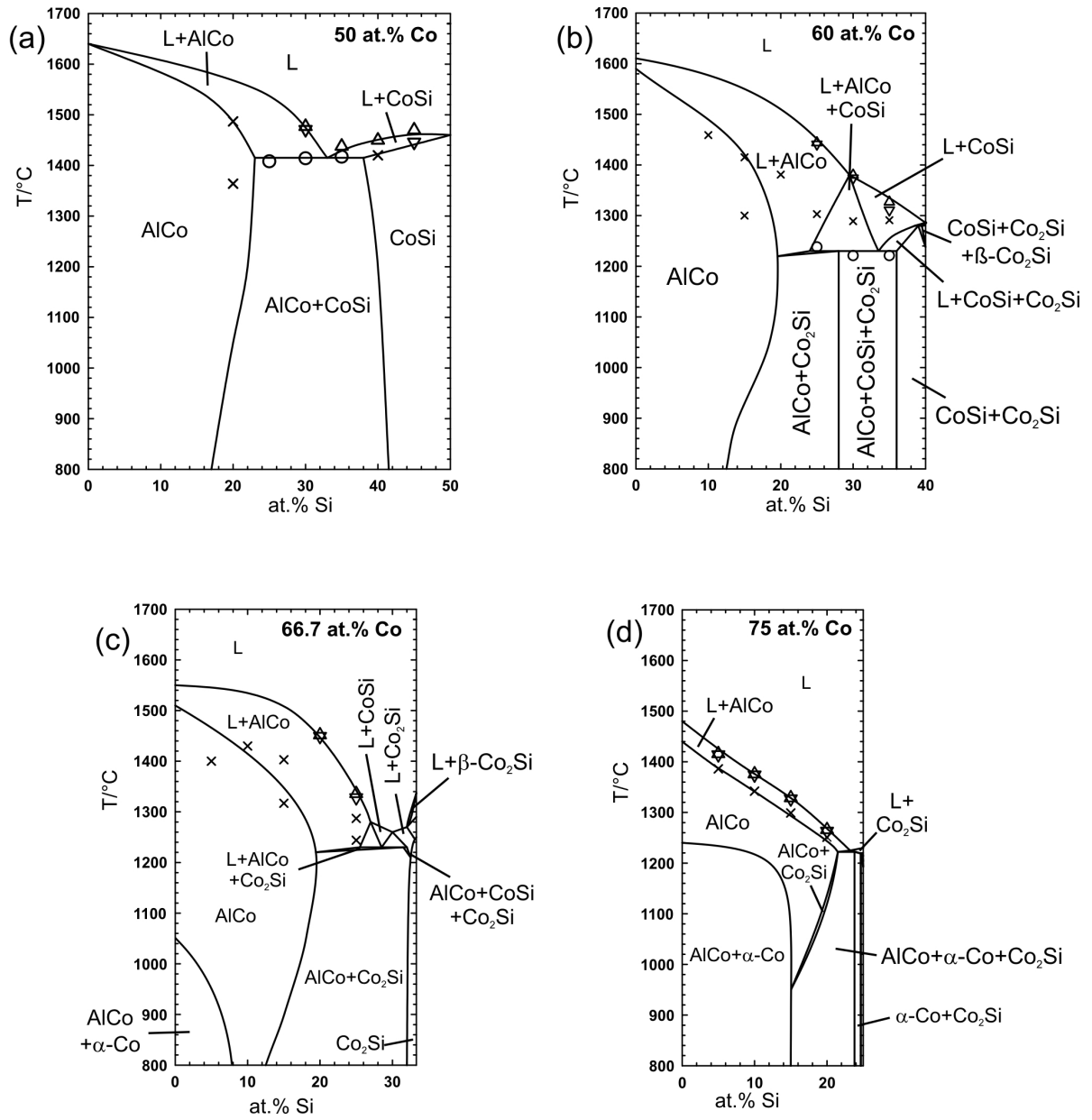


Figure 27: Vertical sections through the Al-Co-Si system at (a) 50, (b) 60, (c) 66.7 and (d) 75 at.% Co. Circles: invariant effects, crosses: non invariant effects; triangles up: liquidus on heating, triangles down: liquidus on cooling.

Table 16: Experimental results of the thermal analysis in the Al-Co-Si system.**All samples were measured in Alumina crucibles at a heating rate of 5 K/min.**

Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₉₀ Co ₅ Si ₅	600, 21d	576	625	862	856
Al ₈₀ Co ₅ Si ₁₅	600, 21d	575	687	767	742
Al ₇₀ Co ₅ Si ₂₅	600, 21d	575	727	762	744
Al ₆₀ Co ₅ Si ₃₅	600, 21d	573	730	838	824
Al ₄₅ Co ₅ Si ₅₀	600, 21d	574, 734	767	1055	1052
Al ₃₅ Co ₅ Si ₆₀	600, 21d	573, 735	795	1158	1144
Al ₇₅ Co ₁₅ Si ₁₀	600, 21d	572	719, 918	980	942
Al ₆₀ Co ₁₅ Si ₂₅	600, 21d	737	787	865	837
Al ₅₀ Co ₁₅ Si ₃₅	600, 21d	734, 799	857		866
Al ₄₀ Co ₁₅ Si ₄₅	600, 21d	735, 801, 850	927	998	993
Al ₃₂ Co ₁₅ Si ₅₃	600, 21d	795, 851	964	1072	1063
Al ₂₅ Co ₁₅ Si ₆₀	600, 21d	846, 974	1050	1140	1134
Al ₁₈ Co ₁₅ Si ₆₇	600, 21d	845, 974	1113	1200	1196
Al _{13.5} Co ₁₅ Si _{71.5}	600, 21d	842, 972	1156	1238	1229
Al ₇ Co ₁₅ Si ₇₈	600, 21d	970	1207	127	1276
Al ₇₄ Co ₂₂ Si ₄	800, 28d		908	1127	1111

Results and Discussion

Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₇₀ Co ₂₂ Si ₈	800, 28d	885		1084	1069
Al ₆₆ Co ₂₂ Si ₁₂	800, 28d	742, 887, 948	833,0000	1030	1015
Al ₆₂ Co ₂₂ Si ₁₆	800, 28d	733	818,0000	971	919
Al ₄₆ Co ₂₂ Si ₃₂	800, 28d	796, 851	740,0000	970	973
Al ₆₈ Co ₂₄ Si ₈	800, 28d	887	952, 1065	1100	1084
Al ₆₄ Co ₂₄ Si ₁₂	800, 28d	894, 943, 743	818, 970	1043	1043
Al ₆₀ Co ₂₄ Si ₁₆	800, 28d	955, 741	968	1033	1010
Al ₅₆ Co ₂₄ Si ₂₀	800, 28d	909, 736,	967		992
Al ₅₅ Co ₂₅ Si ₂₀	600, 21d	969, 908	893		1030
Al ₄₂ Co ₂₅ Si ₃₃	600, 21d	846, 917	910	1080	1063
Al ₃₀ Co ₂₅ Si ₄₅	600, 21d	843, 982	972	1104	1094
Al ₂₃ Co ₂₅ Si ₅₂	600, 21d	846, 971	1010	1178	1148
Al ₁₀ Co ₂₅ Si ₆₅	600, 21d	970	1178	1244	1228
Al ₇₀ Co ₂₆ Si ₄	800, 28d	1034	1122, 1145		1190
Al ₆₆ Co ₂₆ Si ₈	800, 28d	953, 1027	1104		1145
Al ₆₂ Co ₂₆ Si ₁₂	800, 28d	957, 952	1055	1164	1125
Al ₆₀ Co ₂₆ Si ₁₄	800, 28d	963	1045		1123
Al ₅₉ Co ₂₆ Si ₁₅	900, 21d	960	1030	1101	1110
Al ₅₈ Co ₂₆ Si ₁₆	800, 28d	966, 917	1033		1110

Results and Discussion

Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₅₄ Co ₂₆ Si ₂₀	800, 28d	910, 966	1001		1099
Al ₅₀ Co ₂₆ So ₂₄	800, 28d	910	960	1098	1097
Al ₄₈ Co ₂₆ Si ₂₆	900, 21d	911	949		1100
Al ₄₆ Co ₂₆ Si ₂₈	800, 28d	907		1099	1092
Al ₄₄ Co ₂₆ Si ₃₀	900, 21d	910			1082
Al ₄₂ Co ₂₆ Si ₃₂	800, 28d	911, 847	953	1112	1098
Al ₆₈ Co ₂₈ Si ₄	800, 28d	1072, 1030	1113, 1145	1302	1231
Al ₆₄ Co ₂₈ Si ₈	800, 28d	954, 1065	986, 1104	1296	1243
Al ₆₀ Co ₂₈ Si ₁₂	800, 28d	959	1066	1252	1234
Al ₅₆ Co ₂₈ Si ₁₆	800, 28d	960	921, 1032		1250
Al ₅₂ Co ₂₈ Si ₂₀	800, 28d	909, 967	998		1191
Al ₄₈ Co ₂₈ Si ₂₄	800, 28d	907, 921	952	1195	1159
Al ₄₄ Co ₂₈ Si ₂₈	800, 28d	912		1196	1134
Al ₆₆ Co ₃₀ Si ₄	800, 42d		1129, 1157	1588	
Al ₅₈ Co ₃₀ Si ₁₂	800, 42d	1064, 961, 949	1074	1330	1308
Al ₅₄ Co ₃₀ Si ₁₆	800, 42d	957	925, 1026	1335	1325
Al ₅₀ Co ₃₀ Si ₂₀	800, 42d	964	918, 997	1298	1272
Al ₄₂ Co ₃₀ Si ₂₈	800, 42d	908	946	1248	1225
Al ₃₈ Co ₃₀ Si ₃₂	800, 42d	907	962	1232	1218

Results and Discussion

Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₃₅ Co ₃₀ Si ₃₅	900, 21d	907	939	1207	1196
Al ₂₅ Co ₃₀ Si ₄₅	900, 21d	980	940	1189	1182
Al ₆₀ Co ₃₅ Si ₅	900, 21d		1070, 1120, 1152	1517	1503
Al ₅₅ Co ₃₅ Si ₁₀	900, 21d	1067	1118, 1110	1511	1510
Al ₅₀ Co ₃₅ Si ₁₅	900, 21d		1044	1429	1427
Al ₄₅ Co ₃₅ Si ₂₀	900, 21d		1012, 1245	1435	1426
Al ₄₀ Co ₃₅ Si ₂₅	900, 21d	1226, 958	926	1386	1375
Al ₃₅ Co ₃₅ Si ₃₀	900, 21d	1230	922, 943		
Al ₃₀ Co ₃₅ Si ₃₅	900, 21d	908, 922		1315	1305
Al ₂₅ Co ₃₅ Si ₄₀	900, 21d		956, 972, 1047	1279	1275
Al ₂₀ Co ₃₅ Si ₄₅	900, 21d	980	933, 1247	1265	1245
Al ₁₅ Co ₃₅ Si ₅₀	900, 21d	983, 1223		1270	1266
Al ₁₀ Co ₃₅ Si ₅₅	900, 21d	1226			1263
Al ₅ Co ₃₅ Si ₆₀	900, 21d		1285	1312	1277
Al ₃₀ Co ₄₀ Si ₃₀	800, 28d		1413		
Al ₃₄ Co ₄₀ Si ₂₆	800, 28d		1450		
Al ₃₅ Co ₅₀ Si ₁₅	900, 28d				
Al ₃₀ Co ₅₀ Si ₂₀	900, 28d		1364, 1487		
Al ₂₅ Co ₅₀ Si ₂₅	900, 28d	1408			

Results and Discussion

Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₂₀ Co ₅₀ Si ₃₀	900, 28d	1414		1477	1471
Al ₁₅ Co ₅₀ Si ₃₅	900, 28d	1417		1438	
Al ₁₀ Co ₅₀ Si ₄₀	900, 28d		1420	1450	
Al ₅ Co ₅₀ Si ₄₅	900, 28d			1470	1446
Al ₃₅ Co ₆₀ Si ₅	900, 28d				
Al ₃₀ Co ₆₀ Si ₁₀	900, 28d		1459	1459	
Al ₂₅ Co ₆₀ Si ₁₅	900, 28d		1300, 1415		
Al ₂₀ Co ₆₀ Si ₂₀	900, 28d		1381	1444	1441
Al ₁₅ Co ₆₀ Si ₂₅	900, 28d	1238	1303	1380	1374
Al ₁₀ Co ₆₀ Si ₃₀	900, 28d	1221	1289	1327	1311
Al ₅ Co ₆₀ Si ₃₅	900, 28d	1221	1291		
Al _{28.3} Co _{66.7} Si ₅	900, 28d		1400		
Al _{23.3} Co _{66.7} Si ₁₀	900, 28d		1430		
Al _{18.3} Co _{66.7} Si ₁₅	900, 28d		1317, 1403		
Al _{13.3} Co _{66.7} Si ₂₀	900, 28d			1452	1449
Al _{8.3} Co _{66.7} Si ₂₅	900, 28d		1287, 1244	1336	1328
Al ₂₀ Co ₇₅ Si ₅	900, 28d		1386	1416	1414
Al ₁₅ Co ₇₅ Si ₁₀	900, 28d		1342	1376	1374
Al ₁₀ Co ₇₅ Si ₁₅	900, 28d		1299	1329	1327
Al ₅ Co ₇₅ Si ₂₀	900, 28d		1251	1266	1263

Table 17: Ternary invariant phase reactions in the Al-Co-Si system determined by DTA.

Reaction	T / °C	Phase	Composition / at. %		
			Al	Co	Si
E: L=Al+Al ₉ Co ₂ +Si	574	L	~87.0	~1.0	~12.0
		Al	100	0.0	0.0
		Al ₉ Co ₂	78.0	18.0	3.0
		Si	0.0	0.0	100
U: L+φ=Al ₉ Co ₂ +Si	735	L	~68.0	~6.0	~26.0
		φ	55.0	24.5	20.0
		Al ₉ Co ₂	74.0	18.7	6.6
		Si	0.0	0.0	100
U: L+γ=Al ₉ Co ₂ +φ	740	L	~70.0	~7.0	~23.0
		γ	60.1	25.6	14.3
		Al ₉ Co ₂	74.7	18.5	6.6
		φ	54.9	24.6	20.5
U: L+ε=Si+φ	795	L	~62.0	~10.0	~28.0
		ε	45.3	26.3	28.4
		Si	0.0	0.0	100
		φ	54.9	24.6	20.5
U: L+α=Si+ε	845	L	~56.0	~12.0	~32.0
		α	30.0	29.9	42.1
		Si	0.0	0.0	100
		ε	44.4	26.2	29.4
U: L+Al ₃ Co=Al ₉ Co ₂ +γ	885	L	~73.0	~13.0	~14.0
		Al ₃ Co	72.0	25.4	2.6
		Al ₉ Co ₂	74.7	18.7	6.6
		γ	59.5	25.5	15.0

Results and Discussion

Reaction	T / °C	Phase	Composition / at. %		
			Al	Co	Si
U: $L+\beta=\alpha+\epsilon$	~908	L	~53.0	~20,0	~27,0
		β	26.8	37,4	35,8
		α	30.4	30,1	39,5
		ϵ	45.3	26,4	28,3
P: $L+\gamma+\epsilon=\phi$	909	L	~58.0	~18.0	~24.0
		γ	58.0	26.0	16.0
		ϵ	46.6	26.4	27.0
		ϕ	54.9	24.6	20.5
U: $L+\delta=\gamma+\epsilon$	~910	L	~56.0	~20.0	~24.0
		δ	44.0	32.0	24.0
		γ	56.5	26.0	17.5
		ϵ	48.0	26.0	26.0
P: $L+\beta+\delta=\epsilon$	~912	L	~54.0	~21.0	~25.0
		β	27.0	37.0	36.0
		δ	44.0	32.0	24.0
		ϵ	47.5	26.0	26.5
Ua: $L+o-Al_{13}Co_4=Al_3Co+Al_9Co_2$ *	885>T<974	L	~84.0	~12.0	~4.0
		$o-Al_{13}Co_4$	76.5	23.5	0.0
		Al_3Co	73.0	25.0	2.0
		Al_9Co_2	80.8	18.2	1.0
U: $L+\chi=Al_3Co+\gamma$	952	L	~63.0	~20.0	~17.0
		χ	60.2	30.8	9.0
		Al_3Co	71.5	25.5	3.0
		γ	59.0	26.0	15.0

Results and Discussion

Reaction	T / °C	Phase	Composition / at. %		
			Al	Co	Si
P: $L + \delta + \chi = \gamma$	954	L	~61.0	~21.0	~18.0
		δ	43.5	32.0	24.5
		χ	59.2	30.8	10.0
		γ	59.0	26.0	15.0
U: $L + (AlCo) = \delta + \chi$	965	L	~59.0	~23.0	~18.0
		(AlCo)	33.0	40.5	26.5
		δ	42.5	32.5	25.0
		χ	61.0	31.0	8.0
U: $L + CoSi_2 = Si + \alpha$	970	L	~37.0	~18.0	~45.0
		$CoSi_2$	4.1	33.3	62.6
		Si	0.0	0.0	100
		α	22.2	29.8	48.0
P: $L + CoSi_2 + \beta = \alpha$	980	L	~40.0	~20.0	~40.0
		$CoSi_2$	6.4	34.5	59.1
		β	17.7	39.5	42.8
		α	24.5	30.0	45.5
U: $L + Al_5Co_2 = Al_3Co + \chi$	1030	L	~68.0	~21.0	~11.0
		Al_5Co_2	69.5	28.5	2.0
		Al_3Co	71.5	25.5	3.0
		χ	60.5	30.5	9.0
P: $L + (AlCo) + Al_5Co_2 = \chi$	1067	L	~67.0	~23.0	~10.0
		(AlCo)	42.0	45.0	13.0
		Al_5Co_2	68.5	28.5	3.0
		χ	60.5	30.5	9.0

Results and Discussion

Reaction	T / °C	Phase	Composition / at. %		
			Al	Co	Si
Ub: L+h-Al ₁₃ Co ₄ =Al ₃ Co+o-Al ₁₃ Co ₄ *	T<1092	L	~82.0	~17.5	~0.5
		h-Al ₁₃ Co ₄	76.0	24.0	0.0
		Al ₃ Co	74.0	25.0	1.0
		o-Al ₁₃ Co ₄	76.5	23.5	0.0
Pa: L+ε-Co+Co ₂ Si =Co ₃ Si *	1214<T<1230	L	~0.05	~75.7	~24.25
		ε-Co	0.05	82.0	17.95
		Co ₂ Si	0.45	68.0	31.55
		Co ₃ Si	0.1	74.75	25.15
Uc: L+(α-Co)=ε-Co+Co ₂ Si *	T<1230	L	~0.25	~75.05	~24.7
		(α-Co)	0.1	85.0	14.9
		ε-Co	0.1	82.0	17.9
		Co ₂ Si	0.5	68.0	31.5
Ud: L+(AlCo)=(α-Co)+Co ₂ Si *	T<1230	L	~1.5	~75.5	~23.0
		(AlCo)	4.0	76.0	20.0
		(α-Co)	2.0	83.0	15.0
		Co ₂ Si	2.0	66.7	31.3
U: L+(CoSi)=CoSi ₂ +β	1220	L	~20.0	~35.0	~45.0
		(CoSi)	5.0	50.0	45.0
		CoSi ₂	6.0	34.0	60.0
		β	17.0	40.0	43.0
U: L+(CoSi)=(AlCo)+Co ₂ Si	1230	L	~4.0	~70.0	~26.0
		(CoSi)	9.0	50.0	41.0
		(AlCo)	23.5	53.5	23.0
		Co ₂ Si	1.0	67.0	32.0

Results and Discussion

Reaction	T / °C	Phase	Composition / at. %		
			Al	Co	Si
P: L+(AlCo)+ β = δ	1230	L	~50.0	~28.5	~21.5
		(AlCo)	34.0	41.0	25.0
		β	27.0	38.0	35.0
		δ	42.0	33.0	25.0
Ue: L+ β -Co ₂ Si=(CoSi)+Co ₂ Si *	1230<T<1286	L	~1.5	~65.0	~33.5
		β -Co ₂ Si	0.0	66.7	33.3
		(CoSi)	1.0	50.0	49.0
		Co ₂ Si	0.5	66.7	32.8
U: L+(AlCo)=(CoSi)+ β	1385	L	~21.0	~44.0	~35.0
		(AlCo)	30.5	43.5	26.0
		(CoSi)	11.5	49.0	39.5
		β	26.0	42.5	31.5
Max1: L=(AlCo)+ β *	T>1400	L	~26.5	~41.5	~32.0
		(AlCo)	31.0	45.0	24.0
		β	24.0	40.0	36.0
Max2: L=(AlCo)+(CoSi)	1415	L	~18.0	~50.0	~32.0
		(AlCo)	27.0	50.0	23.0
		(CoSi)	12.0	50.0	38.0

* Reaction not determined experimentally

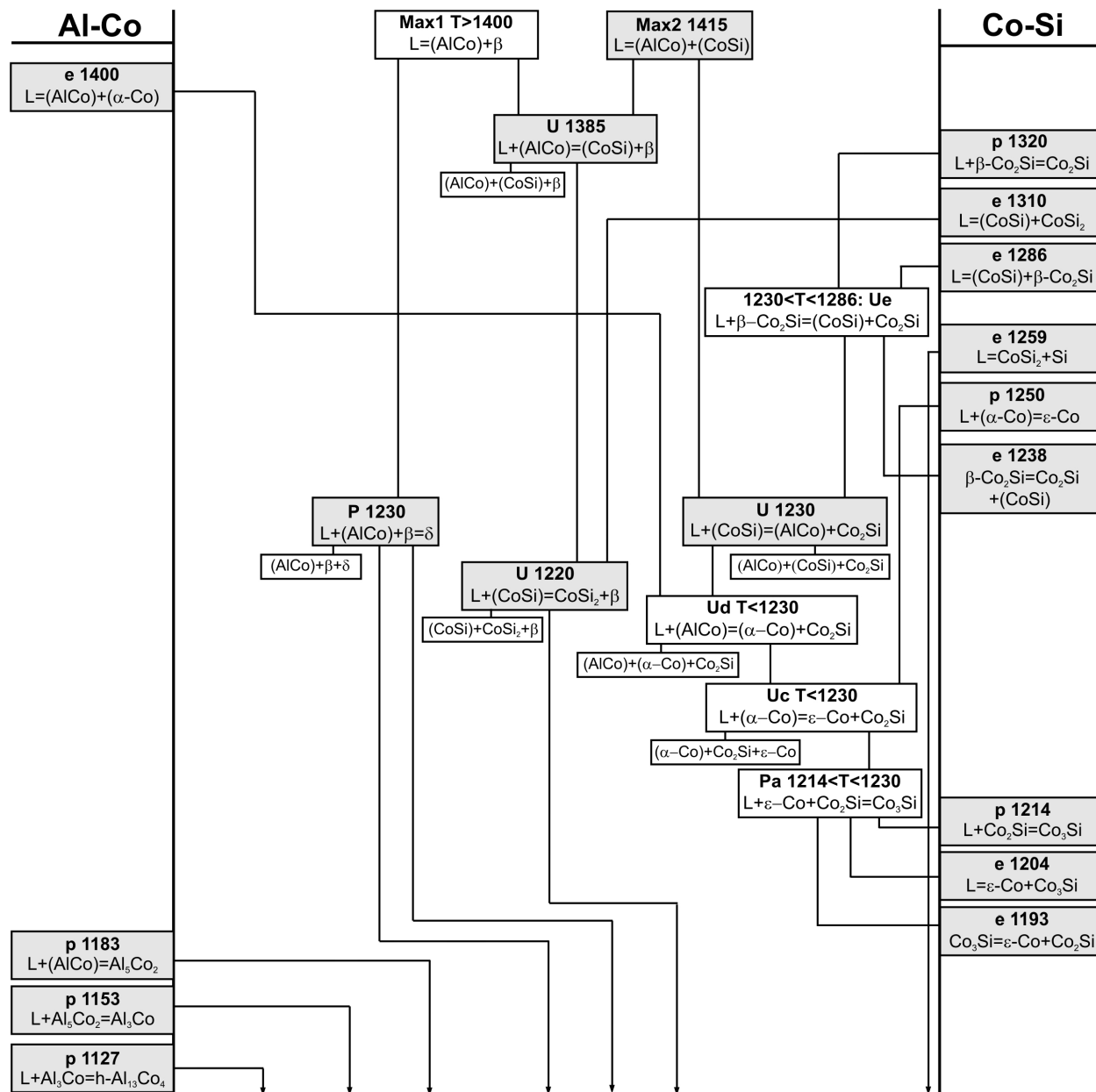
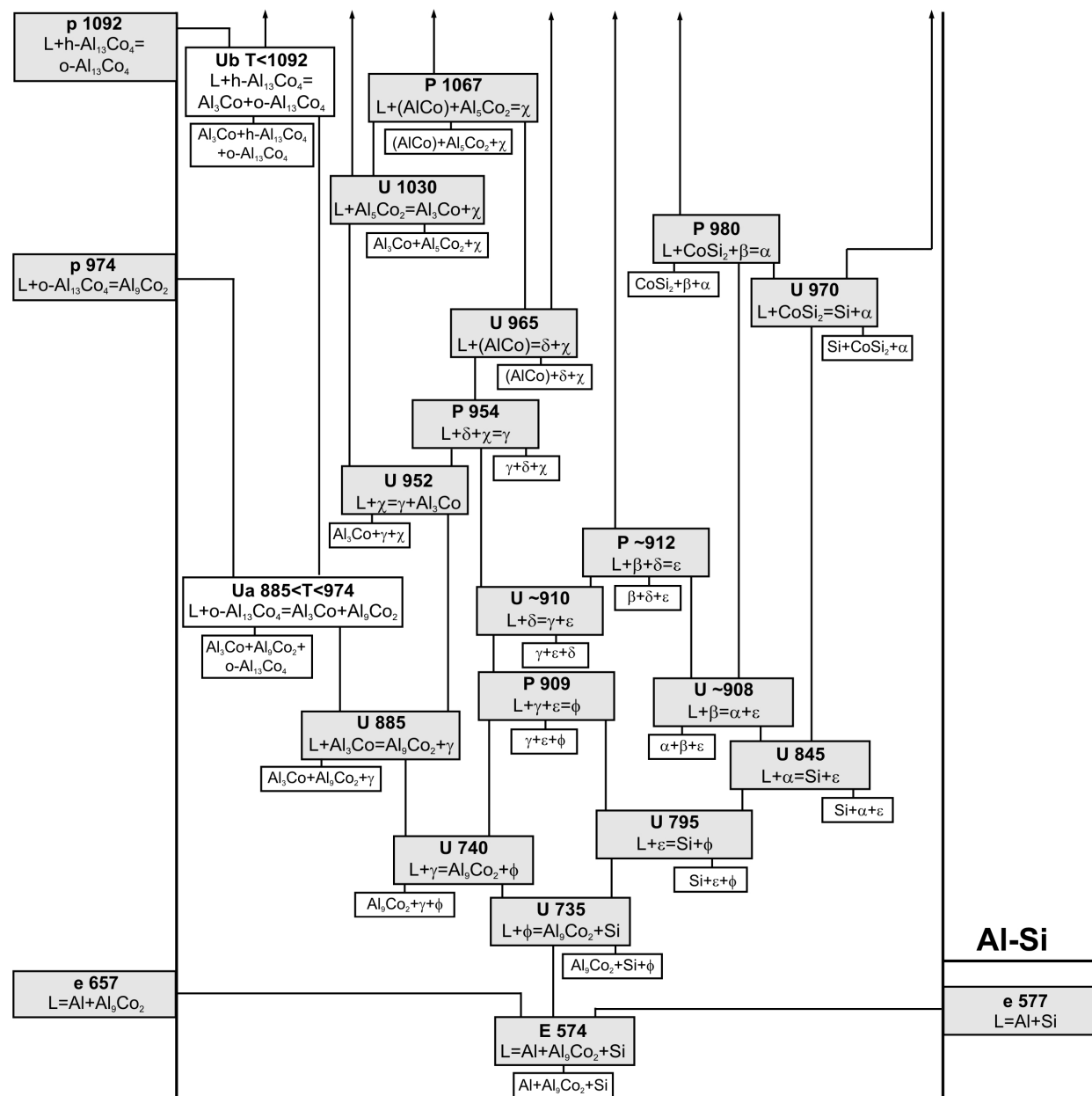


Figure 28: Ternary reaction scheme (Scheil diagram) of the Al-Co-Si system. Gray fields: measured reaction temperatures, white fields: estimated reaction temperatures.



In a very narrow composition- and temperature range between 908 and 912 °C there is a cascade of four invariant reactions and the exact separation of them in the DTA measurement was not possible. The ternary phases α , γ , δ , ϵ , ϕ and χ decompose peritectically at temperatures between 909 and 1230 °C. The β -phase melts congruently at a temperature above 1400 °C, but the exact melting point was not measured due to determination limits at these high temperatures. To prove the assumption of a congruent melting point of β , as cast samples were investigated in the composition range of the β -phase. The results do not show any evidence for peritectic melting behaviour of β .

The interpretation of the ternary phase reactions near the binary Co-Si system was quite complicated: in the vertical section at 60 at.% Co we measured unambiguously invariant effects at 1230 °C in samples situated in the three phase field [(AlCo)+(CoSi)+(Co₂Si)]. This reaction we interpreted to be $L + (\text{CoSi}) = (\text{AlCo}) + \text{Co}_2\text{Si}$. Based on this reaction we propose that the transition reaction $L + (\text{AlCo}) = (\alpha\text{-Co}) + \text{Co}_2\text{Si}$ takes place underneath and the three phase field $L + (\text{AlCo}) + (\alpha\text{-Co})$ evolving from this reaction leads to the binary eutectic reaction $L = (\text{AlCo}) + (\alpha\text{-Co})$ at 1400 °C. Consequently below 1230 °C and very near to the binary Co-Si system the transition reaction $L + (\alpha\text{-Co}) = \epsilon\text{-Co} + \text{Co}_2\text{Si}$ and the peritectic reaction $L + \epsilon\text{-Co} + \text{Co}_2\text{Si} = \text{Co}_3\text{Si}$ connect the ternary system with the binary Co-Si system.

All liquidus values determined by DTA were combined with literature data for the limiting binary phase diagrams to yield a liquidus surface projection of the whole system. The corresponding diagram in Figure 29 shows the liquidus isotherms between 700 and 1600 °C as dotted lines. The liquidus valleys that separate the different fields of primary crystallization are shown as solid lines with arrows indicating the direction toward lower temperature. The compositions of the liquid phase in the various ternary invariant reactions listed in Table 17 are shown as circles in Figure 29. To gain additional knowledge on the primary crystallization several samples were analyzed after DTA-measurement, but these investigations have not been successful. The samples crossed several invariant reactions when cooling slowly in the DTA and the primary solidification cannot be seen. Samples directly after arc melting could bring better results but these attempts have not been done. Anyhow, we gained sufficient liquidus temperatures by the DTA-measurements to construct the liquidus surface projection.

Results and Discussion

The liquidus surface is dominated by the two large fields of primary solidification of the high melting compound (AlCo) and of Si. The primary crystallization fields of (CoSi₂), (CoSi), β and (α -Co) show a considerable dimension. In the Al-rich corner of the phase diagram the fields of primary solidification of the various phases change within a narrow composition range. One of the two maxima we found to exist is situated in the saddle between the (AlCo) and β primary crystallization field, the other maximum is located between the (AlCo) and (CoSi) primary crystallization fields. The latter maximum can be interpreted as quasi-binary eutectic reaction $L=(\text{AlCo})+(\text{CoSi})$ (cf. Figure 27 (a); section at 50 at% Co). The other maximum $L=(\text{AlCo})+\beta$ is a result of the reaction scheme and we estimate the temperature to be above 1400 °C. The proposed congruent melting point of β was not determined exactly but it is estimated to be around the composition Al₂₆Co₄₀Si₃₄ at a temperature of approximately 1450 °C.

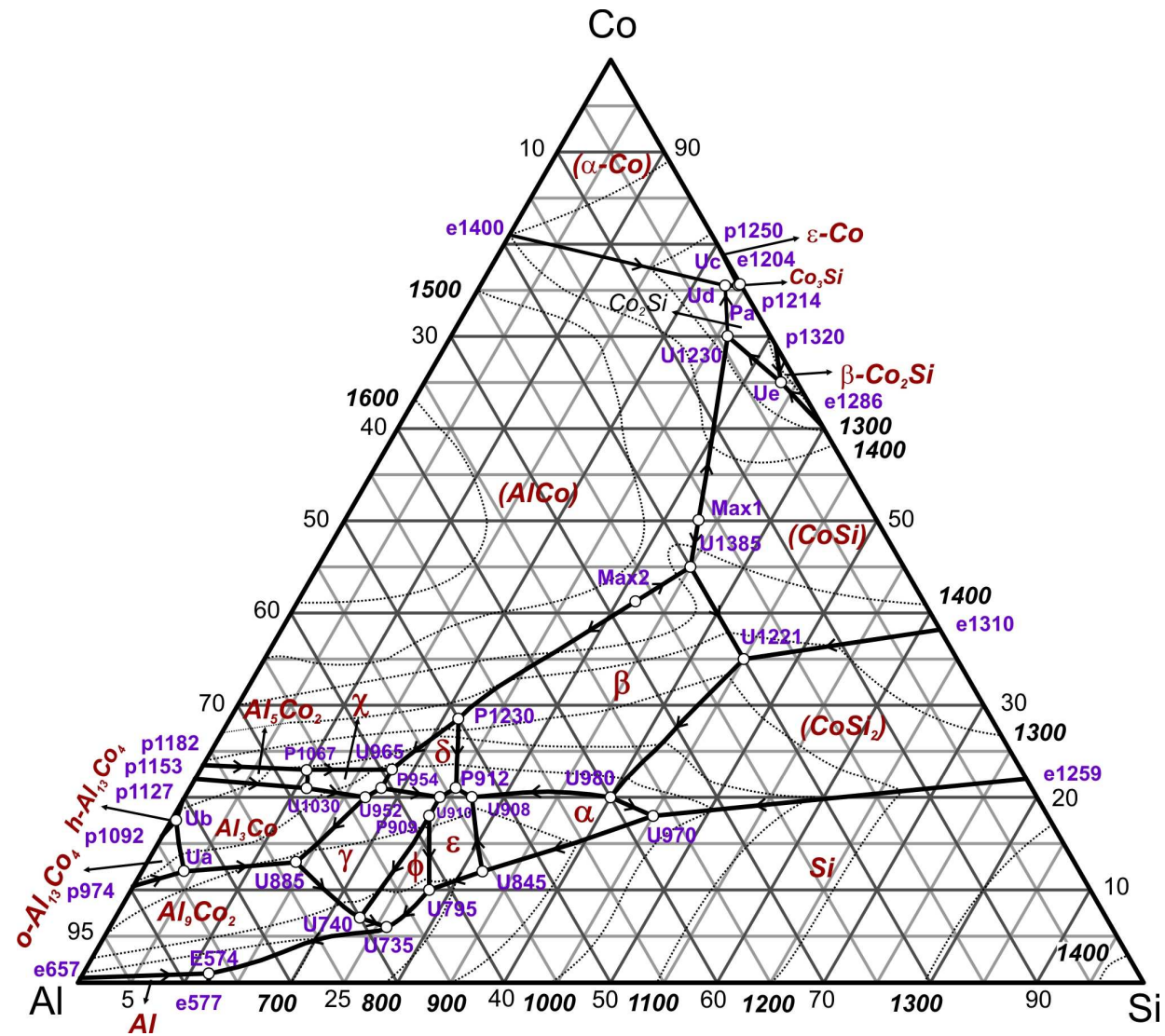


Figure 29: Liquidus surface projection of Al-Co-Si including fields of primary crystallisation. Solid lines: liquidus valleys; dotted lines: isotherms; circles: invariant points.

5.2. The Al-Si-V system

The results in the Al-Si-V system include isothermal sections at 500 and 620 °C in the Al-rich part and at 850 and 1300 °C in the V-rich part. In course of these studies the new ternary phase τ was discovered. Vertical sections at 10, 20, 35 and 50 at.% V were investigated by DTA-measurements leading to a reaction scheme and a liquidus surface projection of the entire ternary system. In Figure 30 all investigated samples are shown with the respective annealing temperature. For the construction of the isothermal sections only selected samples were determined by means of EPMA measurements.

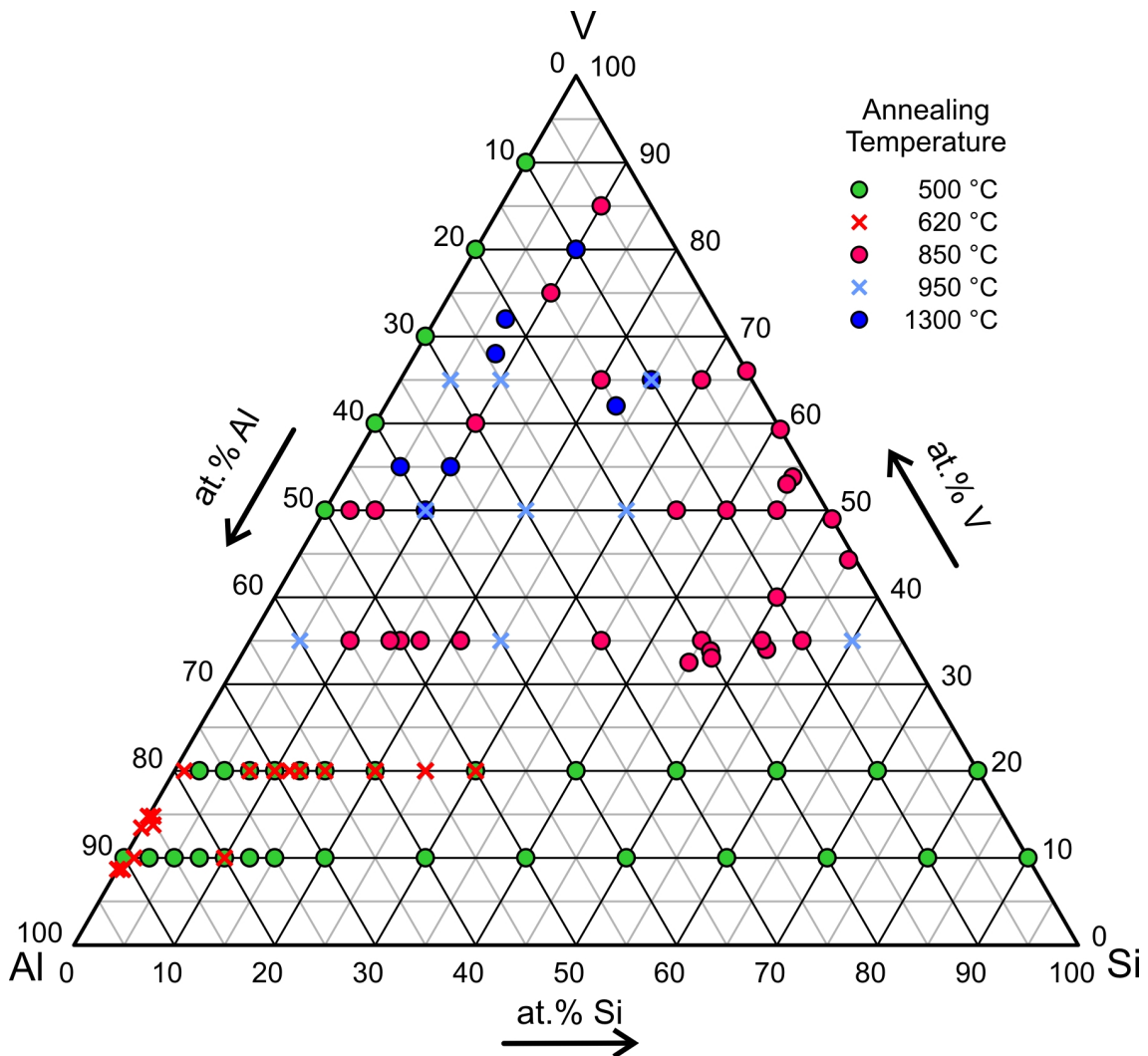
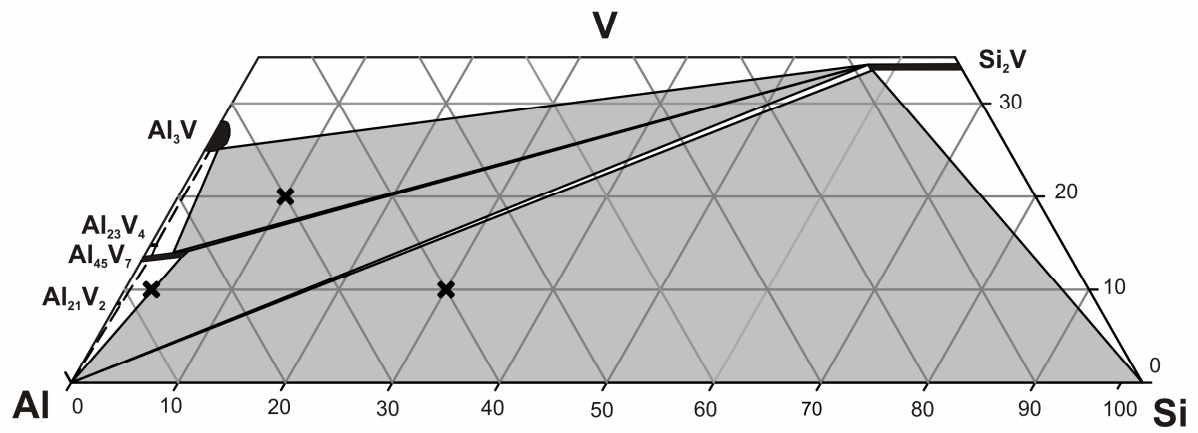


Figure 30: Investigated samples in the Al-Si-V system.

5.2.1. Isothermal sections at 500 and 620 °C

The partial isothermal sections at 500 and 620 °C constructed based on XRD and EPMA measurements are shown in Figure 31 and Figure 32, respectively. The corresponding compositions in the different phase fields are given in Table 18. The solubility of the other elements in (Al) and (Si) can be considered to be insignificant. The phase equilibria in the V-poor part of the phase diagram differ from those given by former authors. Gebhardt and Josef [62] proposed that Al_{23}V_4 is the phase with the highest solubility in the ternary and that Al_{45}V_7 does not show any solubility of Si. Correspondingly, the authors found Al_{23}V_4 in equilibrium with Si_2V and proposed the existence of the three-phase fields $[(\text{Al})+\text{Al}_{23}\text{V}_4+\text{Si}_2\text{V}]$ and $[\text{Al}_3\text{V}+\text{Al}_{23}\text{V}_4+\text{Si}_2\text{V}]$. According to our own investigations however, Al_{45}V_7 is the phase with the highest solubility for Si (up to 3.7 at.% at 620 °C), and, as a consequence, this phase is found in equilibrium with Si_2V . The three-phase fields $[(\text{Al})+\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}]$ and $[\text{Al}_3\text{V}+\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}]$ were found at 500 as well as at 620 °C. The substitution of Al by Si in monoclinic Al_{45}V_7 causes a change of the lattice parameters from $a = 25.604(14)$ Å, $b = 7.6213(13)$ Å, $c = 11.081(12)$ Å and $\beta = 128.92^\circ$ in the binary [25] to $a = 25.5395(12)$ Å, $b = 7.6331(4)$ Å, $c = 11.0433(7)$ Å and $\beta = 128.979(3)^\circ$ in the limiting solubility. For the hexagonal phase Si_2V , which was found to dissolve up to 8.5 at.% Al, the cell parameters increase from $a = 4.562(3)$ Å and $c = 6.359(4)$ Å [25] in the binary to $a = 4.6054(1)$ and $c = 6.4276(2)$ at the ternary composition limit. We did not find relevant solubility of Si in Al_{21}V_2 and Al_{23}V_4 : Al_{21}V_2 was not found in any of the ternary samples and even the sample with only 0.5 at.% Si ($\text{Al}_{90.8}\text{Si}_{0.5}\text{V}_{8.7}$) contained no Al_{21}V_2 . Thus the three-phase field $[(\text{Al})+\text{Al}_{21}\text{V}_2+\text{Al}_{45}\text{V}_7]$ does not show any significant extension in the ternary. Al_{23}V_4 was found in a sample with 0.5 at.% Si, but not in a sample with 1.0 at.% Si (cf. Table 18). An extended illustration of the phase equilibria in the vicinity of the binary Al-V system is shown in Figure 32 (b). The composition of the liquid phase occurring in the section at 620 °C (Figure 32) was not determined by EPMA, but only estimated based on the binary Al-Si phase diagram and our liquidus surface projection (see section 5.2.5.). Therefore the tie triangles $[\text{L}+(\text{Si})+\text{Si}_2\text{V}]$ and $[\text{L}+(\text{Al})+\text{Si}_2\text{V}]$ are shown in dashed lines in Figure 32. In Figure 33 BSE images of samples annealed at 500 and 620 °C showing the three-phase fields of $[(\text{Al})+(\text{Si})+\text{Si}_2\text{V}]$, $[(\text{Al})+\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}]$ and $[\text{Al}_3\text{V}+\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}]$ are given.



**Figure 31: Partial isothermal section through the Al-Si-V system at 500 °C.
Crosses: nominal composition of the samples investigated by EPMA.**

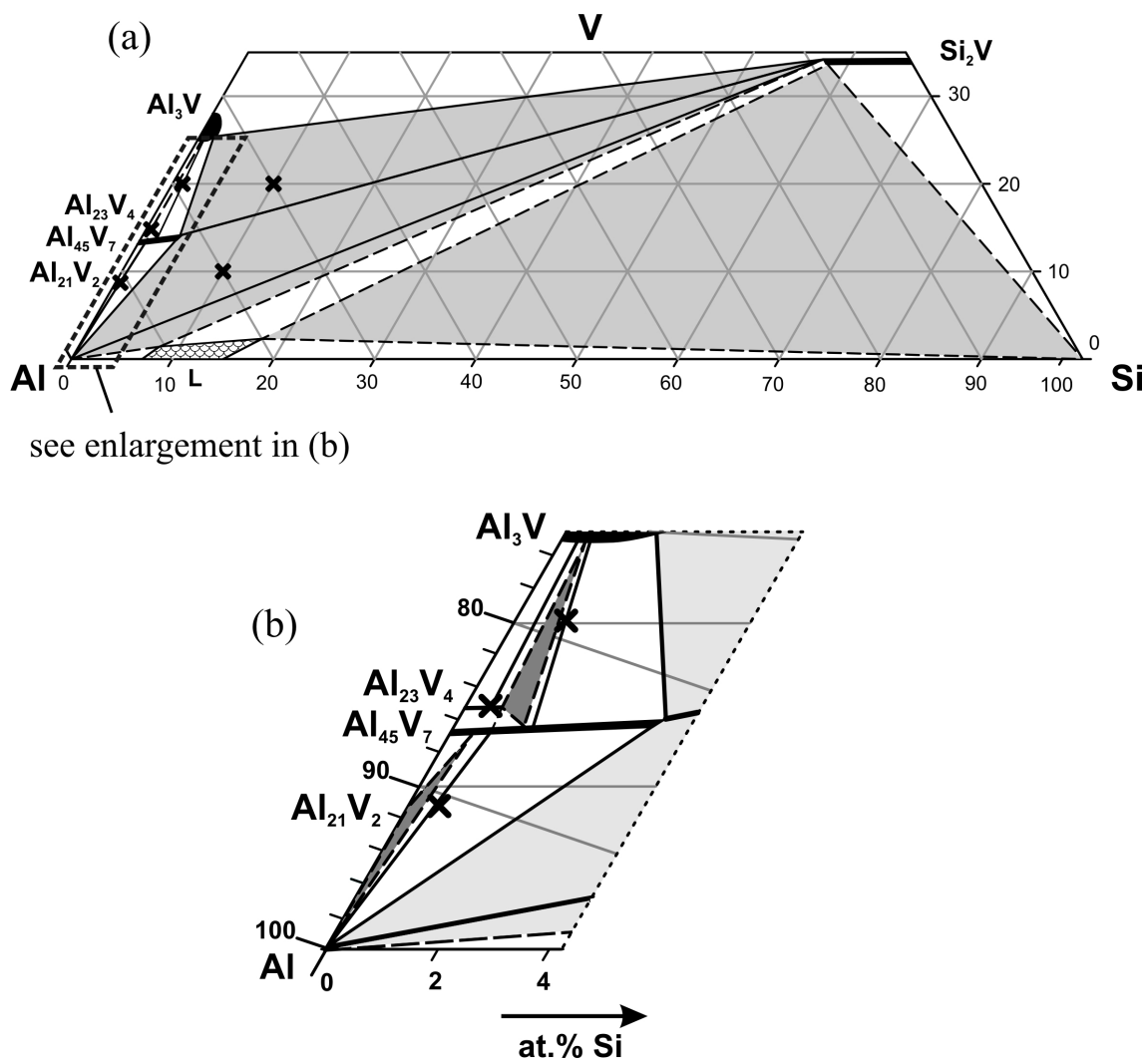


Figure 32: Partial isothermal section through the Al-Si-V system at 620 °C. Crosses: nominal composition of the samples investigated by EPMA. (b) Enlargement of the Al-rich corner.

Table 18: Phase composition in various samples in the Al-Si-V system annealed at 500 and 620 °C determined by EPMA.

Nominal sample composition	T / °C of annealing	Phase field	Phase composition by EPMA /at. %			
				Al	Si	V
$\text{Al}_{60}\text{Si}_{30}\text{V}_{10}$	500	[(Al)+(Si)+ Si_2V]	(Al)	100	0.0	0.0
			(Si)	0.0	100	0.0
			Si_2V	8.4(1)	58.0(1)	33.6(1)
$\text{Al}_{70}\text{Si}_{10}\text{V}_{20}$	500	[$\text{Al}_3\text{V}+\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}$]	Si_2V	8.5(2)	57.3(4)	34.2(4)
			Al_{45}V_7	83.9(1)	2.6(2)	13.5(1)
			Al_3V	73.7(1)	1.2(1)	25.1(1)
$\text{Al}_{87.5}\text{Si}_{2.5}\text{V}_{10}$	500	[(Al)+ Al_{45}V_7]	(Al)	100	0.0	0.0
			Al_{45}V_7	85.6(1)	0.7(1)	13.7(1)
$\text{Al}_{80}\text{Si}_{10}\text{V}_{10}$	620	[(Al)+ $\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}$]	(Al)	100	0.0	0.0
			Al_{45}V_7	82.2(3)	3.7(1)	14.1(3)
			Si_2V	8.5(2)	57.3(4)	34.2(4)
$\text{Al}_{70}\text{Si}_{10}\text{V}_{20}$	620	[$\text{Al}_3\text{V}+\text{Al}_{45}\text{V}_7+\text{Si}_2\text{V}$]	Al_3V	73.2(1)	1.4(1)	25.4(1)
			Al_{45}V_7	82.3(1)	3.7(1)	14.1(1)
			Si_2V	8.5(2)	57.3(4)	34.2(4)
$\text{Al}_{84.7}\text{Si}_{0.5}\text{V}_{14.8}$	620	[$\text{Al}_3\text{V}+\text{Al}_{23}\text{V}_4$]	Al_3V	--	--	--
			Al_{23}V_4	84.4(2)	0.5(1)	15.2(2)
$\text{Al}_{79}\text{Si}_1\text{V}_{20}$	620	[$\text{Al}_3\text{V}+\text{Al}_{45}\text{V}_7$]	Al_3V	74.4(2)	0.6(2)	25.0(4)
			Al_{45}V_7	84.5(3)	1.6(1)	13.9(2)
$\text{Al}_{90.8}\text{Si}_{0.5}\text{V}_{8.7}$	600	[(Al)+ Al_{45}V_7]	(Al)	100	0.0	0.0
			Al_{45}V_7	82.9(2)	3.5(1)	13.6(2)

-- not measured due to fine microstructure

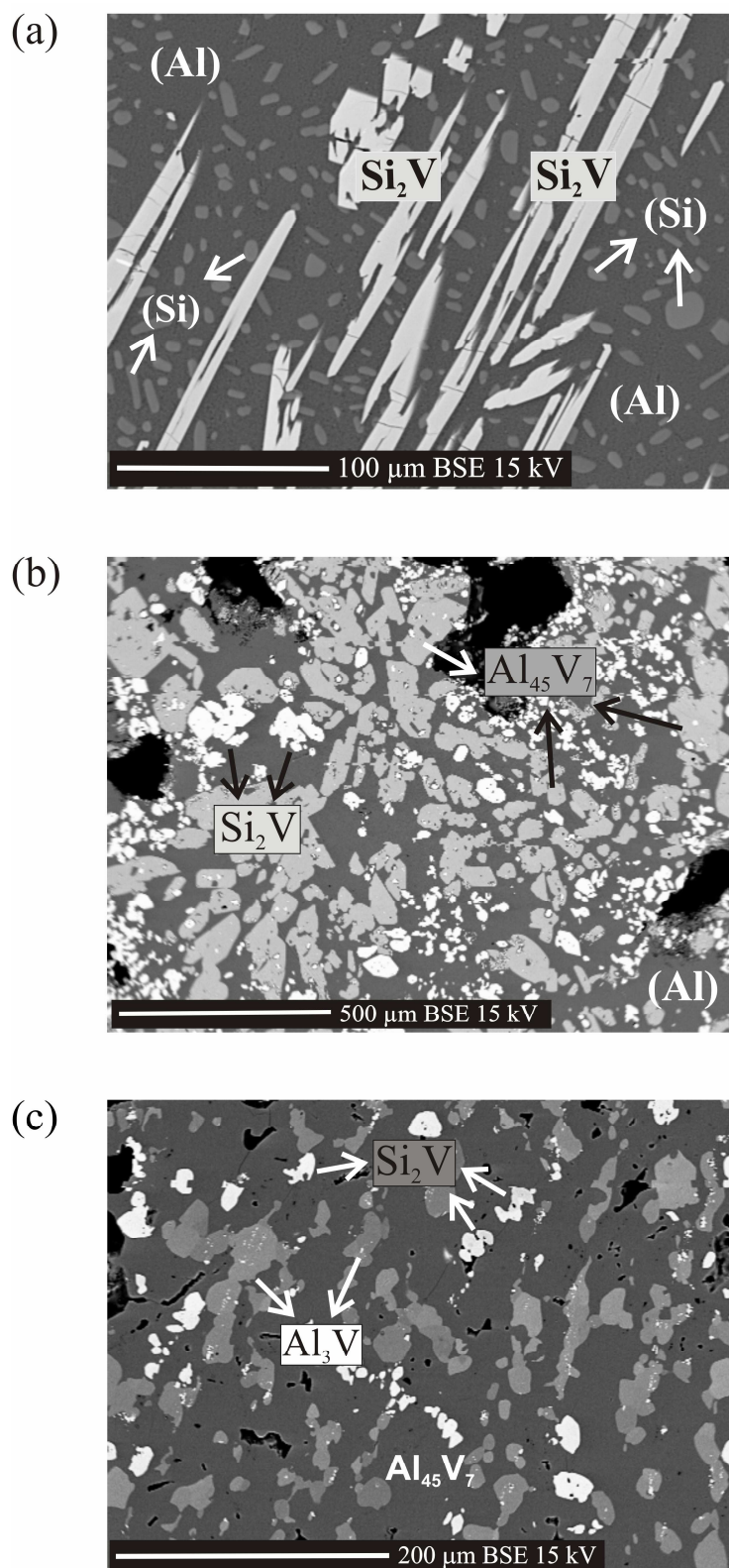


Figure 33: BSE images of the samples (a) $\text{Al}_{60}\text{Si}_{30}\text{V}_{10}$ annealed at 500 °C, (b) $\text{Al}_{80}\text{Si}_{10}\text{V}_{10}$ annealed at 620 °C and (c) $\text{Al}_{70}\text{Si}_{10}\text{V}_{20}$ annealed at 620 °C.

5.2.2. Isothermal section at 850 °C

Phase equilibria at 850 °C were studied in the V-rich part between 35 and 100 at.% V and the resulting partial isothermal section is shown in Figure 34 together with the nominal composition of the samples in the respective three and two phase fields. Table 19 shows the exact phase compositions determined in the various three phase fields of the isothermal section at 850 °C. Similar to the section at 620°C, the composition of the liquid was not measured by EPMA but estimated according to liquidus data for the adjacent binaries and according to our liquidus surface projection of the ternary system (see section 5.2.5.). The most striking difference of our section to previous phase diagram versions is the existence of a new ternary phase τ with the approximate composition $\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$. This phase was found in equilibrium with Al_3V , Si_2V and Si_3V_5 . Details on the crystal structure of this phase are given in section 5.2.4.

The solubility limit of Al in Si_2V at 850 °C was determined to be 5.4 at. % and is considerably lower than the solubility at 620 °C (8.5 at.% Al). Al_3V , Al_8V_5 , and Si_3V_5 show minor solubility in the ternary (in the order of 1-2 at.%). The phase Si_5V_6 does not show any noticeable solubility of Al and the three-phase field [$\text{Si}_2\text{V}+\text{Si}_3\text{V}_5+\text{Si}_5\text{V}_6$] is restricted to a very small area adjacent to the binary Si-V system (Figure 34). The maximal solubility of Al in SiV_3 was measured to be 6.6 at.%. Although Si_3V_5 was reported to be a line compound in the binary, we found considerable differences in the V-content of Si_3V_5 in different ternary samples. Thus we decided to re-investigate the composition limits of binary Si_3V_5 . In the two binary samples with the nominal composition $\text{Si}_{40.7}\text{V}_{59.3}$ and $\text{Si}_{34}\text{V}_{66}$ annealed at 850 °C we found the phase ranging between 61.3 and 63.2 at.% V. The homogeneity range of Si_3V_5 can also be seen by the slight variation of the cell parameters in the two different two-phase fields [$\text{SiV}_3+\text{Si}_3\text{V}_5$] and [$\text{Si}_3\text{V}_5+\text{Si}_5\text{V}_6$]. The cell parameters of V-rich and V-poor tetragonal Si_3V_5 determined by powder XRD are $a = 9.4245(1) \text{ \AA}$, $c = 4.7573(1) \text{ \AA}$ and $a = 9.4305(1) \text{ \AA}$, $c = 4.7538(1) \text{ \AA}$, respectively. In the V-richer part we observed the three phase fields [$\text{Al}_8\text{V}_5+\text{SiV}_3+\text{Si}_3\text{V}_5$] and [$\text{Al}_8\text{V}_5+\text{SiV}_3+(\text{V})$] and the large two phase region of [$\text{SiV}_3+(\text{V})$]. Samples located in the two phase field [$\text{SiV}_3+(\text{V})$] exhibit a very fine microstructure which makes the measurement of the composition of the respective phases by means of EPMA impossible. In XRD-measurements the presence of the phases SiV_3 and (V) were measured unambiguously and the cell parameters of the phases were determined by Rietveld refinement. Vegard's law was applied to get

information about the composition of the solid solution of Al in (V) in order to fix the tie lines shown in Figure 34. For this purpose the cell parameters of pure vanadium [25] and of $\text{Al}_{45}\text{V}_{55}$ (sample $\text{Al}_{30}\text{Si}_{10}\text{V}_{60}$) were used for linear interpolation. Since the solubility of Si in (V) is very small the variation of the cell parameter can be attributed only to the substitution of the V-atoms by Al-atoms. In Figure 35 the corresponding graph can be seen.

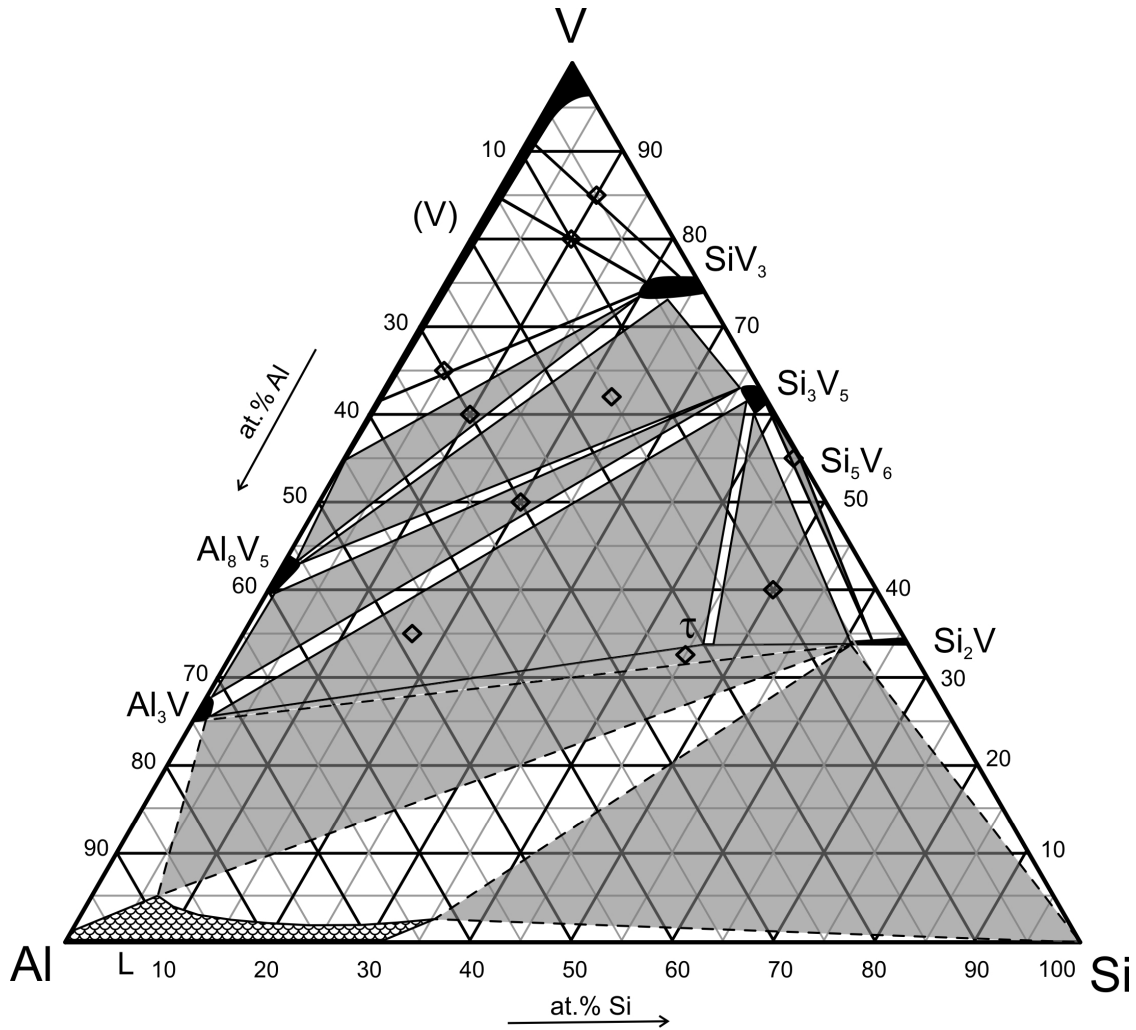


Figure 34: Isothermal section through the Al-Si-V system at 850 °C. Diamonds: nominal composition of the samples investigated by EPMA.

Table 19: Phase composition in various three-phase fields of the Al-Si-V system annealed at 850 °C determined by EPMA.

Nominal sample composition	Phase field		Phase composition by EPMA / at. %		
			Al	Si	V
Al _{22.5} Si ₄₅ V _{32.5}	[Al ₃ V+Si ₂ V+ τ]	Al ₃ V	72.6(3)	1.9(4)	25.5(2)
		Si ₂ V	--	--	--
		τ	19.5(1)	46.6(1)	33.9(1)
Al ₄₈ Si ₁₇ V ₃₅	[Al ₃ V+Si ₃ V ₅ + τ]	Al ₃ V	72.0(3)	1.8(4)	25.6(4)
		Si ₃ V ₅	1.8(4)	37.2(4)	61.0(5)
		τ	20.1(3)	45.9(4)	34.0(2)
Al ₁₀ Si ₅₀ V ₄₀	[Si ₂ V+Si ₃ V ₅ + τ]	Si ₂ V	5.4(2)	60.8(3)	33.8(1)
		Si ₃ V ₅	1.7(4)	39.1(4)	59.2(3)
		τ	19.1(1)	47.2(2)	33.7(1)
Al _{0.7} Si _{44.3} V ₅₅	[Si ₂ V+Si ₃ V ₅ +Si ₅ V ₆]	Si ₂ V	3.1(2)	62.5(3)	34.4(2)
		Si ₃ V ₅	0.1(1)	38.7(3)	60.2(2)
		Si ₅ V ₆	0.0(1)	45.5(3)	54.5(2)
Al ₃₀ Si ₂₀ V ₅₀ *	[Al ₃ V+Al ₈ V ₅ +Si ₃ V ₅]	Al ₃ V	71.6(5)	0.6(4)	27.8(6)
		Al ₈ V ₅	59.5(5)	0.9(2)	39.6(3)
		Si ₃ V ₅	1.8(4)	35.2(4)	63.0(4)

Results and Discussion

Nominal sample composition	Phase field		Phase composition by EPMA / at. %		
			Al	Si	V
Al ₁₅ Si ₂₃ V ₃₂	[Al ₈ V ₅ +SiV ₃ +Si ₃ V ₅]	Al ₈ V ₅	55.3(4)	1.7(1)	43.0(5)
		SiV ₃	3.9(4)	23.0(1)	73.1(5)
		Si ₃ V ₅	1.8(1)	35.2(1)	63.0(1)
Al ₇₀ Si ₁₀ V ₂₀	[Al ₈ V ₅ +SiV ₃ +(V)]	Al ₈ V ₅	55.9(2)	1.2(1)	42.9(2)
		SiV ₃	6.6(3)	20.0(8)	73.4(3)
		(V)	44.9(3)	0.3(1)	54.8(2)
Al ₃₀ Si ₅ V ₆₅	[SiV ₃ +(V)]	SiV ₃	--	--	--
		(V)	--	--	--
Al ₁₀ Si ₁₀ V ₈₀	[SiV ₃ +(V)]	SiV ₃	--	--	--
		(V)	--	--	--
Al ₅ Si ₁₀ V ₈₅	[SiV ₃ +(V)]	SiV ₃	--	--	--
		(V)	--	--	--

* annealed at 950 °C

-- not measured due to fine microstructure

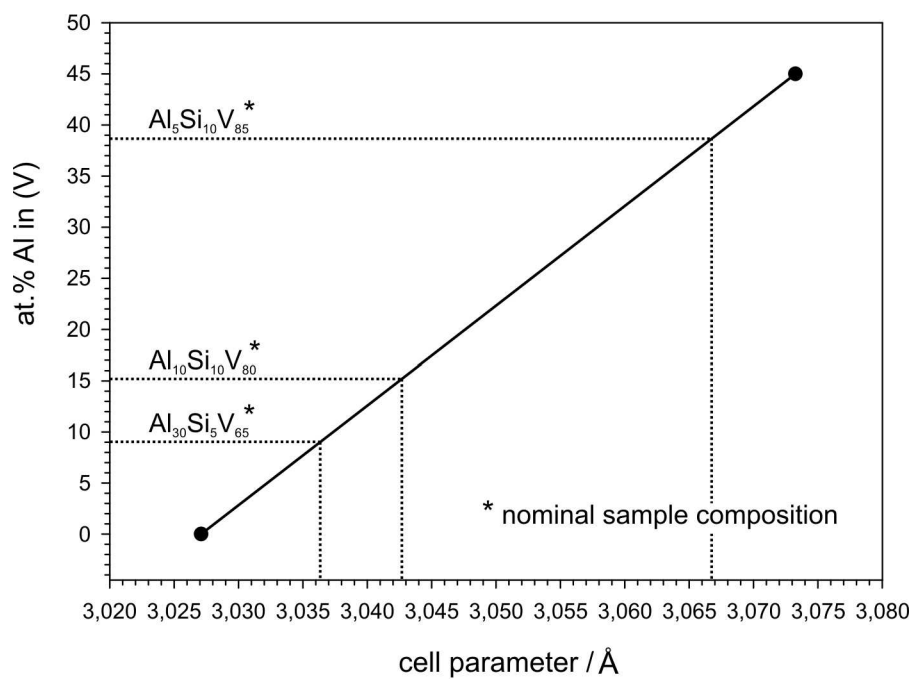


Figure 35: Determination of the Al-concentration in (V) for two-phase samples using lattice parameter interpolation according to Vegard's law.

Results and Discussion

In the binary Si-V system Savickij et al. [10] measured the solubility of SiV_3 to be 24.3-24.7 at.% Si at 800°C. Recently Zhang et al. [49] gave a thermodynamic reassessment of the entire Si-V system and calculated the maximum solubility of SiV_3 to be 20-25 at.% Si at 1837 °C. At a temperature of 900°C the solubility decreases completely. Our results indicate that also the binary phase SiV_3 exhibits certain extension at 850 °C, and not to be so narrow like Zhang et al. [49] calculated in their assessment. So we used the phase boundaries given by Savickij et al. [10] in our sections at 850 °C and 1300 °C as binary reference.

Beside tetragonal Si_3V_5 we found traces (1-5 at.%) of hexagonal Si_3V_5 (Mn_5Si_3 -type) in the ternary samples as well as in the binary Si-V samples. It is well known, that Mn_5Si_3 -type phases may be stabilized by heteroatoms and this was also found to be true for binary Si_3V_5 [40]. In presence of heteroatoms (e.g. O, C, B etc.) these phases bind the atoms in a performed cavity within their crystal structure and are stabilized strongly that way. In this respect we assume that oxygen impurities are responsible for the formation of the hexagonal Si_3V_5 phase. Most likely, these oxygen impurities are due to interstitially solved oxygen in the V used for sample preparation. Since we found the interstitially stabilized Nowotny phase also in the binary Si-V samples it can be ruled out that it is stabilized by Al.

5.2.3. Isothermal section at 1300 °C

The results of our measurements at 1300 °C are shown in Figure 36 and the corresponding compositions determined by means of EPMA are listed in Table 20.

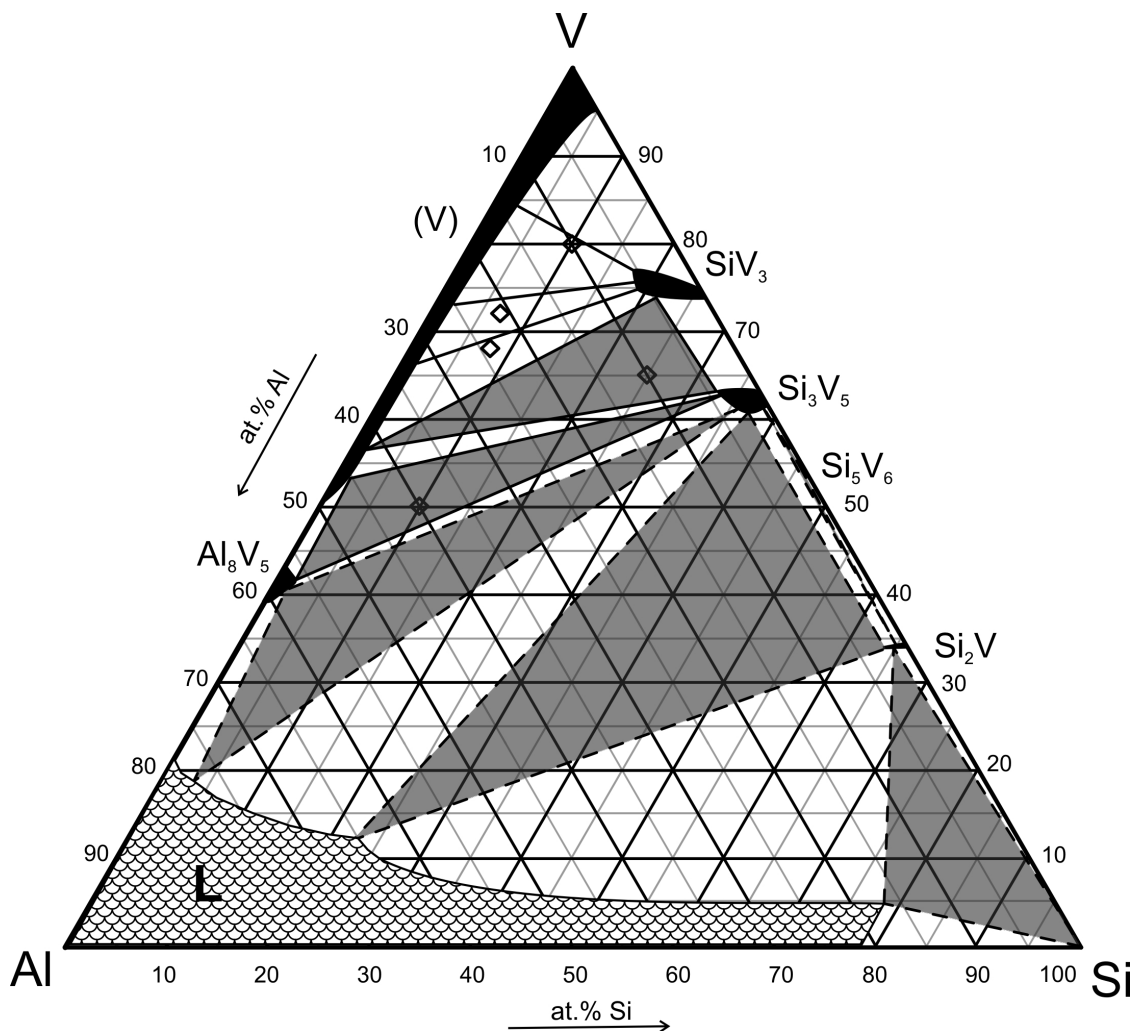


Figure 36: Isothermal section through the Al-Si-V system at 1300 °C. Diamonds: nominal composition of the samples investigated by EPMA.

Table 20: Phase composition in various samples of the Al-Si-V system annealed at 1300 °C determined by EPMA.

Nominal sample composition	T / °C of annealing	Phase field	Phase composition by EPMA /at. %			
				Al	Si	V
Al ₄₀ Si ₁₀ V ₅₀	1300	[Al ₈ V ₅ +Si ₃ V ₅ +(V)]	Al ₈ V ₅	56.4(5)	2.0(2)	41.6(4)
			Si ₃ V ₅	3.5(1)	33.7(1)	62.8(2)
			(V)	45.2(4)	1.6(2)	53.2(7)
Al ₁₀ Si ₂₅ V ₆₅	1300	[SiV ₃ +Si ₃ V ₅ +(V)]	SiV ₃	4.7(1)	21.5(2)	73.8(1)
			Si ₃ V ₅	4.1(1)	32.8(4)	63.1(1)
			(V)	42.2(3)	1.4(2)	56.4(2)
Al ₂₄ Si ₈ V ₆₈	1300	[SiV ₃ +(V)]	SiV ₃	6.2(1)	19.1(1)	74.7(2)
			(V)	32.0(1)	1.7(1)	66.3(1)
Al ₂₁ Si ₇ V ₇₂	1300	[SiV ₃ +(V)]	SiV ₃	6.1(6)	18.4(9)	75.5(8)
			(V)	24.6(1)	1.8(1)	73.6(1)
Al ₁₀ Si ₁₀ V ₈₀	1300	[SiV ₃ +(V)]	SiV ₃	5.3(4)	17.8(9)	76.9(7)
			(V)	13.5(1)	2.1(1)	84.4(1)

Results and Discussion

In contrast to the isothermal section at 850 °C one can see, that the three phase fields $[\text{Al}_8\text{V}_5+\text{Si}_3\text{V}_5+(\text{V})]$ and $[\text{SiV}_3+\text{Si}_3\text{V}_5+(\text{V})]$ exist. This result is in accordance with the work of Müller [63], who determined the V-rich part of the ternary Al-Si-V-system at 1000 °C. Annealing experiments were done to confirm that our results at 850 and at 1300 °C are equilibrium situations and that a solid-solid transition reaction $\text{Si}_3\text{V}_5+(\text{V})=\text{Al}_8\text{V}_5+\text{SiV}_3$ takes place above 850 °C. On the one hand the sample $\text{Al}_{15}\text{Si}_{23}\text{V}_{62}$ annealed at 850 °C exhibiting the phases Al_8V_5 , SiV_3 and Si_3V_5 was annealed at 1180 °C for three weeks. Subsequent EPMA measurements proved that the three phases SiV_3 , Si_3V_5 and (V) were formed. On the other hand a sample with the same overall composition annealed at 1300 °C and therefore exhibiting the phases SiV_3 , Si_3V_5 and (V) in large grains, was annealed at 850 °C for seven weeks. XRD-measurements of this sample however did still show the same phases. With the assumption that the respective reaction $\text{Si}_3\text{V}_5+(\text{V})=\text{Al}_8\text{V}_5+\text{SiV}_3$ is hindered kinetically due to long diffusion distances in the coarse microstructure of the sample, the same sample was powdered, pressed to a pellet and again annealed at 850 °C for five weeks. After this procedure the phase Al_8V_5 was formed and (V) was not longer found. In an attempt to further specify the temperature of the solid state transition reaction, the sample $\text{Al}_{40}\text{Si}_{10}\text{V}_{50}$ was annealed at 950 °C directly after arc melting. It showed the phases Al_8V_5 , Si_3V_5 and (V), indicating the equilibrium above the transition reaction. The two situations after annealing at 850 °C and 950 °C are shown in Figure 37. By means of DTA-measurements we tried to determine the exact reaction temperature but since solid-state reactions generally show only small heat effects and the transition is presumably very slow, this was not possible. Considering our measurements and the results given in [63] we conclude that the reaction takes place between 850 and 950 °C.

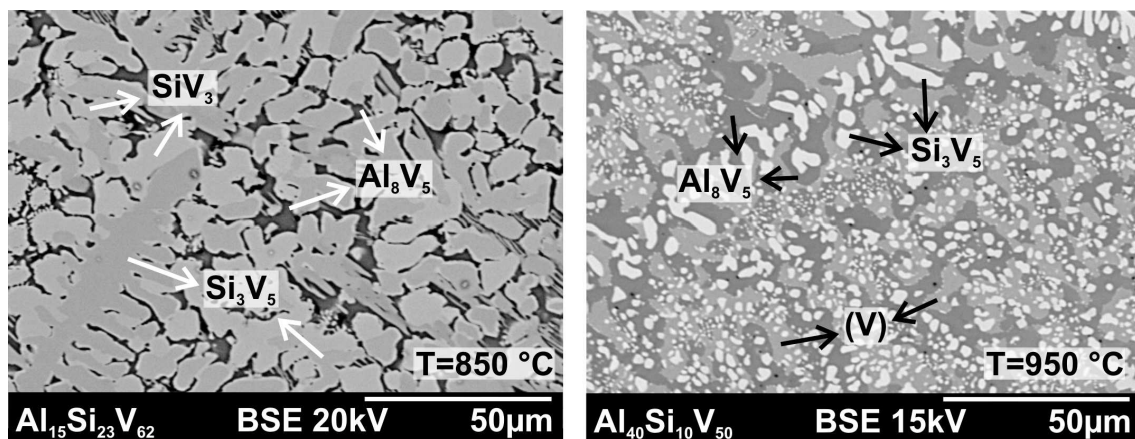


Figure 37: Back scattered electron image of the samples $\text{Al}_{15}\text{Si}_{23}\text{V}_{62}$ and $\text{Al}_{40}\text{Si}_{10}\text{V}_{50}$ annealed at 850 and 950 $^{\circ}\text{C}$.

5.2.4. Crystal structure of τ ($\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$)

The composition of the new compound was determined by means of EPMA and corresponds to the chemical composition $\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$. The structure was determined from powder data. A sample with the nominal composition $\text{Al}_{19.7}\text{Si}_{46.5}\text{V}_{33.8}$ was annealed for four weeks at 850 °C, ground and pressed to a pellet. This pellet was annealed for another two weeks at the same temperature. The powder pattern of this sample was successfully indexed using the TOPAS software [22] and yielded an orthorhombic cell with the cell parameters $a = 8.0856(1) \text{ \AA}$, $b = 4.6921(1) \text{ \AA}$ and $c = 8.4954(1) \text{ \AA}$. Based on the observed cell parameters, the atomic coordinates of TiSi_2 ($Fddd$, $oF24$) [68] was chosen in the starting set for subsequent Rietveld refinements. The refined powder pattern is shown in Figure 38.

Results and Discussion

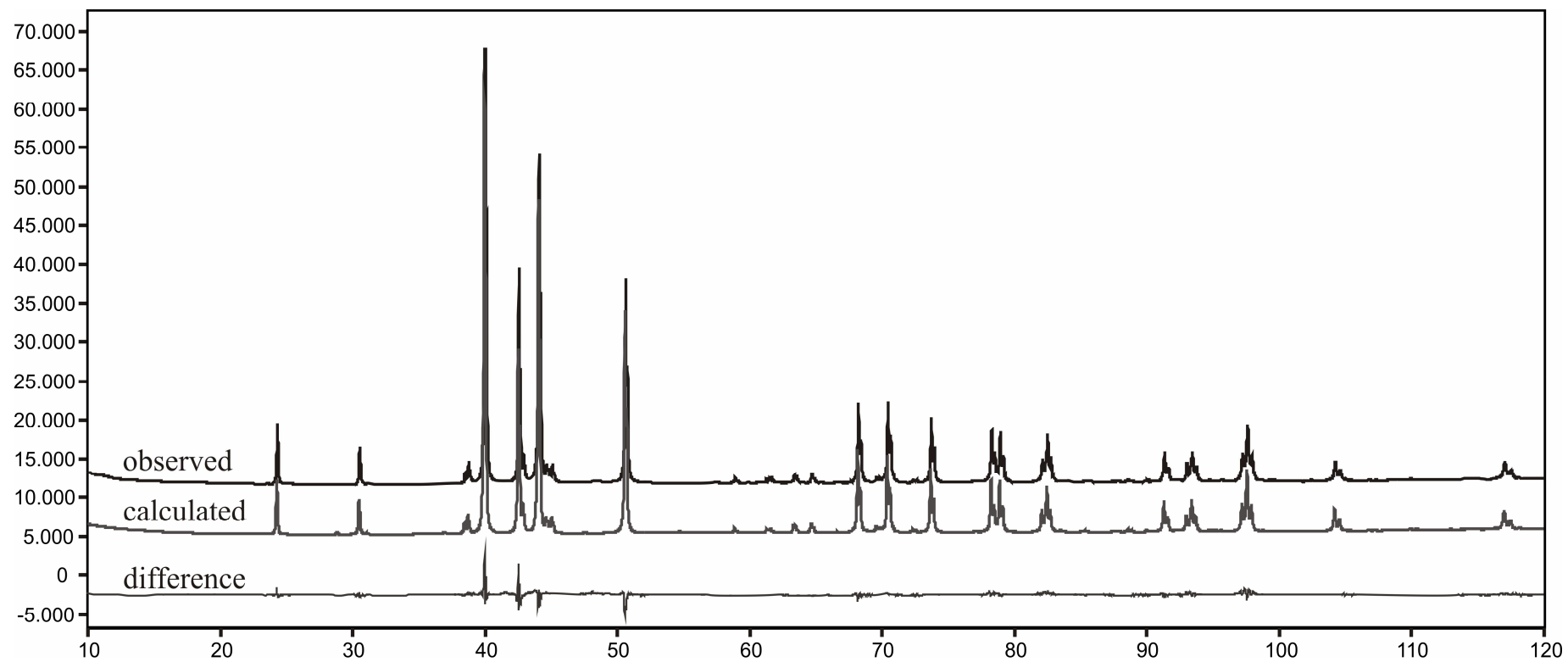


Figure 38: X-ray powder pattern of a sample with the nominal composition $\text{Al}_{19.7}\text{Si}_{46.5}\text{V}_{33.8}$. Black line: measured pattern, gray line: calculated pattern, dark gray line: difference.

Results and Discussion

For additional single crystal XRD, a sample with the nominal composition $\text{Al}_{76}\text{V}_{10}\text{Si}_{14}$ i.e. within the primary crystallization field of τ (compare next section) was prepared in the arc furnace. It was subsequently cooled slowly from 1150 to 1000 °C applying a cooling rate of 0.1 Kmin^{-1} in order to grow single crystals suitable for structure determination. Unit cell parameters were obtained by least-squares refinements of 2 θ values. Corrections for Lorentz polarization and absorption effects (multi-scan method) were applied. The crystal structure was solved by direct methods in the space group *Fddd* and subsequently refined using the SHELXS and SHELXL-97 program packages [69-71]. The results are compiled in Tables 21 and 22. Further details of the crystal structure investigation were deposited in the *Fachinformationszentrum Karlsruhe*¹ under the depository number CSD 420729. The final refinement was performed with neutral atomic scattering functions of V [position 8(*a*)] and Al:Si = 3:7 [position 16(*e*)]. It is to be mentioned that this allocation is based on the chemical composition and on crystal chemical considerations. Due to the special atomic coordinates, a trial refining the crystal structure wrongly with V atoms at position 16(*e*) and Al:Si = 3:7 at position 8(*a*) converged amazingly at $R = 0.022$ and $wR2 = 0.051$ [$U_{\text{iso}} = 0.0107(2)$ for both sites without restriction] which is only moderately increased as compared to the correct refinement (Tables 21 and 22).

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**Table 21: Single crystal X-ray data-collection
and structure refinements of $\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$.**

Empirical formula	$\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$
Crystal system, space group	Orthorhombic, $oF24 / Fddd$
<i>Cell dimensions</i>	
$a / \text{\AA}$	8.091(3)
$b / \text{\AA}$	4.697(2)
$c / \text{\AA}$	8.501(3)
$V / \text{\AA}^3$	323.1(1)
$\rho_{\text{calc}} / \text{g cm}^{-3}; \mu (\text{MoK}\alpha) / \text{mm}^{-1}$	4.37; 6.9
Z	8
Crystal dimensions / μm	60 x 90 x 40
number of images; rotation angle per image / $^\circ$	622; 2
scan mode (at 13 distinct ω -angles)	φ -scans
scan time / s/ $^\circ$; frame size / pixels	195; 621x576
detector-to-sample distance / mm	30
measured reflections	5329
unique reflections (n); reflections with $F_o > 4\sigma(F_o)$	181; 154
$R_{\text{int}} = \Sigma F_o^2 - F_o^2(\text{mean}) / \Sigma F_o^2$	0.028
extinction parameter	0.0098(9)
$R1 = \Sigma (F_o - F_c) / \Sigma F_o$ (181; 154 reflections)	0.019; 0.015
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$	0.041
$\text{GooF} = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n-p) \}^{0.5}$	1.054
max Δ/σ ; number of variable parameters (p)	< 0.001; 10
final difference Fourier map / $\text{e}\text{\AA}^{-3}$	-0.34 to +0.37

$$^* R1 = \Sigma (| |F_o| - |F_c| |) / \Sigma F_o$$

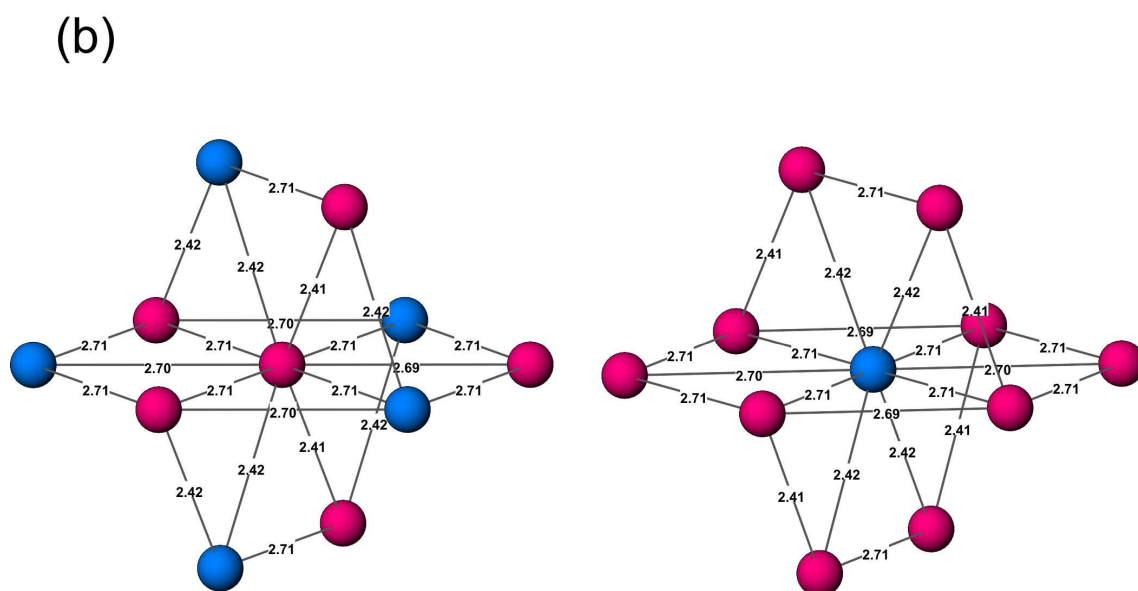
$$^{**} wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$$

Table 22: Fractional atomic coordinates and displacement parameters of $\text{Al}_{0.60}\text{Si}_{1.4}\text{V}$. Origin at -1.

	Wykoff letter	Site symmetry	x	y	z	U_{equiv}
M	16(e)	2..	0.45912(3)	0.125	0.125	0.0075(1)
V	8(a)	222	0.125	0.125	0.125	0.0081(1)

M = 0.3 Al + 0.7 Si

A graphical representation of the structure is given in Figure 39. The crystal structure of $\text{Al}_{0.6}\text{Si}_{1.4}\text{V}$ consists of close-packed *pseudo*-hexagonal layers parallel to (001). Atoms in neighbouring layers are centred above or below the V-M and M-M bonds within the layer, short V-V contacts are avoided within as well as between the layers. Four of these symmetrically equivalent layers form a translation period (stacking sequence ABCD). In this structure type the coordination number of M and V is 10 which can be seen clearly in Figure 39 (b). Each M position (M = Al or Si, respectively) is aligned with the V position in three different bond lengths of 2 x 2.4160 Å, 2 x 2.7069 Å and 1 x 2.6995 Å, respectively. Additionally, the M position is coordinated by M atoms with bond distances of 2 x 2.4139 Å, 2 x 2.7106 Å and 1 x 2.6920 Å. The V position is coordinated by the M atoms with three different bond lengths of 4 x 2.4160 Å, 4 x 2.7069 Å and 2 x 2.6995 Å, respectively. Nowotny [72] investigated the crystallization behaviour of transition metal silicides and found out that there is a connection between the crystal structure and the valence electron concentration (VEC). According to his study silicides with VEC between 4.52 and 5.0 adopt the tetragonal MoSi_2 structure type. Decreasing the VEC the hexagonal CrSi_2 structure is favoured between 4.01 and 4.67 VEC. VSi_2 is an example for this crystal type with a VEC of 4.22. From 4.02 to 4.21 VEC the silicides crystallize mainly in the orthorhombic TiSi_2 -type and the fact that the phase τ with VEC=4.13 exhibits this structure type fits very well to this theory.



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5.2.5. Ternary phase reactions and liquidus surface projection

The ternary phase reactions in the system Al-Si-V were studied by DTA at medium and high temperature in four vertical sections at constant V contents of 10, 20, 35 and 50 at.% V. For regular DTA measurements two heating- and cooling- cycles were performed in each measurement in order to test if equilibrium conditions can be reestablished within the samples at the selected heating/cooling rate of 5 K min⁻¹. Starting temperature was 500, 620 and 850 °C i.e. the respective annealing temperature. The maximum temperature reached in these experiments was 1490 °C. Metastable thermal effects were observed in most samples in the second heating cycles. The experimental data points for thermal effects shown in Figures 40 and 41 (large and small circles as well as crosses) thus represent mainly DTA results obtained on first heating of the annealed samples. The liquidus values (triangles) were evaluated from the heating- and cooling-curves, respectively. The results of our DTA-experiments are given in Table 23. Although minor parts of the sections are not completely covered with experimental data points, the full sections are given in Figures 40 and 41 for the sake of clarity.

Altogether, 13 invariant four-phase equilibria were derived from these data. A summary of these invariant phase reactions including the averaged reaction temperatures and the approximate compositions of the involved phases which were assessed based on a combination of all available experimental data (XRD, EPMA and DTA) is given in Table 24.

The ternary phase reactions proposed by Gebhardt and Joseph [62] differ strongly from our data concerning temperatures and interpretation of the results. One should keep in mind that Gebhardt and Joseph mainly determined their data by means of cooling experiments, only some of their samples were measured using DTA and they report of small temperature effects. The fact that they determined different phase fields at 500 °C results in the different interpretation of the data.

In our study it was possible to determine all invariant reaction temperatures experimentally; the sole exception is the temperature of U₂: $L + Al_{21}V_2 = (Al) + Al_{45}V_7$ which was not found experimentally due to the very small existence range of the phase

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Al_{21}V_2 . This temperature was estimated to be $\sim 664^\circ\text{C}$. The transition reaction U2 and the peritectic decomposition of Al_{45}V_7 (P1: $\text{L} + \text{Al}_3\text{V} + \text{Si}_2\text{V} = \text{Al}_{45}\text{V}_7$) which was determined to be at 745°C can be seen in Figure 40 (a2) which is an enlargement of the very Al rich part of the vertical section at 10 at.% V. In some samples of the vertical section at 20 at.% V we observed small thermal effects which we did not find in the corresponding region in the vertical section at 10 at.% V. These effects do not exhibit any trend allowing rationalization in terms of an equilibrium reaction. Until now it was not possible to process a proper hypothesis to explain these effects. However, we believe that they are not corresponding to any equilibrium reaction in the phase diagram, as they are always small and their position in the ternary sections is not consistent with the rest of the experimental data; i.e. they are found between the invariant reaction P1 and U4 in the section at 20 at.% V, but not in the same region at 10 at.% V. In DTA measurements of the sample $\text{Al}_{30}\text{Si}_{20}\text{V}_{50}$ we found only one invariant effect at 1390°C . The effect corresponding to the invariant reactions U6 at 1224°C is missing. However, the reaction U6 was measured in other samples in the vertical sections at 20 and 35 at.% V as well as in the sample $\text{Al}_{20}\text{Si}_{30}\text{V}_{50}$ (see figures 40 and 41), unambiguously.

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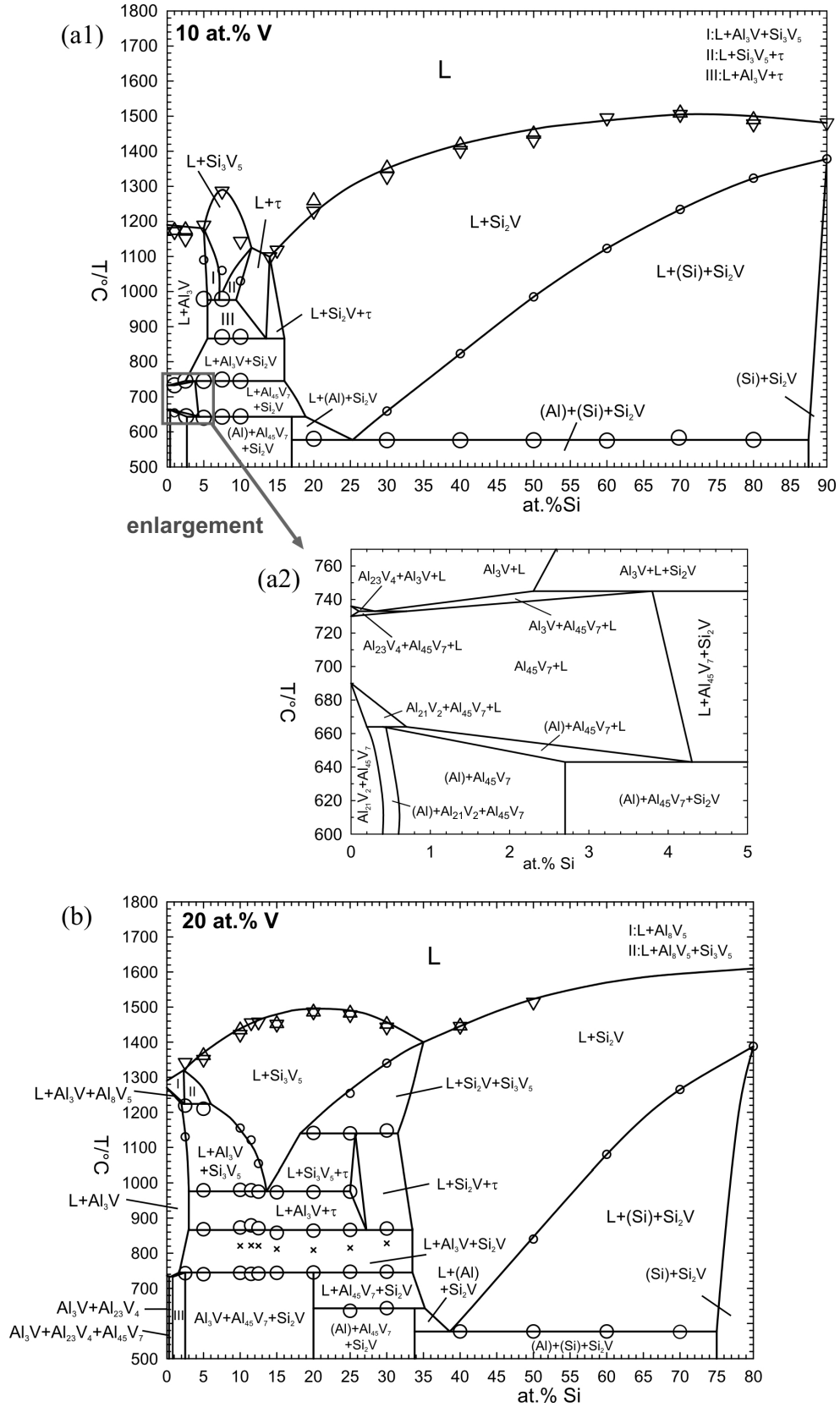


Figure 40: Vertical sections in Al-Si-V at (a) 10 at.% V and (b) 20 at.% V. Large circles: invariant thermal effects; triangles up: liquidus on heating; triangles down: liquidus on cooling; small circles and crosses: other thermal effects.

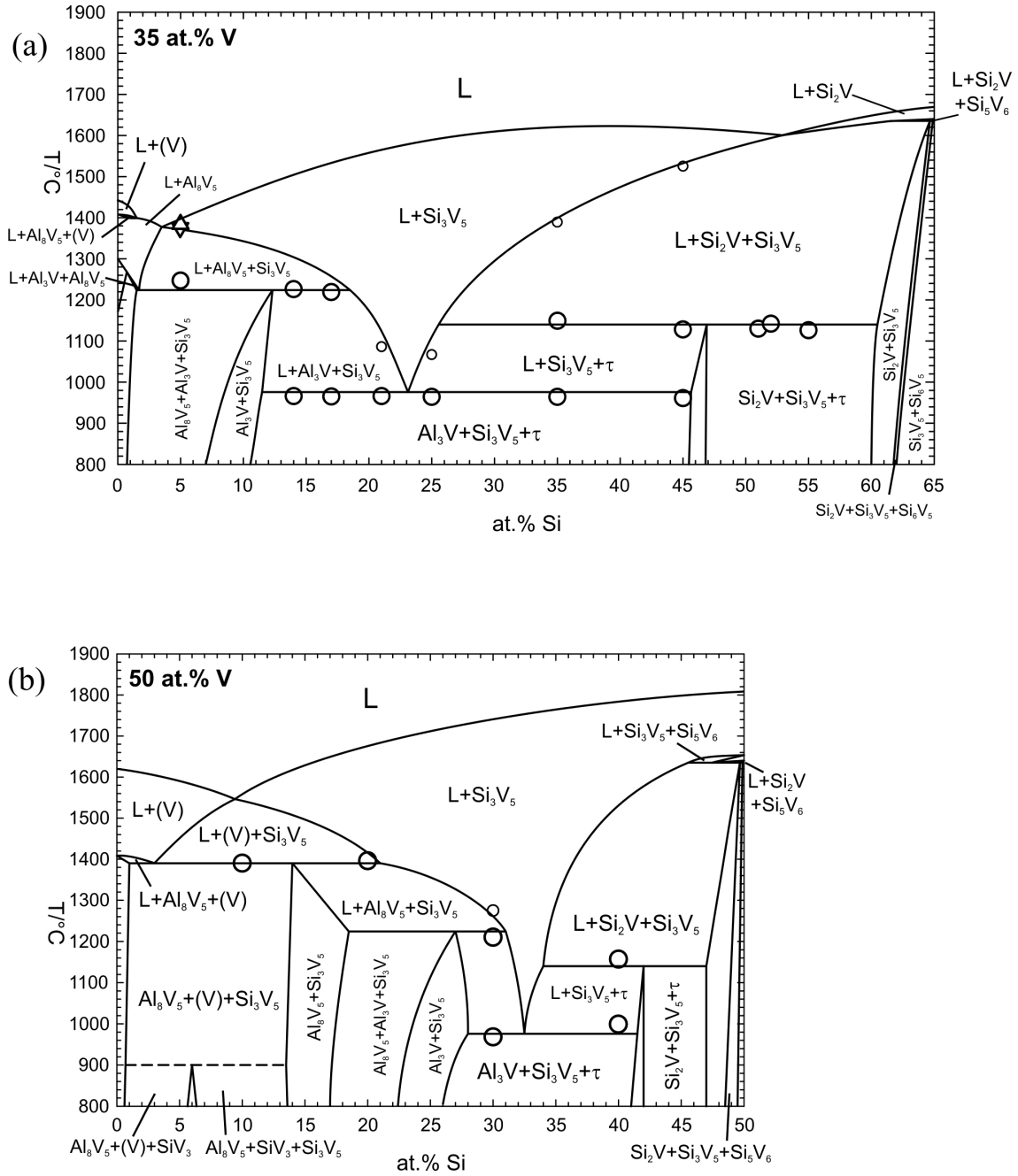


Figure 41: Vertical sections in Al-Si-V at (a) 35 at.% V and (b) 50 at.% V. Large circles: invariant thermal effects; triangles up: liquidus on heating; triangles down: liquidus on cooling; small circles: other thermal effects.

Table 23: Experimental results of the thermal analysis in the Al-Si-V system.
All samples were measured in alumina crucibles at a heating rate of 5 K/min.

Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₈₉ Si ₁ V ₁₀	620, 14d	733	654	1175	1172
Al _{87.5} Si _{2.5} V ₁₀	500, 21d	646, 746		1176	1150
Al ₈₅ Si ₅ V ₁₀	500, 21d	640, 745, 979	1090		1189
Al _{82.5} Si _{7.5} V ₁₀	500, 21d	870, 643, 749, 979	1060		1286
Al ₈₀ Si ₁₀ V ₁₀	500, 21d	644, 745, 871	1030		1143
Al ₇₆ Si ₁₄ V ₁₀	620, 14d				1099
Al ₇₅ Si ₁₅ V ₁₀	620, 14d				1118
Al ₇₀ Si ₂₀ V ₁₀	500, 21d	580		1259	1229
Al ₆₀ Si ₃₀ V ₁₀	500, 21d	576	659	1352	1328
Al ₅₀ Si ₄₀ V ₁₀	500, 21d	576	823	1418	1402
Al ₄₀ Si ₅₀ V ₁₀	500, 21d	576	985	1449	1432
Al ₃₀ Si ₆₀ V ₁₀	500, 21d	575	1123		1495
Al ₂₀ Si ₇₀ V ₁₀	500, 21d	578	1234	1509	1505
Al ₁₀ Si ₈₀ V ₁₀	500, 21d	577	1323	1490	1478
Si ₉₀ V ₁₀	500, 21d		1378		1481
Al _{77.5} Si _{2.5} V ₂₀	500, 21d	743, 1219	1130		1342
Al ₇₅ Si ₅ V ₂₀	500, 21d	740, 868, 979 1210	1228	1362	1351

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Nominal sample composition	Annealing	Invariant effects	Temperature / °C		
			Other effects	Liquidus on heating	Liquidus on cooling
$\text{Al}_{70}\text{Si}_{10}\text{V}_{20}$	500, 21d	744, 873, 980	1155, 821	1435	1422
$\text{Al}_{68.5}\text{Si}_{11.5}\text{V}_{20}$	620, 21d	741, 879, 979	1121, 822		1455
$\text{Al}_{67.5}\text{Si}_{12.5}\text{V}_{20}$	620, 16d	742, 871, 975	1054, 821		1457
$\text{Al}_{65}\text{Si}_{15}\text{V}_{20}$	620, 21d	744, 858, 973	812	1453	1451
$\text{Al}_{60}\text{Si}_{20}\text{V}_{20}$	620, 21d	745, 864, 974, 1141	809	1486	1486
$\text{Al}_{55}\text{Si}_{25}\text{V}_{20}$	620, 21d	636, 747, 866, 975, 1140	1254, 815	1483	1478
$\text{Al}_{50}\text{Si}_{30}\text{V}_{20}$	620, 21d	644, 747, 870, 1148	1340, 828	1451	1443
$\text{Al}_{40}\text{Si}_{40}\text{V}_{20}$	500, 21d	577		1446	1445
$\text{Al}_{30}\text{Si}_{50}\text{V}_{20}$	500, 21d	577	840		1514
$\text{Al}_{20}\text{Si}_{60}\text{V}_{20}$	500, 21d	577	1080		
$\text{Al}_{10}\text{Si}_{70}\text{V}_{20}$	500, 21d	576	1265		
$\text{Si}_{80}\text{V}_{20}$	500, 21d		1388		
$\text{Al}_{60}\text{Si}_5\text{V}_{35}$	950, 14d	1247			1375
$\text{Al}_{51}\text{Si}_{14}\text{V}_{35}$	850, 28d	966, 1226			
$\text{Al}_{29}\text{Si}_{17}\text{V}_{35}$	850, 28d	965, 1219			
$\text{Al}_{44}\text{Si}_{21}\text{V}_{35}$	850, 28d	966	1086		
$\text{Al}_{40}\text{Si}_{25}\text{V}_{35}$	950, 14d	964	1067		
$\text{Al}_{30}\text{Si}_{35}\text{V}_{35}$	850, 28d	964, 1149	1389		
$\text{Al}_{20}\text{Si}_{45}\text{V}_{35}$	850, 28d	961, 1128,	1525		

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Nominal sample composition		Annealing	Invariant effects	Temperature / °C		
				Other effects	Liquidus on heating	Liquidus on cooling
$\text{Al}_{14}\text{Si}_{51}\text{V}_{35}$		850, 28d	1130,			
$\text{Al}_{13}\text{Si}_{52}\text{V}_{35}$		850, 28d	1142			
$\text{Al}_{10}\text{Si}_{55}\text{V}_{35}$		850, 28d	1126			
$\text{Al}_{40}\text{Si}_{10}\text{V}_{50}$		950, 14d	1390			
$\text{Al}_{30}\text{Si}_{20}\text{V}_{50}$		950, 14d	1396			
$\text{Al}_{20}\text{Si}_{30}\text{V}_{50}$		950, 14d	968, 1210	1275		
$\text{Al}_{10}\text{Si}_{40}\text{V}_{50}$		850, 28d	1157	1013		
$\text{Al}_{15}\text{Si}_{23}\text{V}_{62}$	high temperature DTA	850, 15d	1574			
$\text{Al}_{0.7}\text{Si}_{44.3}\text{V}_{55}$	high temperature DTA	850, 15d	1635			

Table 24: Ternary invariant phase reactions determined by DTA in the Al-Si-V system.

Reaction	T / °C	Phase	Composition / at.%		
			Al	Si	V
E1: L=(Al)+(Si)+Si ₂ V	577±1	L	~87.75	~12.15	~0.1
		(Al)	100	0	0
		(Si)	0	100	0
		Si ₂ V	8.6	58.1	33.3
U1: L+Al ₄₅ V ₇ =(Al)+Si ₂ V	643±3	L	~92.0	~6	~2
		Al ₄₅ V ₇	82.5	3.5	14
		(Al)	100	0	0
		Si ₂ V	7.7	59	33.3
U2: L+Al ₂₁ V ₂ =(Al)+Al ₄₅ V ₇	~664	L	~99.3	~0.5	~0.2
		Al ₂₁ V ₂	91.3	0	8.7
		(Al)	100	0	0
		Al ₄₅ V ₇	85.6	0.7	13.7
U3: L+Al ₃ V=Al ₂₃ V ₄ +Al ₄₅ V ₇	733±1	L	~99.2	~0.2	~0.6
		Al ₃ V	74.5	0.5	25
		Al ₂₃ V ₄	84.8	0.4	14.8
		Al ₄₅ V ₇	85.6	0.7	13.7
P1: L+Al ₃ V+ Si ₂ V=Al ₄₅ V ₇	745±5	L	~93.3	~3.6	~3.1
		Al ₃ V	73.4	1.3	25.3
		Si ₂ V	6.6	60.1	33.3
		Al ₄₅ V ₇	82.2	3.7	14.1

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Reaction	T / °C	Phase	Composition / at. %		
			Al	Si	V
U4: $L + \tau = Al_3V + Si_2V$	866±7	L	~87.0	~7.5	~5.5
		τ	19.5	47.2	33.3
		Al_3V	73.4	1.3	25.3
		Si_2V	5.3	61.4	33.3
U5: $L + Si_3V_5 = Al_3V + \tau$	976±3	L	~87.0	~5.5	~7.5
		Si_3V_5	2.0	38.6	59.4
		Al_3V	73.0	2	25
		τ	19.5	47.2	33.3
P2: $L + Si_2V + Si_3V_5 = \tau$	1140±7	L	~74.0	~14	~12
		Si_2V	4.0	62.7	33.3
		Si_3V_5	2.0	38.6	59.4
		τ	19.5	47.2	33.3
U6: $L + Al_8V_5 = Al_3V + Si_3V_5$	1224±2	L	~83.2	~1.8	~15.0
		Al_8V_5	56.6	1.4	42.0
		Al_3V	73.0	2.0	25.0
		Si_3V_5	2.0	38.6	59.4
U7: $L + (V) = Al_8V_5 + Si_3V_5$	1390	L	~60.5	~4	~35.5
		(V)	44.5	0.5	55.0
		Al_8V_5	55.6	1.4	43.0
		Si_3V_5	1.7	35.3	63.0

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Reaction	T / °C	Phase	Composition / at. %		
			Al	Si	V
U8: L + SiV ₃ = Si ₃ V ₅ + (V)	1574	L	~35.0	~10.0	~55.0
		SiV ₃	5.0	22.0	73.0
		Si ₃ V ₅	1.7	35.5	63.0
		(V)	44.5	0.5	55.0
U9: L + Si ₅ V ₆ = Si ₂ V + Si ₃ V ₅	1635	L	~9.0	~54.0	~37.0
		Si ₅ V ₆	0.0	45.5	54.5
		Si ₂ V	0.2	65.8	34.0
		Si ₃ V ₅	0.5	37.5	62.5
U: Si ₃ V ₅ + (V) = Al ₈ V ₅ + SiV ₃ annealing experiments; not measured by DTA	850 < T < 950	Al ₈ V ₅	55.5	1.5	43.0
		(V)	45.0	0.5	54.5
		SiV ₃	4.0	23.0	73.0
		Si ₃ V ₅	0.5	37.5	62.5

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High temperature DTA was used to measure the temperatures of invariant phase reactions higher than 1490 °C. For this purpose samples in the respective three phase fields $[\text{SiV}_3+\text{Si}_3\text{V}_5+(\text{V})]$ ($\text{Al}_5\text{Si}_{23}\text{V}_{62}$) and $[\text{Si}_2\text{V}+\text{Si}_3\text{V}_5+\text{Si}_5\text{V}_6]$ ($\text{Al}_{0.7}\text{Si}_{44.3}\text{V}_{55}$) were heated in high temperature DTA with a heating rate of 5 K min^{-1} . Starting temperature was 1400°C. In order to avoid a possible reaction of the liquid with the alumina crucibles, the measurements were stopped after the first visible effect and not heated further to the liquidus temperatures. These measurements allowed to determine the invariant reactions in the V-rich part at elevated temperatures. A ternary reaction scheme (Scheil diagram) is shown in Figure 42. All liquidus values determined by DTA were combined with literature data for the limiting binary phase diagrams to yield a liquidus surface projection within the entire investigated composition range. The corresponding diagram in Figure 43 shows the liquidus isotherms between 600 and 1900 °C as dotted lines. It should be emphasized, that the isotherms between 1500 and 1900 °C are estimates, as no liquidus temperatures above 1490 °C were determined. The isotherms reflect information on the binary melting temperatures and information on invariant ternary reaction temperatures. The liquidus valleys that separate the different fields of primary crystallization are shown as solid lines with arrows indicating the direction toward lower temperature. The compositions of the liquid phase in the various ternary invariant reactions listed in Table 24 are shown as circles in Figure 43. The three invariant reactions E1, U2 and U3 can be seen clearly in Figure 43 (b) which is an enlargement of the very Al rich part of the liquidus surface projection. In order to reach additional information about the compositions of the liquid phase taking part in the invariant four phase reactions and to construct the liquidus surface projection, as cast samples at various compositions were investigated for primary crystallization and the sample compositions are shown in Figure 43 as triangles. An overview of all investigated as cast samples is given in Table 25 together with information about primary solidification. The sample $\text{Al}_{75}\text{Si}_5\text{V}_{10}$ was not measured after arc melting but after DTA-measurement i.e. it was heated and subsequently cooled slowly with a cooling- rate of 5 Kmin^{-1} . In Figure 44 the primary crystallization of Si_3V_5 can be seen as white grains in the BSE image of the respective sample. This confirms the extension of the Si_3V_5 crystallization field towards the Al-rich corner of the phase diagram.

In Figure 45 BSE images of as cast samples in four different primary crystallization fields are shown. The liquidus surface projection is dominated by the huge primary

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solidification field of Si_3V_5 . In Figure 45 (a), a sample is shown near the liquidus valley which leads from P2 to U9. The white crystals were measured to be Si_3V_5 . In Figure 45 (b) the white grains of Si_5V_6 are the primary crystallized phase and the narrow solidification field of this high temperature phase is represented by the sample $\text{Al}_5\text{Si}_{56}\text{V}_{39}$. Figure 45 (c) shows a sample in the primary crystallization field of (V). The as cast sample $\text{Al}_{32}\text{Si}_{11}\text{V}_{57}$ shown in Figure 45 (d) exhibits SiV_3 as primary crystals. Together with the as cast sample $\text{Al}_{37}\text{Si}_{19}\text{V}_{53}$ located directly on the liquidus valley between U7 and U8 it offers valuable information about the composition of the liquid phase taking part in the transition reaction U8.

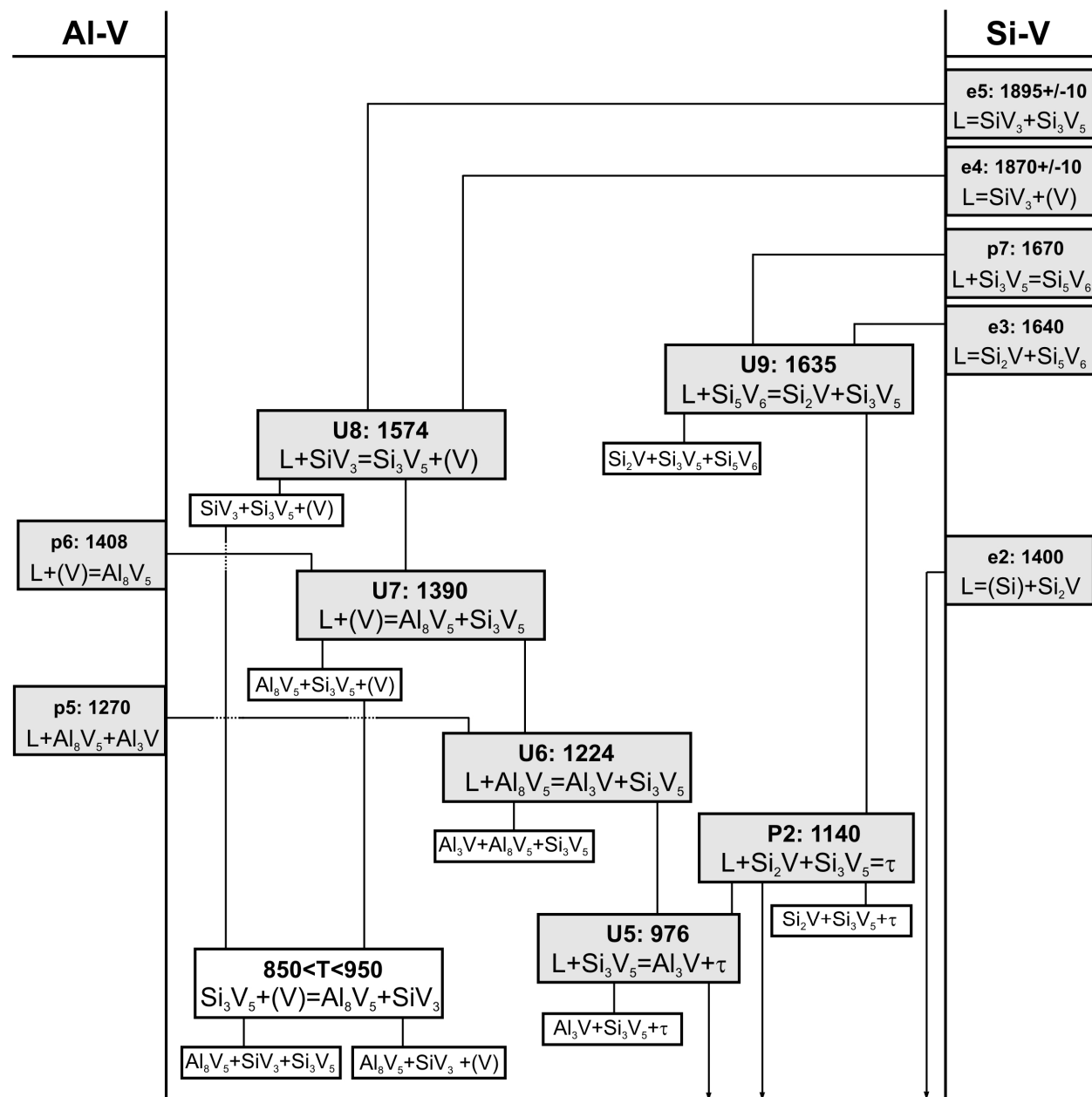
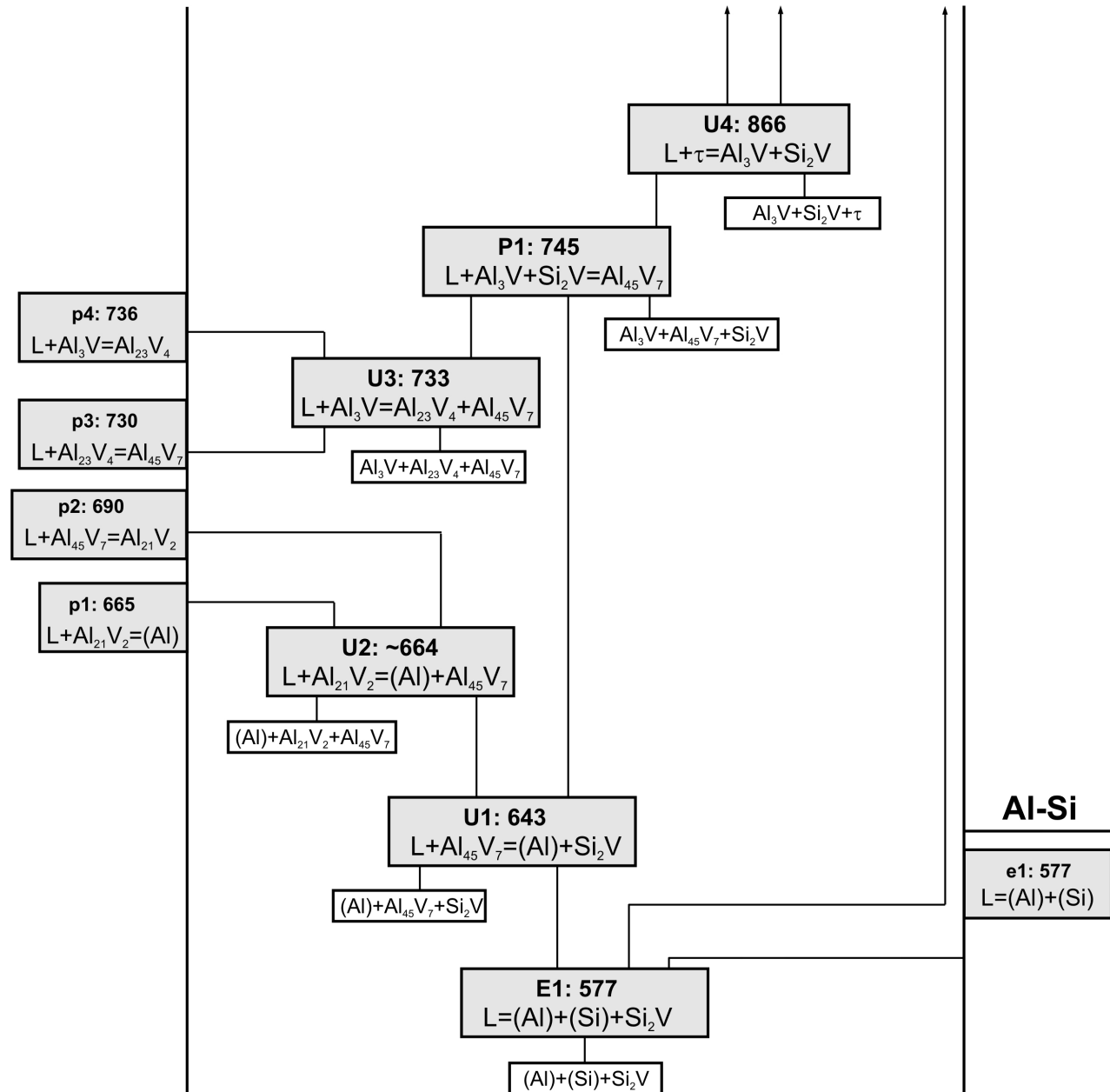


Figure 42: Ternary reaction scheme (Scheil diagram) of the Al-Si-V system. Gray fields: measured reaction temperatures, white fields: estimated reaction temperatures.



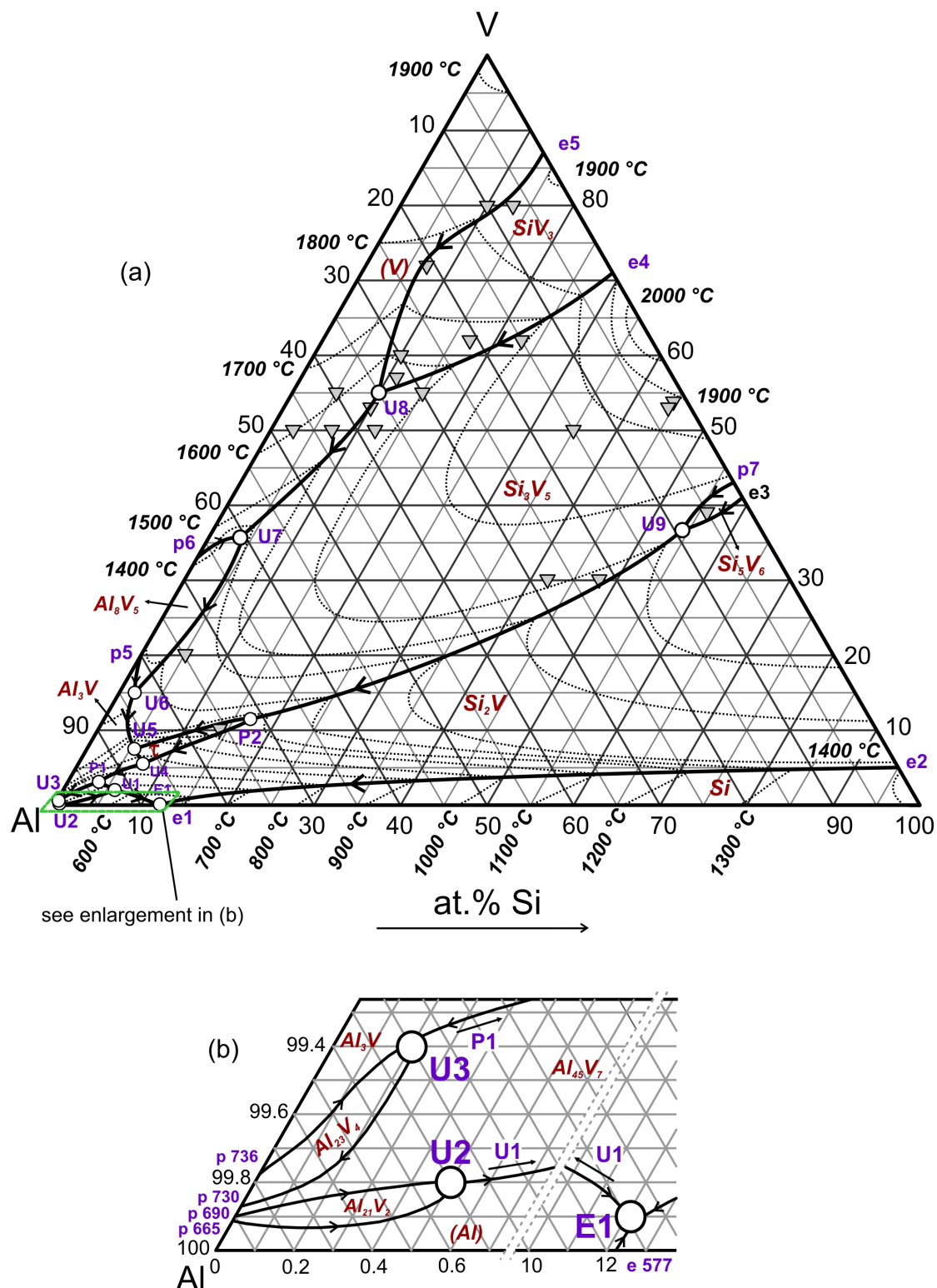


Figure 43: Liquidus surface projection of Al-Si-V including fields of primary crystallisation. Solid lines: liquidus valleys; dotted lines: isotherms; circles: invariant points; triangles: investigated as cast samples.

Table 25: Primary crystallization investigated from as cast samples.

Nominal sample composition		Primary crystallization
$\text{Al}_{75}\text{Si}_5\text{V}_{20}$	after DTA-measurement	Si_3V_5
$\text{Al}_{76}\text{Si}_{14}\text{V}_{10}$		τ
$\text{Al}_{1.5}\text{Si}_{44.7}\text{V}_{53.8}$		Si_3V_5
$\text{Al}_{2.5}\text{Si}_{44.5}\text{V}_{53}$		Si_3V_5
$\text{Al}_{15}\text{Si}_{35}\text{V}_{50}$		Si_3V_5
$\text{Al}_{47.5}\text{Si}_{2.5}\text{V}_{50}$		(V)
$\text{Al}_{30}\text{Si}_{10}\text{V}_{60}$		SiV_3
$\text{Al}_{15}\text{Si}_{23}\text{V}_{62}$		Si_3V_5
$\text{Al}_{30}\text{Si}_{15}\text{V}_{55}$		Si_3V_5
$\text{Al}_{40}\text{Si}_5\text{V}_{55}$		(V)
$\text{Al}_{10}\text{Si}_{10}\text{V}_{80}$		(V)
$\text{Al}_{21}\text{Si}_7\text{V}_{72}$		SiV_3
$\text{Al}_{28}\text{Si}_{42}\text{V}_{30}$		Si_3V_5
$\text{Al}_{22}\text{Si}_{48}\text{V}_{30}$		Si_3V_5
$\text{Al}_5\text{Si}_{56}\text{V}_{39}$		Si_5V_6
$\text{Al}_{43}\text{Si}_7\text{V}_{50}$		(V)
$\text{Al}_{38}\text{Si}_{12}\text{V}_{50}$		Si_3V_5
$\text{Al}_{37}\text{Si}_{10}\text{V}_{53}$		Si_3V_5 / (V)
$\text{Al}_{32}\text{Si}_{11}\text{V}_{57}$		SiV_3
$\text{Al}_{21}\text{Si}_{17}\text{V}_{62}$		SiV_3
$\text{Al}_7\text{Si}_{13}\text{V}_{80}$		SiV_3

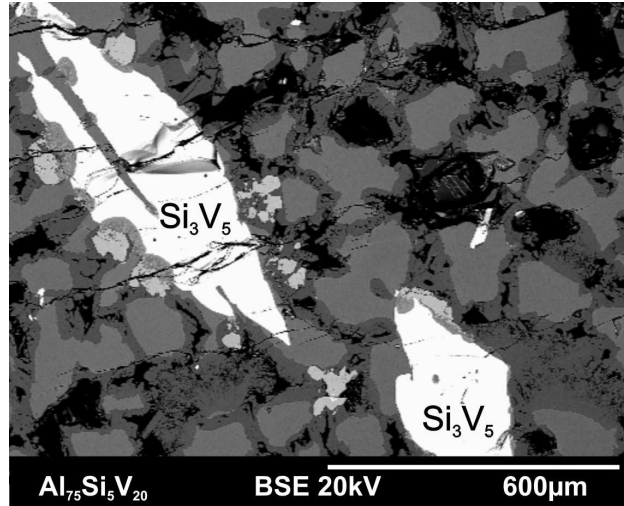


Figure 44: Back scattered electron image of a sample with the nominal composition $\text{Al}_{75}\text{Si}_5\text{V}_{20}$ after cooling with 5 Kmin^{-1} . White grains: primary crystals of Si_3V_5 .

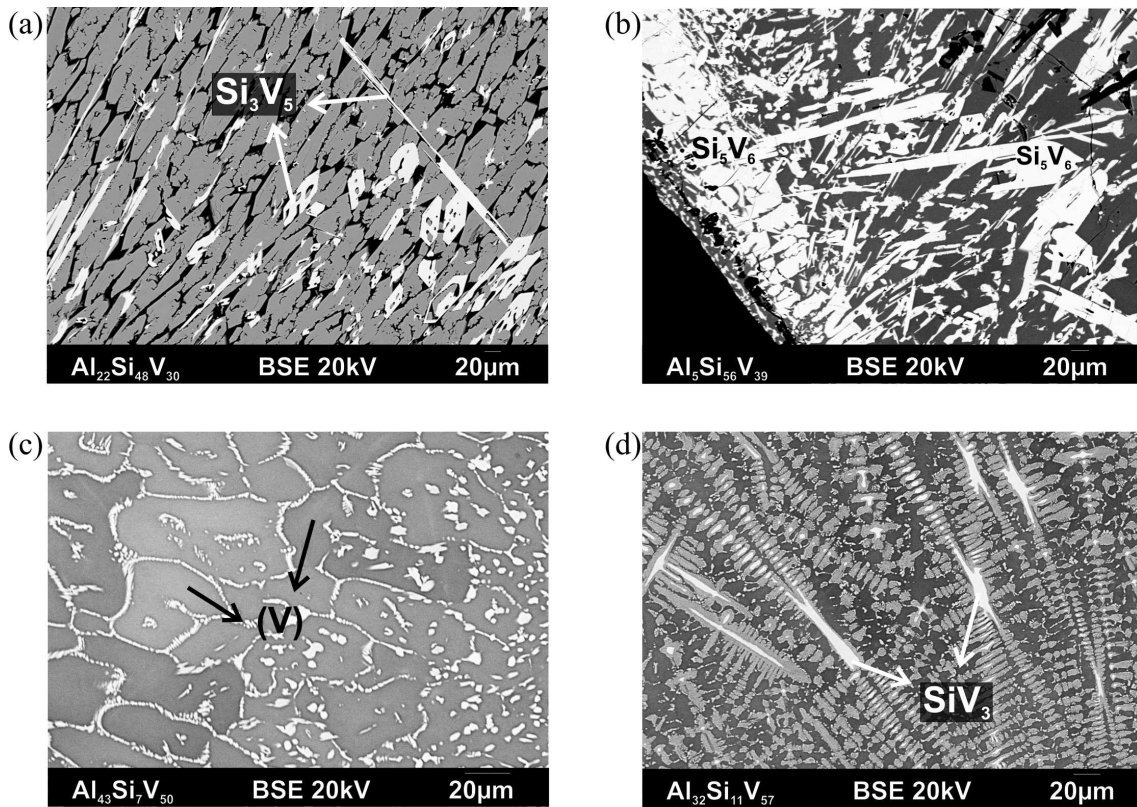


Figure 45: Back scattered electron images of as cast samples with the nominal compositions (a): $\text{Al}_{22}\text{Si}_{48}\text{V}_{30}$, (b): $\text{Al}_5\text{Si}_{56}\text{V}_{39}$, (c): $\text{Al}_{43}\text{Si}_7\text{V}_{50}$ and (d): $\text{Al}_{32}\text{Si}_{11}\text{V}_{57}$. Primary crystals are highlighted.

5.3. The new binary low temperature compound AlV

Beside ternary alloys, binary samples were prepared and investigated to check literature data of the binary limiting systems. In the course of this study we discovered a new binary AlV compound at lower temperatures.

The sample preparation of the binary Al-V alloys and the sample characterization in principle followed the method of the ternary Al-Si-V samples described in the experimental section. Samples with the nominal composition $\text{Al}_{50}\text{V}_{50}$, annealed at 620 and 500 °C, respectively, showed significantly different X-ray powder patterns (Figure 46). While the pattern observed for 620 °C was identified as a mixture of Al_8V_5 and the solid solution of Al in bcc-V, the sample annealed at 500 °C showed a completely different pattern which could not be identified with any known crystal structure in the Al-V system. However, the pattern showed strong peaks near to the peaks of bcc-(V) pointing to some relations to this simple structure. In Figure 47 a BSE image of a sample with the nominal composition $\text{Al}_{50}\text{V}_{50}$ annealed at 500 °C is shown. The composition of the new binary compound was determined by means of EPMA and corresponds to the chemical composition $\text{Al}_{50.1(5)}\text{V}_{49.9(4)}$. Beside the main phase AlV, small amounts of the darker phase Al_8V_5 can be seen. For the latter phase the composition was measured to be 60.2(5) at.% Al and 49.8(5) at.% V by means of EPMA.

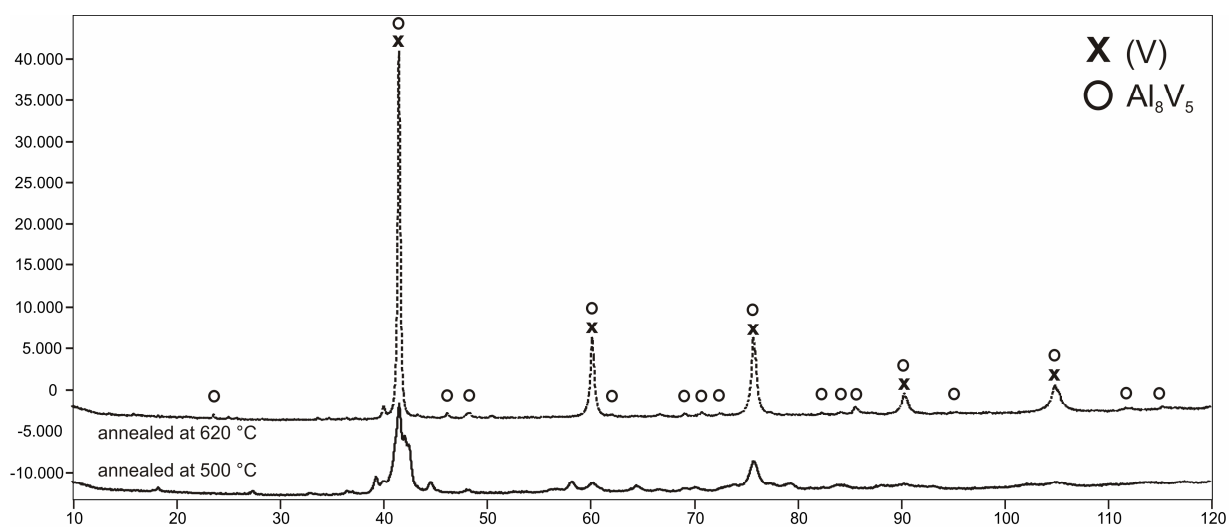


Figure 46: Comparison of the X-ray powder patterns of samples annealed at 620 °C (dashed line) and 500 °C (solid line).

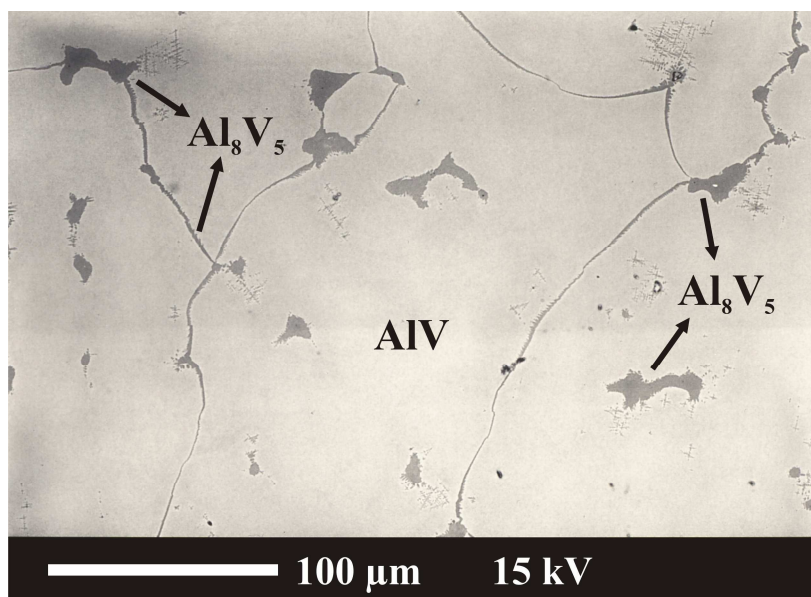


Figure 47: Back scattered electron image of a sample with the nominal composition $\text{Al}_{50}\text{V}_{50}$ annealed at 500 °C.

The sample containing the new AlV-phase was investigated by DTA in order to determine the transition temperature, but no noticeable effect was found in the temperature range between 500 and 620 °C. In order to determine the exact decomposition temperature, different annealing temperatures (590, 560, 545, 540, 535 and 530 °C) were applied; the annealing time was 4 weeks. At 535 °C we observed the best pattern; i.e. the (V) main peak (011) at around 41.5 ° (2 θ) was not visible as dominant peak. Starting from 540 °C, the (V) (011) peak started to grow and at 590 °C the pattern was completely converted to simple bcc. Thus we concluded that the formation temperature of the new phase is below 540 °C. The crystals isolated from the sample annealed at 535 °C were of low quality and could not be used for structure determination. In order to gain single crystals for structure determination several attempts were made to improve the crystal quality and size: a sample which was annealed at 535 °C was oscillated around the hypothetic decomposing temperature of 540 °C several times. The respective temperature program can be seen in Figure 48. A similar procedure was successfully used to grow suitable single crystals in a pure solid-solid reaction in the Al-Ni-Si-system [73]. In the current case, however, subsequent single crystal measurements indicated that the sample was crystallized insufficiently and showed mosaic like crystallization. Therefore structure determination was impossible.

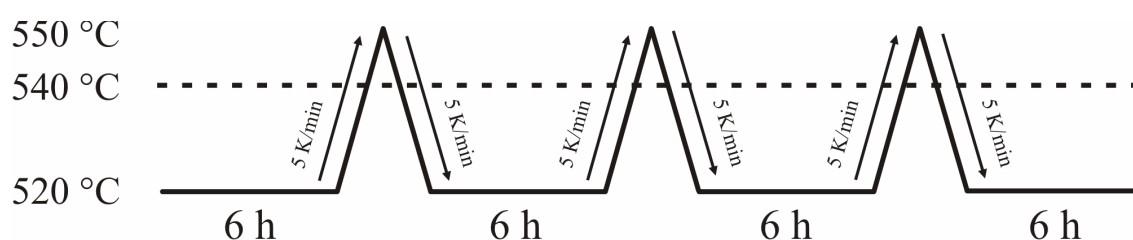


Figure 48: Temperature program for the oscillation annealing used for the improvement of crystal quality.

Results and Discussion

In another attempt we tried to use iodine as crystallization aid. For this purpose the coarsely powdered sample and about 10 mg of I_2 were put into a quartz glass tube which subsequently was evacuated and sealed. For annealing in the muffle furnace two different procedures were applied. On the one hand isothermal annealing at 535 °C for 6 weeks was performed. These samples again exhibited mosaic like crystallization of the new phase, not suitable for single crystal XRD. The other annealing experiments were done using a temperature program which can be seen in Table 26. The temperature was risen over the decomposition temperature up to 560 °C with the aim to gain better crystallization on slow cooling.

Table 26: Temperature program with I_2 as crystallization aid.

Segment	Temperature	Cooling-/ heating rate	Duration
Heating	560 °C	1 K/min	
Cooling	535 °C	1 K/min	
Isothermal			100 h
Heating	560 °C	1 K/min	
Cooling	535 °C	1 K/min	
Isothermal			100 h

Figure 49 shows a comparison of the XRD patterns of a sample annealed regularly at 535 °C and a sample annealed with I_2 as crystallization aid with temperature program. As can be seen, also the use of I_2 was not successful to form high quality crystals and cycling between 560 and 535 °C even yielded in the complete decomposition of the new phase into (V) and Al_8V_5 . Given the slow kinetics at this rather low temperature, long term annealing experiments have been done at 450 and 535 °C with crystallization aid for 5 months. After the annealing at 535 °C AlV was not longer found and the sample annealed at 450 °C exhibited the three phases AlV, (V) and Al_8V_5 . These results provide the hypothesis that AlV is a metastable phase, which is formed from (V) with around 50 at.% Al obtained after the initial arc melting step. AlV is formed on annealing at low temperatures as intermediate metastable phase Through long term annealing it decomposes to the equilibrium phases Al_8V_5 and (V), but only when the temperature is high enough for diffusion. The diffusion is too slow at 450 °C to

Results and Discussion

decompose the phase totally after 5 months. At 535 °C the faster diffusion provides the decomposition of AlV and Al_8V_5 and (V) are formed.

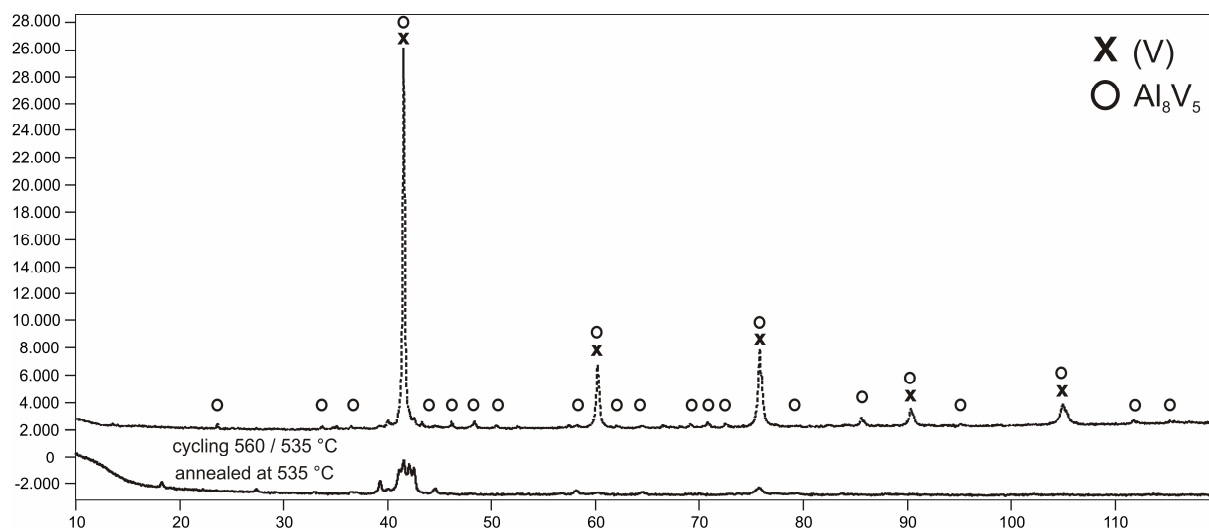


Figure 49: Comparison of the X-ray powder patterns of samples after annealing at 535 °C (solid line, X-ray measurement was done with monochromator) and after cycling between 560 and 535 °C using I_2 as crystallization aid (dashed line).

Results and Discussion

As we were not able to prepare good single crystals, we tried to determine the unit cell of the phase from powder data. Indexing of the powder pattern of the sample annealed at 535 °C was performed using the TOPAS software [22]. Due to the rather low crystallinity of the compound (the domain size refined with a fundamental parameter approach was 26 nm), the diffraction peaks were rather broad, and the distinction of partly overlapping peaks was not always unambiguous. The most suitable result indicates the phase to be of tetragonal symmetry, possible space group $P4_22_12$ with the cell parameters $a = 10.8450(7)$ Å and $c = 4.3755(2)$ Å, respectively. The cell parameter for bcc-(V) at the same composition at higher temperatures was determined to be $a = 3.0692(1)$ Å. This value is associated to the cell parameters of the suggested tetragonal cell by the factor $\sqrt{2}$ for c and by the factor $\frac{5}{2}\sqrt{2}$, for a , respectively. This indicates a possible superstructure relation to the simple bcc structure and a more or less diffusionless transformation between bcc-(V) and the here suggested tetragonal structure of AlV is probable. In Table 27 the positions and intensities of the observed peaks are listed together with the Miller indices and the theoretical positions of the diffraction lines of the tetragonal cell. With few exceptions, the peaks match very well with the theoretical position. For four peaks two different $h k l$ are listed because of ambiguity. Although the cell proposed here is quite reasonable given the cell parameter relations to bcc-(V), the solution should still be taken with some caution, as the crystalline quality of the investigated samples was not sufficient for unambiguous indexing.

Single crystal measurements will be essential for structure determination but up to now attempts with regard to gain suitable single crystals have not been effective. Maybe TEM measurement can provide further information on the crystal structure even with a sample which is not pure of AlV.

Table 27: Result of the indexing of the powder pattern of a sample annealed at 535 °C.

Obs. Position / 2 θ	Area	h k l	Theor. Position / 2 θ
18.31	2.65	2 1 0	18.28
27.41	4.28	2 1 1	27.43
32.99	2.96	3 1 1	33.16
36.60	4.97	3 2 1	36.21
37.03	3.41	4 2 0	37.04
39.33	35.81	0 4 1	39.05
40.09	13.06	4 1 1	39.96
41.15	68.16	0 0 2	41.23
41.59	102.10	4 3 0	41.60
42.13	82.93	0 1 2	42.10
42.57	78.47	5 1 0	42.47
		4 2 1	42.59
44.61	23.37	0 2 2	44.63
56.80	9.77	4 2 2	56.62
		6 3 0	56.91
58.22	39.63	5 4 1	58.38
60.23	22.62	5 5 0	60.30
64.60	22.69	4 4 2	64.58
70.07	10.78	3 1 3	70.05
73.92	16.13	0 4 3	73.70
		6 6 0	74.13
75.35	25.51	7 5 0	75.32
		8 2 1	75.41
75.74	80.89	7 1 2	75.67
76.06	50.93	4 2 3	76.09
77.49	23.04	7 2 2	77.45
79.41	32.32	5 1 3	79.64

6. Summary

6.1. Summary (English)

The thesis presented here was performed in the course of a larger research project with the aim to clarify the phase equilibria of ternary systems of the 3d transition metals with aluminum and silicon. As a contribution to this project phase diagram investigations were carried out for the two ternary systems Al-Co-Si and Al-Si-V.

The ternary Al-Co-Si system was described quite well in literature concerning isothermal sections at 600, 800 and 900 °C. Seven ternary compounds have been found to exist in the Al-rich part. So far the system was not investigated by thermal analysis and no information on the melting behaviour of the ternary phases were available. Based on existing literature data and with the aim to describe the entire ternary Al-Co-Si system, two isothermal sections in the Co-rich part of the phase diagram at 1050 and 1200 °C were investigated. By means of DTA-measurements of samples covering the whole system, 14 vertical sections at 5, 15, 22, 24, 25, 26, 28, 30, 35, 40, 50, 60, 66.7, and 75 at.% Co were constructed. These investigations yielded a liquidus surface projection and a reaction scheme (Scheil diagram) of the complete ternary system. We found the ternary compounds α , γ , δ , ϵ , ϕ and χ to melt peritectically whereas the phase β melts congruently. Additionally, diffusion couple investigations were performed in the system. The two couples AlCo/Si and AlCo/Co₂Si annealed at 900 and 1050 °C, respectively are in excellent agreement with the isothermal sections at the respective temperatures and the diffusion paths were developed. Contact formation in the couples Al/CoSi₂ and Al/CoSi at 550 °C were done by a liquid-solid interface and the interpretation of the results are therefore not straight forward. Nevertheless, diffusion paths also in these couples could be proposed.

Literature in the Al-Si-V system was scarce and referred mainly to the very Al-rich part. Besides, an isothermal section at 1000 °C in the V-rich part was given. In course of the present study the ternary system was investigated in isothermal sections at 500 and 620 °C in the Al-rich part, and at 850 and 1300 °C in the V-richer part. The ternary compound τ was discovered and its chemical composition was measured to be Al_{0.6}Si_{1.4}V. The powder pattern of this sample was successfully indexed and yielded an orthorhombic TiSi₂-type cell (*Fddd*, *oF24*) with the cell parameters $a = 8.0856(1)$ Å,

Summary

$b = 4.6921(1) \text{ \AA}$ and $c = 8.4954(1) \text{ \AA}$. These results could be confirmed by single crystal XRD. By means of thermal analysis the ternary compound was measured to melt peritectically at 1400 °C. The ternary system was investigated in four vertical sections at 10, 20, 35 and 50 at.% V by DTA measurements. To get detailed information about the position of the liquidus valleys several as cast samples were investigated concerning primary crystallization. A combination of all data yielded a liquidus surface projection and a reaction scheme of the entire Al-Si-V system.

In this work, beside ternary alloys, binary samples were prepared and investigated to check literature data of the binary limiting systems, and in the course of this study we discovered a new binary AlV compound at lower temperatures. By means of annealing experiments between 450 and 560 °C with and without crystallization aid several attempts to produce the phase pure for indexing the powder XRD or to gain single crystals for single crystal measurements were done. But until now these efforts failed and we consider the phase to be metastable. Maybe small area electron diffraction (SAED) in TEM measurement could provide further information on the crystal structure of this binary phase.

6.2. Zusammenfassung (Deutsch)

Die hier vorliegende Arbeit wurde im Laufe eines größeren Forschungsprojektes durchgeführt. Ziel dieses Projektes war die Untersuchung von Phasengleichgewichten von ternären Legierungssystemen der 3d-Übergangsmetalle mit Aluminium und Silizium. Als Beitrag zu diesem Projekt wurden die Phasendiagramme der ternären Systeme Al-Co-Si und Al-Si-V untersucht.

Über das ternäre Al-Co-Si-System waren in der Literatur bereits isotherme Schnitte bei 600, 800 und 900 °C beschrieben. Sieben ternäre Phasen im aluminiumreichen Teil des Phasendiagrammes sind bekannt. Thermische Analyse wurde in dem System bislang noch nicht durchgeführt, weshalb es keine Informationen über das Schmelzverhalten der ternären Verbindungen gab. Um das gesamte ternäre Phasendiagramm aufklären zu können, wurden im Zuge dieser Arbeit zwei isotherme Schnitte im kobaltreichen Teil bei 1050 und 1200 °C untersucht. Basierend auf DTA-Messungen von Proben, die den gesamten Bereich abdecken wurden 14 vertikale Schnitte bei 5, 15, 22, 24, 25, 26, 28, 30, 35, 40, 50, 60, 66,7 und 75 at.% Co konstruiert. Diese Untersuchungen führten zur Liquidusoberfläche und zu einem Reaktionsschema (Scheil-Diagramm) des gesamten ternären Systems. Laut unserer Messungen schmelzen die ternären Verbindungen α , γ , δ , ϵ , ϕ und χ peritektisch, die Phase β schmilzt hingegen kongruent. Zusätzliche wurden Diffusions-Paare im Al-Co-Si-System untersucht. Die beiden Diffusions-Paare AlCo/Si und AlCo/Co₂Si, welche bei 900 beziehungsweise 1050 °C zur Reaktion gebracht wurden, stimmen mit den entsprechenden Isothermen ausgezeichnet überein und die Diffusionswege konnten ermittelt werden. Bei den beiden Diffusions-Paaren Al/CoSi₂ und Al/CoSi, die bei 550 °C getempert wurden, wurde der Kontakt über eine fest-flüssig Zwischenschicht gebildet, weshalb die Interpretation nicht so klar wie bei den klassischen Diffusions-Paaren. Dennoch werden auch hier Diffusions-Wege vorgeschlagen.

Literaturdaten über das ternäre Al-Si-V-System waren rar und bezogen sich hauptsächlich auf den aluminiumreichen Teil. Daneben war ein isothermer Schnitte bei 1000 °C bekannt. Im Zuge dieser Arbeit wurden im Al-Si-V-System isotherme Schnitte bei 500 und 620 °C im aluminiumreichen Teil und bei 850 und 1300 °C im vanadiumreicheren Teil untersucht. Die ternäre Verbindung τ wurde entdeckt, deren Zusammensetzung als Al_{0,6}Si_{1,4}V bestimmt wurde. Das Pulverdiffraktogramm der Phase

Summary

wurde indiziert und führte zu einer orthorhombischen Zelle des TiSi_2 -Typs ($Fddd$, $oF24$) mit den Zellparametern $a = 8,0856(1) \text{ \AA}$, $b = 4,6921(1) \text{ \AA}$ und $c = 8,4954(1) \text{ \AA}$. Dieses Ergebnis wurde mit Einkristalldiffraktometrie bestätigt. Es wurde festgestellt, dass sich τ peritektisch bei $1400 \text{ }^\circ\text{C}$ zersetzt. Im Al-Si-V-System wurden 4 Isoplethen bei 10, 20, 35 und 50 at.% V mittels DTA-Analyse gemessen. Zusätzlich wurden Proben direkt nach dem Lichtbogenschmelzen bezüglich Primärkristallisation untersucht. Durch die Kombination aller Ergebnisse wurden eine Liquidusoberfläche und ein Reaktionsschema (Scheil-Diagramm) für das gesamte ternäre Al-Si-V-System entwickelt.

Um binäre Literaturdaten zu überprüfen, wurden im Laufe dieser Arbeit neben ternären Legierungen auch binäre Proben untersucht. Im Zuge dessen wurde im binären Al-V-System die neue Phase AlV bei niedrigeren Temperaturen entdeckt. Durch Glühversuche zwischen 450 und $560 \text{ }^\circ\text{C}$ mit und ohne Kristallisationsmittel wurde versucht, die Phase rein herzustellen, um Pulverdiffraktometrie oder Einkristallmessungen durchführen zu können. Bisher waren diese Versuche jedoch vergeblich und wir nehmen an, dass es sich um eine metastabile Phase handelt. Vermutlich könnten TEM-Messungen weitere Informationen über die Kristallstruktur dieser binären Phase bringen.

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8.3. Curriculum Vitae

Personal Information

Name:	Bearix HUBER
Title:	Magister rerum naturalium
Date of birth:	May 5th, 1977
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Education and Studies

1983-1987	Basic School, A-7000 Eisenstadt
1987-1995	Grammar School, A-7000 Eisenstadt, A-1090 Vienna
1995	June
	School-leaving examination
January–June 1997	Stay in Italy: Trieste, Rome
1997-2000	Higher Technical School, A-1160 Vienna
June 2000	School-leaving examination with distinction
2001-2006	Chemistry and Physical Education for Teaching, University of Vienna
August 2006	Magister rer. nat. with distinction
2007-2010	PhD studies, University of Vienna

Professions

1999-2001	Laboratory of medical diagnostics, A-1090 Vienna
2004-2007	Tutor at the Faculty of Chemistry
Since 2007	Research assistant, employed at the Austrian Science Foundation

Research interests

Thermochemistry and phase diagrams of inorganic materials
Lead-free solder materials

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Other activities

- February 2008 4 weeks research stay at the Eindhoven University of Technology
– Department of Chemical Engineering and Chemistry (Prof. Kodentsov), The Netherlands
- October 2008 1 week STSM (“Preparation of micro- and nano- sized solder materials via precursor route and identification of the products”) under the ASO-Brno project No. 1-2007 at the University of Plovdiv, Bulgaria

Memberships

Austrian Chemical Society (GÖCh)
Society of Austrian Chemistry Teachers (VCÖ)

Selected contributions to conferences

1. B. Huber, K.W. Richter, A. Mikula, H. Ipser, „Cp – Messungen an flüssigen Legierungen im binären System Bi – Ga“, poster, *11. Österreichische Chemietage*, Leoben, Austria 09/2005.
2. B. Huber, K.W. Richter, A. Mikula, H. Ipser, „Thermochemische Charakterisierung von flüssigen Legierungen mit Entmischungstendenzen: Das System Bismuth – Gallium“, oral presentation, *4. Workshop Anorganische Chemie in Österreich*, Eisenstadt, Austria 04/2006.
3. B. Huber, K.W. Richter, A. Mikula, H. Ipser, „Thermochemical characterization of the Bi-Ga system“, poster, *High Temperature Materials Chemistry XII*, Vienna, Austria 09/2006.
4. B. Huber, K.W. Richter, „Phase Equilibria in the Al – V – Si System“, poster, *12. Österreichische Chemietage*, Klagenfurt, Austria 09/2007.
5. B. Huber, K.W. Richter, „Phase Equilibria in the Al – V – Si System“, oral presentation, *TOFA 2008 – Discussion Meeting on Thermodynamics of Alloys*, Krakau, Polen 06/2008.
6. B. Huber, K.W. Richter, „Phase Equilibria in the Al – V – Si System“, poster, *7th Chemistry Conference*, Plovdiv, Bulgaria 10/2008.
7. B. Huber, K.W. Richter, „Phasengleichgewichte im System Al – V – Si“, oral presentation, *5. Workshop Anorganische Chemie in Österreich*, Graz, Austria 03/2008.
8. B. Huber, K.W. Richter, „Phase Equilibria in the Al – Co – Si System“, oral presentation, *13. Österreichische Chemietage*, Wien, Austria 08/2009.

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9. B. Huber, K.W. Richter, „Phase Equilibria in the Systems Al – V – Si and Al-Co-Si“, oral presentation, Peking and Schanghai, China 09/2009
10. B. Huber, A. Kodentsov, K.W. Richter, “Phase Equilibria and Diffusion Couples in the Al-Co-Si system”, oral presentation, *TOFA 2010 – Discussion Meeting on Thermodynamics of Alloys*, Porto, Portugal 09/2010.

Papers

1. B. Huber, K.W. Richter, H. Flandorfer, A. Mikula and H. Ipser, „Thermodynamic characterization of liquid alloys with demixing tendency: Bi-Ga”, *International Journal of Materials Research*, (2008).
2. B. Huber and K.W. Richter, „Phase equilibria in the Al-V-Si system“, *Intermetallics*, (2010).
3. B. Huber and K.W. Richter, „Observation of the new binary low temperature compound AlV”, *Journal of Alloys and Compounds*, (2009).
4. B. Huber, A. Kodentsov and K.W. Richter, “The Al-Co-Si System”, *Intermetallics*, (2010).
5. B. Huber and K.W. Richter, “Phase equilibria in the Al-Si-V system: The vanadium rich part”, *Intermetallics*, (2010).