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"Investigation of the Al-Ge-Ni phase diagram with a view to joining application for Nickel Aluminides"

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"For my parents and Dolores"

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1. Introduction

During the last several decades, intermediate compounds, based on aluminides of transition metals have been under investigation due to their optimal properties at high temperatures. As Among the most promising intermetallic alloys, nickel aluminides such as γ' -Ni₃Al and β -NiAl, have to be mentioned. The major advantages of nickel aluminides are primary the low density and corrosion resistance and secondary the mechanical properties, such as good tensile and compressive yield strengths at high temperatures supplemented by a high creep strength. Nickel aluminides are nowadays used in terms of nickel-base superalloys, which usually contain high amounts of chromium, leading to pronounced corrosion resistance, as well as several other transition metals and main group elements, making these materials rather complex. There is quite a huge amount of research done, improving chemical and thermal resistance as well as mechanical properties, as these properties make nickel-base superalloys popular wherever high thermal and mechanical stresses are expected. These alloys are applied in turbine blades of aircraft and space vehicle engines, power generating gas turbines and marine propulsion turbines, respectively, where materials are subjected to elevated temperatures. Gas turbine engines are ideally operating after the Brayton cycle, where an isentropic compressed air-fuel mixture is isobarically combusted in a combustion chamber before it is accelerated towards the propulsion turbine. In fact the efficiency of all types of gas turbine engines is increasing with rising turbine inlet temperatures, due to higher enthalpies of the combustion gas, which is transferred into mechanical energy, powering the turbine. The attainment of higher efficiency is thus limited by the ability of the applied materials to withstand high temperatures and mechanical stresses. Besides excessive material science, to achieve optimal material properties and develop special resistant coatings, a complex cooling system as well as structural design is therefore established.

Since applied parts of nickel-base superalloys are moulded in complex procedures, using elevated temperatures, they are very expensive. A successful application of these materials thus requires suitable and cost-effective joining techniques such as welding, diffusion bonding and brazing. Since welding of AlNi strengthened nickel-base superalloys exhibits difficulties due to formation of cracks at the weld joint, induced by thermal shocks, and diffusion bonding, where two substrates are compressed together at high pressure (~100MPa) to realize solid state diffusion, is very time and cost intensive, the only applicable joining technique of these alloys is brazing [1]. There exists a hybrid joining process known as diffusion brazing (7.1.), sometimes also called transient liquid-phase (TLP) joining or transient liquid phase

bonding (TLPB), respectively, which is a very popular technique for joining and repairing of nickel base alloys, where two substrates with a lower melting braze material inserted between them are annealed for a short time. The respective filler material provides a definitely lower melting point than the two component parts and melts partially or totally during the annealing process. Thus diffusion brazing has the extraordinary merit of filling joints of every dimension and is producing well-round fillets at the edges of the joint. It therefore combines the desired joint filling and less importance of flat surfaces of the substrates from traditional brazing together with the greater flexibility in respect to service temperature of the joined parts from conventional welding and diffusion bonding.

Since brazing materials need to provide definitely lower melting points than the substrates but should possess similarities in respect to the chemical composition of the substrate, melting point depressant elements have to be added to the braze alloy. The nowadays most commonly applied melting point depressant elements for diffusion brazing of nickel-base superalloys, B, P, Cu and Si, lead in most cases to brittle phases in the joining area, which consequently decreases the mechanical strength [2-4]. For the investigation of a new brazing material the promotion of forming phases, similar to the bulk, as well as the suppression of precipitating brittle phases have to be considered. In the present study Ge was selected as a melting point depressant element of nickel aluminides, due to its affinity of forming deep eutectics with lots of important elements, such as Al, Fe, Ni and Ti. Previous investigations of single crystalline Ni-Ge brazed nickel-base superalloys PWA 1483 and René N5 was successfully processed by Neumeier et al [5]. As brazing alloys they have used binary Ni-Ge alloys with 20wt.% and 23wt.% Ge, respectively. Diffusion brazing experiments were carried out at 1160 and 1200°C, which was slightly lower than the respective melting temperatures of the braze materials. Subsequently nanoindentation tests of the joints possessed strength levels, which were comparable to the base materials.

In the current work a characterisation and optimisation of a novel braze alloy, based on nickel aluminides, with Ge as melting point depressant element has been done by fundamental research of the ternary Al-Ge-Ni phase diagram. Two partial isothermal sections at 400°C and 700°C and vertical sections at 10, 20, 35at.% nickel and at constant Al:Ni ratio of 1:3 were investigated, to clarify phase relations in the whole temperature range. A partial reaction scheme as well as liquidus projection in the Ni poor part were also constructed.

Further fundamental wetting and diffusion brazing experiments were practised with two selected brazing alloys, using AlNi and AlNi₃ as substrate materials, at processing temperatures of 900 and 1000°C, respectively.

2. Basic materials

2.1. Aluminium [6]

Atomic number	13		
Classification	Boron group, 13 th		
Electron configuration	[Ne] $3s^2 3p^1$		
Appearance	argentic		
State of matter	solid		
Atomic mass (g·mol ⁻¹)	26.982		
Covalent radius (pm)	125		
Melting point (K)	933.5		
Density (g·cm ⁻³)	2.699		



Fig. 1: Aluminium cut wire shot [7]

Table 1: Characteristics of Aluminium [6]

Natural occurrence

Aluminium is the third most abundant element in the geosphere with a mass fraction of about 7.7%. Because of its huge chemical affinity to oxygen, it does not occur natively but as oxidic compounds. Most deposits of aluminium are in the forms of corundum (Al_2O_3), hydrargillite ($Al(OH)_3$), boehmite (AlO(OH)) and several combinations with other metal oxides and metal hydroxides, respectively. In the latter case the most popular are the alumosilicates, like feldspars, e.g. potassium feldspar ($K[AlSi_3O_8]$), and micas. As alteration products of the feldspars, the clays, and in further sequence the bauxites are to mention.

Extraction

For industrial purposes aluminium is extracted from red bauxite, after the *Bayer-process*, which also contains 20-25 % iron (III) oxide and 1-5% silicon oxide. Finely grounded bauxite is heated for several hours with soda lye (35-38%) in an autoclave at 140-250 °C. During this process sodium aluminate (Na [Al(OH)₄]) is produced with a reaction equilibrium totally at the aluminate side, whereas the iron (III) oxide is not solved in the soda lye. Afterwards the solution is filtered and the aluminium hydroxide is precipitated. The aluminium hydroxide will be annealed at 1200-1300 °C to get dissipated into the α -aluminium oxide. The aluminium oxide will be subjected to the fused-salt electrolysis admixed with cryolite (Na₃AlF₆) to allow for a moderate melting point at about 940-980 °C. As electrodes, carbon blocks are used with an operating voltage of about 4.5-5.0 V.

Physical properties

Aluminium crystallizes in a cubic close packing (cF4) with the space group $Fm\overline{3}m$ [8]. The Mohs hardness is 2.75 [9]. Due to the mechanical properties aluminium is the most technically applied light metal. Because of its small Young's modulus of 70 GPa [10] it is possible to create 0.004 mm thick aluminium foils. Furthermore, aluminium is paramagnetic and has a specific electrical conductivity of $3.767 \cdot 10^5$ S/cm which is 0.66 times the conductivity of copper.

Chemical properties

Aluminium basically occurs trivalent and gets oxidized by most non-metals. It forms intermediate compounds with almost all metals. With oxygen it assumes several oxidic compounds, a process which leads to a permanent oxide-layer on air (passivation). Aluminium reacts with non oxidizing acids such as hydrochloric acid but not with oxidizing ones, like nitric acid, because of the characteristic passivation it creates. In water and weak acids a protective $Al(OH)_3$ layer is formed whereas in strong acids and bases the $Al(OH)_3$ layer gets dissolved by forming Al^{3+} and aluminate $(Al(OH)_4)$, respectively.

2.2. Germanium [6]

Atomic number	32
Classification	Carbon group, 14 th
State of matter	solid
Appearance	grey white
Atomic mass (g·mol ⁻¹)	72.61
Electron configuration	$[Ar] 3d^{10}4s^24p^2$
Covalent radius (pm)	122
Melting point (K)	1211.4
Density (g·cm ⁻³)	5.323



Fig. 2: Germanium piece [11]

Table 2: Characteristics of Germanium [6]

Natural occurrence

Germanium occurs with a mass fraction of $1.4 \cdot 10^{-4}$ in the geosphere. The worldwide production of Germanium is roughly 100 tonnes [12]. Its main deposits are in the forms of sulphides, like thio-germanates, and rarely in form of argyrodite (Ag₈GeS₆) and germanite (Cu₆FeGe₂S₈), respectively. Germanium is currently recovered as a by-product from sphalerite zinc ores where it is concentrated in amounts of up to 0.3 % [13], especially from sediment-hosted, massive Zn-Pb-Cu(-Ba) deposits and carbonate-hosted Zn-Pb deposits [14].

Extraction

The most common way to extract germanium oxide (GeO₂), which is the pre-product for the germanium production, is to dissolve it with sulphuric acid away from the germanite containing flue gas, which occurs during the reprocessing of zinc ores. With the addition of soda lye the mixture has a germanium oxide content of about 2-10 %. After the conversion of germanium oxide into germanium chloride (GeCl₄) and further distillation of the volatile GeCl₄, germanium oxide is manufactured by hydrolysis and afterwards reduced with hydrogen to germanium. Ultrapure germanium is realised by zone melting.

Physical properties

Germanium (*cF8*), which is a semi-conductor, crystallizes such as α -silicon, namely in the diamond structure, where four of the eight tetrahedron holes of the face-centered cubic structure are occupied. Its space group is $Fd\overline{3}m$ [15]. Since germanium is a semi-metal it is very brittle, like tellurium, and has the Mohs hardness 6.0 [16]. Germanium expands during crystallisation because of the lower coordination number in the solid state.

Chemical properties

Germanium mainly occurs bivalent and tetravalent and is more or less stable at room temperature. It cannot be solved in non-oxidic acids and diluted sulphuric acid but it reacts to the dioxide (GeO₂) with oixidic acids such as nitric acid and concentrated sulphuric acid. Because of its affinity to the tetravalent oxidation state to reach the s^0 electron configuration it almost only occurs with the oxidation state +4 in nature.

2.3. Nickel [6]

Atomic number	28
Classification	Nickel group, 10 th
State of matter	solid
Appearance	silvery white
Atomic mass (g·mol ⁻¹)	58.69
Electron configuration	$[Ar] 4s^{1}3d^{9}$
Covalent radius (pm)	115
Melting point (K)	1728
Density (g·cm ⁻³)	8.908



Fig. 3: Nickel sheet [17]

Table 3: Characteristics of Nickel [6]

Natural occurrence

The mass fraction of nickel in the geosphere is approximately $7.2 \cdot 10^{-3}$. Native sources of nickel are only present in iron meteorites and especially in the earth's core. In the lithosphere nickel is mainly deposited in nickel containing ores. The major degradable nickel ores are pentlandite ((Ni,Fe)₉S₈), which is a nickel containing magnetic pyrite, and garnierite ((Mg,Ni^{II})₃(OH)₄[Si₂O₅]).

Extraction

Nickel is technically extracted from magnetic pyrites containing nickel, copper and iron. After slaging the disturbing iron oxide and iron sulphide, copper-nickel-matte is achieved. The matte is the shredded and melted with sodium sulphide where two separated layers of the liquefied material are generated. The head of the liquid phase is a disulfide of nickel and copper and on the bottom nickel sulphide is concentrated. Afterwards the bottom is calcinated to nickel oxide and reduced with carbon to rough nickel. Further purification like electrolytic refining or the conventional Mond process are used to realise more pure nickel.

Physical properties

Nickel crystallizes in the face-centered cubic structure (*cF4*) and the space group is $Fm\overline{3}m$ [18]. It is a hard metal with the Mohs hardness around 4 [19] and it is ductile. Due to its mechanical properties it is forgeable and takes a high polish. Nickel, like iron and cobalt, is ferromagnetic at room temperature (Curie-temperature 375 °C) and has a specific electrical conductivity of $1.46 \cdot 10^5$ S/cm which is six times lower than that of silver. Its Young's modulus is about 210 GPa [20].

Chemical properties

Nickel forms a common oxide layer and is therefore stable in a concentrated nitric acid but not in a diluted one. In non-oxidic acids the oxidation is slow and in alkali hydroxides nickel is stable up to 400 $^{\circ}$ C. Its most observed oxidation number is +2.

3. Literature

3.1. Binary subsystems

3.1.1.Al – Ge

The Aluminium – Germanium phase diagram has been entirely investigated, over the whole composition range, due to its significance in the semiconductor technology.

Initial assessment work on the Al-Ge system has been done by Ansara et al [21] and McAlister and Murray [22] where the latter authors considered solid solution limits of germanium and aluminium in their calculations. Primarily based on thermodynamic data of previous experimental work of Kroll et al [23], Stohr et al [24], Glazov et al [25] and McAlister and Murray made a first critical assessment [22] shown in Figure 4. The phase diagram shows a simple binary eutectic at 420°C with the eutectic point at 28.4 at.% germanium. The eutectic temperature has not been determined reliably but it has been estimated from electrochemical cell data of Eslami et al [26] of 417 \pm 3 °C. They have further presented a solubility of about 2.0 at.% Al in (Ge) and approximately 1.1 at.% Ge in (Al) at the eutectic temperature.



Subsequently, a re-evaluation of the Al-Ge system by Srikanth et al [28] has shown that the solid solution for (Ge) of McAlister and Murray [22] is in good agreement with experimental results of Glazov et al [25], shown in Figure 5. The solid solution of (Al) however is inconsistent with earlier electron probe microanalysis measurements of Minamino et al [29], who reported a maximal Ge solubility of about 2.56 at.% (Fig.5). Figure 5 also exhibits X-ray diffraction studies of Stohr and Klemm [24] and He⁺ backscattering experiments of Caywood [30], respectively.



Fig. 5: Solid solution of (Al) and (Ge) [28]



Fig. 6: Comparison of calculated and experimental Phase diagram of Al-Ge [28]

According to the presented results, a re-optimisation of the Al-Ge phase diagram (Fig. 6) has been achieved by Srikanth et al [28], incorporating the more reliable data of Minamino et al, the previously work of McAlister and Murray [22] and SGTE data for pure elements [31].

In contrast to McAlister and Murray the eutectic temperature is indicated at 696.85 K (Tab.4) and the solid solution of (Al) is around 2.6 at.% Ge. The two phases (Al) and (Ge) are shown in Table 5. The corresponding data in Table 4 and 5 were consulted in the present work.

		_	-
Reaction	Composition	Temperature	Reaction type
	(at.% Ge)	(°C)	
$L \leftrightarrow (Al) + (Ge)$	28 2.6 98.7	423.7	eutectic
L↔Al	0	660.5	melting
L⇔Ge	100	938.3	melting

 Table 4: Binary phase equilibria in the Al-Ge phase diagram [28]

 Table 5: Crystal structure data for the Al-Ge phase diagram [28]

Phase	Composition	Pearson	Space	Structure	Strukturbericht
	(at.% Ge)	symbol	group	type	designation
(Al)	0 - 2.6	cF4	Fm-3m	Cu	<i>A</i> 1
(Ge)	98.7 - 100	cF8	Fd-3m	C (diamond)	A4

3.1.2.Al – Ni

Due to the popularity of using nickel aluminides in several technical applications, the entire Al-Ni phase diagram has been investigated.

An early survey was given by Hansen [32] which was later adopted by Nash [33], shown in Figure 7. The re-investigated diagram of Nash differs from that of Hansen through the inclusion of the Al_3Ni_5 phase, based on recent work of Robertson and Wayman [34], refinement of the AlNi phase boundaries and a reconsideration of the (Ni) solid solution of Alexander and Vaughan [35].



Fig. 7: Al-Ni phase diagram by Nash [33]; Prediction of Alexander (above) [35]and Schramm (below) [36]

Moreover a conflict had to be decided by Nash, predicated on the publications of Alexander and Vaughan and Schramm [36] who argued for different interpretations of the peritectic reaction of the Ni₃Al phase (Fig. 7). Nash recommended the peritectic reaction $L+AlNi\leftrightarrow AlNi_3$ at 1395 °C based on Alexander and Vaughan whereas Schramm predicted the melting reaction $L+(Ni)\leftrightarrow AlNi_3$ at 1362 °C. However, the results of Schramm were later supported by several works [37-39], confirmed with transmission electron microscopy (TEM), differential thermal analysis (DTA) and metallography. They all observed two invariant reactions in a very closely temperature range (~2 °C). In a newer update (Fig. 8) of the Al-Ni phase diagram Okamoto [40] considered the results of Schramm [36] and several re-examinations of the AlNi+AlNi₃ two-phase field with microprobe analysis by [38, 39, 41].

Furthermore the AlNi₃+(Ni) two-phase field was also slightly modified by Jia [41] in respect to the assessed data given by Nash [33], which were all determined before the seventies and exhibited huge fluctuations. The composition of the Al₃Ni₂ phase at 1133 °C was altered to less than 40 at.% Ni contrary to Nash [33].



Fig. 8: Al-Ni phase diagram of Okamoto [40]

The reaction temperatures of the eutectic $(L \leftrightarrow AlNi + AlNi_3)$ and the peritectic $(L+(Ni)\leftrightarrow AlNi_3)$ reactions, shown in Table 7, were re-studied by Hilbert et al [38] and considered in the present work.

The presented Al-Ni phase diagram consists of two fcc solid solutions, (Al) and (Ni), one line-compound (Al₃Ni) and four non- stoichiometric phases (Al₃Ni₂, AlNi, Al₃Ni₅, AlNi₃) shown in Table 6. AlNi, Al₃Ni and Ni₃Al are formed peritectically whereas AlNi is generated congruently from the liquid at 1638°C. The Al₃Ni₅ phase which is supposed to be an equilibrium phase, by Robertson and Wayman [34], who applied X-ray diffraction, optical and electron microscopy techniques, crystallizes through a solid-state reaction of AlNi and AlNi₃. The two intermediate compounds Al₃Ni₂ (Al₃Ni₂-type) and AlNi (CsCl-type) were reported previously to be related concerning to their crystal structures.

 Al_3Ni_2 is formed by ordered vacancies on the Ni position in the AlNi structure. A new hexagonal arrangement of the unit cell is thus required which leads to a bigger cell with a higher amount of atoms. Therefore the powder pattern of Al_3Ni_2 shows additionally reflections.

The corresponding data in Table 6 and 7 were consulted in the present work.

Phase	Composition	Pearson	Space	Structure	Strukturbericht
	(at.% Ge)	symbol	group	type	designation
(Al)	0 - 0.11	cF4	Fm-3m	Cu	A1
Al ₃ Ni	25	oP16	Pnma	Fe3C	$D0_{11}$
Al ₃ Ni ₂	36.8 - 41.5	hP5	P-3m1	Al ₃ Ni ₂	$D5_{13}$
AlNi	42 - 69.2	cP2	Pm-3m	CsCl	<i>B</i> 2
Al ₃ Ni ₅	64 - ~68	oC16	Cmmm	Ga_3Pt_5	
AlNi ₃	72 - 77.6	cP4	Pm-3m	AuCu ₃	$L1_2$
(Ni)	78.8 - 100	cF4	Fm-3m	Cu	<i>A</i> 1

 Table 6: Crystal structure data for the Al-Ni phase diagram [33, 40]

 Table 7: Binary phase equilibria in the Al-Ge phase diagram [40]

Reaction	Composition		ion	Temperature	Reaction
	(at.% Ni))	(°C)	type
$L \leftrightarrow Al$		0		660.5	melting
$L \leftrightarrow Al_3Ni + (Al)$	2.7	25	0.11	639.9	eutectic
$L + Al_3Ni_2 \leftrightarrow Al_3Ni$	15	36.8	25	854	peritectic
$L + AlNi \leftrightarrow Al_3Ni_2$	26.9	42	38	1133	peritectic
L ↔ AlNi		50		1638	congruent
AlNi +AlNi ₃ ↔Al ₃ Ni ₅	60.8	72	66	700	peritectoid
$L \leftrightarrow AlNi + AlNi_3$	73.6	70	75	1360	eutectic
$L + (Ni) \leftrightarrow AlNi_3$	74.2	78.8	75.1	1362	peritectic
$L \leftrightarrow Ni$		100		1455	melting

3.1.3.Ge – Ni

The Ge-Ni phase diagram is a rather complex system which forms several high- and lowtemperature intermediate phases as well as some superstructures. The system has been investigated over the whole composition range but cannot be considered well established, especially in the range of 20 to 50 at.% Ge.

A first survey of the phase diagram was given by Nash et al [42] according to the results of Dayer and Feschotte [43] and Ellner et al [44]. Ellner et al have partially re-examined the Ge-Ni phase diagram in the region from 20 to 45 at.% germanium (Fig. 9), which contains all the intermediate compounds of the system. A γ ' high-temperature phase, reported by Ruttewit et al [45], could not be confirmed by Ellner et al and Dayer and Feschotte. In contrast to the work of Dayer and Feschotte, Ellner et al determined the phases GeNi_{2 (r)}, GeNi_{2 (h)}, Ge₃Ni₅ and Ge₁₂Ni₁₉ as to be separated.



Fig. 9: Ge-Ni phase diagram in the range of 25-45at.% Ge [44]

The γ and Ge₂Ni₅ high-temperature phases were presented by both authors [43, 44], but with a different melting behaviour. Ellner et al interpreted the reaction as $L+GeNi_{2(h)}\leftrightarrow Ge_2Ni_5$, whereas Dayer and Feschotte suggested $L+\gamma \leftrightarrow Ge_2Ni_5$. The published Ge-Ni phase diagram by Nash et al [42], shown in Figure 10, exhibits the version of Dayer and Feschotte [43], who used metals with a higher purity and made a number of differential



thermal analysis measurements. It is to notice that both authors have used different notations for the occurring phases.

Fig. 10: Ge-Ni phase diagram of Nash [42]

The peritectic formation of GeNi takes place at 850°C, and the eutectic reaction temperature of $L \leftrightarrow GeNi+(Ge)$ is about 762 °C, according to Dayer and Feschotte. Furthermore the phases β GeNi₃, ϵ Ge₃Ni₅ and ϵ 'Ge₃Ni₅ were observed to be formed congruently. Dayer and Feschotte also measured the solubility of the nickel solid solution with electron probe microanalysis and presented values around 12 at.% Ge. The whole melting behaviour is listed in Table 9.

The separation of the Ge₃Ni₅ phase, as it was considered by Nash et al [42], is based on results of Ellner et al [44], who applied DTA, optical microscopy and X-ray measurements. Ellner found that the Ge₃Ni₅ phase is splitted into two filled NiAs structured phases, Ge₂Ni₃ and ϵ Ge₃Ni₅, and a monocline superstructure Ge₁₂Ni₁₉. However it is to mention that the phase boundaries of the Ge₁₂Ni₁₉ phase were not investigated precisely, only by the means of DTA. Moreover a monocline low-temperature modification of the Ge₃Ni₅ phase with around 37.5 at.% Ge (ϵ 'Ge₃Ni₅) has been found to exist, as well as an superstructure of the Ge₃Ni₅ phase with the chemical composition GeNi₂. A complete compilation of the crystal structure data is shown in Table 8.

Phase	Composition	Pearson	Space	Structure	Strukturbericht
	(at.% Ge)	symbol	group	type	designation
(Ni)	0 - 12	cF4	Fm-3m	Cu	A1
$\beta GeNi_3$	22.5 - 25	cP4	Pm-3m	AuCu ₃	$L1_2$
$\gamma GeNi_3$	25.6				
δGe_2Ni_5	28	hP84	P6 ₃ /mmc	Pd_5Sb_2	
GeNi ₂	33.5	oP12	Pnma	Co ₂ Si	<i>C</i> 23
ε'Ge ₃ Ni ₅	~37	mC32	<i>C</i> 2	Ni ₅ Ge ₃	
εGe ₃ Ni ₅	33.8 - 38	hP4	P6 ₃ /mmc	NiAs	$B8_1$
Ge ₁₂ Ni ₁₉	38 - 41	mC62	C2	Ni ₁₉ Ge ₁₂	
Ge ₂ Ni ₃	41 - 43	hP4	P6 ₃ /mmc	NiAs	$B8_1$
GeNi	50	oP8	Pnma	MnP	<i>B</i> 31
(Ge)	~100	cF8	Fd-3m	C(diamond)	<i>A</i> 4

 Table 8: Crystal structure data for the Ge-Ni phase diagram [42]

Table 9: Binary phase equilibria in the Ge-Ni phase diagram [42]

Reaction	Composition		Temperature	Reaction	
	(at.% Ni)			(°C)	type
$L \leftrightarrow Ni$		0		1455	melting
$L \leftrightarrow (Ni) + \beta GeNi_3$	23	~16	~23.3	1124	eutectic
$L \leftrightarrow \beta GeNi_3$		~24		1132	congruent
$L + \beta GeNi_3 \leftrightarrow \gamma GeNi_3$	27.3	~25	~25.6	1118	peritectic
$L + \gamma GeNi_3 \leftrightarrow \delta Ge_2Ni_5$	28.9	25.6	28	1102	peritectic
$\gamma GeNi_3 {\leftrightarrow} \beta GeNi_3 {+} \delta Ge_2Ni_5$	25.6	~25	28	1082	eutectoid
$\delta Ge_2Ni_5 {\leftrightarrow} \beta GeNi_3 {+} \epsilon Ge_3Ni_5$	28	25	33.6	1045	eutectoid
$L \leftrightarrow \delta Ge_2Ni_5 + \epsilon Ge_3Ni_5$	29	28	33.6	1099	eutectic
$\beta GeNi_3 + \epsilon Ge_3Ni_5 \leftrightarrow GeNi_2$	25	34.5	33.5	506	peritectoid
εGe ₃ Ni ₅ ↔GeNi ₂ +ε'Ge ₃ Ni ₅	36.3	33.5	37	290	eutectoid
$\varepsilon Ge_3Ni_5 \leftrightarrow \varepsilon'Ge_3Ni_5$		37.4		~398	congruent
$L \leftrightarrow \epsilon Ge_3Ni_5$		36.5		1185	congruent
$L + \epsilon Ge_3Ni_5 \leftrightarrow Ge_{12}Ni_{19}$	~45.5	38.8	39	1050	peritectic
$L + Ge_{12}Ni_{19} \leftrightarrow Ge_2Ni_3$	47	~41.5	~41.7	990	peritectic
$L + Ge_2Ni_3 \leftrightarrow GeNi$	~45	54.5	50	850	peritectic
$Ge_2Ni_3 \leftrightarrow Ge_{12}Ni_{19} + GeNi$	~39.6	~39.2	50	515	eutectoid
$\epsilon Ge_3Ni_5 \leftrightarrow \epsilon'Ge_3Ni_5 + Ge_{12}Ni_{19}$	~37.7	~37.5	~38	~394	eutectoid
$Ge_{12}Ni_{19} \leftrightarrow \epsilon'Ge_3Ni_5 + GeNi$	~38.2	~37.6	50	382	eutectoid
$L \leftrightarrow \text{GeNi} + (\text{Ge})$	67	50	~100	762	eutectic
$L \leftrightarrow Ge$		100		938.3	melting

3.2. Previous investigation of the ternary system: Al-Ge-Ni

The ternary phase diagram Al-Ge-Ni was previously studied by Yanson et al [46], who constructed an isothermal section at 770 K, which is given in Figure 11.

For sample preparation Yanson et al have used an electric arc furnace. The samples were sealed in silica ampoules and annealed at 770 K for about 1000 hours before they were quenched in cold water. The determination of the phase compositions have been done with X-ray powder diffraction (XRD) and additional optical microscopy has been applied.

A ternary compound Σ , with the empirical formula Ni₄AlGe according to the ternary phase Ni₄AlSi in the related Al-Si-Ni system, was reported but not further characterised. Moreover a solubility of about 3 at.% Ge in the Al₃Ni₂ binary phase was indicated, as well as a solubility of 7 at.% Ge in AlNi. A continuous solid solution of the two $L1_2$ phases AlNi₃ and GeNi₃ was determined by the means of optical microscopy. The continuous solid solution was also examined by Ochiai et al [47], who employed X-ray methods and metallography, and demonstrated the existence of a continuous solid solution at 1273 K.



Fig. 11: Isothermal section of the system Al-Ge-Ni at 770 K [46]

4. Theoretical basics and experimental methods

4.1. Phase diagrams [48, 49]

Phase diagrams, also known as constitutional diagrams or equilibrium diagrams, describe the state of a materials system in thermodynamic equilibrium as a function of temperature, pressure and composition.

A phase is characterised to have a homogeneous chemical composition and uniform physical properties. Besides its appearance in one of the three states of matter, solid, liquid or gaseous it further has relatively distinct mechanical properties.

In materials chemistry the most attention is turned on metals and metal oxides and the phase diagrams among them. Phase diagrams are nowadays the most important tools for demonstrating all occurring phases as well as their thermodynamic behaviour at different intensive properties (temperature, pressure), for a selected one- or more-component system. They are used on the one hand to better understand solidification processes which is important to explain e.g. mechanical properties and on the other hand to characterize appearing compounds and phases as well as their reactions. For example it is necessary to know what happens with a material in the whole temperature and pressure range, where it is applied, to avoid unwanted phase transformations and with it changes of its properties. Phase transformations can occur through different types of transitions which are usually first order and second order transitions. First order transitions are e.g. congruent phase melting or invariant phase reactions, at which the first derivation of the Gibbs-energy (enthalpy, entropy and volume) has a discontinuity. Second order transitions, like magnetic transformations, are continuous transitions and have no discontinuity of H, S and V, but of the heat capacity c_p .

From the thermodynamical point of view a phase diagram exhibits all equilibrium phases which are stable at given conditions. Multi component phase diagrams are mainly specified in form of x/T diagrams where the pressure is kept constant at atmospheric pressure. The equilibrium state of a certain phase diagram is defined when the free energy G (1)

$$G = H - T \cdot S \tag{1}$$

is at a minimum, with *H* as the heat content or enthalpy $(J \cdot mol^{-1})$, *S* the entropy $(J \cdot mol^{-1}K^{-1})$ and *T* the absolute temperature (K). The phase boundaries and hence the equilibria of all phases among themselves can be constructed by a combination of all ΔG curves of the phases in the system.

Moreover the construction of phase diagrams on the basis of experimental investigations claims for several thermodynamic rules. Foremost of these is the Gibb's phase rule (2),

$$P + F = C + 2 \tag{2}$$

which is modified for condensed systems (p = const.) to the "condensed phase rule" (3),

$$P+F'=C+1\tag{3}$$

where P represents the number of phases which are in equilibrium, C means the order of the system (e.g. 2 for a binary system) and F is the degree of freedom or rather the number of variables that can be varied independently.

4.2. Isothermal methods for phase diagram investigation

4.2.1.X-ray powder diffraction and Rietveld refinement: Phase identification [50]

The X-ray powder diffraction (XRD) is the most important method for phase identifications in solid state chemistry. By the means of XRD it is possible to analyse all crystalline substances due to their periodic electron density over a long range order.

The method is based on diffraction phenomena of electromagnetic radiation. The radiation applied for XRD investigations is X-ray radiation (e.g. $CuK\alpha_1$ = 1.540596 Å) due to general inter atomic distances of crystalline substances around 2 Å. The X-ray radiation is produced by conventional X-ray tubes where electrons, which are emitted from a heated tungsten cathode, are accelerated towards a target which is layered by a metal (Cu, Mo, Co, Fe) in respect to the required wavelength of the X-ray radiation. Electrons are then knocked out of inner orbitals of the respective element and get re-occupied by electrons of outer shells. The different binding energies of the electrons which are taking part at the transition lead to emission of a characteristic X-ray quantum. Because of differences in the probability of electron transitions the spectrum shows different intensities of the characteristic X-rays. A schematic emission spectrum of a Cu X-ray tube is shown in Figure 12.



Fig. 12: Schematic spectrum of copper

Beside the characteristic X-ray radiation of the most probable electron transitions of copper (CuK α_1 , CuK α_2 , CuK β) a huge amount of the kinetic energies of the incident electrons is transferred on so-called white radiation (Bremsstrahlung). To gain useful intensities of the characteristic X-ray radiation for XRD, the acceleration voltage has to be around 20-60 kV.

XRD is based on the constructive interference of diffracted X-ray beams after entering a solid substance. A model for diffraction is given by the Bragg approach which is graphically represented in Figure 13. While a crystalline substance is geometrically built up of atom layers, the incident X-ray radiation is diffracted at the high electron densities of atoms.



Fig. 13: Theoretical description of X-ray diffraction

If path differences, shown as red line, are equal to n times the applied X-ray wavelength, the diffracted beams interfere constructively. The respective Bragg equation is given in (4).

$$2d\sin\theta = n\lambda\tag{4}$$

Thus each hypothetical plane in the crystal structure leads to interference at a certain angle and gives a reflection in the diffraction pattern. As a nomenclature the Miller indices (*hkl*) are used to describe the different lattice planes in the crystal. The spacing of a certain plane set (*hkl*) can be calculated from the lattice parameters, using different equations for the 7 crystal systems. The intensity of a diffracted X-ray beam is affected by the arrangement of atoms within the unit cell. The intensity *I* is proportional to the square of the absolute value of the structure factor *F* (5-6), which describes the scattering power of the unit cell.

$$I_{hkl} \propto \left| F_{hkl} \right|^2 \tag{5}$$

$$F_{hkl} = \sum_{j} N_{j} f_{j} \cdot e^{-B_{j} \frac{\sin^{2} \theta}{\lambda^{2}}} \cdot e^{2\pi i (hx_{j} + ky_{j} + lz_{j})}$$
(6)

In equation (7) N_j is the multiplicity of the atomic position (x_j, y_j, z_j) and B_j is the temperature factor of atom *j*. *fj* is known as the scattering factor of atom *j*, occupying the position (x_j, y_j, z_j) , which is temperature dependent and decreases with increasing diffraction angle. The highest possible value for f_j is the respective atomic number of atom *j*. Furthermore there are additional factors which influence the intensity e.g. multiplicity factor *P*, Lorentz factor *L*, polarisation factor *P*, absorption factor *A*.

Instrumental setup

The generated X-ray beam can enter the sample in two different modes, the transmission and reflection mode, respectively. The transmission mode, as it is employed in the Guinier-Huber technique, uses a fine focus X-ray tube and a monochromator (e.g. Ge single crystal) to provide that only CuK α_1 radiation enters the sample. Diffracted beams are then detected with an image plate detector in transmission condition. Conventional image plate detectors are working with an X-ray sensitive BaFBr: Eu2⁺ layer. Incident X-rays are producing colour centres which were then read with a laser which stimulates emission of radiation in the visible range. These photons are then detected with a photomultiplier. The feature of the Gunier-Huber technique is the simultaneously detection of the whole powder XRD pattern which leads to higher intensities at shorter measurement periods.

The reflection mode is applied in the corresponding Bragg-Brentano pseudo-focusing geometry where the sample and the detector ($\theta/2\theta$ instrumentation) or the X-ray source and the detector (θ/θ instrumentation) are moving on a circle. The X-ray radiation is entering the sample after passing several slits (e.g. collimator) to guarantee linear incident beams. Further slits and filters (e.g. $K\beta$) are positioned between sample and detector to avoid that scattering beams and stray radiation enters the detector. Several types of detectors are used e.g. scintillation counter, solid state and one dimensional detector. The scintillation counter is a classical method where X-ray beams generate photons (flashes) in the visible range, after entering a conventional Tl doped NaI crystal, which are then detected by photomultiplier. Solid state detectors are energy dispersive, based on semiconducting technique, where incident X-rays are producing electron/hole pairs. The generated charge is proportional to the energy of the X-rays and the resolution is limited by the band gap energy of the respective semiconducting material (~3.8 eV for Si). Solid state detectors are often applied for metals such as Mn, Fe and Co, which exhibit strong X-ray fluorescence. The fastest and most common detectors in respect to powder XRD are the one dimensional detectors where a number of small silicon strips are arranged along a line. θ is described simultaneously (increment: ~0.01°) by adding the signals, detected in a certain range around θ . Thus and due to several statistical and systematically errors reflections are given as peaks in the diffraction pattern.

Rietveld refinement

A powder XRD pattern is given as a two dimensional plot of the diffraction angle θ on the abscissa against the intensity, measured in X-ray counts, on the ordinate. The most important information, gained from a powder pattern, are the positions of the diffraction lines, linked to unit cell dimensions, and the intensities of the different reflections, linked to e.g. atomic positions, site occupations and different electron densities.

The evaluation of powder XRD patterns is practised by comparison of theoretically calculated patterns with the observed diffraction patterns from the measurements. The method of structure refinement from X-ray powder data was presented by Hugo Rietveld. In the so-called Rietveld refinement the diffraction pattern is calculated based on structure-, profile-and instrument- related parameters. The software for powder pattern evaluation used in this evaluation is DIFFRAC^{*plus*}TOPAS, provided by Bruker AXS.

The refinement is working after a least square algorithm by comparing calculated with observed intensities (7).

$$\chi_1^2 = \frac{\sum_i w_i (y_{Oi} - y_{Ci})^2}{\sum_i w_i y_{Oi}}$$
(7)

 y_{Oi} and y_{Ci} are the respective observed and calculated intensities at point *i* and w_i is a weight factor which considers different weights of the data points. Reflection data points are thus much more weighted than background data points. The corresponding y_{Ci} is calculated, using the fundamental parameter approach, on the basis of instrumental and phase specific parameters. For each phase in a diffraction pattern the calculation follows equation (8),

$$y_{Ci} = y_{Bi} + S \cdot \sum_{hkl} \left| F_{hkl} \right|^2 \cdot P \cdot \left(\frac{1 + \cos^2 2\Theta_i}{\sin^2 \Theta_i \cos \Theta_i} \right) \cdot e^{\frac{-2B \sin^2 \Theta}{\lambda^2}} \cdot \Phi(2\Theta_i - 2\Theta_{hkl}) \cdot P_{hkl} \cdot A \cdot S_r \cdot E$$
(8)

where y_{Bi} describes the background at *i* (polynomial function) and *S* the scaling factor for each phase. P_{hkl} and S_r are additional functions for possible preferred orientation and surface roughness whereas *A* and *E* consider absorption and extinction, respectively. The function Φ describes the profile of the reflections (Gauss or Lorentz-type). The quality of a refinement can be noticed by reliability values, the so-called R-values, which describe the coincidence between calculated and observed patterns. Smaller R-values means better fits and are thus aspired.

4.2.2. Optical microscopy [51]

The most conventional imaging mode for the examination of microstructures, by using a reflected-light microscope, is the bright field mode (Fig. 14) e.g. for the determination of primary crystallisation or the estimation of grain sizes.

The light beam enters at first a collector lens which produces a bundle of parallel beams that pass then a dichroic mirror. Subsequently the diffracted beam enters an objective (collecting lens) which focuses it on a focal

point if the sample is in focus of the lens. Reflected beams come through the tubus lens where a real image is produced. This real image can be observed through an ocular which works in principle as a loupe. The contrast is given due to surface properties like reflectivity, colour and roughness.

Additional help, for the observation of different grains as well as their difference in hardness, can be obtained by dark field imaging (Fig. 15) where the beam primarily passes a mirror system and gets deviated from the normal optical path. After coming through a ring mirror and a dark channel system the beam enters the sample at a low angle. Only beams that get reflected by surface structures such as scratches, grain boundaries, holes or cracks enter the aperture and can be

noticed. Scratches are mostly a product of the hardness of a phase due to stronger abrasive at the prior grinding and polishing process. Perfect flat areas do not show any differences in the contrast but they will be seen as black areas.

For the observation of different crystallites as well as the discovery of single crystals, polarisation optics is a reinforced method (Fig. 16).

Linear polarized light is induced by a polarizer which is diffracted at a dichroic mirror. The beam passes the sample where the polarization plane is modified, according to optical properties of the phases. The reflected beam enters an analyzer, which is positioned at ninety degrees



Fig. 16: Polarization optics

angle to the polarizer, in order to obtain contrast due to the different optical properties and



Fig. 14: Bright field imaging

ocula

aperture

Fig. 15: Dark field imaging

tubus lens

sample

ring

collecto

mirror system

condensing lens

orientations of the crystallites. Strong and weak polarizing surfaces can be identified by rotating the sample relative to the incident beam. Cubic crystals are isotropic due to their refractivity and do not rotate the polarization plane of a linear polarized beam. Therefore they show the same colour in every orientation.

For imaging of small differences in height of the grains, which gives important information about its hardness, the differential interference contrast (DIC) optics is applied (Fig. 17). The incident beam is polarized and enters a birefringent prism where it is separated into two parts. According to height differences at the surface of the sample, due to the grinding process, the separated beams have different optical path lengths. After passing an



Fig. 17: DIC optics

analyzer they interfere according to their optical path difference. For a better contrast a colour filter (λ -plate) is applied.

The investigation of the microstructure reveals lots of important information which are necessary for sample characterisation. Useful information of the following issues can be obtained:

- thermal history of a sample (annealed or slowly cooled)
- crystallisation sequence
- reaction sequence and type of reactions
- grain sizes and grain size distribution
- segregation
- amount of phases
- precipitation (solid-solid transition)
- miscibility gaps
- twinning and martensitic transformation

4.2.3. Scanning electron microscopy and electron probe microanalysis

Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) are used for qualitative and quantitative examination as well as imaging of microstructures and occurring phases, respectively. The imaging is applied similar to optical microscopy but with a higher resolution.

At both techniques an electron beam, produced from a heated cathode (tungsten, LaB_6 tip) in a Wehnelt cylinder, is focussed through electromagnetic lenses to less than 1µm spot size at the sample. To avoid charging at the sample's surface the sample has to be either conductive or coated with a conductive material (sputtering). The collision of electrons with solid material leads to several effects, shown in Figure 18.



Fig. 18: Interaction of the primary electrons with the sample

Back scattered electrons (BSE) as well as secondary electrons (SE) are used for imaging. An image is constructed by scanning a certain surface area with the electron beam line by line. Since secondary electrons are ionisation products of sample atoms, they have very low energies (most probably: 3-5 eV) and leave the sample only in a narrow area near the surface. Thus SE contrast is given due to the topography of the surface. Back scattering electrons are generated by multiple elastic and inelastic scattering of electrons of the primary beam at the high electron densities of atoms. In this case contrast is given by different average atomic numbers of the phases.

Qualitative and quantitative information is gained from the investigation of the characteristic X-ray radiation emitted from the sample. The characteristic X-ray radiation is

generated when an electron of the primary beam removes an inner shell electron whose shell is then immediately re-filled by a higher energy electron of an outer shell (Fig. 19). The energy difference of the respective electron levels is emitted as an X-ray quantum, characteristic for the corresponding atom. There are only a few electron transitions (K-, L-, Mlines) which are suitable for qualitative and quantitative

the

analysis

according

to



Fig. 19: Characteristic lines [51]

probabilities. To gain significant intensities of the measured lines, the acceleration voltage of the primary beam has to be higher than the energy differences of the respective electron levels.

transition

difference in

For determination of characteristic X-ray radiation, energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) are applied. EDS uses an energy dispersive detector where X-rays are generating electron/ hole pairs on a photosensitive Si layer. Signals are counted in different energy channels which results in a two dimensional plot with the energy of the X-rays on the abscissa and the counts on the ordinate. The resolution of the detector is limited by the band gap energy of the respective photosensitive layer. Since EDS measures the whole spectrum simultaneously, it is a very fast method and thus commonly used in scanning electron microscopy.

Wavelength dispersive spectroscopy is usually applied in electron probe microanalysis (Fig. 20), where the characteristic X-rays are monochromated on different orientated crystals (Bragg approach) and then counted with a scintillation detector, which is moving along a focussing circle. WDS spectra are thus given with the diffraction angle on the abscissa against

intensity on the ordinate. Since the detector and the crystal move while measuring, the method is slower than EDS. The resolution of WDS however, is much higher, which makes this method promising for accurate qualitative and quantitative analysis.

To gain quantitative reliably results, conventional ZAF matrix correction is employed to consider matrix effects of the sample material.



Fig. 20: Electron probe micro analyzer [51]

4.3. Dynamic methods for phase diagram investigation

4.3.1. Differential thermal analysis DTA: Investigation of phase reactions

Differential thermal analysis is a dynamic method where physical properties of a sample are followed, while the sample is subjected to a certain temperature program. It is applied for the investigation of reaction temperatures of first and second order transitions. Due to the fact that every phase transition is connected with a heat exchange, either exothermal or endothermal, these effects can be measured by the means of differential thermal analysis.

Figure 21 presents schematically the measurement setup of a DTA, where a sample and a reference are heated up to a certain temperature in a tubular furnace. Both, the sample and the reference, are positioned in suitable crucibles (e.g. Al₂O₃), which can withstand at least the maximum temperature of the selected temperature program and do not react in any form with the materials. As reference (e.g. Ti-plates) a material is applied which shows no phase transitions in the range of the temperature program, and has a high affinity to oxygen as well as a higher melting point than the sample. The sample and the reference are heated up to a certain temperature under inert gas (e.g. Ar), until the sample is fully melted. To avoid disturbing oxygen the reference additionally acts as a getter. During the measurement the temperatures of the sample and the reference, respectively, are followed by two thermocouples, which measure the temperature at the bottom of the crucibles.



Fig. 21: DTA measurement setup

The DTA signal is evaluated as a two dimensional plot with the temperature difference ΔT (T_{Ref} - T_S) on the ordinate and the reference temperature T_{Ref} on the abscissa. There are two sorts of effects, invariant (F = 0) and non-invariant (F > 0), which exhibit typical shapes in the DTA curve. Invariant reactions take place at a fixed temperature while non-invariant reactions occur within a temperature interval. While heat is transferred between the furnace, crucible, sample (reference) and the thermocouple the DTA signals are often deviated from the ideal shape.

5. Experimental section

5.1. Sample preparation

5.1.1. Basic materials and individual alloys

For the investigation of the Al-Ge-Ni system several individual samples with strategically selected compositions have been prepared (Tab. 10, Fig. 22). As basic materials following metals have been used which provide high purities, necessary for the sensible equilibration in solid state chemistry.

-Aluminium slug, 3.175 mm x 6.35 mm, 99.999 % (5N), Fa. Johnson Matthey Chemicals
-Germanium pieces, 3-9 mm, 99.999 % (M5N), Fa. Johnson Matthey Chemicals
-Nickel Foil, 1 mm, 99.99 % (4N), Fa. Advent, Research Materials Ltd.

The samples have been weighted with a semi-micro balance and an accuracy of about ± 0.5 mg and ± 0.1 at.%, respectively. The total sample masses are generally 1000 mg but also 800 mg for aluminium rich samples due to the lower density.



Fig. 22: Prepared samples for phase diagram investigation

Sample	Nominal composition/ at%			Actual	Total mass		
/ ID	Al	Ge	Ni	Al	Ge	Ni	/ mg
TR01	75.00	15.00	10.00	75.02	15.00	9.98	1000
TR02	75.00	5.00	20.00	74.98	5.02	20.01	1000
TR03	55.00	25.00	20.00	54.99	25.00	20.02	1000
TR04	35.00	45.00	20.00	35.01	45.01	19.98	1000
TR05	15.00	65.00	20.00	15.05	65.00	19.95	1000
TR06	60.00	5.00	35.00	59.97	5.06	34.97	1000
TR07	50.00	15.00	35.00	49.97	15.02	35.00	1000
TR08	40.00	25.00	35.00	39.98	25.03	34.99	1000
TR09	30.00	35.00	35.00	29.94	35.07	35.00	1000
TR10	20.00	45.00	35.00	19.96	45.05	34.99	1000
TR11	10.00	55.00	35.00	9.96	55.05	34.99	1000
TR12	45.00	5.00	50.00	44.98	5.03	49.99	1000
TR13	30.00	20.00	50.00	29.97	20.05	49.98	1000
TR14	5.00	45.00	50.00	4.97	45.04	49.99	1000
TR15	35.00	5.00	60.00	34.99	5.02	59.99	1000
TR16	30.00	10.00	60.00	29.94	10.03	60.02	1000
TR17	25.00	15.00	60.00	24.96	15.02	60.02	1000
TR18	15.00	25.00	60.00	15.03	25.01	59.96	1000
TR19	10.00	30.00	60.00	10.04	30.03	59.92	1000
TR20	5.00	35.00	60.00	4.91	35.07	60.02	1000
TR21	20.00	10.00	70.00	19.98	10.05	69.98	1000
TR22	15.00	15.00	70.00	15.01	15.01	69.98	1000
TR23	10.00	20.00	70.00	10.08	20.00	69.92	1000
TR24	5.00	25.00	70.00	5.00	25.02	69.98	1000
TR25	24.00	6.00	70.00	23.95	6.04	70.01	1000
TR26	23.00	10.00	67.00	23.01	10.03	66.96	1000
TR27	21.50	15.00	63.50	21.57	15.00	63.43	1000
TR28	20.00	20.00	60.00	19.99	20.02	60.00	1000
TR29	18.50	26.50	55.00	18.51	26.52	54.97	1000
TR30	17.00	33.00	50.00	17.05	32.99	49.96	1000
TR31	14.00	45.00	41.00	14.01	45.00	40.99	1000
TR32	9.00	65.00	26.00	8.99	65.01	26.00	1000
TR33	3.50	85.50	11.00	3.50	85.53	10.97	1000
TR36	65.00	15.00	20.00	64.99	15.00	20.00	1000
TR37	45.00	35.00	20.00	45.04	34.98	19.98	1000
TR38	25.00	55.00	20.00	25.04	54.93	20.02	1000
TR39	5.00	75.00	20.00	5.06	74.94	20.00	1000
TR40	3.00	27.00	70.00	3.04	27.01	69.95	1000
TR41	19.00	24.00	57.00	19.02	24.02	56.96	1000
TR42	15.00	26.00	59.00	15.04	25.98	58.98	1000
TR43	16.00	51.00	33.00	16.03	50.99	32.98	1000

Table 10: Nominal and actual compositions of all prepared samples

*Actual compositions were calculated from the weighed masses by the balance

Sample	Nominal composition/ at%			Actual composition/ at%			Total mass
/ ID	Al	Ge	Ni	Al	Ge	Ni	/ mg
TR44	20.50	5.00	74.50	20.53	4.99	74.48	1000
TR45	15.00	10.00	75.00	15.01	9.99	75.01	1000
TR46	10.00	15.00	75.00	10.03	14.99	74.98	1000
TR47	4.00	20.00	76.00	3.98	20.01	76.02	1000
TR48	13.00	5.00	82.00	13.01	5.00	81.99	1000
TR49	5.00	11.00	84.00	4.95	11.02	84.03	1000
TR54	15.00	40.00	45.00	15.00	40.00	45.00	1000
TR55	10.00	60.00	30.00	9.99	60.00	30.02	1000
TR56	13.00	50.00	37.00	13.00	50.02	36.98	1000
TR57	7.00	73.00	20.00	7.01	73.00	19.99	1000
TR58	46.00	10.00	44.00	46.00	10.00	43.99	1000
TR59	40.00	10.00	50.00	40.00	10.01	50.00	1000
TR60	35.00	10.00	55.00	34.97	10.01	55.02	1000
TR61	30.00	10.00	60.00	30.03	10.01	59.96	1000
TR62	23.00	10.00	67.00	23.01	10.00	66.99	1000
TR63	85.00	5.00	10.00	85.00	5.01	9.98	800
TR64	65.00	25.00	10.00	65.00	25.00	10.01	800
TR65	50.00	40.00	10.00	49.99	39.99	10.02	1000
TR66	34.00	56.00	10.00	34.00	55.99	10.01	1000
TR67	15.00	75.00	10.00	15.08	74.95	9.98	1000
TR68	8.50	81.50	10.00	8.55	81.44	10.01	1000
TR69	5.50	84.50	10.00	5.50	84.51	9.98	1000
TR70	2.00	88.00	10.00	2.07	87.93	10.00	1000
TR71	67.50	18.00	14.50	67.51	18.00	14.49	800
TR74	24.79	40.53	34.68	24.80	40.53	34.67	1000
TR79	22.00	43.00	35.00	22.01	43.07	34.92	1000
TR80	24.00	40.00	36.00	23.98	40.07	35.95	1000
TR81	19.00	50.00	31.00	18.98	50.01	31.01	1000
TR82	16.00	57.00	27.00	15.92	57.06	27.02	1000
TR83	32.00	37.00	31.00	31.99	37.03	30.98	1000
TR84	26.00	43.00	31.00	26.03	42.97	31.00	1000
TR85	23.00	44.00	33.00	22.96	44.05	32.98	1000

*Actual compositions were calculated from the weighed masses by the balance
5.1.2. Arc furnace melting

The weighted samples have been melted with an arc furnace (Johanna Otto GmbH, MAM1, Fig. 23) under argon atmosphere (Argon 5.0, >99.999Vol.%). The electric arc is provided by a moveable tungsten needle, which acts as an anode, and the sample which forms the cathode. After applying a potential the arc is initialised by touching the tungsten needle with a tungsten-bold, which is positioned on a water-cooled



Fig. 23: Common arc furnace [52]

copper plate in the recipient. Due to electron collision ionisation of the argon atoms a low temperature plasma arises which can attain around 3000 °C. By moving the tungsten needle above the sample, which is placed in a small cavity (chill-mould) of the copper plate, the material melts immediately to a pill. By varying the current it is possible to control the temperature. To avoid traces of oxygen in the recipient, which leads to oxidation of the sample during the melting process, a zirconium pearl (getter) is melted before the samples, to bind the oxygen. To guarantee a homogeneous distribution of the basic materials the pill is melted three times by turning it upside down and always weighed back to check for possible mass loses. It was found that the mass loses were negligible in all samples.

5.1.3. Equilibration

The melted pills were further annealed at certain temperatures and durations to obtain respective equilibration of the different phases of each sample. The annealing temperatures were chosen to be slightly lower than relevant invariant reaction in the binary subsystems.



For the annealing routine the samples had to be under vacuum ($\sim 10^{-3}$ mbar) which was realized by placing them into alumina crucibles and further melting

them into evacuated silica glass tubes (Fig.24) with the help of an H_2/O_2 Fig. 24: Sample flame.

Two different methods were applied for annealing. On the one hand the pills were directly melted into silica glass and on the other hand they were powdered and pressed into pills before annealing, to allow for short diffusion paths. In the latter case the pill was powdered by the use of a tungsten carbide mortar and sieved (Mesh: 0.125 μ m) before it was pressed by a hydraulic press (Larzep EC10.13) with 15kN for 5 minutes.

Afterwards the samples were annealed at certain temperatures in conventional muffle furnaces for different durations. For the investigation of the thermodynamic equilibria at the annealing temperatures the samples had to be quenched in cold water. Table 11 shows the annealing conditions as well as the further analyzing methods to which the samples were subjected.

Sample	Annealing	Annealing	Analyzing methods				
/ ID	temperature/ °C	duration	XRD	OM	ESEM	EPMA	DTA
TR01	400	14 days	Х	Х	X	Х	
TR01*	400	14 days	Х				Х
TR02	400	14 days	Х	Х	X	Х	
TR02 [*]	400	14 days	Х				Х
TR03	650 + 400	7 + 7 days	Х	Х	X	Х	
TR03 [*]	400	2 months	Х				Х
TR04	650 + 400	7 + 7 days	Х	Х	X		
TR04 [*]	400	2 months	Х				Х
TR05	650 + 400	7 + 7 days	Х	Х	X	Х	
TR05 [*]	700	14 days	Х				Х
TR06	650 + 400	7 + 7 days	Х	Х	X		Х
TR07	650 + 400	7 + 7 days	Х	Х	X		Х
TR08	650 + 400	7 + 7 days	Х	Х	X		Х
TR09	650 + 400	7 + 7 days	Х	Х	X	Х	Х
TR09 [*]	700	14 days	Х				
TR10	650 + 400	7 + 7 days	Х	Х	X	Х	Х
TR10 [*]	700	14 days	Х				
TR11	650 + 400	7 + 7 days	Х	Х	X	Х	Х
TR11 [*]	700	14 days	Х				
TR12	700	20 days	Х	Х		Х	Х
TR13	700	20 days	Х	Х		Х	Х
TR14	700	20 days	Х	Х		Х	Х
TR15	700	20 days	Х	Х		Х	Х
TR16	700	20 days	Х	Х		Х	Х
TR17	700	20 days	Х	Х		Х	Х
TR18	700	20 days	Х	Х		Х	Х
TR19	700	20 days	Х	Х		Х	Х
TR20	700	20 days	Х	Х		Х	Х
TR21	700	20 days	Х	Х		Х	Х
TR22	700	20 days	Х	Х		Х	Х

Table 11: Annealing conditions and applied methods of the respective samples

Sample	Annealing	Annealing	Analyzing methods				
/ ID	temperature/ °C	duration	XRD	OM	ESEM	EPMA	DTA
TR23	700	20 days	Х	Х		Х	Х
TR24	700	20 days	Х	Х		Х	Х
TR25	700	20 days	Х	Х		Х	Х
TR26	700	20 days	Х	Х		Х	Х
TR27	700	20 days	Х	Х		Х	Х
TR28	700	20 days	Х	Х		Х	Х
TR29	700	20 days	Х	Х		Х	Х
TR30	700	20 days	Х	Х		Х	Х
TR31	700	20 days	Х	Х		Х	Х
TR32	700	20 days	Х	Х		Х	Х
TR33	700	20 days	Х	Х		Х	Х
TR36	400	6 weeks	Х	Х	X		Х
TR37	400	6 weeks	Х	Х			Х
TR38	400	6 weeks	Х	Х			Х
TR39	700	6 weeks	Х	Х			Х
TR40	700	6 weeks		Х			Х
TR41	700	4 weeks	Х	Х	Х		Х
TR42	700	4 weeks	Х	Х	X		Х
TR43	700	3 weeks	Х	Х			
TR44	800	2 months	Х				
TR45	800	2 months	Х				
TR46	800	2 months	Х				
TR47	800	2 months	Х				
TR48	800	2 months	Х				
TR49	800	2 months	Х				
TR54	700	4 weeks					Х
TR55	700	3 weeks					Х
TR56	700	3 weeks					Х
TR57	700	3 weeks					Х
TR58 [*]	700	2 months	Х				
TR59 [*]	700	2 months	Х				
TR60*	700	2 months	Х				
TR61 [*]	700	2 months	Х				
TR62 [*]	700	2 months	X				
TR63 [*]	400	4 weeks	Х				Х
TR64 [*]	400	4 weeks	Х				Х
TR65 [*]	400	4 weeks	Х				Х
TR66 [*]	400	4 weeks	Х				Х

Sample	Annealing	Annealing	Analyzing methods				
/ ID	temperature/ °C	duration	XRD	OM	ESEM	EPMA	DTA
TR67 [*]	500	4 weeks	Х				Х
TR68 [*]	700	4 weeks	Х				Х
TR69*	700	4 weeks	Х				Х
$\mathrm{TR70}^{*}$	700	4 weeks	Х				Х
TR71	400	4 weeks	Х	Х	X		Х
TR74	700	6 weeks	Х				
TR79	700	5 weeks	Х	Х	X		Х
TR80	700	5 weeks	Х	Х	X		
TR81	700	5 weeks	Х	Х	X		
TR82	700	5 weeks	Х	Х	X		Х
TR83 [*]	700	4 weeks	Х				Х
TR84 [*]	700	4 weeks	Х				
TR85 [*]	700	4 weeks	Х				

* Samples were powdered and pressed (see 5.1.3. Equilibration)

After freezing the thermodynamic equilibria by quenching the samples in cold water, further isothermal and dynamic methods were applied to determine phase relations in the system. X- ray studies (XRD, single crystal diffraction) as well as optical microscopy (OM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were combined with differential thermal analysis (DTA) measurements to get an full overview of the phase diagram. It was not possible to produce surface grindings of the powdered and pressed samples (Tab.11, asterisked samples) after the annealing process due to the minor compactness of the pills.

5.2. X-ray diffraction

5.2.1.X-ray powder diffraction (XRD)

Phase identifications as well as precise lattice parameters of the different phases were obtained by the means of X-ray powder diffraction (XRD). The measurements were done using on the one hand the Guinier-Huber technique (Guinier camera 670, Fig.25) with Cu-K α_1 radiation of a fine focus X-ray tube and an image plate detector (measurement period: 1h, 10 detection loops), and on the other hand a conventional powder diffractometer in Bragg-Brentano pseudo-focusing geometry (Bruker D8 Discover Serie 2, Fig. 25) with a $\theta/2\theta$ arrangement, a variable slit aperture with 12 mm length of illuminated sample area and a silicon strip detector (LynxEyeTM, measurement period: 1h).





Fig. 25: Guinier camera 670; Bruker D8 Discover Serie 2

For the XRD measurement a small piece (~10 mg) of each sample (Tab.11) was powdered with a tungsten carbide mortar until the powder was not shining anymore (~10 μ m particle size). More ductile samples were powdered with a ball mill and afterwards stress annealed for about 15 minutes. In the case of the Bruker diffractometer the powder was placed on a silicon wafer with Vaseline whereas for the Guinier camera it was fixed on a plastic foil which leaded to a broad peak, dedicated to the foil, at a small angel. Guinier measurements were adjusted with IP Guinier Camera G670 5.0 basic software. Measurements at the Bruker diffractometer were operated with DIFFRAC^{plus} XRD Commander software.

5.2.2. Single crystal X-ray diffraction

For the investigation of the new ternary phases a Nonius Kappa CCD diffractometer, equipped with a monocapillary optics collimator, a graphite monochromatized MoK α radiation and a position sensitive planar X-ray detector, was applied. The measured reflections were refined with the software SHELX-97.

5.3. Metallography

5.3.1. Embedding

For further investigation with optical microscopy (OM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) the samples (Tab. 11) had to be embedded

(Struers LaboPress-1) in phenolic hot mounting resin (Struers, PolyFast, thermosetting, carbon as filler material) and then ground and polished. A small piece of each sample with a nearly flat surface and a spoonful of the resin were put into the embedding cylinder and heated to 180 °C with 15 kN for about 6 minutes. After cooling with cold water for 3 minutes the embedded samples were ground and polished with a grinding machine (Metaserv 2000, grinder/polisher) which can be seen in Figure 27. The grinding was performed with silicon carbide abrasive paper with different mesh sizes (240, 400, 600, 800,

1000, and 1200). Further polishing with abrasive corundum

Fig. 27: Metaserv 2000



Fig. 26: Surface grinding

powder, applied on a fabric plate, was used to realise a visual flat surface necessary for microscopic investigations. With the help of the dark-field-mode of a reflected-light microscope the polished surfaces were checked for possible scratches. Figure 26 shows a well prepared metallographic sample which was used for further analysis.

5.3.2. Optical microscopy

The microstructure and was analyzed with a binocular reflected-light microscope (Zeiss Axiotech 100, Fig. 28). Conventional imaging modes (see 4.2.2) like bright field and dark field imaging as well as differential interference contrast (DIC) and polarisation (360° rotary stage) optics have been applied in order to gain all information of the microstructure. Magnifications of about 50, 100, 200 and 500 have been used for imaging.



Fig. 28: Axiotech 100 [53]

5.3.3. Scanning electron microscopy

Qualitative investigations of as-cast and annealed samples were practised on an environmental scanning electron microscope (Zeiss Supra 55 VP ESEM, Fig. 29) operating with energy dispersive spectroscopy (EDS), and using an 120 μ m aperture. An acceleration voltage of 20 kV has been settled according to the excitation energies of the elements (5.3.4.). Pure cobalt has been applied for an energy calibration of the EDX detector signal. For imaging of the microstructures a back scatter detector as well as a



Fig. 29: Zeiss Supra 55 VP [54]

secondary electron detector was employed. The composition of each phase was measured at three or more spots in order to minimize statistical errors and obtain more reliable results.

5.3.4. Electron probe micro analysis

Quantitative analysis of the phase compositions were performed by a Cameca SX electron probe 100 (Fig. 30) equipped with four high sensitive diffracting crystals. Measurements were carried out with an acceleration voltage of 15 kV and a beam current of 10nA using a wavelength dispersive Xray detector (WDX) to measure the characteristic



Fig. 30: Cameca SX-100 EPMA [52]

X-ray radiation and a back scatter detector to make images of the microstructures. Pure aluminium, germanium and nickel were employed as standard materials. Conventional ZAF matrix correction was applied to calculate final compositions from the measured X-ray intensities.

 Aluminium:
 K_{α} -line, 1.4867 keV [55]

 Germanium:
 K_{α} -line, 9.8864 keV [55]

 Nickel:
 K_{α} -line, 7.4782 keV [55]

5.3.5. Differential thermal analysis

Phase transitions and thermal reactions were determined by differential thermal analysis performed on a DTA 404 PC (Netzsch, Selb, Germany, Fig.31), using open alumina crucibles. The measurements were carried out under a constant argon flow (50ml/min) with titanium as a reference material. The temperature was measured with type-S (Pt/Pt10%Rh) thermocouples which were calibrated at the melting points of pure Al, Au and Ni. The



Fig. 31: DTA 404 PC [56]

samples weighed usually around 100mg and were positioned in good thermal contact to the crucibles. The recipient was evacuated three times and purged with argon. Starting temperatures were defined, on the basis of the binary phase reactions, at 380 and 680 °C. The end-temperatures (T_{max}) were estimated for each sample to be higher than its melting point. For every sample two heating and cooling cycles were carried out (Fig.32). After measuring the samples were re-weighted in order to check possible mass changes. No systematic mass changes were observed in this regard.



Fig. 32: General temperature program for DTA measurements

6. Results and discussion

6.1. Partial isothermal section at 400 °C

An initial characterisation of the samples annealed at 400 °C were done by the means of Xray powder diffraction, single crystal X-ray diffraction, electron probe microanalysis and scanning electron microscopy. On the basis of the gained results a partial isothermal section at 400 °C was drawn (Fig. 34) which is hardly comparable with prior results of Yanson et al [46] (Fig. 11).

The applied samples and additional results are shown in Table 12. It is to mention that several samples were not in equilibrium after annealing at 400 °C. Therefore additional samples, which were powdered and pressed (homogenization) before annealing, have been synthesized. However, it was possible to reduce the amount of the fourth phase of each sample by further annealing, which helped to verify the phase field where it is localized. For instance, a sample with the nominal composition of $Al_{75}Ge_{15}Ni_{10}$ (TR01, TR01*), lying in the Al-Ge- τ_2 three phase field, and additionally showed Al_3Ni , was almost in equilibrium after homogenization as can be seen in Figure 33.



Fig. 33: XRD powder pattern; Comparison of homogenized and not homogenized TR01; green curve: pure Al₃Ni; not identified reflections are from the unknown τ_2 phase (EPMA: Al₆₇Ge₁₉Ni₁₄)

The lattice parameters which are given in Table 12, evaluated from the homogenized samples, are similar to that of the non homogenized samples. In samples with the nominal compositions $Al_{75}Ge_{15}Ni_{10}$ (TR01), $Al_{75}Ge_5Ni_{20}$ (TR02), $Al_{55}Ge_{25}Ni_{20}$ (TR03) and $Al_{15}Ge_{65}Ni_{20}$ (TR05) four phases have been found with XRD as well as EPMA. The assumed non-equilibrium phases were marked in Table 12. A sample at $Al_{20}Ge_{45}Ni_{35}$ (TR10) did not exhibit grains of (Ge) but the XDR pattern definitely showed (Ge) reflections although with low intensity.

Sample ID	le ID Phase analysis			EPMA/ SEM			
/ nom.comp.	Phase XRD		XRD	Al	Ge	Ni	
(at.%)	1 nase	Lattice parameter (Å)	%	(at.%)	(at.%)	(at.%)	
	(Al)	a = 4.0511(1)	-	97.9	1.7	0.4	
TR01	Al ₃ Ni ^b	a = 6.6211(4), b = 7.3724(5), c = 4.8154(3)	-	74.9	0.4	24.8	
Al ₇₅ Ge ₁₅ Ni ₁₀	(Ge)	a = 5.6605(1)	-	2.4	97.6	~0 ^c	
	τ_2	unknown structure	-	67.9	18.3	13.8	
	(Al)	<i>a</i> = 4.0509(1)	-	97.8	1.8	0.4	
TR02	Al ₃ Ni	a = 6.6167(1), b = 7.3708(2), c = 4.8152(1)	-	74.8	0.1	25.1	
Al ₇₅ Ge ₅ Ni ₂₀	(Ge) ^b	a = 5.6598(1)	-	1.7	98.3	~0 ^c	
	τ_2	unknown structure	-	67.5	17.2	15.3	
TD 26 ^a	Al ₃ Ni	a = 6.6165(1), b = 7.3711(1), c = 4.8153(1)	-	74.1	0.8	25.1	
Al Ge Ni	(Ge)	a = 5.6608(1)	-	1.7	98.3	~0 ^c	
A1650C151120	τ ₂	unknown structure	-	67.0	17.8	15.2	
	(Al) ^b	<i>a</i> = 4.0524(5)	3	98.2	1.6	0.2	
TR03	Al ₃ Ni	a = 6.6166(2), b = 7.3718(2), c = 4.8156(1)	50	74.6	0.2	25.2	
Al ₅₅ Ge ₂₅ Ni ₂₀	(Al ₃ Ni ₂)	a = 4.0408(1), c = 4.8806(1)	6	57.1	2.9	40.0	
	(Ge)	a = 5.6617(1)	41	1.8	98.2	~0 ^c	
	(AlNi) ^b	<i>a</i> = 2.8199(1)	7	46.5	5.0	48.5	
TR05	(Ge)	a = 5.6589(1)	22	0.7	99.3	~0 ^c	
Al15Ge65Ni20	τ_1	a = 10.7512(1), b = 5.7056(8), c = 5.6990(8)	5	17.7	48.9	33.4	
	τ ₄	<i>a</i> = 5.6495(1)	66	25.7	39.9	34.4	
TR07 ^a	(Al ₂ Ni ₂)	a = 4.0396(1), c = 4.8806(1)		56.7	3.9	39.4	
AlsoGe15Ni25	(Ge)	a = 5.6608(1)	80	2.4	97.6	~0 ^c	
1 1 30 0 0 1 31 (1 3 3			20		,,,,,,		
TDOO		4.0505(1) 4.0254(1)		10.0	12.7	20.0	
	(AI_3INI_2)	a = 4.0525(1), c = 4.8554(1)	82	40.0	13.7	39.8 0°	
AI40Ge25INI35	(Ge)	u = 5.0572(1)	18	1.4	98.0	~0	
	(AlNi)	<i>a</i> = 2.8872(1)	26	46.1	5.2	48.7	
TR09	(Ge)	a = 5.6576(1)	21	1.0	99.0	~0 ^c	
Al ₃₀ Ge ₃₅ Ni ₃₅	τ_4	a = 5.6405(1)	53	26.8	38.2	35.0	
	(AlNi)	<i>a</i> = 2.8867(1)	11	45.6	5.4	49.0	
TR10	τ_1	a = 10.7534(2), b = 5.7035(1), c = 5.6989(1)	85	17.2	49.1	33.8	
Al20Ge45Ni35	τ_4	a = 5.5905(2)	2	24.8	40.5	34.7	
	(Ge) ^b	a = 5.6457(5)	2	-	-	-	

Table 12: XRD	. EPMA and SEM	results for th	he investigation (of the nartia	l isothermal	section at 400°C
Table 12. MAD	, LI MILLANG DELM	i counto i u	ne myesugauon v	n une parua	i isounci mai	

TR11 Al ₁₀ Ge ₅₅ Ni ₃₅	(Ge) GeNi _{T1}	a = 5.6589(1) a = 5.3891(2), b = 3.4381(1), c = 5.8173(2) a = 10.7575(2), b = 5.7128(1), c = 5.7075(1)	10 29 61	0.7 0.8 15.0	99.3 49.2 51.3	~0 ^c 50.0 33.7

^a Samples were measured with SEM; τ_1 measured with single crystal diffraction; τ_2 not identified yet; τ_4 refined with NiSi₂-structure (CaF₂-type structure) and indexed with DIFFRAC^{*plus*} TOPAS software;

^b 4th phase which was supposed to be not in equilibrium

^c The Ni solubility of (Ge) was assumed to be 0 due to the literature (3.1.3.)

Additional samples, lying within the partial isothermal section were characterised by XRD (Tab. 11, Fig. 22) but not headed in Table 12. Their results were in good agreement with the given partial isothermal section (Fig. 33). For comparison of the lattice parameter Table 13 presents all crystal structures of the binary subsystems which were relevant for the present study.

In the present isothermal section nine three phase fields $[(Al)-Al_3Ni-\tau_2, (Al)-(Ge)-\tau_2, Al_3Ni-(Ge)-\tau_2, Al_3Ni-(Ge)-\sigma_2, Al_3Ni-(Al$



Fig. 34: Partial isothermal section at 400 °C. Large circles: nominal compositions of samples; small circles: measured phase compositions; dashed lines: assumed phase fields

Phases	Lattice	Structure	Space	Reference
1 muses	parameter (Å)	type	group	
(Al)	a = 4.0492	Cu	Fm-3m	[8]
	a = 6.5982			
Al ₃ Ni	b = 7.3515	CFe ₃	Pnma	[57]
	c = 4.8021			
(AlaNia)	a = 4.0363	AlaNia	P-3m1	[57]
(1131112)	c = 4.9004	1 1131 112	1 3111	[37]
(AlNi)	a = 2.848	CsCl	Pm-3m	[58]
(Ge)	a = 5.656	С	Fd-3m	[15]
	a = 5.381			
GeNi	b = 3.428	MnP	Pnma	[59]
	c = 5.811			

Table 13: Crystal structure data of binary phases relevant for the partial isothermal section at 400 °C

The solid solubility of Ge in Al₃Ni was found to be very small around 0.4 at.% (EPMA) whereas the solubility in (Al₃Ni₂) is much higher (~13.6 at.%, SEM). It seems that Al is partially replaced by Ge due to the constant Ni content of the homogeneity range at approximately 40 at.%. With raising Ge content the lattice parameter *a* is increasing from a = 4.0363-4.0525 Å and *c* is decreasing from c = 4.9004-4.8354 Å. Concerning to the EPMA results of the (Al₃Ni₂) phase in the ternary it is assumed that the Al solubility of Al₃Ni₂, in the binary, has to be lower than found in the literature.

The homogeneity range of the (AlNi) phase was difficult to interpret due to fluctuating EPMA results. It was supposed that these fluctuations are due to the high melting point (~1638 °C) of the congruent melting AlNi phase. Solidification temperatures of ternary samples, which primary crystallize (AlNi), are therefore higher and it is difficult to reach equilibrium on annealing at 400 °C. For this reason samples with smaller amounts of (AlNi) were used for evaluations in order to obtain more reliable results. The solubility of the (AlNi) phase at 400 °C was measured to be around 5.2 at.%. The lattice parameters were found to vary between a = 2.8480-2.8859 Å (TR09).

The EPMA measurements of the pure (Ge) phase exhibited some problems regarding the ternary solubility of Al and Ni. The measured solubility of Al in (Ge) was approximately 2.4 at.% which is slightly higher than expected from the literature [28]. The solubility of Ni in (Ge), however, was found around 5 at.%, much higher as it is stated by Nash [42] for binary Ge-Ni. It was assumed that Ni could not segregate entirely of (Ge) during quenching of the

samples and thus small Ni grains lead to elevated Ni contents in (Ge), which is not plausible. Thus the Ni solubility of (Ge) was assumed as to be more or less zero, because no reliable specification could be given. The solubility of GeNi, for instance, was measured to be approximately 0.8 at.% which is realistic by comparing it with the Al solubility of same-structured NiSi in the related Al-Ni-Si system by Richter et al [60]. However, the Ni content of GeNi was around 50 at.%, which is more than supposed.

In addition to binary phases, three new ternary compounds have been found in the present isothermal section at 400 °C. All phases were found to be stable within small measured composition ranges around $Al_{15.0}Ge_{51.5}Ni_{33.5}$ (τ_1), $Al_{67.5}Ge_{18.0}Ni_{14.5}$ (τ_2) and $Al_{25.5}Ge_{40.0}Ni_{34.5}$ (τ_4).

6.1.1. Crystal structure of the ternary compound $Al_xGe_{2-x}Ni(\tau_1)$

An intermediate phase within the composition range of approximately $Al_{15.0}Ge_{51.3}Ni_{33.8} - Al_{17.2}Ge_{49.1}Ni_{33.8}$, measured with EPMA (Tab. 12) and confirmed with XRD, was designated as τ_1 in the current study. A sample with the nominal composition $Al_{16}Ge_{51}Ni_{33}$ (TR43) was produced for generating a pure powder pattern of τ_1 (Fig. 35). The sample exhibited thermodynamic equilibrium between τ_1 and another unknown phase τ_4 , discussed later (6.1.3.). τ_1 was primarily indexed from the XRD pattern, using DIFFRAC^{plus} TOPAS software, with an orthorhombic unit cell.



Fig. 35: Powder pattern of a Al₁₆Ge₅₁Ni₃₃ (TR43) sample; black curve below: Ge₂Ni (CaF₂-type, τ_4) phase; red curve: reflections of the Al_xGe_{2-x}Ni (CoGe₂-type, τ_1) and Ge₂Ni (CaF₂-type, τ_4) phases

The attempt to extract single crystals of τ_1 was not successful due to a fine microstructure (Fig. 36), which suggests for a peritectic formation. It looked like that both phases are very

brittle due to lots of holes produced during the grinding process. The invariant reaction temperature was measured with DTA at approximately 809 ± 1 °C, with the proposed corresponding reaction $L+\tau_4+(AlNi) = \tau_1$. Details are discussed later (6.3.) Based on the partial liquidus projection (6.3.), a sample with the nominal composition Al₆Ge₆₃Ni₃₁ was slowly cooled from 820 to 700 °C in order to



Fig. 36: Polarisation image of $Al_{16}Ge_{51}Ni_{33}$ (TR43) with 20× magnification

produce single crystals of τ_1 . The corresponding microstructure can be seen in Figure 37. The primary crystallised phase was verified with SEM to be τ_1 . The single crystals were further confirmed with polarisation optics and extracted by crashing the sample. A suitable single crystal with the dimensions $0.02 \text{mm} \times 0.02 \times 0.1 \text{mm}$ was chosen for single crystal XRD. The measurement was carried out at 30mm crystal- detector distance and 2° rotation per frame. The exposure time was 100 sec per degree with 539 frames in total. The unit cell was found to be orthorhombic, as it was expected from indexing, with the cell parameter a = 10.760(2) Å, b = 5.715(1) Å and c = 5.713(1) Å and the space group *Cmca*. The phase crystallizes in the binary CoGe₂- type structure and was refined with SHELX-97 [61], based on structure data for high pressure Ge₂Ni of Takizawa [62]. The final single crystal X-ray data collection as well as cell parameters are presented in Table 14.



Fig. 37: BSE image of a slowly cooled sample with the nominal composition Al₆Ge₆₃Ni₃₁

Empirical formula	$Al_{0.44}Ge_{1.56}Ni_1$
Crystal system, space group	Orthorhombic, Cmca
Cell dimensions	
a / Å	10.760 (2)
b / Å	5.715 (1)
c / Å	5.713 (1)
V / Å ³	351.310(1)
ρ_{calc} / g·cm ⁻³ ; $\mu(MoK\alpha)$ / mm ⁻¹	5.985; 27.73
Z	8
Crystal size/ mm ³	0.02×0.02×0.1
Scan time/ s/°; frame size/ pixels	100; 621×576
Total reflections	2210
Unique reflections (<i>n</i>); reflections with $F_o > 4\sigma(F_o)$	405; 377
$R_{int} = \Sigma F_o^2 - F_o^2(\text{mean}) / \Sigma F_o^2$	0.0582
$R1 = \Sigma \left(/ F_o - F_c \right) / \Sigma F_o $	0.0234
$w\mathbf{R}^{2} = \left[\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma wF_{o}^{4}\right]^{1/2}$	0.0555
GooF = $[\Sigma w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$	1.169
Extinction parameter	0.0049(6)
Max Δ/σ ; number of variable parameters (<i>p</i>)	< 0.001; 20
Final difference Fourier map / eÅ ⁻³	0.29

Table 14: Selected data collection and refinement parameters for $Al_xGe_{2-x}Ni(\tau_1)$

The crystal structure τ_1 consists of three different atomic positions, where one is totally filled with Ni atoms and two are mixing positions of Al and Ge with the occupation factors and anisotropic displacement parameters presented in Tables 15-16. The chemical composition, calculated from the refinement (Al_{14.67}Ge_{51.99}Ni_{33.33}), is in excellent agreement with EPMA results (Al_{14.45}Ge_{52.80}Ni_{32.76}) and corresponds to Al_{0.44}Ge_{1.56}Ni₁.

Table 15: Atomic coordinates and equivalent isotropic displacement parameters for $Al_xGe_{2-x}Ni(\tau_1)$

Atomic	Wykoff	Occupation	Х	У	Z	U_{eq}
position	letter	_		-		-
Ni	8(d)	1.0	0.11656(4)	0	0	0.0092(1)
M1	8(f)	0.96(1)Ge+	0	0.15432(6)	0.34454(6)	0.0097(1)
		0.04(1)Al				
M2	8(e)	0.65(1)Ge+	0.25000	0.24831(8)	0.25000	0.0100(1)
		0.35(1)Al				

Atomic	<i>U</i> 11	U22	<i>U</i> 33	U23	<i>U</i> 13	<i>U</i> 12
Ni	0.0077(2)	0.0105(2)	0.0095(2)	0	0	0
M1	0.0116(2)	0.0091(2)	0.0086(2)	0	0	0
M2	0.0089(2)	0.0111(2)	0.0101(2)	0	0.0001(1)	0

Table 16: Anisotropic displacement parameters for $Al_xGe_{2-x}Ni(\tau_1)$

It is to mention that these compositions are both given at 700 °C. Phase stability of $Al_xGe_{2-x}Ni$ at 400 °C was measured within the range x = 0.45-0.52. The structure is arranged of alternate stacking of Ni and M layers along the *a*-axis which can be seen in Figure 38.



Fig. 38: Crystal structure of $Al_xGe_{2-x}Ni(\tau_1)$; view along the *a*- axis (left); 3D view perpendicular to the *a*- axis (right)

Rather surprisingly, close Ni-Ni contacts were found in the structure (Fig. 39). These contacts were found in dimmers with a Ni-Ni distance around 2.508 Å, which is almost the distance in *fcc* Ni. Ni is coordinated of four M1 atoms, four M2 atoms and one Ni atom in the first coordination sphere. The polyhedron was found to be a square anti prism with one additional Ni position (Fig. 40). Both M positions show two different distances to the Ni position, which are added in the Figure.

The M1 atom has four Ni atoms and one M1 atom as nearest neighbours. There are also two different distances between the Ni and M1 atoms. The atomic coordination forms a rectangular pyramid with the Ni atoms positioned on the base. The average distance for M1-M1 was found to be around 2.503 Å.



Fig. 39: Ni dimers along *a*-axis of $Al_xGe_{2-x}Ni(\tau_1)$



Fig. 40: Atomic coordination of the Al_xGe_{2-x}Ni (τ_1) structure for the first coordination sphere

The M2 atoms are tetrahedral coordinated from Ni atoms. The bond angles between the Ni-M2-Ni atoms are found to be around 109.19-109.62°, which leads to an almost regular tetrahedron. A complete compilation of all atomic distances of the $Al_xGe_{2-x}Ni$ structure is given in Table 17.

The $CoGe_2$ structure was previously designated from Takizawa [62] as to be an intermediate structure between the CaF_2 and the $CuAl_2$ structure. The

Fable 17: Interatomic distances and	bond
angles of Al _x Ge _{2-x} Ni (τ ₁)	

	distance/ Å
Ni-Ni	2.508(4)
Ni-M1	2.495(1)
	2.503(9)
Ni-M2	2.473(9)
	2.484(1)
M1-M1	2.503(2)
M1-M2	2.796(8)
M2-M2	2.857(6)
	2.858(6)

relation is due to similar atomic coordinations within the three structure types. The cubic coordination, as it occurs in the CaF₂- type, is shifted to a square anti prism with one additional transition metal position (CoGe₂) and two additional transition metal positions (CuAl₂), respectively, in the first coordination sphere. The CaF₂ structure also exhibits the tetrahedral arrangement of the group 14 element whereas the CuAl₂ structure maintains the

rectangular pyramidal coordination. Both atom arrangements are also present in the $CoGe_2$ structure. Further intermetallic phases, which crystallize in the $CoGe_2$ structure type, were found to exist, such as $RhSn_2$ and $PdSn_2$.

6.1.2. A new ternary compound at $Al_{67.5}Ge_{18.0}Ni_{14.5}(\tau_2)$

The presence of a new ternary compound with a composition close to $Al_{67.5}Ge_{18.0}Ni_{14.5}$ was confirmed with XRD and micro probe analysis. The EPMA results are given in Table 12. The XRD pattern (Fig. 41) of a homogenized sample with the nominal composition $Al_{75}Ge_{15}Ni_{10}$ (TR01*) was used for an indexing attempt with DIFFRAC^{*plus*} TOPAS software. Moreover no convincing solution was found. The observed diffraction data of τ_2 are shown in Table 18.



Fig. 41: Powder XRD pattern of a sample with the nominal composition $Al_{75}Ge_{15}Ni_{10}$; red curve: refined (Al) and (Ge) phase; non identified reflections are from the unknown τ_2 phase

d _{obs}	Iobs	d_{obs}	Iobs	d_{obs}	I _{obs}
15.5366	0.57	44.9200	100.00	66.5626	6.25
19.0556	0.92	46.3834	59.52	67.6943	2.98
24.6561	27.06	47.8118	17.91	69.9360	17.89
27.0491	27.36	49.2057	24.02	72.1452	11.65
29.2674	17.10	50.5762	14.72	75.4197	26.30
31.3400	13.64	51.9197	8.88	77.5692	13.02
33.2957	14.49	53.2240	4.16	79.7011	26.81
35.1558	11.56	57.0597	2.17	81.8178	6.71
36.9313	15.14	59.5132	26.35	82.8761	14.56
38.6474	13.64	61.9145	12.42	88.1164	21.25
40.2847	17.15	64.2603	16.99	98.6010	17.39

 τ_2 was recognized to be in thermodynamic equilibrium with (Al), (Ge) and Al₃Ni. It is formed peritectically by the reaction $L + Al_3Ni + (Ge) = \tau_2$ at 444 ± 2 °C, compare to 6.3. Moreover it was not possible to gain singe crystals from samples, containing τ_2 , due to very fine microstructures (Fig.42) as a result of peritectical formation. Therefore several samples were prepared by slowly cooling with nominal compositions within the primary crystallisation field of τ_2 , as it is predicted in the liquidus projection (6.3.). Due to a very small field of primary crystallisation the attempt was not crowned with success.

An important fact, however is that τ_2 is not polarising visible light which can be seen in Figure 42. It is thus save to assumed that the phase is crystallizing in the cubic system which is also supposed by observing the powder pattern, concerning the continuous spacing.

Single crystal measurements are planned for the future to investigate the ternary phase τ_2 .



Fig. 42: Polarisation image of a sample with the nominal composition Al₇₅Ge₁₅Ni₁₀ (TR01)

6.1.3. A new ternary compound at $Al_{25.5}Ge_{40.0}Ni_{34.5}(\tau_4)$

A new ternary compound with the chemical composition of approximately $Al_{25.5}Ge_{40.0}Ni_{34.5}$, designated as τ_4 in the present study, was primarily determined with EPMA (Tab. 12) and confirmed by means of XRD. A sample with the nominal composition $Al_{24.79}Ge_{40.53}Ni_{34.68}$ (TR74) was produced in order to gain a single phase pattern of τ_4 , shown in Figure 43. The sample was found to be located within a two-phase field, revealing thermodynamic equilibrium between τ_4 and (AlNi). Not identified reflections were indexed using DIFFRAC^{plus} TOPAS software, which yielded the best consistency for a *fcc* cell with

the lattice parameter a = 5.6475 Å and the volume V = 180.12 Å³, respectively. The observed cell suggested the well known CaF₂possible structural structure as model. Refinement was done with the structure data from NiSi₂ of Ackerbauer et al [63]. For refinement the occupation factor of the Ni position was set to 1, whereas the Si position was assumed to be a mixing position of Al and Their site occupation factors were Ge. calculated from the measured composition

Table 19:	Powder X-ray diffraction data of
	Ge ₂ Ni (CaF ₂ -type)

h	k	l	d_{obs}	Iobs
1	1	1	3.2598	12.40
0	0	3	2.8231	6.55
0	2	2	1.9962	100.00
3	1	1	1.7024	19.13
2	2	2	1.6299	4.89
0	0	4	1.4115	29.00
3	3	1	1.2953	11.24
0	4	2	1.2625	9.12
4	2	2	1.1525	71.63
3	3	3	1.0866	2.35
5	1	1	1.0866	7.04

(EPMA) of τ_4 and thus are 0.61 for Al and 0.39 for Ge. The additionally refined displacement factor for the position Al/Ge (M) is 1.839.



Fig. 43: Powder XRD pattern (Guinier) of a sample with the nominal composition $Al_{24.79}Ge_{40.53}Ni_{34.68}$; circles: reflections of the CaF₂- structured τ_4 phase; squares: reflections of the AlNi structure

The resulting refinement is presented in Figure 43, with a R_{wp} value of about 5.385. As lattice parameters a = 2.8825(1) Å for (AlNi) and a = 5.6462(1) Å for τ_4 were found. Respective *hkl* values as well as spacing and relative intensities of observed reflections are shown in Table 19.

The crystal structures as well as atomic coordination of the two atomic positions are shown in Figure 44. It is to mention that Ni is coordinated in a cubic arrangement with an atomic distance between Ni and M atoms of 2.445 Å, less than in the related atomic arrangement of τ_1 , which is a distorted anti prism with approximately 2.500 Å Ni-M distance. Another similarity between τ_1 and τ_4 is the tetrahedral coordination of M atoms with Ni atoms found in both structures with average atomic distances of around 2.473 Å in τ_1 and 2.445 Å in τ_4 .



Fig. 44: Crystal structure of τ_4 perpendicular to the *c*-axis (left, grey atoms: Ni, blue atoms: M); atomic coordination of Ni in the first coordination sphere (middle); atomic coordination of M in the first coordination sphere (right)

The CaF₂- structured τ_4 phase, stoichiometrically described as Al_xGe_{2-x}Ni, is only stable within a small homogeneity range between Al_{24.8}Ge_{40.5}Ni_{34.7} and Al_{26.8}Ge_{38.2}Ni_{35.0}, supported with EPMA. The measured Ni content was found to be slightly higher than expected from the stoichiometric composition. All in all it seems that the composition of τ_4 is shifted slightly to the Ni rich side which is not expected from the structure and is not evidenced with single crystal XRD in the present study.

Phase relations of τ_4 are discussed in 6.3.. The microstructure of a sample with the nominal composition Al₃₀Ge₃₅Ni₃₅, shown in Figure 45, provides thermodynamic equilibrium between (AlNi), (Ge) and τ_4 (concerning to Fig. 34). The microstructure shown in Figure 45 may be interpreted as peritectic because (AlNi) is totally surrounded by τ_4 .



Fig. 45: BSE image of a sample with the nominal composition $Al_{30}Ge_{35}Ni_{35}$ (TR09)

The corresponding peritectic reaction was assessed to be $L+(AlNi)+(Ge) = \tau_4$ with the reaction temperature of 822 ± 2 °C, determined with DTA. The reaction temperature is close to the peritectic formation temperature of τ_1 which is at 809 ± 1 °C. τ_1 gets peritectically formed of τ_4 in the reaction $L+(AlNi)+\tau_4 = \tau_1$.

Another remarkable property of CaF_2 structured τ_4 is the almost perfect lattice match to Ge, which could be a promising material for epitaxial films grown on Ge. The phases are shown to be in thermodynamic equilibrium within a very narrow two phase field. Their lattice mismatch was found to be less than -0.2 %.

The presence of lattice match between nickel disilicides and silicon was previously studied by Richter et al [64]. Perfect lattice match between two disilicides, with the compositions NiSi_{1.74}Al_{0.26} and NiSi_{1.83}Ga_{0.17}, and Si was achieved. It was revealed that both element combinations exhibit extended solubilities in the ternary. By application of Vegard's rule compositions with perfect lattice match to Si were found. Perfect lattice match in this case is probably not conceivable due to the small homogeneity range of τ_4 but is an important topic in respect to related phase diagrams.

6.2. Partial isothermal section at 700 °C

An initial characterisation of the samples annealed at 700 °C was done by the means of Xray powder diffraction, single crystal X-ray diffraction and electron probe microanalysis. According to the received results a partial isothermal section at 700 °C could be drawn which is presented in Figure 46. The results were hardly comparable with prior investigations of Yanson et al [46]. The continuous solid solution between the binary $L1_2$ phases AlNi₃ and GeNi₃ as well as the extended ternary solution of AlNi could be confirmed. A predicted ternary compound Σ , with the empirical formula Ni₄AlGe, was not found in the present study, but a ternary phase τ_3 , with the approximate composition Al₁₅Ge₂₆Ni₅₉, which is discussed below. The isothermal section at 700 °C includes lots of three phase equilibria which were not all determined experimentally, especially in the area of Ge₃Ni₅, Ge₁₂Ni₁₉ and Ge₂Ni₃. Additionally some assumed phase fields [L-Al₃Ni-(Al₃Ni₂), L-(Al₃Ni₂)-(Ge), (AlNi)-(Al₃Ni₂)-(Ge), (AlNi)-(Ge)- τ_4 , (Ge)- τ_1 - τ_4 , (AlNi)- τ_1 - τ_4], estimated from the isothermal section at 400 °C, are . Measured EPMA values as well as lattice parameters of samples which were used for the construction of the section are compiled in Table 21. All relevant binary structures are additionally given in Table 20.



Fig. 46: Partial isothermal section at 700 °C. Large circles: nominal compositions of samples used for the isothermal section; small circles: measured phase compositions with EPMA; dashed lines: assumed phase fields; phase boundary of Ni₁₉Ge₁₂ was estimated

Phases	Lattice parameter (Å)	Structure type	Space group	Reference
Al	a = 4.0492	Cu	Fm-3m	[8]
Al ₃ Ni	a = 6.5982, b = 7.3515, c = 4.8021	Fe ₃ C	Pnma	[57]
Al ₃ Ni ₂	a = 4.0363, c = 4.9004	Al ₃ Ni ₂	P-3m1	[57]
AlNi	a = 2.848	CsCl	Pm-3m	[58]
AlNi ₃	a = 3.608	AuCu ₃	Pm-3m	[65]
βGeNi ₃	a = 3.572	AuCu ₃	Pm-3m	[66]
eGe ₃ Ni ₅	a = 3.913, c = 5.064	InNi ₂	P6 ₃ /mmc	[67]
Ge ₁₂ Ni ₁₉	a = 11.63,1b = 6.715, c = 10.048	Ni ₁₉ Ge ₁₂	C2	[44]
Ge ₂ Ni ₃	a = 3.863, c = 4.998	NiAs	P6 ₃ /mmc	[44]
GeNi	a = 5.381, b = 3.428, c = 5.811	MnP	Pnma	[59]
Ge	a = 5.656	С	Fd-3m	[15]

Table 20: Crystal st	ructure data of binary phas	ses relevant for the par	rtial isothermal section	n at 700 °C
	acture and or sindry prime	ses rere and ror and par		

Table 21: XRD, EPMA and SEM results for the investigation of the partial isothermal section at 700 $^\circ C$

Sample ID	Phase analysis				EPMA/ SEM		
/ nom.comp.	Phase	XRD		Al Ge		Ni	
(al.%)		Lattice parameter (Å)	%	(at.%)	(at.%)	(at.%)	
TD 12	(AlNi)	a = 2.8884(2)	63	42.0	8.3	49.8	
	GeNi	a = 5.4012(4), b = 3.4318(2), c = 5.8160(4)	31	1.2	48.8	50.0	
AI ₃₀ Ge ₂₀ INI ₅₀	(Ge ₃ Ni ₅)	a = 3.8981(4), b = 4.9358(1)	6	9.9	33.7	56.4	
TR14	(AlNi)	a = 2.8890(3)	7	42.2	8.3	49.6	
Al ₅ Ge ₄₅ Ni ₅₀	GeNi	a = 5.3904(1), b = 3.4372(1), c = 5.8172(1)	93	1.2	48.7	50.1	
TR15	(AlNi)	a = 2.8630(2)	-	36.9	3.8	59.3	
Al ₃₅ Ge ₅ Ni ₆₀	(Ge ₃ Ni ₅)	refinement not possible	-	19.0	15.3	65.7	
TR17	(AlNi)	a = 2.8812(1)	34	38.1	6.5	55.4	
Al ₂₅ Ge ₁₅ Ni ₆₀	(Ge ₃ Ni ₅)	a = 3.9690(2), c = 4.9993(2)	66	13.4	22.1	64.5	
TR18	(AlNi)	refinement not possible	-	41.7	8.2	50.2	
Al. Gen Ni	(Ge ₃ Ni ₅)	a = 3.9413(2), c = 5.0022(3)	-	9.3	27.2	63.5	
m15002511160	τ ₃	a = 7.8771(1), c = 14.9990(2)	-	16.9	23.2	59.9	

TR19	(Ge ₃ Ni ₅)	a = 3.9136(1), c = 5.0125(2)	64	6.2	31.9	61.9
Al ₁₀ Ge ₃₀ Ni ₆₀	τ ₃	a = 7.8636(1), c = 15.0197(2)	36	13.1	27.7	59.3
TR20	(Ge ₃ Ni ₅)	a = 3.8871(1), c = 5.0109(2)	75	5.0	34.2	60.8
Al ₅ Ge ₃₅ Ni ₆₀	τ ₃	a = 7.8261(3), c = 15.0029(7)	25	10.0	31.6	58.4
TR22	(AlNi ₃)	a = 3.5780(3)	43	18.1	8.9	73.0
Al ₁₅ Ge ₁₅ Ni ₇₀	(Ge ₃ Ni ₅)	a = 3.9842(3), c = 5.0089(6)	57	14.6	19.4	66.0
TR23	(GeNi ₃)	a = 3.5742(2)	61	11.7	14.0	74.3
Al ₁₀ Ge ₂₀ Ni ₇₀	(Ge ₃ Ni ₅)	a = 3.9763(3), c = 5.0101(6)	39	11.0	23.0	66.0
TR24	(GeNi ₃)	<i>a</i> = 3.5727(1)	62	4.1	20.8	75.1
Al ₅ Ge ₂₅ Ni ₇₀	$_{5}Ni_{70}$ (Ge ₃ Ni ₅) $a = 3.9637(3), c = 5.0301(6)$		38	6.1	28.4	65.5
TR26	(AlNi)	refinement not possible	-	37.0	3.0	60.0
Al ₂₃ Ge ₁₀ Ni ₆₇	(AlNi ₃) (Ge ₃ Ni ₅)	a = 3.5751(1) a = 4.0584(3), c = 4.9050(6)	-	19.0 20.0	7.5 13.4	73.5 66.6
TR27	(AlNi)	<i>a</i> = 2.8718(1)	27	17.4	17.5	65.1
Al _{21,5} Ge ₁₅ Ni _{63,5}	(Ge ₃ Ni ₅)	a = 3.9857(1), c = 4.9920(2)		37.6	5.7	56.7
TR29	(AlNi)	a = 2.8890(1)	18	42.4	8.2	49.4
Al _{18,5} Ge _{26,5} Ni ₅₅	(Ge ₃ Ni ₅) τ_3	a = 3.9061(1), c = 4.9972(1) a = 7.8130(1), c = 14.9935(4)	31 51	- 10.3	- 32.4	57.3
TD21	(AlNi)	<i>a</i> = 2.8865(1)	8	43.8	9.0	47.3
$Al_{14}Ge_{45}Ni_{41}$	GeNi t ₁	<i>a</i> =5.3886(2), <i>b</i> =3.4383(1), <i>c</i> =5.8148(2) <i>a</i> =10.7559(4), <i>b</i> =5.7103(3), <i>c</i> =5.7043(3)	40 52	1.2 16.4	48.8 49.6	50.0 34.1
TP22	(Ge)	a = 5.6592(1)	30	0.3	99.7	~0 ^a
$Al_9Ge_{65}Ni_{26}$	GeNi	a = 5.3849(1), b = 3.4409(6), c = 5.8112(1)	11	0.8	49.8	49.4
	τ_1	a = 10.7619(4), b = 5.7165(3), c = 5.7090(3)	59	14.7	52.4	32.9

 $*\tau_3$ was measured with single crystal diffraction and is discussed below ^a The Ni solubility of (Ge) was assumed to be 0 due to the literature (3.1.3.)

The solid solubilities of Ge in Al₃Ni and (Al₃Ni₂) were not measured at 700 °C and were drawn similar to the section at 400 °C. The two three phase fields L-Al₃Ni-(Al₃Ni₂) and L-(Al₃Ni₂)-(Ge) in the Ni-lean part of the section are estimated from the partial liquidus projection (6.3.).

The determination of the solid solubility of (AlNi) turned out to be difficult. It was found that the (AlNi) phase of samples, which were lying on the same tie-lines, exhibited completely different Ge contents. According to the explanation in 6.1., samples which were localized farther of (AlNi) tended to have more reliable Ge values due to their lower melting point. Four samples with the nominal compositions $Al_{45}Ge_5Ni_{50}$ (TR12), $Al_{30}Ge_{20}Ni_{50}$ (TR13), $Al_{17}Ge_{33}Ni_{50}$ (TR30) and $Al_5Ge_{45}Ni_{50}$ (TR14), which are all lying on a same tie-line between GeNi and (AlNi) with constant Ni content, were consulted to determine the real solubility of (AlNi). The respective solubilities (3.6 – 6.8 at.%), measured with EPMA, were found to be in linear behaviour (Vegard's rule) with the corresponding lattice parameters (2,8872 - 2,8890 Å), as it was expected. The plot is given in Figure 47. An additional sample with the nominal composition $Al_{40}Ge_{10}Ni_{50}$ (TR59) was produced in form of a pressed pill and annealed for two month at 700 °C. It was supposed that this sample is in thermodynamic equilibrium, but it was not possible to measure it directly with EPMA due to less compactness of the pressed pill. Its respective (AlNi) phase was refined with *a* = 2.8893(1) Å which leaded to a calculated Ge solubility of approximately 8.3 at.%.



Fig. 47: Lattice parameter a of (AlNi) versus composition (Vegard's rule)

The calculated Ge content is reliable by comparing it with the value of a sample with the nominal composition $Al_{14}Ge_{45}Ni_{41}$ (TR31), which was determined to be 9.0 at.% (compare Tab. 21). This sample is located on a tie triangle which enters (AlNi) close to the tie-line of (AlNi)-GeNi. A similar Ge content was thus expected.

The Ge solubility of the Ni richer side of the non stoichiometric (AlNi) phase could only be estimated based on comparison of lattice parameters of a homogenized {a = 2.8768(2) Å} and a non-homogenized {a = 2.8760(1) Å} sample with the same nominal composition of Al₃₀Ge₁₀Ni₆₀ (TR61, TR16). Due to the increase of lattice parameter *a* with rising Ge content at 50.0 at.% Ni (Fig.47), it was supposed that the non-homogenized sample shows a too low Ge content, which was measured at 3.6 at.%. The confirmation of this assumption was the measured value (5.7 at.%) of a sample (Al_{21.5}Ge_{15.0}Ni_{63.5}, TR27) which lies on the same tieline as the discussed ones. The comparison of the lattice parameter with the corresponding samples (TR16, TR61) was not possible because the pattern could not be refined well, due to very low amount of (AlNi) within the sample.

In the Ni rich part of the system a continuous solid solution of the two $L1_2$ phases AlNi₃ and β GeNi₃ was assumed from the EPMA results. It was tried to confirm the single phase field with powder XRD using Vegard's rule. The evaluation of powder patterns from samples, lying in the assumed single phase field (TR44-TR47), with increasing Ge content was not precise enough to generate a reliable plot. Due to small differences of atomic radii of Al and Ge, AlNi₃ and β GeNi₃ exhibit a very similar lattice parameter *a*.

The solid solubility of Al in MnP- structured GeNi was measured to be approximately 1.2 at.%, which is slightly higher than at 400°C (0.8 at.%). Within three different three-phase fields, the phase GeNi was found to be in thermodynamic equilibrium with the ternary phase τ_1 (Al_xGe_{2-x}Ni) and the binary compounds (AlNi) and (Ge₃Ni₅).

The ternary phase τ_1 (Al_xGe_{2-x}Ni), which is also present at 400°C and decomposes at around 809 ± 1 °C, possesses a small homogeneity range of about x = 0.44-0.52, similar to that at 400°C which was determined around x = 0.45-0.52.

Moreover the predicted binary superstructure $Ge_{12}Ni_{19}$ by Ellner et al [44] was not found in the ternary samples but an extended solubility of the filled NiAs structure (Ge₃Ni₅) in the ternary. The limiting solubility of (Ge₃Ni₅) was determined at a Ni content of about 67.0 at.%, where the secondary Ni position 2*d* is fully occupied, to be approximately 20.0 at.% Al. An extended solubility of around 10.3 at.% was also found in the Ni poorer part of the homogeneity range of (Ge₃Ni₅). The (Ge₃Ni₅) phase was measured with powder XRD and further refined by using the respective EPMA values of the phase for each sample. It was assumed that the Ge position is partially occupied with Al and the second Ni position 2*d* gets filled up with increasing Ni content. The displacement factor was in this case additionally refined. The Rietveld refinement showed nice results. A pattern of a sample within a two phase field of a ternary phase τ_3 and (Ge₃Ni₅) with the nominal composition Al₁₀Ge₃₀Ni₆₀ (TR19) is given in Figure 48, showing a R_{wp} value of 2.066.



Fig. 48: Powder XRD pattern of a sample with the nominal composition Al₁₀Ge₃₀Ni₆₀ (TR19)

Consequently the binary phases Ge_2Ni_3 and Ge_3Ni_5 were determined to form a common solid solution in the ternary. All powder XRD patterns, which include this NiAs-type structure, were refined by using the filled Ni₂In type (Ge₃Ni₅) with site occupation on 2*d* based on the corresponding EPMA results. Furthermore a small two phase field between (Ge₃Ni₅) and Ge₁₂Ni₁₉ in the ternary was assumed to exist and drawn with dashed lines within the isothermal section.

In the range of Al_{16.9}Ge_{23.2}Ni_{59.9} to Al_{10.0}Ge_{31.6}Ni_{58.4} a new ternary compound was found to exist and designated as τ_3 in the current study. Structure and homogeneity range will be discussed in 6.2.1. The ternary phase was determined, with EPMA and powder XRD, to be in thermodynamic equilibrium with (AlNi) and (Ge₃Ni₅) within two different three phase fields (AlNi)-(Ge₃Ni₅)- τ_3 . One three phase field was only drawn with dashed lines according to a sample with the nominal composition Al_{18.5}Ge_{26.5}Ni_{55.0} (TR29). EPMA measurement of this sample did not exhibit presence of τ_3 but the XRD pattern showed characteristic τ_3 reflections. The existence of the three phase field is thus not verified because τ_3 could also be formed during quenching of the sample. The assumed three phase field was estimated to touch τ_3 at approximately Al_{10.6}Ge_{31.6}Ni_{58.4} (TR20) {a = 7.8130(1) Å, c = 14.9936(4) Å for TR29; a =7.8261(2) Å, c = 15.0029(7) Å for TR20}. Higher amounts of Al in τ_3 , were found to significantly raise the *a* parameter. For example, a sample with the nominal composition Al₁₅Ge₂₅Ni₆₀ (TR18) showed lattice parameters of a = 7.8771(1) Å and c = 14.9990(2) Å.

6.2.1. Crystal structure of a new ternary compound at $Al_yGe_{9.y}Ni_{13\pm x}(\tau_3)$

The new ternary intermetallic compound τ_3 was characterised by the means of XRD and electron probe microanalysis. A sample with the nominal composition Al₁₅Ge₂₆Ni₅₉ (TR42) was prepared and annealed for 4 weeks at 700°C, in order to obtain a pure powder XRD pattern of τ_3 , given in Figure 50. It is to mention that the pattern is refined with data of single crystal XRD determination, mentioned below. The sample was found to exhibit pure τ_3 which was confirmed by scanning electron microscopy. Further investigations of the microstructure

with polarization optics (Fig. 49) indicated the presence of suitable single crystals for single crystal XRD measurements. The sample was crushed with a mortar and a single crystal with the approximate dimensions $0.04 \times 0.03 \times 0.07$ mm³ was selected for structure determination. Single crystal measurement was carried out at room temperature and reflections were collected at a crystal-detector distance of 30 mm. 781 frames in total were measured with 2°



Fig. 49: Polarisation image of a sample with the nominal composition $Al_{15}Ge_{26}Ni_{59}$ (TR42) with 20x magnification

rotation and 2×80 s exposure time per frame. The obtained reflections could be indexed with a trigonal unit cell with the corresponding cell parameters a = 7.871 (2) Å and c = 15.019 (1) Å. Structure refinement was employed with SHELX-97 [61] software based on structure data for the phase Al_ySi_{9-y}Ni_{13±x} of Richter [68]. The final single crystal X-ray data collection as well as cell parameters, atomic positions and anisotropic displacement parameters are presented in Tables 22-24.



Fig. 50: Powder XRD pattern of a sample with the nominal composition $Al_{15}Ge_{26}Ni_{59}$ (TR42) with reliability factor $R_{wp} = 2.14$; red curve: refinement with data of single crystal XRD determination

Empirical formula	Al _{3.3} Ge _{5.7} Ni _{12.9}
Crystal system, space group	Trigonal, P 3 ₁ 21
Cell dimensions	
<i>a</i> / Å	7.8706 (22)
<i>c</i> / Å	15.0184 (11)
$V / \text{\AA}^3$	805.7 (1)
$\rho_{\text{calc}} / \text{g·cm}^{-3}; \mu(MoK\alpha) / \text{mm}^{-1}$	7.830; 38.09
Z	3
Crystal size/ mm ³	0.04×0.03×0.07
Scan time/ s/°	80
Total reflections	11316
Unique reflections (<i>n</i>); reflections with $F_o > 4\sigma(F_o)$	1791; 2356
$R_{int} = \Sigma F_o^2 - F_o^2(\text{mean}) / \Sigma F_o^2$	0.0771
$R1 = \Sigma \left(\frac{ F_o }{F_c} \right) \sum F_o $	0.0288
$w\mathbf{R}^{2} = \left[\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma wF_{o}^{4}\right]^{1/2}$	0.0646
GooF = $[\Sigma w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$	0.969
Extinction parameter	0.00046 (18)
Max Δ/σ ; number of variable parameters (<i>p</i>)	< 0.001; 109
Final difference Fourier map / eÅ ⁻³	0.31

Table 22: Selected data collection and refinement parameters for $Al_yGe_{9-y}Ni_{13\pm x}$

Table 23: Atomic coordinations and isotropic displacement parameters for $Al_yGe_{9\text{-}y}Ni_{13\pm x}$

Atomic	Wykoff	Occupation	Х	у	Z	U_{eq}
position	letter					
M1	6с	0.72(1)Ge + $0.28(1)$ Al	0.6181(1)	0.3089(2)	0.07803(3)	0.0116(1)
M2	6c	0.46(1)Ge + 0.54(1)Al	0.3100(2)	0.1914(2)	0.92150(4)	0.0114(2)
M3	6c	0.79(1)Ge + 0.21(1)Al	0.3352(1)	0.1682(1)	0.25053(3)	0.0123(1)
M4	6c	0.77(1)Ge + 0.23(1)Al	0.3098(2)	0.1165(1)	0.5895(1)	0.0115(1)
M5	3b	0.18(1)Ge + 0.82(1)Al	0.4952(2)	0	5/6	0.0102(3)
Ni1	3b	1	0.0014(3)	0	5/6	0.0101(1)
Ni2	6с	1	0.5029(1)	0.9948(2)	0.9974(1)	0.0099(1)
Ni3	6с	0.969(1)	0.6791(1)	0.3412(2)	0.2453(1)	0.0131(1)
Ni4	6с	1	0.3389(2)	0.1788(1)	0.4265(1)	0.0117(1)
Ni5	6с	1	0.4998(2)	0.0009(3)	0.1662(1)	0.0103(1)
Ni6	6c	0.984(2)	0.3394(2)	0.1618(2)	0.7532(1)	0.0109(1)
Ni7	3a	1	0.0036(3)	0	1/3	0.0102(1)
Ni8	3a	1	0.4925(1)	0	1/3	0.0095(1)

Atomic	<i>U</i> 11	U22	<i>U</i> 33	<i>U</i> 23	<i>U</i> 13	<i>U</i> 12
position	-	-				-
M1	0.0162(3)	0.0093(6)	0.0109(2)	0	0	0.0075(6)
M2	0.0103(8)	0.0074(7)	0.0125(3)	0	0.0014(6)	0.0015(2)
M3	0.0115(2)	0.0089(2)	0.0174(2)	0.0003(2)	0.0005(3)	0.0057(2)
M4	0.0096(6)	0.0171(3)	0.0099(2)	0.0008(1)	0.0005(4)	0.0080(6)
M5	0.010(1)	0.013(2)	0.0087(6)	0.004(1)	0.0019(6)	0.006(1)
Ni1	0.0104(6)	0.013(1)	0.0079(3)	0	0	0.0066(6)
Ni2	0.0111(6)	0.0111(6)	0.0080(2)	0	0	0.0058(2)
Ni3	0.0118(3)	0.0111(6)	0.0168(2)	0	0	0.0060(6)
Ni4	0.0108(5)	0.0096(3)	0.0153(2)	0.0011(2)	0	0.0053(5)
Ni5	0.0102(3)	0.0107(5)	0.0081(2)	0	0.0004(1)	0.0037(5)
Ni6	0.0092(5)	0.0095(5)	0.0138(2)	0	0	0.0044(2)
Ni7	0.0119(6)	0.009(1)	0.0090(3)	0	0	0.0043(5)
Ni8	0.0106(6)	0.010(1)	0.0079(2)	0	0	0.0050(5)

Table 24: Anisotropic displacement parameters for AlyGe9.yNi13±x

The Al_vGe_{9-v}Ni_{13±x} structure was found to crystallize in the ternary Ga₃Ge₆Ni₁₃ structure type, which was originally described by Bhargava and Schubert [69]. The cell contains 66 atoms in total with the corresponding Pearson symbol hP66 and Z = 3. Eight Ni positions, two are only partially filled, with site occupation factors 0.969(1) and 0.984(2), as well as five mixing positions of Al and Ge were refined. The measured composition of τ_3 (Al_{15.0}Ge_{26.2}Ni_{58.8}), determined at the respective sample with the nominal composition Al₁₅Ge₂₆Ni₅₉ (TR42), was found to be in excellent agreement with the calculated composition from structure refinement (Al_{15,1}Ge_{25,8}Ni_{58,7}). The present structure type was previously designated to be closely related to the Ni₂In type with doubled a and b axes and tripled c axis. Figure 51 gives a unit cell of a Ni₂In-type T₂M crystal, where T represents a transition metal and M a main group element of the groups 13 through 16 in periodic table. Two general atomic positions (0,0,0; 2a) and (1/3,2/3,1/4; 2c), occupied with T atoms, and one general M position (2/3, 1/3, 1/4; 2d) are describing the Ni₂In structure. This structure is also known as the filled NiAs structure with the difference of the additional 2c position at the expanded voids, which is completely filled with T atoms. The corresponding stoichiometrical relation between T and M atoms in Ni₂In is 2:1 but can be lower in case of Ni concentration less than 66.7 at.%. In the latter case the 2c position is only partially occupied.



Fig. 51: Ni₂In structure (left), NiAs structure (right); T atoms: transition metal, M atoms: main group element

As it was indicated the $Al_yGe_{9-y}Ni_{13\pm x}$ structure is a vacancy and replacement homeotype structure of the Ni₂In type. The number of atoms in $Al_yGe_{9-y}Ni_{13\pm x}$ (Fig. 52) is reduced from 72 (6×12) for a fully occupied Ni₂In homeotype to 66, due to ordered vacancies on the 2*c* corresponding positions of the Ni₂In structure. Additionally one of the 2*a* corresponding atoms of Ni₂In is replaced by M atoms (position M5). The theoretical stoichiometry of Ni₁₃M₉ is thus provided. The atomic positions of Ni₁₃M₉ can be described as follows: Ni1, Ni2, Ni5, Ni7, Ni8 and M5 correspond to the 2*a* atoms of the Ni₂In-type; Ni3, Ni4 and Ni6 correspond to the randomly occupied 2*d* atoms; M1-M4 correspond to the fully occupied 2*c* atoms.

An additional representation of the first coordination spheres of all representative atomic positions is shown in Figure 53. Atomic distances are drawn up to 3 Å.



Fig. 52: Crystal structure of Al_yGe_{9-y}Ni_{13±x}; view perpendicular to the *c* axis (left) and along *c* axis (right); dark grey atoms: Ni1,Ni2,Ni5,Ni7,Ni8 positions, turquoise atoms: M⁵ position, bright grey atoms: Ni3,Ni4,Ni6 positions, blue atoms: M1-M5 positions; surrounded position: representation of ordered vacancies



Fig. 53: Atomic coordination of the representative atomic positions 2*a* (left), 2*d* (middle), 2*c* (right); blue atoms corresponds to main group atoms, grey atoms corresponds to Ni atoms

Ni1 and Ge5 are representatives for the corresponding 2a position, where the latter one is coordinated by eight Ni atoms and six M atoms. The coordination number of Ni1 is reduced to twelve, concerning to only six Ni atoms, due to ordered vacancies on the 2c position. It is important to mention that the antistructure position M5 is always at maximum distance to the vacancies. Moreover representatives of the corresponding 2c and 2d positions are drawn with the respective positions Ge1, Ni3 and Ni6, respectively.

Due to the description of the current phase with $Al_yGe_{9-y}Ni_{13\pm x}$ two compositional variabilities are indicated. The present single crystal structure determination leaded to an empirical formula of $Ni_{12.8}M_9$ which is slightly lower than the stoichiometric relation of $Ni_{13}M_9$ of the respective $Ga_3Ge_6Ni_{13}$ structure. Besides EPMA results also presented higher amounts of Ni corresponding to a formula of $Ni_{13.4}M_9$. By observing the site occupation factors of the respective 2c positions Ni3, Ni4 and Ni6 it is save to assume that the compositional variability of Ni is due to partial filling of vacancies in case of $Ni_{13.4}M_9$ and additional vacancy formation in case of lower Ni contents, respectively.

The compositional variability, concerning to the partially replacement of Ge with Al atoms, is indicated with the parameter *y* in $Al_yGe_{9-y}Ni_{13\pm x}$. An interesting point is the difference of site occupations of the five M positions within the structure. The respective 2*a* position M5 was found to be preferably occupied with Al [*sof* = 0.819(2)]. M2 shows a small overstaffing of Al with *sof* = 0.539(3), whereas M1, M3 and M4 show strong overstaffing of Ge, with the site occupation factors given in Table 23.

6.3. Ternary phase reactions and liquidus projection

Several samples (Tab. 11), annealed at 400 and 700 °C, were further characterised with differential thermal analysis (DTA) to determine phase reactions as well as respective isothermal reaction temperatures. Based on the results three vertical sections at constant Ni concentration of 10, 20 and 35 at.% and one partial vertical section with constant Al:Ni ratio of 1:3 were constructed to represent phase relations at variable temperatures. For each sample two heating/cooling cycles were performed at a rate of 5 K/min in order to check if equilibrium conditions, at the respective annealing temperature, are reproducible. It was found that most of the DTA samples, especially in the Ni poor part of the system, were not in equilibrium after the first heating/cooling circle. However temperatures of all thermal effects which were found in both heating cycles were in good agreement to each other. All non-invariant as well as invariant effects, measured in the first heating curves, were taken for the graphical representation shown in Figures 54-57. Besides, the liquidus values were calculated as mean values from both cycles. Although most of the cooling curves exhibited strong supercooling their liquidus values were additionally considered.



Fig. 54: Vertical section at 10 at.% Ni; large circles: invariant thermal effects, small circles: non-invariant thermal effects, triangles up: liquida on heating, triangles down: liquida on cooling, dotted lines: assumed phase boundaries



Fig. 55: Vertical section at 20 at.% Ni; large circles: invariant thermal effects, small circles: non-invariant thermal effects, triangles up: liquida on heating, triangles down: liquida on cooling, dotted lines: assumed phase boundaries



Fig. 56: Vertical section at 35at.% Ni; large circles: invariant thermal effects, small circles: non-invariant thermal effects, triangles up: liquida on heating, triangles down: liquida on cooling, dotted lines: assumed phase boundaries



Fig. 57: Partial vertical section at constant Al:Ni ratio of 1:3; large circles: invariant thermal effects, small circles: non-invariant thermal effects, triangles up: liquida on heating, triangles down: liquida on cooling, dotted lines: assumed phase boundaries

The vertical sections were constructed by a combination of XRD, DTA and EPMA results. Phase boundaries at the annealing temperatures were taken from the isothermal sections. Phase reactions as well as phase relations were determined by the help of the isothermal sections and DTA measurements. Within the four vertical sections thirteen invariant reactions were found involving the liquid phase, including one degenerated eutectic, three ternary peritectic, eight II-class transition reactions and one maximum. The three ternary peritectic reactions P1, P2 and P3 correspond to the incongruent formations of τ_2 , τ_1 and τ_4 , respectively. All reactions as well as averaged isothermal reaction temperatures and estimated compositions of the involved phases, are presented in Table 25. The respective compositions of the liquid phase were estimated from the liquidus projection, given below.

Vertical sections at 10, 20 and 35 at.% Ni were drawn based on results of the samples presented in Table 11. In the very narrow temperature range of 421-446 °C three reactions (E1, P1, U1) take place.
Deastion	T/°C Phase		Comp	osition	/ at.%
Reaction	I/ C	rnase	Al	Ge	Ni
E1: L = (Al) + (Ge) + τ_2	423 ± 2	L	71.3	28.6	0.1
		(Al)	98.0	1.8	0.2
		(Ge)	1.0	99.0	0.0
		τ_2	67.5	18.5	14.0
U1: L+ Al ₃ Ni = (Al) + τ_2	437 ± 2	L	71.5	27.5	1.0
		Al ₃ Ni	24.8	0.5	74.7
		(Al)	98.0	1.8	0.2
		τ_2	68.0	18.0	14.0
P1: L + Al ₃ Ni + (Ge) = τ_2	444 ± 2	L	70.5	28.5	1.0
		Al ₃ Ni	24.8	0.5	74.7
		(Ge)	1.0	99.0	0.0
		τ_2	68.0	17.5	14.5
U2: $L + (Al_3Ni_2) = Al_3Ni + (Ge)$	558 ± 2	L	59.0	40.0	1.0
		(Al_3Ni_2)	57.5	2.5	40.0
		Al ₃ Ni	24.8	0.5	74.7
		(Ge)	1.0	99.0	0.0
U3: $L + (AlNi) = (Al_3Ni_2) + (Ge)$	852 ± 2	L	28.0	63.0	9.0
		(AlNi)	46.5	6.5	47.0
		(Al ₃ Ni ₂)	46.0	14.0	40.0
		(Ge)	0.6	99.4	0.0
Max1: $L = (AlNi) + (Ge)$	~860	L	14.8	68.2	17.0
		(AlNi)	46.5	6.5	47.0
		(Ge)	0.5	99.5	0.0
U4: L = (Ge) + GeNi + τ_1	763 ± 3	L	0.0	67.0	33.0
		(Ge)	0.7	99.3	0.0
		(GeNi)	0.5	50.0	49.5
		$ au_1$	13.2	53.8	33.0
U5: L + (AlNi) = GeNi + τ_1	790 ± 4	L	4.0	60.0	36.0
		(AlNi)	45.0	7.0	48.0
		(GeNi)	0.7	49.8	49.5
		τ_1	17.0	50.0	33.0
U6: L + $\tau_4 = (Ge) + \tau_1$	798 ± 3	L	6.3	66.7	27.0
		$ au_4$	25.5	40.0	34.5
		(Ge)	0.7	99.3	0.0
		$ au_1$	15.0	52.0	33.0

 Table 25: Ternary invariant reactions relevant for the presented vertical sections of the Al-Ge-Ni phase diagram

Continue of Table 25					
Depation	T/°C	Dhaga	Composition / at.%		
Reaction	1/ C	r nase	Al	Ge	Ni
P2: L + τ_4 + (AlNi) = τ_1	809 ± 1	L	8.5	61.0	30.5
		$ au_4$	25.0	40.0	35.0
		(AlNi)	46.0	6.0	48.0
		$ au_1$	17.5	49.0	33.5
P3: L+ (AlNi) + (Ge) = τ_4	822 ± 2	L	8.0	66.5	25.5
		(AlNi)	46.2	6.3	47.5
		(Ge)	0.8	99.2	0.0
		$ au_4$	25.5	40.0	34.5
U7: $L + (Ge_3Ni_5) = (AlNi) + GeNi$	844 ± 3	L	2.0	55.0	43.0
		(Ge ₃ Ni ₅)	11.5	33.0	55.5
		(AlNi)	7.0	43.5	49.5
		GeNi	0.7	49.8	49.5

Continue of Table 25

The ternary eutectic E1, with the isothermal reaction temperature measured at 423 ± 2 °C, was found to be degenerated concerning to the binary eutectic in the Al-Ge subsystem at 423.7 °C [28]. The eutectic crystallization behaviour was confirmed by very fine microstructures of as-cast samples near to the eutectic point (Fig.58).



Fig. 58: As-cast sample with the nominal composition Al_{68.5}Ge_{28.5}Ni₃

Moreover a saddle was found corresponding to the maximum L = (AlNi)+(Ge). The invariant temperature was assumed from the liquidus projection at approximately 860 °C. It is to mention that the section at 10 at.% Ni shows the saddle right to the liquidus valley of the primary crystallisation fields of (AlNi) and (Ge), compare to the liquidus projection (Fig. 62),

whereas the vertical sections at 20 and 35 at.% Ni show it on the left side. Thus an almost pseudo binary eutectic is supposed to exist along (AlNi)-(Ge), separating the ternary phase diagram into two parts.

A degenerated transition reaction, designated as U4, was found to exist in the Al lean part of the phase diagram concerning to the binary eutectic L=Ge+GeNi in the Ge-Ni subsystem. The reaction temperature was found to be 763 ± 3 °C, slightly higher than the binary eutectic temperature, given at 762 °C [42]. The degeneration was confirmed by the microstructure of a slowly cooled sample with the nominal composition Al₉Ge₆₃Ni₂₈, exhibiting definitely the binary eutectic microstructure of (Ge)+ GeNi, (Fig.59).



Fig. 59: Slowly cooled sample with the nominal composition $Al_9Ge_{63}Ni_{28}$

The partial vertical section at constant Al:Ni ratio of 1:3 was not determined precisely in the Ni rich part of the phase diagram due to limited amount of samples in the region of τ_3 . DTA results of samples located in this region, presented invariant effects in the range of 1218-1246 °C and several non-invariant effects in the temperature range of 700-800 °C. Further work will be done in respect to the determination of phase relations in this region. Concerning the Ge rich part of the vertical section (Fig.57) the ternary peritectic reaction P2 at 809 ± 1°C is given only in a very small range. The presence was thus not experimentally supported but theoretically from all available results.

As mentioned above, the assumed pseudo eutectic divides the ternary phase diagram into two partial reaction schemes, which are demonstrated in the Scheil diagrams in Figures 60-61. Both reaction schemes start from Max1 with the respective three phase field L+(AlNi)+(Ge). The partial reaction schemes are consistent with all available data as well as rules of equilibrium thermodynamics.



Fig. 60: Partial reaction scheme (Scheil diagram) for the Al rich part of the Al-Ge-Ni phase diagram



Fig. 61: Partial reaction scheme (Scheil diagram) for the Al lean part of the Al-Ge-Ni phase diagram

Based on the results of all vertical sections as well as primary crystallisation and melting points of several selected samples a partial liquidus projection was drawn, given in Figure 62. The projection exhibits three extended primary crystallisation fields of (Ge), (Al_3Ni_2) and (AlNi), respectively. One maximum (Max1) is situated in the saddle between the two congruent melting phases (Ge) and (AlNi). The valleys in the Ni lean part of the projection were found to run very narrow to the binary Al-Ge subsystem due to a very steep increase of the liquidus surface by addition of small amounts of Ni.

 τ_2 was found to crystallize only in a very small area, limited by the three invariant ternary reactions E1, P1 and U1. Thus the attempt to generate single crystals from slowly cooled samples in this area was not successful. The liquidus valley, joining from the Ni rich part of the phase diagram, was estimated from melting points of respective samples located in this area. There is no information about the Ni rich part of the liquidus projection yet but phase equilibria and crystallisation behaviour are currently under investigation.



Fig. 62: Partial liquidus surface projection of the ternary Al-Ge-Ni system including the fields of primary; solid lines: liquid valleys, dotted lines: isotherms, filled black circles: invariant reaction points

7. Application: Diffusion brazing of nickel aluminides

Since applied parts of nickel-base superalloys are moulded in complicated procedures at elevated temperatures, they are very expensive. A successful application of these materials thus requires suitable and cost-effective joining techniques such as welding and brazing. In this case diffusion brazing, sometimes also called transient liquid-phase (TLP) joining or transient liquid phase bonding (TLPB), is a very popular technique for joining and repairing of nickel base alloys. Two substrates (joining parts) with a filler material (braze material) inserted between them are annealed for a short time. The respective filler material provides a definitely lower melting point than the two component parts and melts partially or totally during the annealing process. As a melting point depressant element Ge seems to be very promising, as it forms deep eutectics with Al and Ni. Based on the phase diagram studies two ternary Al-Ge-Ni alloys were selected for further joing tests. Preliminary wetting and brazing tests were carried out with conventional AlNi and Ni₃Al substrates. All experiments, which are examined in the present study, were processed at the Eidgenössische Materialprüfungs-und Forschungsanstalt (EMPA) in Zürich (Switzerland).

7.1. Diffusion brazing (TLP)

Diffusion brazing, also called transient liquid phase (TLP) joining or transient liquid phase bonding (TLPB), is a hybrid joining method which is successfully applied several decades for joining and repairing of nickel base alloys in the aerospace industry. It is the high temperature analogue of diffusion soldering, performed at elevated process temperatures above 450 °C.

The joint configuration comprises two component parts, called substrates, and a brazing material, inserted between them. Since brazing materials need to provide definitely lower melting points than the substrates but should possess similarities in respect to the chemical composition of the substrate, melting point depressant elements have to be added to the braze alloy. The joining process is predominantly practised under vaccum or inert gas conditions and is stepwise given in Figure 63. Brazing materials are usually applied as very thin preform or foil interlayer between two substrates which are softly clamped together. The assemble is afterwards annealed, at a temperature just above the melting point of the brazing material, which melts and wets the substrate surfaces. The ability of filling the joint gaps as well as forming well-round fillets at the edges of the joint is dependent of the wettability of the substrate by the liquid brazing material. Initial wetting tests are thus profitable. During the annealing process, elements of the liquid braze alloy are diffusing into the substrate material

and vice versa. This leads to an increase of the melting point of the braze material due to the change of its composition with time. An isothermal solidification of the liquid, forming a microstructure similar to the bulk material, is desirable. Slow cooling after joining suppresses the induction of thermal stresses in the joint area.



Fig. 63: Theoretical steps of diffusion brazing [70]

Diffusion brazing provides very narrow joints which benefits mechanical properties and thermal conductivity. In addition thus less amount of brazing material is required. Brazing materials should further contain as few intermetallic compounds as possible to avoid brittle joints which reduce mechanical strength.

7.2. Experimental procedure

AlNi and Ni₃Al substrates were prepared by induction melting, using aluminium slugs (99.999 %, Fa. Johnson Matthey Chemicals) and nickel slugs (99.98 %, Alfa Aesar), with the respective stoichiometric compositions $Al_{50}Ni_{50}$ and $Al_{25}Ni_{75}$. For both, wetting and brazing experiments, plates were cut with a precision cut-off machine (Accutom-50, Struers), using alumina and silicon carbide cut-off wheels. The substrates were afterwards ground with silicon carbide abrasive paper (400, 600, 800, 1000, 2500, 4000 Mesh) and diamond polished, using 3 and 1µm suspensions, to realize flat surfaces for better contact as well as to remove the aluminium oxide layer. Further cleaning in the ultrasonic bath, using acetone (per analysis), and degassing at 1000 °C for one hour in a high vacuum furnace at 10⁻⁶ mbar (TORVAC, Fig. 64) was carried out to prevent the joint area from dust.



Fig. 64: High vacuum furnace (TORVAC) with Mo heating plates

Two brazing alloys with suitable melting points of approximately 900 and 1000 °C, compatible in respect to industrial applications, were chosen on the basis of the vertical section at constant Al:Ni ratio of 1:3 (Fig.65), with the respective nominal compositions $Al_{10}Ge_{60}Ni_{30}$ (TR72_900 °C) and $Al_{13}Ge_{48}Ni_{39}$ (TR73_1000 °C). The alloys were produced according to 5.1.2.-5.1.3 and annealed for about three weeks at 700 °C. Further powdering was operated by the means of ball milling with steal balls. The powdered alloys were mixed with an organic binder (powder: octyl acetate = 10:1) to produce pastes for better application. For wetting experiments small amounts of the paste were punctually applied whereas for brazing tests the whole substrate surface was covered with paste and then masked with a second polished substrate. The organic binder was afterwards evaporated in a compartment dryer at 150 °C for one hour.

Both, wetting and brazing experiments, were carried out in a high vaccum furnace at 10⁻⁶ mbar. For examination of participating phases in the diffusion areas, cross sections were produced by cutting and embedding. The microstructures were investigated with scanning electron microscopy (FEI NovaNanoSEM 230) and electron probe microanalysis (JXA-8800RL JEOL).



Fig. 65: Partial vertical section at constant Al:Ni ratio of 1:3; large circles: invariant thermal effects, small circles: non-invariant thermal effects, triangles up: liquida on heating, triangles down: liquida on cooling, dotted lines: assumed phase boundaries

7.2.1. Wetting experiments

Small amounts of the brazing material/ octyl acetate pastes ($Al_{10}Ge_{60}Ni_{30}$ / TR72_900 °C, $Al_{13}Ge_{48}Ni_{39}$ / TR73_1000 °C) were punctually applied on AlNi and AlNi₃ substrates and further evaporation of the binder was practised.

Substrate Brazing alloy	AlNi	AlNi ₃	Process temperature	Process duration
Al ₁₀ Ge ₆₀ Ni ₃₀ TR72_900	3 experiments	3 experiments	900 °C	30 min
Al ₁₃ Ge ₄₈ Ni ₃₉ TR73_1000	3 experiments	3 experiments	1000 °C	30 min

Table 26: Test assembles for wetting experiments

Three tests of each assemble (Tab.26) were performed in order to obtain reproducibility of the processes. The experiments were all done in a high vaccum furnace (10^{-6} mbar) at the respective temperatures, dependent from the melting point of the brazing material, for 30 minutes process duration.

7.2.2. Brazing experiments

For brazing experiments (Tab. 27) the whole surface of the respective substrate was covered with the corresponding braze material and then masked with a second polished substrate. After evaporation of the organic binder, the experiments were carried out in a high vacuum furnace (10^{-6} mbar) for 30 minutes process duration. Two experiments of each assemble were primary performed without any additional pressure application, except the own weight of the upper substrate. A secondary experiment was practised under a small pressure of approximately 0.35-0.8 kPa, realized with small Ni cylinders. Both assembles are schematically shown in Figure 66.



Fig. 66: Diffusion brazing experiments without pressure (left) and with 6.5g Ni cylinder (right)

Table 27:	Test	assembles	for	brazing	experiments
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Substrate Brazing alloy	AlNi	AlNi ₃	Process temperature	Process duration
Al ₁₀ Ge ₆₀ Ni 30 TR72_900	2 + 1(pressure) experiments	2 + 1(pressure) experiments	900 °C	30 min
Al ₁₃ Ge ₄₈ Ni ₃₉ TR73_1000	2 + 1(pressure) experiments	2 + 1(pressure) experiments	1000 °C	30 min

7.3. Results and discussion

7.3.1. Wetting experiments

BSE images of cross sections of the respective wetting experiments are shown in Figures 68-71. All determined phases could be well characterised on the basis of the established ternary phase diagram. The samples are found to exhibit lots of cracks, most notable on the drop borders of the experiments with AlNi₃ as substrate material, which was assumed to have occurred while cutting the samples (compare 7.2.). The cracks are formed in all



Fig. 67: TR72_900/ AlNi

directions which is rather an indication for brittle phases in the joints than for thermal induced cracks. Besides, each drop presented a slag like deposition on its surface, which is representatively shown in Figure 67. This was ascribed to abrasion during the ball milling process of the alloys (7.2.).

The wetting angles for AlNi₃ as substrate material were determined to be approximately 39° for TR72 and 20° for TR73, respectively, whereas for AlNi the wettability was much lower (wetting angles: 55° for TR72, 40° for TR73).



Fig. 68: Wetting experiment of TR72_900 with AlNi



Fig. 69: Wetting experiment of TR72_900 with AlNi₃



Fig. 70: Wetting experiment of TR73_1000 with AlNi



Fig. 71: Wetting experiment of TR73_1000 with AlNi₃

However, the wettability was definitely higher at the experiments with TR73 (Al₁₃Ge₄₈Ni₃₉), not least because of the higher processing temperature of 1000°C. The wetting angels were evaluated by the means of the BSE images and thus only taken for comparison.

Moreover all test assembles presented reactions between the respective alloy and the bulk material. The diffusion areas were much larger for AlNi₃, and measured to be around 240 μ m for TR72 and 190 μ m for TR73. All experiments did express a huge presence of ternary intermetallic phases in the diffusion areas.

7.3.2. Brazing experiments

The corresponding brazing experiments depicted similar results (Fig. 72-75) in respect to the microstructure of the joints. As it was expected from the wetting experiments, interdiffusion areas were much more extended by using $AlNi_3$ as substrate material.



Fig. 72: Brazing experiment of TR72_900 with AlNi



Fig. 73: Brazing experiment of TR72_900 with AlNi₃



Fig. 74: Brazing experiment of TR73_1000 with AlNi



Fig. 75: Brazing experiment of TR73_1000 with AlNi₃

As it was found in the wetting experiments, the AlNi₃ substrate did not dissolve Ge, which was expected from the isothermal section (compare Figure 46), where a continuous solid solution of the two $L1_2$ structures AlNi₃ and GeNi₃ was determined. Instead a very fine microstructure of (AlNi) and Ge₃Ni₅ is formed in the vicinity of the substrate.

While the brazing experiments with AlNi₃ as substrate material did express large interdiffusion areas over the whole surface of both substrates, the brazing experiments with AlNi as substrate material did show less reaction between brazing alloy and substrate. The latter have often formed very narrow interdiffusion areas, like in Figure 74. Huge cracks where found at the edges of these joints. It seemed that during solidification of the brazing materials the thermal compression leaded to lacks of brazing material and thus forms holes and cracks, wherever reactions were less strong. In the case of the test assembles in Figures 73 and 75, these cracks were found to be central in the initial gap regions, due to the strong reactions between brazing alloys and AlNi₃ substrates. These initial gap regions showed for both brazing alloys very fine microstructures from Ge₃Ni₅ and τ_3 and are thus expected to be very brittle, which is another reason of forming cracks favourable at these places of the joints. The latter experiments did additionally exhibit voids which were all located on the same height in the diffusion area and thus were assumed to be so-called Kirkendall voids. These Kirkendall voids were previously verified in β -NiAl and γ '-Ni₃Al by Aloke [71]. They are often formed when diffusing atoms have definitely different diffusion coefficients.

Moreover all brazing experiments were additionally practised with a small pressure of

approximately 0.35-0.8 kPa, applied on the joining parts. The corresponding microstructures were all comparable with the prior experiments, where no supplemental pressure was employed. Unfortunately the applied pressure induced at measurement assembles where AlNi was used as a substrate material, that brazing material left the joint in form of small droplets (Fig. 76). This behaviour was only observed when AlNi was used as substrate material. It was assumed



Fig. 76: Brazing experiment

that due to less interdiffusion the dispensable liquid brazing material is pressed out of the joint.

All in all further optimization of the process parameters are planned to do, to reduce the amount of brittle phases in the microstructure as well as to realize continuous joints which offer similar hardness to the substrate materials. In this respect micro hardness tests will be performed.

8. Summary

Nickel aluminides, like γ '-Ni₃Al and β -NiAl, are used in high temperature alloys, which are applied in aircraft and space vehicle engines, power generating turbines and marine propulsion turbines. Nickel aluminides are nowadays used in terms of nickel-base superalloys which usually contain high amounts of chromium, as well as several other transition metals and main group elements, making these materials rather complex. Since applied parts of nickel-base superalloys are moulded in complicated procedures at elevated temperatures, they are very expensive. A successful application of these materials thus requires suitable and cost-effective joining techniques such diffusion brazing (TLP). During this process two substrates with a filler material inserted between them are annealed for a short time. As filler materials, alloys with a lower melting temperature than the two component parts, but similar chemical compositions, are applied, to provide optimal diffusion during the annealing process.

In this work, germanium has been chosen, as melting point depressing element, as it forms deep eutectics with Al and Ni. The aim of the present work was to investigate the ternary phase diagram Al-Ge-Ni, in order to optimize the filler composition and to better understand the interface reactions occurring during the brazing process.

The ternary phase diagram was studied by a combination of optical microscopy, X-ray powder diffraction, Electron probe microanalysis and Differential thermal analysis. Two partial isothermal sections at 400 °C and 700 °C and vertical sections at 10, 20 and 35 at.% nickel as well as one vertical section at constant Al:Ni ratio 1:3 were investigated. The results were hardly comparable with prior results of Yanson et al [46]. At least four new ternary phases have been found to exist in the system. Two ternary intermetallic phases were determined with single crystal diffraction and designated with the empirical formula Al_xGe₂. _xNi (NiGe₂-type, τ_1) and AlyGe_{9-y}Ni_{13±x} (Ga₃Ge₆Ni₁₃-type, τ_3). Furthermore, one phase was identified from its powder diffraction pattern, using DIFFRAC^{plus} TOPAS software, and designated as Al_xGe_{2-x}Ni (CaF₂-type, τ_4). One additionally phase was determined by EPMA and powder XRD at the composition Al_{67.5}Ge_{18.0}Ni_{14.5} (τ_2).

Moreover phase relations and solubility limits were studied in detail for the Ni-poor part of the system. A partial liquidus projection and a partial reaction scheme were examined. In total twelve invariant reactions (1 degenerated eutectic, 3 peritectic reactions, 7 transition reactions, 1 maximum) were found in the Ni-poor part.

Furthermore, fundamental wetting- and diffusion-brazing experiments were performed with two selected brazing alloys, using AlNi and AlNi₃ as substrate materials, at processing temperatures of 900 and 1000 $^{\circ}$ C, respectively.

9. Zusammenfassung

Nickel- Aluminide, wie γ '-Ni₃Al and β -NiAl, finden heutzutage in Form von Nickelbasis-Superlegierungen, aufgrund ihrer herausragenden mechanischen Eigenschaften sowie hohen Stabilität gegenüber thermischen und chemischen Einflüssen, Anwendung in Flugzeugmotoren und Gasturbinen. Nickelbasis- Superlegierungen sind aufgrund ihrer komplexen chemischen Zusammensetzungen und aufwendigen Herstellung sehr kostenintensiv. Eine wirtschaftliche Anwendung dieser Materialien erfordert daher geeignete Reparatur- und Fügeverfahren. Ein in den letzten Jahren häufig praktiziertes Fügeverfahren ist Diffusions- Hartlöten (TLP). Bei diesem Verfahren wird ein Lötmaterial mit ähnlich chemischer Zusammensetzung, jedoch niedrigerer Schmelztemperatur, zwischen die entsprechenden Fügeteile appliziert, und die Anordnung für eine gewisse Zeit getempert.

In der aktuellen Arbeit wurde Germanium als ein den Schmelzpunkt erniedrigendes Element verwendet, weil es mit Al bzw. Ni tief schmelzende Eutektika bildet. Das Hauptziel war eine grundlagenorientierte Aufklärung des ternären Phasendiagramms Al-Ge-Ni, zur Eruierung von geeigneten Lötmaterialien sowie deren Schmelzverhalten während des Lötprozesses.

Das ternäre Phasendiagramm wurde mit einer Kombination aus optischer Mikroskopie, Röntgenpulverdiffraktometrie, Elektronenmikroskopie und Differential- Thermoanalyse untersucht. Es wurden zwei partielle isotherme Schnitte bei 400 und 700 °C sowie drei vertikale Schnitte bei 10, 20, 35 at.% und ein vertikaler Schnitt bei konstantem Al:Ni Verhältnis von 1:3 konstruiert. Die Ergebnisse waren mit jenen von früheren Untersuchungen von Yanson et al [46] kaum vergleichbar. Es konnten mindestens vier neue intermetallische ternäre Phasen gefunden werden. Zwei Phasen, mit den empirischen Formeln Al_xGe_{2-x}Ni (NiGe₂-type, τ_1) and AlyGe_{9-y}Ni_{13±x} (Ga₃Ge₆Ni₁₃-type, τ_3), wurden mithilfe von Einkristallröntgenstrukturanalyse aufgeklärt. Die Struktur von Al_xGe_{2-x}Ni (CaF₂-type, τ_4), wurde aus Röntgenpulverdaten ermittelt. Die Existenz einer weiteren Phase, mit der chemischen Zusammensetzung Al_{67.5}Ge_{18.0}Ni_{14.5} (τ_2), konnte mit EPMA und XRD Messungen eindeutig belegt werden.

Zusätzlich wurden die Phasengleichgewichte im Ni- armen Bereich des ternären Phasendiagramms untersucht, wobei eine partielle Liquidusprojektion und ein partielles Reaktionsschema (1 degeneriertes Eutektikum, 3 Peritektika, 7 Übergangsreaktionen, 1 Maximum) konstruiert werden konnten.

Anhand des Phasendiagramms wurden zwei Legierungen ausgewählt, um Benetzungs- und Lötexperimente an AlNi und AlNi₃ Fügeteilen, bei 900 und 1000 °C, durchzuführen.

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