Influence of carbon on the formation of \(\gamma/\gamma^\prime\)

microstructure and \(\kappa\)-phase in the WC/Co–Ni–Al–W system: ab initio calculations and experimental studies

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ABSTRACT

Modifications of the binder phase (\(\gamma\)) of cemented carbides have the potential to increase the hardness and wear resistance of the whole material. Partially, coherent precipitations with L1₂ structure (\(\gamma^\prime\)) promise these improved properties without sacrificing tensile strength or toughness. \(\gamma^\prime\) is a metastable phase in the Al–Co–W ternary system in the form of Co₃(Al,W) which is stabilized by the substitution of cobalt with nickel. Superalloys of the composition Co–(30Ni)–9Al–7 W with different carbon contents were prepared by inductive melting, and the resulting microstructures were analysed using SEM–EDS, XRD and Vickers hardness. Cemented carbides with \(\gamma/\gamma^\prime\) binder microstructure were prepared via DTA, and the phase equilibria in the composite material were investigated experimentally and in silico. It was shown that nickel stabilizes the \(\gamma^\prime\) phase in superalloys as well as in cemented carbides. Carbon leads to the formation of an additional phase with E₂¹ structure (\(\kappa\)). DTA measurements of cemented carbides with different aluminium–cobalt–nickel mixtures as binder gave an overview of the compositional influence. Enthalpies of formation for compounds with L1₂ and E₂¹ structure were calculated using ab initio methods and compared to experimental results.
**GRAPHICAL ABSTRACT**

**Introduction**

The aluminium–carbon–cobalt–nickel–tungsten system is of high interest for theoretical and experimental investigations in order to facilitate the use of superalloys as binder in cemented carbides. Although the addition of carbon to cobalt-based superalloys has been studied in the past [1] and thermodynamic assessments of the aluminium–carbon–cobalt ternary and the aluminium–carbon–cobalt–nickel quaternary systems are also available [2, 3], respectively, there is still much room left for detailed investigations and analysis about the formation of different phases upon changing the composition.

We therefore aimed to study the influence of carbon in the cobalt–nickel–aluminium–tungsten system. Compositionally different superalloys are produced and analysed experimentally by difference thermal analysis, microstructural and XRD investigations and hardness measurements. Cemented carbides are produced by DTA, and the binder regions are searched for γ/γ’ microstructure and additional phases. The formation of the precipitation phases γ’ and κ is studied by means of CALPHAD approach and ab initio calculations.

**Common phases**

A complete list of all possible phases of the aluminium–carbon–cobalt–nickel–tungsten system is given in Table 1, but the phases which are most likely to form, considering the composition ranges, will be discussed here in more detail. The investigated carbon-free superalloys are covered almost entirely by the works of E. Lass et al. [4] and K. Shinagawa et al. [5] where the phase equilibria and microstructures of cobalt-based and cobalt–nickel-based alloys with aluminium concentrations from 8.25 to 17.5 at% and tungsten concentrations from 2.5 to 15 at% are studied. Additionally, Zhu et al. [6] thermodynamically assessed the quaternary system in the cobalt-rich region which also fits the experimentally prepared superalloys from this work. Above the allotropic phase transition of hcp cobalt, a solid solution of cobalt and nickel with fcc structure is formed. This phase is usually denoted as γ and dissolves over 15 at% aluminium [7] and up to 18 at% tungsten [8] in ternary alloys. This can also be reasoned from the binary phase diagrams where quite high aluminium and tungsten contents are predicted to dissolve at higher temperatures in cobalt and nickel. The solubility of these elements is heavily reduced in cobalt at lower temperatures which happens because the hcp allotrope becomes more and more stable.
The big difference between the aluminium–cobalt and aluminium–nickel systems is that \( \gamma' \) is only stable in the latter one. Ni\(_3\)Al is an ordered form of the fcc crystal structure with aluminium at the corners and nickel at the face centres of the cube. The solubility of cobalt in \( \gamma' \) is up to 50 at\% in the ternary aluminium–cobalt–nickel system at 900 °C [9] and the phase becomes stable at even higher cobalt concentrations when tungsten is added [5]. At higher aluminium concentrations, B2 phase—sometimes denoted as \( \beta \)—is formed which is an ordered form of the bcc crystal structure with aluminium in the body centre and cobalt (AlCo) or nickel (AlNi) at the corners [10, 11]. It is easy to assume that AlCo and AlNi form a continuous phase field in the ternary aluminium–cobalt–nickel system because the phases have the same crystal structure and a similar composition range. The calculated ternary phase diagrams from Wang et al. [9] and Zhu et al. [6] confirm this assumption. In the latter work, it is also shown that AlCo has high tungsten solubilities of over 10 at\%, but AlNi does not dissolve even 1 at\% tungsten. This coincides with the findings from Shinagawa et al. where B2 phase is only found in cobalt rich alloys [5].

Cobalt forms two intermetallic phases with tungsten in the composition range from 0 to 50 at\% tungsten. Both, Co\(_3\)W with D\(_{019}\) crystal structure and

| Phase | Lattice | Model | References |
|-------|---------|-------|------------|
| Liquid | (Al,C,Co,Ni,W) | SRS | – |
| \( \gamma \) | (Al,Co,Ni,W)(C,Va) | IS | – |
| \( \gamma' \) | (Al,Co,Ni,W)\(_{0.75}\) (Al,Co,Ni,W)\(_{0.25}\)(C,Va) | 2SL + IS, ordered \( \gamma \) | – |
| \( \kappa \) | (Al,Co,Ni)\(_{0.75}\) (Al,Co,Ni)\(_{0.25}\)(C,Va) | 2SL + IS | – |
| bcc | (Al,Co,Ni,W,Va)\(_{0.5}\)(C,Va)\(_{0.5}\) | IS | – |
| B2 | (Al,Co,Ni,W,Va)\(_{0.5}\)(Al,Co,Ni,W,Va)\(_{0.25}\)(C,Va) | 2SL + IS, ordered bcc | – |
| hcp | (Al,Co,Ni,W,Va)\(_{0.5}\)(C,Va)\(_{0.5}\) | IS | – |
| \( \mu \) | (Al,Co,Ni)\(_{0.75}\)W\(_{2}\)(Co,Ni,W)\(_{0.5}\) | 3SL | – |
| D\(_{019}\) | (Co,Ni)\(_{3}\)Fe(Al,W) | 2SL | – |
| M\(_6\)C | (Co,Ni)\(_{3}\)W\(_{2}\)(Co,Ni,W)\(_{2}\)C | 4SL | – |
| M\(_{12}\)C | (Co,Ni)\(_{4}\)W\(_{6}\)C | 4SL | – |
| Al\(_4\)C\(_3\) | – | SP | [13] |
| Al\(_2\)Co | – | SP | [10] |
| Al\(_5\)Co\(_2\) | – | SP | [10] |
| Al\(_6\)Co\(_2\) | – | SP | [10] |
| Al\(_{10}\)Co\(_4\) | – | SP | [10] |
| \( \alpha \)Al\(_{13}\)Co\(_4\) | – | SP | [10] |
| \( \gamma \)Al\(_{13}\)Co\(_4\) | – | SP | [10] |
| \( \alpha \)Al\(_{13}\)Co\(_4\) | – | SP | [10] |
| Al\(_3\)Ni | – | SP | [11] |
| Al\(_3\)Ni\(_2\) | (Al,Ni)\(_3\)(Al,Ni)\(_2\)(Ni,Va) | 2SL + WS | [11] |
| Al\(_3\)Ni\(_3\) | – | SP | [11] |
| Al\(_3\)W | – | SP | [17] |
| Al\(_4\)W | – | SP | [17] |
| Al\(_5\)W | – | SP | [17] |
| Al\(_7\)W\(_3\) | – | SP | [17] |
| Al\(_{11}\)W | – | SP | [17] |
| Al\(_{17}\)W\(_{23}\) | – | SP | [22] |
| Ni\(_3\)W | – | SP | [25] |
| Ni\(_4\)W | – | SP | [25] |
| Ni\(_5\)W | – | SP | [25] |
| WC | – | SP | [22] |

The lattices are omitted for stoichiometric phases (SP). The other models are substitutional regular solution model (SRS), sublattice model (SL) and interstitial solution model (IS), which is a special case of the Wagner–Schottky model (WS).
Co7W6 with D8\textsubscript{5} crystal structure, show aluminium solubilities of 2.5–5 at% \[4, 6\]. But they are also found in nickel-containing alloys where D0\textsubscript{19} (Co7W) and μ (Co7W\textsubscript{6}) form below and above 50 at\% nickel, respectively \[5\]. Al\textsubscript{2}Ni\textsubscript{5}, Ni\textsubscript{4}W and NiW do not show up in the samples or calculations in \[5\] and \[6\] which can be reasoned from the fact that only cobalt-rich alloys were investigated. Also, these phases might have very low cobalt solubilities. The binary phases of the aluminium–tungsten system do not have to be considered because it is not expected that high amounts of these elements react with each other and they are not found in any of the higher-order systems of the literature data.

Additions of carbon to cobalt-based superalloys have already been investigated by Freund et al. \[1\], and thermodynamic assessments of the aluminium–carbon–cobalt ternary and the aluminium–carbon–cobalt–nickel quaternary systems were carried out by Zheng et al. \[2\] and Ohtani et al. \[3\], respectively. Cobalt and nickel do not form any carbides \[12\], and Al\textsubscript{4}C\textsubscript{3} from the aluminium–carbon binary system \[13\] is not expected to be found for the same reasons as for the aluminium–tungsten compounds. The only additional phase which must be considered is which corresponds to Co\textsubscript{3}AlC or Ni\textsubscript{3}AlC. This phase has E2\textsubscript{1} crystal structure and can be constructed from L1\textsubscript{2} Co\textsubscript{3}Al or Ni\textsubscript{3}Al by placing a carbon atom into the body centre. It is found to be stable in the aluminium–carbon–cobalt ternary system, but has a quite narrow homogeneity range \[2\]. Experimental data for the Ni\textsubscript{3}AlC phase are very scarce. Ohtani et al. theoretically determined phase equilibria for the aluminium–carbon–nickel ternary system, but did not calculate any phase diagrams nor discussed the results thoroughly. But from the ab initio calculated formation enthalpies, one could reason that is not formed since \(\gamma\) is more stable \[3\]. Also, Ni\textsubscript{3}Al seems to dissolve high amounts of carbon with up to 10 at\% \[14, 15\].

**CALPHAD models**

For the five elements of interest in this work, i.e. cobalt, nickel, aluminium, tungsten and carbon, respectively, there are ten binary permutations which is the number of thermodynamic assessments to consider. The aluminium–carbon system is assessed in \[13\] and updated in \[16\] and \[2\], the aluminium–cobalt system is taken from \[10\] with some updated parameters from \[2\] and \[17\], the aluminium–nickel system is assessed in \[11\] and \[18\], the most recent parameters for the aluminium–tungsten system are from \[17\], the carbon–cobalt system is described in \[19\], but the \(\kappa\) phase is added in \[2\], the carbon–nickel system is taken from \[20\] with updates from \[21\], the carbon–tungsten system is assessed in \[22\], the cobalt–nickel system is taken from \[23\], but the description of metastable phases is from \[7\], the cobalt–tungsten system is described in \[19\] and updated in \[17\] and \[24\], and the nickel–tungsten system is taken from \[25\]. Nine of the ten possible ternary permutations are available as assessments, only aluminium–carbon–tungsten is missing, but this system is already well described by the underlying binary systems. The aluminium–carbon–cobalt system was very recently assessed in \[2\], the parameters of aluminium–carbon–nickel are taken from \[14\], but is only described in \[3\], the aluminium–cobalt–nickel system is taken from \[7\], but has also been assessed in \[9\], the parameters of the aluminium–cobalt–tungsten system are found in \[17\], aluminium–nickel–tungsten is assessed in \[26\], but some parameters are missing, carbon–cobalt–nickel and carbon–cobalt–tungsten are taken from \[20\], but the latter one is updated in \[24\], carbon–nickel–tungsten is assessed in \[14\], and the cobalt–nickel–tungsten system is also described in \[20\] with some updated parameters in \[27\].

Quaternary parameters are quite uncommon and they are only found for the carbon–cobalt–nickel–tungsten system which was assessed in \[27\]. The problem with higher-order systems from ternary upwards is that many of them are overfitted and cannot easily be combined to a multi-component database without re-assessment. This is especially true for the quaternary system of aluminium–cobalt–nickel–tungsten from \[6\] which gives reasonable results for the special case of cobalt-rich alloys, but cannot be combined with other systems since the underlying binary and ternary systems are massively modified to fit the experimental data.

**Experimental procedure**

**Ab initio calculations**

Precipitation phases of the quintenary aluminium–carbon–cobalt–nickel–tungsten system were studied
by ab initio calculations. In total, 12 structures of L12 type (\(\gamma'\)) and 15 structures of E21 type (\(\kappa\)) have been assessed.

Ground-state energies of elements in their reference state structure and of compounds were calculated using the projector-augmented wave (PAW) method [28, 29] as implemented in the ABINIT software package [30–32]. The exchange correlation functional was the Perdew–Burke–Ernzerhof form of the generalized gradient approximation [33] and PAW atomic data was taken from the JTH v1.1 dataset [34]. The structures were calculated with full spin polarization and the cell parameters were fully relaxed using the Broyden–Fletcher–Goldfarb–Shanno minimization [35]. A non-shifted Monkhorst–Pack [36] scheme (MP) was used for the automatic generation of \(k\)-points in the irreducible Brillouin zone. The number of bands and their occupation numbers were determined in respect to the Gaussian smearing scheme [37] with a broadening parameter of 0.001 hartree.

The enthalpy of formation \(\Delta H\) for the various structures was calculated according to [2] as the difference between the total energy of the structure and the total energies of the reference state elements it is composed of. For example, the enthalpy of formation of Co3AlC was derived as

\[
\Delta H_{\text{Co}_3\text{AlC}} = E_{\text{Co}_3\text{AlC}}^{\text{E21}} - \left[ \frac{3}{5} E_{\text{Co}}^{\text{hcp}} + \frac{1}{5} E_{\text{Al}}^{\text{fcc}} + \frac{1}{5} E_{\text{C}}^{\text{hcp}} - 1.895\text{kJ} \right]
\]

where \(E_{\text{Co}_3\text{AlC}}^{\text{E21}}\) is the total energy of Co3AlC in E21 structure and \(E_{\text{Co}}^{\text{hcp}}\), \(E_{\text{Al}}^{\text{fcc}}\) and \(E_{\text{C}}^{\text{hcp}}\) are the total energies of hcp cobalt, fcc aluminium and diamond, respectively. The total energy of carbon in its reference state, i.e. graphite, cannot be calculated easily and instead, the total energy of diamond is corrected by the energy difference in respect to graphite (1.895 kJ). All energy values are scaled per mole and atom.

There are two possible ways how the atoms occupy the positions in each structure type which are shown in Fig. 1. The compounds may be denoted as \(\text{A}_3\text{B}\) or \(\text{A}_2\text{BA}\) and \(\text{A}_3\text{BC}\) or \(\text{A}_2\text{BAC}\) for the L12 and E21 structures, respectively. The corners are occupied by the B atom in the former compound of each structure type and by one A atom in the latter one. But the structures in Fig. 1a and b are crystallographic equivalent because they can be converted into each other through translation operations. Thus, only one compound \(\text{A}_3\text{B}\) with L12 structure must be considered. This equivalence is lost through the insertion of a carbon atom into the octahedral void of the face atoms and the structures in Fig. 1c and d will be called E21-I and E21-II, respectively.

### CALPHAD calculations

Thermodynamic equilibrium calculations were carried out using Thermo-Calc version 2020a (Thermo-Calc Software AB). The utilized databases are listed in Table 2.

### Materials preparation and characterization

The detailed description for the preparation of superalloys can be found in a previous paper [40]. The powder mixtures were prepared by mixing the starting powders of WC (mean particle size = 5.65 \(\mu\)m, Wolfram Bergbau und Hütten AG, Austria), tungsten (0.99 \(\mu\)m, Wolfram Bergbau und Hütten AG, Austria), cobalt (Co S160/505, Ceratizit, < 1 \(\mu\)m), nickel (VALE Nickel Powder Type 123 Premium Grade, Hart Materials Ltd. UK, approx. 3–6 \(\mu\)m), aluminium (DG056, < 400 \(\mu\)m, Mepura Austria) and carbon black. All elemental powders were mixed for 2 h in a Turbula mixer.

**Influence of carbon in Co–9Al–7 W–xC and Co–30Ni–9Al–7 W–xC superalloys**

Samples with different carbon content were prepared for the connecting link between superalloys and cemented carbides. The effect of an increasing carbon concentration on the formation of \(\gamma'\), \(\kappa\) and other phases was studied by means of two series of six samples each, one nickel-free and one with a nickel concentration of 30 at% and weighed-in carbon concentrations of 0, 1, 2, 5, 10 and 15 at%. Aluminium and tungsten concentrations were kept constant for all samples at 11 at% and 9 at%, respectively. The alloys were prepared by inductive melting at 1550 °C for a dwell time of 25 min in Ar atmosphere. Subsequently solution and precipitation heat treatment steps were performed at 1300 °C for a dwell time of 12 h and 950 °C for a dwell time of 48 h in Ar atmosphere. The resulting carbon concentrations after the preparation process were determined by combustion carbon analysis (LECO CS230 Carbon Combustion Analyser).
X-ray diffraction (XRD) investigations with Cu-Kα in the range of 2θ = 15–120° and a scanning rate of 30 s/0.02° were carried out to allow the identification of formed phases. For hardness measurements, Vickers indentation on polished cross sections and a load of 30 kg was applied (HV30). An average was calculated based on at least five indents.

Cemented carbides via DTA

A TG–DTA/DSC apparatus (STA 449 C, NETZSCH) was used for the determination of γ′ solvus temperatures in superalloys and for synthesis and subsequent thermal analysis of cemented carbides. The system was protected by argon gas (99.999% purity), additionally, some pieces of titanium foil were placed into the sample room to remove most of the remaining oxygen from the purge gas. Before the start of each measurement, the sample room was evacuated and backfilled with argon three times. The measurements were taken using Proteus Thermal Analysis software (NETZSCH). Phase transformation temperatures were only determined from DSC heating curves to rule out undercooling. First, the reactions were identified in the cooling curves where the temperature differences are more pronounced since the effects elapse faster. Then in heating curves, the temperature was determined as the extrapolated onset and the extrapolated end of peaks for solidus and solvus reactions, respectively.

Cemented carbides with constant binder contents of 20 wt%, but different binder compositions were synthesized. Four binder series with 0.0, 2.5, 5.0 and 7.5 wt% aluminium, each with cobalt-to-nickel ratios of 100:0, 85:15, 50:50, 15:85 and 0:100, were prepared from elemental powder mixtures. Two samples of

Table 2 List of used databases, the relevant defined elements and their sources

| Database | Elements | References |
|----------|----------|------------|
| TCCC1    | C, Co, Ni, W | [38]       |
| TCFE9    | C, Al, Co, Ni, W | [39]       |
| Wang17   | Al, Co, W | [17]        |
| Zhou16   | C, Co, Ni, W | [27]        |
| Zhu14    | Al, Co, Ni, W | [6]         |

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each binder composition were made, one with carbon
deficit (low carbon) and the other with excess carbon
(high carbon), for measurements left and right out-
side the carbon window. This corresponds to 4.2 wt%
and 5.8 wt% carbon, respectively. The regions were
anticipated from preliminary thermodynamic calcu-
lations using Thermo-Calc with the TCFE9 database
for all cobalt-to-nickel ratios, but without considering
the influence of aluminium. 500–700 mg of these
powders was used for each DTA experiment, and
some of them were repeated to check for
reproducibility.

A zigzag temperature profile with two heating and
cooling ramps was applied. The first step was con-
sidered synthesis of the cemented carbide, and the
sample was heated to 1500 °C and cooled to 600 °C
with a rate of 20 K/min including an additional
10 min dwell at the maximum temperature. The
second step was the actual measurement with heat-
ing to 1500 °C and cooling to room temperature at a
rate of 10 K/min. The samples were metallographi-
cally prepared and characterized using SEM/EDS to
identify present phases.

Results and discussion

Ab Initio calculations

Reference state elements

The lattice constants of the calculated elements in
their reference structures are given in Table 3 and
compared to experimentally determined literature
values. The error of the lattice constants is well below
1% for each element.

| Element | Structure | Lattice constant (Å) | Reference value (Å) |
|---------|-----------|---------------------|---------------------|
| C       | Diamond   | 3.570               | 3.567 [41]          |
| Al      | FCC       | 4.039               | 4.046 [42]          |
| Co      | HCP       | a = 2.491           | a = 2.507 [43]      |
|         |           | c = 4.044           | c = 4.070 [43]      |
| Ni      | FCC       | 3.524               | 3.499 [42]          |
| W       | BCC       | 3.185               | 3.155 [42]          |

L1₂ Structures

All twelve possible binary permutations of alu-
minium, cobalt, nickel and tungsten which form a
compound with A₃B configuration were calculated.
The evaluated enthalpies of formation from the total
energies according to Sect. 2.1 are given in Table 4
and compared to reference values where available.
The results agree to each other quite well within a
few kilojoule, especially with [2] where the difference
is below 5% even though another software package
was used for the calculations in this work.

The thermodynamically stable compounds with
L1₂ structure at 0 K are Al₃Co, Co₃Al, Al₃Ni, Ni₃Al
and Co₃W because they have negative enthalpies of
formation. This predicts that these could be found as
(meta) stable phases in the binary systems alu-
minium–cobalt, aluminium–nickel and cobalt–tung-
sten. But only Co₃Al and Ni₃Al are observed
experimentally or described in thermodynamic
assessments with L1₂ structure [17, 44]. The other
compounds are not formed because at this composi-
tion intermetallic phases with different crystal struc-
tures are presumably more stable. Al₃Co is described
as stoichiometric phase of the space group P2/m, but
no value for the enthalpy of formation was found
[17]. Al₃Ni forms crystals of the space group Pnma
with an enthalpy of formation of about – 40 kJ/(mol
atom) [44, 45] which is much more stable than in the
L1₂ structure. The D0₁₉ phase is the stable form of the
Co₃W compound with an enthalpy of formation of
about – 8 kJ/(mol atom) [17] which leaves the L1₂
structure a little less stable.

Co₃Al with L1₂ structure on its own does not form
in the binary system [46], but is readily stabilized
through the addition of tungsten in the form of
Co₃(Al,W) and might even be stable in the ternary
system [4, 47]. L₁₂ Co₃W has a negative enthalpy of
formation and this could facilitate the replacement of
aluminium with tungsten and allow the formation of
a (meta)stable compound. The enthalpy of formation
of L₁₂ Ni₃W on the other hand is positive and thus,
tungsten might destabilize γ' when Ni₃(Al,W) is
formed. But since the enthalpy of formation of L₁₂
Ni₃Al is very negative, a quite high amount of
tungsten may be dissolved before the structure is not
stable anymore. This can be reasoned from the tern-
ary phase diagram where γ' consist of up to 10 at%
tungsten [26]. Still, the destabilizing effect is seen in
the γ' partition coefficients which reveal that tungsten
changes from a γ′ to a γ former at higher concentrations [48].

The most positive enthalpies of formation are found for the compounds with three tungsten atoms on the faces of the L1 2 structures which means they are the most unstable. This limits the maximum amount of tungsten in the γ′ phase, whereas a higher amount of aluminium is possible since Al3Co and Al3Ni are quite stable. Definite conclusions are hard to draw from the other results, but the values are quite important for a thermodynamic description of the L1 2 phase in the aluminium–cobalt–nickel–tungsten system.

### E21 structures

As discussed in Sect. 2.1, two different configurations of the E21 structure are possible, i.e. A3BC with B in the corners and A2BAC with A in the corners which will be called E21-I and E21-II, respectively. The order of the first three atoms is alphabetically and the fourth atom is always the one on the corners, followed by C for the carbon atom in the centre. All permutations with aluminium, cobalt and nickel as A or B were calculated and the results are given in Table 5. Tungsten was not considered for these calculations since it is not found to dissolve into γ′ phase and even seems to destabilize its formation as discussed in Sect. 3.3.2. The calculations agree very well with [2] except for AlCo3CoC where the reference enthalpy of formation is more than 5 kJ/(mol atom) lower. However, this is negligible because the stable configuration is Co3AlC, i.e. the E21-I structure, anyway. In contrast to the results for the L1 2 structures, the differences to [3] are quite pronounced for the κ compounds. But it was already discussed in [2] that the enthalpy of formation for Co3AlC is way too low there. Also, only one configuration of E21 with aluminium always in the corners was considered in their calculations.

The only stable compounds are the E21-I structures Co3AlC and Ni3AlC with aluminium on the corners. The former one is found in the ternary system and has a very small homogeneity range, i.e. is almost stoichiometric, but with a carbon content between 10 and 12 at%. Therefore, it should rather be denoted as Co3AlC, where x is about 0.5 [2, 49, 50]. Ni3AlC is not described as an individual intermetallic compound in the ternary system, but as already discussed, Ni3Al is stable there. The γ′ phase has a high solubility of carbon with up to 10 at% and therefore, forms a homogenous phase field with κ which is nothing else, but L1 2 Ni3Al with a carbon atom in the body centre to form E21-I [3, 14, 15].

Co3AlC is more stable than Ni3AlC which could explain why the former phase seems to be more readily formed in cemented carbides (see Sect. 3.3.2). Tungsten stabilizes the L1 2 structure of the cobalt compounds, but seems to destabilize it in the nickel compounds which could further influence the formation of E21 in this system. Co3Al is not found to be stable in the binary system, but with carbon in the body centre the structure is stabilized by almost 7 kJ/(mol atom).

Aluminium seems to preferably occupy the corners since Al2Co3AlC, Co3AlC and Ni3AlC are the more

| Compound | Enthalpy of formation (kJ/(mol atom)) | Reference value (kJ/(mol atom)) |
|----------|-------------------------------------|---------------------------------|
| Al3Co   | − 19.69                             | − 20.07 [2]                     |
| Co3Al   | − 16.23                             | − 17.05 [2]                     |
| Al3Ni   | − 20.96                             | − 22.90 [3]                     |
| Ni3Al   | − 41.75                             | − 42.38 [3]                     |
| Al3W    | 6.16                                |                                  |
| W3Al    | 19.75                               |                                  |
| Co3Ni   | 3.86                                |                                  |
| Ni3Co   | 0.96                                |                                  |
| Co3W    | − 4.08                              |                                  |
| W3Co    | 25.36                               |                                  |
| Ni3W    | 11.17                               |                                  |
| W3Ni    | 17.45                               |                                  |

Table 4 Calculated enthalpies of formation for the L1 2 structure type compounds compared to calculated values from literature sources
stable configurations of these compounds, except for Al$_3$NiC which is more stable than its E2$_1$-II pendant Al$_2$NiAlC, probably because nickel also prefers to occupy the corners as can be seen in the enthalpies of formation of Co$_3$NiC and CoNi$_2$NiC versus their other configurations.

Co$_2$NiCoC and Ni$_3$CoC both have two different results because the total energy spiked to a lower value at specific plane wave cut-off energies, but converged to the higher values afterwards. However, the enthalpies of formation for the compounds in the other configuration, i.e. Co$_3$NiC and CoNi$_2$NiC, are lower anyway.

The calculated enthalpies of formation of the cobalt- and nickel-based compounds from Table 4 and 5 for L1$_2$ and E2$_1$ structures, respectively, are plotted against their aluminium concentration in Fig. 2. Ni$_3$AlC resides in a deep well of stability, and since Al$_3$Ni is also quite stable, the slope between the two compounds is not very steep. This could explain why the phase field of the L1$_2$ structure also reaches into regions of higher nickel and aluminium concentrations [44]. Co$_3$Al, on the other hand, is not that stable compared to pure L1$_2$/fcc cobalt which could inhibit its formation. But when carbon is introduced, Co$_3$AlC sits in a steep well between Co$_3$C and Al$_3$CoC which seems to facilitate its formation, but is also responsible for the narrow phase field [22].

| Compound   | Enthalpy of formation (kJ/(mol atom)) | Reference value (kJ/(mol atom)) |
|------------|----------------------------------------|---------------------------------|
| Al$_3$CoC  | 25.22                                  | 24.44 [2]                       |
| Al$_3$CoAlC| 23.23                                  | 22.51 [2]                       |
| Co$_3$AlC  | -23.07                                 | 22.70 [3]                       |
| AlCo$_2$CoC| 17.49                                  | 11.87 [2]                       |
| Al$_3$NiC  | 14.03                                  | -                              |
| Al$_2$NiAlC| 23.52                                  | 12.90 [3]                       |
| Ni$_3$AlC  | -19.17                                 | -28.20 [3]                      |
| AlNi$_2$NiC| 6.98                                   | -                              |
| Co$_3$NiC  | 16.59                                  | -                              |
| Co$_2$NiCoC| 22.72 33.12                            | -                              |
| Ni$_3$CoC  | 25.12 33.06                            | -                              |
| CoNi$_2$NiC| 18.17                                  | -                              |
| Al$_4$C    | 29.98                                  | 29.87 [2] 32.10 [3]             |
| Co$_4$C    | 19.03                                  | 18.73 [2] 19.60 [3]             |
| Ni$_4$C    | 17.46                                  | -                              |

Figure 2 Calculated enthalpies of formation of cobalt (squares) and nickel (triangles)-based L1$_2$ and E2$_1$ structures versus aluminium concentration of the compounds.

Influence of carbon in Co–9Al–7 W–xC and Co–30Ni–9Al–7 W–xC superalloys

Micrographs of the nickel-free alloys of the carbon series are shown in Fig. 3 with a common section and an inlet with the γ/γ′ or γ/k microstructure. The
sample with 0.2 at% carbon already consists of small amounts of an additional white phase which becomes more with increasing carbon concentration. EDS identified the phase as $\eta$ (M$_6$C or M$_{12}$C) or tungsten carbide (WC) because of the high carbon and tungsten concentrations. Graphite is observed in the sample with 10.7 at% carbon. Note that the measured carbon concentrations of the nickel-free Co–9Al–7 W–xC alloy and the nickel-containing Co–30Ni–9Al–7 W–xC are given in Table 6. As expected, quite a lot of carbon is lost during preparation.

$\gamma/\gamma'$ microstructure is only visible in the sample with 0.5 at% carbon and it is not clear why the samples with lower carbon concentrations did not form $\gamma'$. Carbon might has a stabilizing effect on the formation of $\gamma'$ as concluded in [1]. With higher carbon concentrations, $\gamma'$ incorporates carbon into its structure and changes from L1$_2$ Co$_3$(Al,W) to E2$_1$ Co$_3$AlC (x). Very little tungsten between 0.8 at% and 1.3 at% (EDS measurements) is dissolved in this phase. It could be reasoned that most of the tungsten must be consumed by formation of $\eta$ and WC before

Table 6 Carbon concentrations in at% of nickel-free and nickel-containing alloys measured with combustion carbon analysis. The weighed-in target carbon concentrations are given as table headers in at%.

| Alloy system      | 0   | 1   | 2   | 5   | 10  | 15  | at% |
|-------------------|-----|-----|-----|-----|-----|-----|-----|
| Co–9Al–7 W–xC     | 0.0 | 0.2 | 0.5 | 2.6 | 7.1 | 10.7| at% |
| Co–30Ni–9Al–7 W–xC| 0.0 | 0.2 | 0.8 | 3.7 | 9.5 | 14.1| at% |
κ becomes stable. Carbon content in κ was not quantified, but the amount of cobalt is three to four times the amount of aluminium which backs up the identification of κ with EDS. The amount of this phase increases with carbon concentration and covers quite large areas in the sample with 10.7 at% carbon (Fig. 3f).

The micrographs of the nickel-containing samples from the carbon series are also shown in Fig. 3, again with a common section of the samples and an inlet with the γ/γ' or γ/κ microstructure. Analogous to the nickel-free samples, carbides are already observable from the lowest carbon concentration of 0.2 wt% and their amount increases the more carbon is added. The shape of the white phase changes from nodular to blocky at 9.5 at% carbon. From the EDS results in Table 7 it is very likely that η changes to WC with increasing carbon concentrations. Graphite begins to form in a carbon range between 7.1 and 9.5 at% if no influence of the nickel concentration is assumed.

γ' is observable until a carbon concentration of 3.7 at% which is way higher than in the nickel-free samples where this phase is not stable at 2.6 at% carbon already. From 9.5 at% carbon, κ can be observed which was also identified by EDS. Here it is finely dispersed and does not form large areas even at a carbon concentration of 14.1 at%.

XRD results (Table 8) largely confirm the SEM/EDS observations, but also give hint on the partial presence of the B2-phase at the highest carbon concentration in the Co–30Ni–9Al–7 W series which was not visible in the SEM images. Interestingly, no phases except η (M6C or M12C) and WC were detected in the 7.1 at% carbon sample of the Co–9Al–7 W series, whereas SEM images clearly showed the presence of the κ phase. Graphite was only confirmed in the nickel-containing sample with 14.1 at% carbon which can be reasoned from SEM images where only small amounts are visible which might not be detected by XRD.

Thermodynamic calculations of alloys with 9 at% aluminium and 7 at% tungsten, and carbon concentration from 0 to 15 at% at 950 °C were carried out using Thermo-Calc with the TCFE9 and TCCC1 databases. The fraction of present phases were plotted against the carbon content which is shown in Fig. 4a and b for nickel-free alloys and 30 at% nickel, respectively. The calculations yielded the same results for both databases which indicates that the same thermodynamic assessments were used. This leaves the results quite doubtful because aluminium was not defined while using TCCC1 which means that this element does not influence the calculated phase equilibria at all. This also becomes apparent when the compositions of the phases are derived from the calculation results which show that the γ phase constantly has an aluminium concentration of 9 at%. Still, the experimental results for the nickel-free alloys show some similarities to the calculations. M6C/M12C was observed in samples with up to 2.6 at% C and at 7.1 at% blocky WC is identified (see Fig. 3, Table 7 and Table 8) which coincides with the curves in Fig. 4. At higher carbon concentrations η becomes stable again which might be due to the interaction with κ. From the inlet in Fig. 3f, it seems like κ is formed on the edges of WC which leads to carbon depletion and transformation to η. Graphite is predicted to form at carbon contents above 7.5 at% which is also observed in the experimental results. γ' and κ are missing completely which is not surprising clearly visible in spectra. The carbides are guessed from the tungsten-to-cobalt ratios and tungsten-to-cobalt/nickel ratios, respectively, which is unity in η and big in WC [51].

| Table 7 | Phase formation in Co-9Al-7 W-xC and Co-30Ni-9Al-7 W-xC by image analysis and EDS measured composition from carbon series. ✓ and x represent absent and present phases, respectively. EDS Quantification was carried out neglecting carbon, although a peak is |
|---------|-----------------------------------------------------------------|
| Co–9Al–7 W–xC | Co–30Ni–9Al–7 W–xC |
| Carbon | γ' | κ | Carbides | Carbon | γ' | κ | Carbides |
| 0.0 at% C | x | x | x | 0.0 at% C | ✓ | x | x |
| 0.2 at% C | x | x | η | 0.2 at% C | ✓ | x | η |
| 0.5 at% C | ✓ | x | η | 0.8 at% C | ✓ | x | η |
| 2.6 at% C | x | ✓ | η | 3.7 at% C | ✓ | x | η |
| 7.1 at% C | x | ✓ | η/WC, Gr | 9.5 at% C | x | ✓ | η/WC, Gr |
| 10.7 at% C | x | ✓ | η, Gr | 14.1 at% C | x | ✓ | WC, Gr |
because they are not described in the underlying thermodynamic assessments of the used databases. The calculated results in the nickel-containing carbon series differ severely from the experimental observations. With EDS and XRD measurements, the carbides were identified to be $\gamma'$ for the samples with up to 3.7 at% carbon (see Table 7 and Table 8). It is known that the description of cemented carbides with a mixture of cobalt and nickel is erroneous in thermodynamic assessments which were used in TCFE9. This was partially corrected in [27] and these parameters were used in the Zhou16 database, but, unfortunately, repeating the above calculations with this database did not affect the results. The calculated critical carbon concentration for the formation of graphite is a little lower for the nickel-containing alloys. This is reasonable since nickel has a higher tungsten solubility than cobalt [20, 52] and with more tungsten in $\gamma$, less is available to consume carbon through the formation of carbides.

Generally, hardness (HV30) rapidly increases for both carbon series with increasing carbon content followed by a plateau and either an increase (nickel-free series) or decrease (nickel-containing series) for the highest carbon contents (Fig. 5). Furthermore, a distinct difference in hardness can be observed between the two series which can be reasoned from the information in Table 7 and Table 8. At low carbon concentrations $\gamma'$ is only present in the nickel-containing samples which explains the higher hardness. But from 0.5 at% carbon the nickel-free samples contain finely dispersed $\gamma'$ or $\kappa$ phases which are sparse or look rather agglomerated when nickel is present (Fig. 3). This leads to an inversion of the hardness relationship. The decrease in hardness for the highest carbon content of the nickel-containing

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**Table 8** Phase formation in Co–9Al–7 W–xC and Co–30Ni–9Al–7 W–xC by XRD from carbon series. ✓ and × represent absent and present phases, respectively. Gr...Graphite

| Carbon (at%) | γ' | κ | B2 | Carbides          | Carbon (at%) | γ' | κ | B2 | Carbides          |
|-------------|----|----|----|------------------|-------------|----|----|----|------------------|
| 0.0          | ×  | ×  | ×  |                  | 0.0          | ×  | ×  | ×  |                  |
| 0.2          | ×  | ×  | ×  | ×                | 0.2          | ✓  | ×  | ×  | ×                |
| 0.5          | ✓  | ×  | ×  | M6C              | 0.8          | ✓  | ×  | ×  | M6C, M12C        |
| 2.6          | ✓  | ×  | ×  | M6C              | 3.7          | ✓  | ×  | ×  | M6C, WC          |
| 7.1          | ×  | ×  | ×  | M6C, WC          | 9.5          | ×  | ✓  | ×  | WC               |
| 1.7          | ×  | ✓  | ✓  | M6C, WC          | 14.1         | ✓  | ✓  | ✓  | WC, Gr           |

**Figure 4** Calculated present phases in a nickel-free carbon series and b carbon series with 30 at% nickel at 950 °C using Thermo-Calc with TCFE9/TCCC1 database. The amount of $\gamma'$ is the rest to unity.
series appears to be unexpected, as the presence of WC should cause an increase. But it can be explained by the high amount of graphite visible in the SEM images (Fig. 3 l) which adds easily deformable glide planes to the material.

Cemented carbides via DTA

Solidus temperature

The temperature of liquid formation was determined from DTA heating curves, and the results are plotted against the nickel proportion of the binder (fraction of nickel in the cobalt–nickel ratio) in Fig. 6a and b for the low-carbon (4.2 wt% C) and high-carbon (5.8 wt% C) samples, respectively. Red-coloured data points are presumably wrong because overlapped DTA signals were observed and these cannot be separated due to their complex relationship [53]. Therefore, they are excluded from further discussion. Each series with different aluminium content was linearly fit by least-squares regression omitting the rejected results. The solidus temperature is elevated with increasing nickel proportion in all binder series, and the rate of this effect is described by the slope of the linear fit curves. In the samples with low carbon content, the slope becomes less steep when the more aluminium is added. This leads to an inversion of the trend at higher nickel proportions where aluminium addition decreases the solidus temperature. The inversion occurs at the intercept of the 0 wt% aluminium line with the other lines, i.e. at around 60, 35 and 5% nickel proportion for 2.5, 5 and 7.5 wt% binder aluminium concentration, respectively. For the high-carbon series, there is no change of the solidus temperature from 5 to 7.5 wt% aluminium and the fit curves are identical in Fig. 6b.

The results of the series with 0.0 wt% aluminium are further compared to [27] where similar experiments in the system Co–Fe–Ni–W–C were carried out. All measured solidus temperatures are higher in the present work, but the deviations are below 10 K for all high-carbon samples and for the samples with low nickel content in the low-carbon series. Additional literature values from [24, 54] for Co–W–C and Ni–W–C coincide very well with the present results at 100% nickel proportion and the deviations in the nickel-free samples are only 5 K. Therefore, the temperatures of liquid formation and their compositional dependencies seem valid in the present work.

The solidus temperature of cemented carbides was also calculated for binder aluminium concentrations between 0 and 10 wt% using the TCFE9 database and the results are shown along with the corresponding experimental data in Fig. 7. Only binary binder systems, i.e. aluminium–cobalt and aluminium–nickel, were modelled because mixtures of cobalt and nickel as binder are not well defined in TCFE9. A low-carbon and a high-carbon series were calculated with 4.2 and 5.8 wt% carbon, respectively, analogous to the experimental samples. Calculations for the low-carbon–nickel series and the high-carbon–cobalt series in Fig. 7 describe the experimental determined temperatures remarkably well. Aluminium lowers the solidus temperature in the former case and elevates it in the latter one. The calculations for the high-carbon–nickel series show an increasing solidus temperature, but the measured effect is far less pronounced. The calculated low-carbon–cobalt series does not reflect the subtle increase in the solidus temperature which can be seen in the experimental results.

Identification and solvus temperature of precipitation phases

The present phases were identified from SEM micrographs (see Supplementary Data) and the results are given in Table 9 together with the results
Graphite was, as intended, found in every sample of the high-carbon series. On the other hand, could not easily be identified in WC–Co50–Ni50–Al2.5–C4.2 and WC–Co15–Ni85–Al2.5–C4.2 via SEM since no large areas of this phase are visible. This indicates that the carbon window is shifted to higher carbon concentrations and the sample is further in the $g$ region [55]. Although not observed directly in WC–Co50–Ni50–Al2.5–C4.2, it is quite unlikely that no $g$ carbide has formed in this sample since it has been found in every other low-carbon sample. It might just be dispersed very finely as well.

$c'$ is observable in micrographs of five low-carbon samples with 5 and 7.5 wt% binder aluminium concentration. In WC–Co85–Ni15–Al7.5–C4.2 very fine precipitates were detected only at higher magnification. Since $c'$ is also visible in WC–Co15–Ni85–Al7.5–C4.2 and WC–Ni100–Al7.5–C4.2, this phase is expected to be stable in WC–Co50–Ni50–Al7.5–C4.2 as well, but cannot be observed in SEM micrographs. The reason might be that only $g'$ is stable or there is no Z-contrast between $g$ and $g'$. A phase of difference thermal analysis (measurement curves in Supplementary Data). Graphite was, as intended, found in every sample of the high-carbon series. $\eta$, on the other hand, could not easily be identified in WC–Co50–Ni50–Al2.5–C4.2 and WC–Co15–Ni85–Al2.5–C4.2 via SEM since no large areas of this phase are visible. This indicates that the carbon window is shifted to higher carbon concentrations and the sample is further in the $\eta$ region [55]. Although not observed directly in WC–Co50–Ni50–Al2.5–C4.2, it is quite unlikely that no $\eta$ carbide has formed in this sample since it has been found in every other low-carbon sample. It might just be dispersed very finely as well.

$\gamma'$ is observable in micrographs of five low-carbon samples with 5 and 7.5 wt% binder aluminium concentration. In WC–Co85–Ni15–Al7.5–C4.2 very fine precipitates were detected only at higher magnification. Since $\gamma'$ is also visible in WC–Co15–Ni85–Al7.5–C4.2 and WC–Ni100–Al7.5–C4.2, this phase is expected to be stable in WC–Co50–Ni50–Al7.5–C4.2 as well, but cannot be observed in SEM micrographs. The reason might be that only $\gamma'$ is stable or there is no Z-contrast between $\gamma$ and $\gamma'$. A phase

![Figure 6](image_url)

**Figure 6** Solidus temperatures of cemented carbides with different cobalt–nickel–aluminium binder and a excess tungsten (4.2 wt% C) and b excess carbon (5.8 wt% C). The red-coloured data points were excluded from further discussion since the solidus temperature could not be evaluated validly. The reference data are coloured in blue and taken from [24, 27] and [54] for Co–Fe–Ni–W–C, Co–W–C and Ni–W–C, respectively. Steinlechner is from unpublished work carried out at TU Wien where a conventionally prepared cemented carbide with 20 wt% nickel as binder was analysed.

![Figure 7](image_url)

**Figure 7** Calculated (lines) and measured (symbols) solidus temperatures of cemented carbides versus binder aluminium concentration. The red-coloured data points could not be evaluated validly. Calculations were carried out using the TCFE9 database.
transformation can be seen in DTA curves and the temperature fits perfectly into the trend of an increasing \( c' \) solvus with increasing nickel content. \( c/\) phase transformations were also found in measurements of samples with high cobalt ratio in the series with 5 wt% aluminium. The results are a bit unreliable since no two-phase binder microstructure was observed in these samples. But the trend of an increasing \( c' \) solvus with increasing nickel content is a sign for correct interpretation of the measurements.

No \( c' \) precipitation can be measured in WC–Co100–Al7.5–C4.2 although it was determined in WC–Co100–Al5.0–C4.2 and aluminium tends to stabilize \( c' \). But in the aluminium–cobalt–tungsten system the stable composition range for \( c' \) is quite narrow [47] and small deviations could prevent it from forming. A decreasing tungsten solubility with an increasing aluminium concentration was observed which also affects the stability of \( c' \). Figure 8 shows this effect for the low-carbon samples, but details of the binder composition analysis are discussed later.

\( \kappa \) is visible in WC–Co100–Al5–C5.8 and WC–Co85Ni15–Al5–C5.8, and in all high-carbon samples with 7.5 wt% aluminium in binder. It seems like nickel has destabilizing effects on this phase because it is only visible at high cobalt ratios in the samples with 5 wt% aluminium. This finding can also be reasoned from the observations in Sect. 3.2 where \( \kappa \) needs higher carbon concentrations to become stable when nickel is added. When enough aluminium is added \( \kappa \) will be stable at higher nickel concentrations as well. All of this might be indirectly a function of the binder tungsten concentration. As already discussed, more carbon will reduce the amount of tungsten through formation of \( \eta \) and WC, and aluminium tends to decrease the binder tungsten solubility while nickel increases it. Thus, a binder with little nickel and high aluminium concentration will dissolve less tungsten and it is more likely that \( \kappa \) becomes stable. This can also be reasoned from the micrographs where \( \kappa \) frequently appears to form at the edges of WC. The reason behind this may be a depletion of tungsten around the carbides as these

| Basic composition | Low-carbon series (4.2 wt% C) | High-carbon series (5.8 wt% C) |
|-------------------|------------------------------|------------------------------|
| Co-to-Ni ratio    | \( \gamma' \) | \( \eta \) | \( \kappa \) | Graphite |
| 100:0             | 0 | x | x | x | x |
| 85:15             | 0 | x | x | x | x |
| 50:50             | 0 | x | x | x | x |
| 15:85             | 0 | x | x | x | x |
| 100:0             | 2.5 | x | x | x | x |
| 85:15             | 2.5 | x | x | x | x |
| 50:50             | 2.5 | x | x | x | x |
| 15:85             | 2.5 | x | x | x | x |
| 100:0             | 2.5 | x | x | x | x |
| 100:0             | 5.0 | x (887) | x | x | x |
| 85:15             | 5.0 | x (909) | x | x | x |
| 50:50             | 5.0 | x (1093) | x | x | x |
| 15:85             | 5.0 | x (1160) | x | x | x |
| 100:0             | 5.0 | x (1160) | x | x | x |
| 100:0             | 7.5 | x | x | x | x |
| 85:15             | 7.5 | x (991) | x | x | x |
| 50:50             | 7.5 | x (1142) | x | x | x |
| 15:85             | 7.5 | x (1246) | x | x | x |
| 100:0             | 7.5 | x (1293) | x | x | x |

The present phases other than WC and \( \gamma' \) are \( \gamma' \) and \( \eta \) for the low-carbon (4.2 wt% C) samples, and \( \kappa \) and graphite for the high-carbon (5.8 wt% C) samples. \( \checkmark \) and x represent absent and present phases, respectively. DTA measured \( \gamma' \) and \( \kappa \) solvus temperatures in °C are given in parentheses. ? is discussed in text separately.
precipitate from the binder and grow in size. The formation temperature of \( \kappa \) could not be determined for WC–Co100–Al7.5–C5.8 and WC–Ni100–Al7.5–C5.8 although the phase is clearly visible in the micrographs. In the former sample the quaternary phase reaction between liquid, WC, \( \gamma \) and graphite might overlap with the \( \kappa \) formation because the measured solidus temperature is unexpectedly high (see Fig. 6b). In WC–Ni100–Al7.5–C5.8, the reaction heat could be very low and spread out over a wide temperature range. A small peak at 1150 °C can even be observed in the cooling curve, but since it is not seen in the heating curve this value cannot be evaluated. The \( \kappa \) formation temperature increases with the binder nickel concentration in the 5 wt% aluminium series, but decreases in the samples with 7.5 wt% aluminium.

**Binder composition analysis**

The binder composition for all cemented carbides was determined by EDS. As mentioned before, aluminium decreases the tungsten solubility which can be clearly seen in Fig. 8a for the low-carbon samples (4.2 wt% carbon). This effect is quite pronounced because the solubility is decreased by over 60% between the samples with 0 and 7.5 wt% binder aluminium. A similar trend of aluminium decreasing the tungsten concentration is qualitatively also observed for the high-carbon samples (5.8 wt% carbon), Fig. 8b. Nickel increases the tungsten solubility for both the low-carbon and the high-carbon series in Fig. 8, and is well known [20, 52]. Quantitatively, the low-carbon series allows much higher—approx. double or triple—concentrations of tungsten in the binder compared to the high-carbon series.

Thermodynamic equilibrium calculations at 1000 °C were additionally carried out using the

![Figure 8 Solubility of tungsten in the binder (\( \gamma \) phase) in wt% of cemented carbides as a function of the nickel proportion and aluminium concentration. Al was varied between 0.0, 2.5, 5.0 and 7.5 wt%, the Ni proportion was set to 0, 15, 50, 85 and 100% respectively. Symbols are EDS measured, lines are calculated binder tungsten concentration of a the low-carbon (4.2 wt% C) and b the high-carbon (5.8 wt% C) cemented carbide series. Calculations were carried out at 1000 °C using the TCFE9 database. Cemented carbides were prepared from powder mixtures in the DTA. Three EDS measurements inside a section of 15 × 15 μm were taken for each sample, and the confidence interval is given as error bars.](image-url)
TCFE9 database. The trends coincide quite well with the EDS analysis, but the measurements generally result in higher tungsten concentrations, especially for the samples with 0% nickel proportion. There might be a systematic deviation due to experimental limitations, but an influence of the error-prone EDS analysis of carbon can be ruled out since only aluminium, cobalt, nickel and tungsten were considered in the evaluation. The difference most probably arises from the insufficiently defined γ phase in TCFE9 which does not account for aluminium or carbon solubility.

**Discussion/summary**

A comparison of the samples of this work will be carried out using calculated ternary phase diagrams. Figure 9a shows such a plot for the aluminium–cobalt–tungsten system at 950 °C calculated using Thermo-Calc with the Zhu14 database. All samples from the ternary are included as symbols in the diagram, i.e. the binder compositions of the DTA cemented carbides from Sect. 3.3 and the Co–9Al–7 W–xC samples from the influence of carbon, Sect. 3.2.

The DTA samples have different symbols depending on the present phases which were determined by metallographic and thermoanalytic methods. The γ' and κ phases are considered stable at 950 °C if the measured solvus is above this temperature. Carbon is not included in the calculations since it is not described in the Zhu14 database, but the effects might be derived as difference to the aluminium–cobalt–tungsten system. Most of the samples have a single-phase γ binder only, which coincides quite well with the calculated results. The samples which are inside two-phase regions with D019 or B2 are on the edge of the calculated phase fields, so it is not surprising that no additional phases were found metallographically. The two samples with γ/κ microstructure imply that there is a tie line for the formation of κ between 2 and 5 at% tungsten. From the stoichiometric composition of Co3AlC it could be reasoned that the upper limit of the two-phase region is around 20 at% aluminium.

The samples from the carbon influence investigation start inside the γ single-phase field (indicated by the symbol in Fig. 9a) and move to lower tungsten concentrations since tungsten binds in the form of carbides when carbon is added. Eventually, they cross the κ tie line. But before that, γ' seems to be stabilized which was already discussed based on Fig. 9c.

Nickel stabilizes the γ' phase, which was discussed extensively here and in a previous paper [40] and can again be identified in Fig. 9b for a cobalt-to-nickel ratio of 85:15. The four DTA samples with the lower aluminium concentrations are again predicted and experimentally confirmed to have γ single-phase binder. The two γ/κ samples are in about the same region as their equivalents in Fig. 9a. The calculated and experimentally determined results for a fixed cobalt-to-nickel ratio of 50:50 in Fig. 9c also coincide very well with each other. The γ/κ region seems to have become smaller because only the DTA sample with the highest aluminium concentration shows this microstructure, but the tie line is still somewhere between 2 and 5 at% tungsten.

Calculated alloys with fixed cobalt-to-nickel ratios of 15:85 and 0:100 are plotted together with the corresponding DTA samples in Fig. 9d and e, respectively. The calculations reflect the experimental results very well for the samples with high nickel content. The κ phase is again found only at high aluminium and low tungsten concentrations, but inside the γ'/κ two-phase region of the aluminium–cobalt–nickel–tungsten system.

**Conclusions**

The phase equilibria in cemented carbides with superalloys of the aluminium–cobalt–nickel–tungsten system as binder phase were investigated with focus on several aspects. The following conclusions can be drawn from the results:

1. The addition of nickel in aluminium–cobalt–tungsten stabilizes the γ' phase which leads to higher solvus temperatures. This stability is lost when carbon is introduced to the system. First, very small carbon additions seem to promote the precipitation of γ'. But then, the amount of dissolved tungsten in the γ matrix is reduced through the formation of carbides and γ' vanishes. However, the absence of tungsten facilitates the formation of another precipitate phase, κ, which seems to be especially stable in cobalt-rich samples.
2. $\gamma/\gamma'$ binder microstructure of cemented carbides is hard to obtain because the maximum tungsten concentration is limited and depends on the overall carbon content. But nickel does not only stabilize the $\gamma'$ phase, it also elevates the amount of dissolved tungsten in the binder phase of cemented carbides. This might be the reason why only nickel-containing samples worked out as intended in this work.

3. Aluminium additions of up to 15 at% to the binder of cemented carbides have moderate effects on the temperature of the quaternary phase reactions. But it was shown that other phase transformations at lower temperatures occur which yield $\gamma$, $\gamma/\gamma'$ and $\gamma/\kappa$ binder microstructures. These results may be useful for the thermodynamic description of the aluminium–carbon–cobalt–nickel–tungsten system.

4. Ab initio calculated enthalpies of formation of the $\gamma$ and $\kappa$ compounds coincide with literature data, reflect the experimental results and might also be used for assessing the quintenary system thermodynamically.

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References

[1] Freund LP, Bauer A, Benker L, Neumeier S, Göken M (2015) Formation of cuboidal Co3AlC precipitates in carbon-containing Co–Al–W-based superalloys. Adv Eng Mater 17(8):1113–1118
[2] Zheng W, He S, Wang J, Mao H (2018) Thermodynamic evaluation of the Co-Al-C system by coupling Ab initio calculations and CALPHAD approach. J Ph Equili Diffus 39(5):538–548
[3] Ohtani H, Yamano M, Hasebe M (2004) Thermodynamic analysis of the Co–Al–C and Ni–Al–C systems by incorporating ab initio energetic calculations into the CALPHAD approach. Calphad 28(2):177–190
[4] Lass EA, Grist RD, Williams ME (2016) Phase equilibria and microstructural evolution in ternary Co-Al-W between 750 and 1100 °C. J Ph Equilib Diffus 37(4):387–401
[5] Shinagawa K, Omori T, Sato J, Oikawa K, Ohnuma I, Kainuma R, Ishida K (2008) Phase equilibria and microstructure on $\gamma$-ph. in Co-Ni-Al-W System, Mater Trans 49(6):1474–1479
[6] Zhu J, Titus MS, Pollock TM (2014) Experimental investigation and thermodynamic modeling of the co-rich region in the Co-Al-Ni-W quaternary system. J Ph Equilib Diffus 35(5):595–611
[7] Liu XL, Lindwall G, Gheno T, Liu Z-K (2016) Thermodynamic modeling of Al–Co–Cr, Al–Co–Ni, Co–Cr–Ni ternary systems towards a description for Al–Co–Cr–Ni. Calphad 52:125–142
[8] Dincer O, Pehlivanoğlu MK, Çalışkan NK, Karakaya İ, Kalkanlı A (2015) Processing and microstructural characterization of liquid phase sintered tungsten–nickel–cobalt heavy alloys. Int J Refract Met Hard Mater 50:106–112
[9] Wang Y, Zhou P, Peng Y, Du Y, Sundman B, Long J, Xu T, Zhang Z (2016) A thermodynamic description of the Al–Co–Ni system and site occupancy in Co + AlNi3 composite binder phase. J Alloys Compd 687:855–866
[10] Stein F, He C, Dupin N (2013) Melting behaviour and homogeneity range of B2 CoAl and updated thermodynamic description of the Al–Co system. Intermetallics 39:58–68
[11] Ansara I, Dupin N, Lukas HL, Sundman B (1997) Thermodynamic assessment of the Al-Ni system. J Alloys Compd 247(1):20–30
[12] Guillermet AF (1988) Thermodynamic Properties of the Fe-Co-Ni-C System. Z Met 79:524–536
[13] Gröbner J, Lukas HL, Aldinger F (1995) Thermodynamic calculations in the Y-Al-C system. J Alloys Compd 220(1):8–14
[14] Wang Y, Chen C, Zhang Z, Long J, Xu T, Liu X, Zhang L, Peng Y, Zhou P, Du Y (2014) Phase equilibria in the Al–C–Ni–W quaternary system. Int J Refract Met Hard Mater 46:43–51
[15] Hosoda H, Inamura T (2011) Evaluation of solubility limit of carbon in Ni3AlC1-x. MRS Proceedings 1295 mrsf10–1295-n02–09
[16] Connetable D, Lacaze J, Maugis P, Sundman B (2008) A Calphad assessment of Al–C–Fe system with the carbide modelled as an ordered form of the fcc phase. Calphad 32(2):361–370
[17] Wang P, Xiong W, Kattner UR, Campbell CE, Lass EA, Kontsev OY, Olson GB (2017) Thermodynamic reassessment of the Al-Co-W system. J Ph Equilib Diffus 26(2):152–160
[18] Dupin N, Ansara I, Sundman B (2001) Thermodynamic reassessment of the ternary system Al-Cr-Ni. Calphad 25(2):279–298
[19] Guillermet AF (1989) Thermodynamic properties of the Co-W-C system. MTA 20(5):935–956
[20] Guillermet A (1989) The Co-Fe-Ni-W-C phase diagram: a thermodynamic description and calculated sections for (Co-Fe-Ni)-bonded cemented WC tools. Z Met 80:83–94
[21] Lee B-J (1992) On the stability of Cr carbides. Calphad 16(2):121–149
[22] Jonsson S (1995) Phase relations in quaternary hard materials
[23] Guillermet AF (1987) Assessment of the thermodynamic properties of the Ni-Co system. Z Met 78:639–647
[24] Markström A, Frisk K, Sundman B (2005) A revised thermodynamic description of the Co-W-C system. J Ph Equilib Diffus 26(2):152–160
[25] Gustafson P (1988) A thermodynamic evaluation of the Cr-Ni-W system. Calphad 12(3):277–292
[26] Popović J, Brož P, Buršič J (2008) Microstructure and phase equilibria in the Ni–Al–W system. Intermetallics 16(7):884–888
[27] Zhou P, Peng Y, Buchegger C, Du Y, Lengauer W (2016) Experimental investigation and thermodynamic assessment of the C-Co–Fe–Ni–W system. Int J Refract Met Hard Mater 54:60–69
[28] Blöchl PE (1994) Projector augmented-wave method. Phys Rev B 50(24):17953–17979
[29] Kresse G, Joubert D (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. Phys Rev B 59(3):1758–1775
[30] Gonzé X, Amadon B, Antonius G, Arnardi F, Baguet L, Beuken JM, Biedier J, Bottin F, Bouchet J, Bousquet E, Brouwer N, Brueneval F, Brunin G, Cavignac T, Charraud JB, Chen W, Côté M, Cottenier S, Denier J, Geneste G, Ghosez P, Giantomassi M, Gillet Y, Gingras O, Hamann DR, Hautier G, He X, Helbig N, Holzwarth N, Jia Y, Jollet F, Lafargue-Dit-Hauret W, Lejaeghere, Marques K MAL, Martin A, Martins C, Miranda HC, Naccarato F, Persson K, Petretto G, Planes V, Pouillon Y, Prokhorenko S, Ricci F, Rignanes GM, Romero AH, Schmitt MM, Torrent M, van Setten MJ, Van Troeye B, Verstraete MJ, Zéra G, Zwanziger JW (2020) The abinitproject: Impact, environment and recent developments. Comput Phys Commun, 248:107042
[31] Romero AH, Allan DC, Amadon B, Antonius G, Applen court T, Baguet L, Biedier J, Bottin F, Bouchet J, Bousquet E, Brueneval F, Brunin G, Caliste D, Cote M, Denier J, Dreyer C, Ghosez P, Giantomassi M, Gillet Y, Gingras O, Hamann DR, Hautier G, Jollet F, Jomard G, Martin A, Miranda HPC, Naccarato F, Petretto G, Pike NA, Planes V, Prokhorenko S, Rangel T, Ricci F, Rignanes GM, Royo M, Stengel M, Torrent M, van Setten MJ, Van Troeye B, Verstraete MJ, Wiktor J, Zwanziger JW, Gonzé X (2020) ABINIT: overview and focus on selected capabilities. J Chem Phys 152(12):124102
[32] Torrent M, Jollet F, Bottin F, Zéra G, Gonzé X (2008) Implementation of the projector augmented-wave method in the ABINIT code: application to the study of iron under pressure. Comput Mater Sci 42(2):337–351
[33] Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77(18):3865–3868
[34] Jollet F, Torrent M, Holzwarth N (2014) Generation of projector augmented-wave atomic data: a 71 element validated table in the XML format. Comput Phys Commun 185(4):1246–1254
[35] Head JD, Zerner MC (1985) A Broyden—Fletcher—Goldfarb—Shanno optimization procedure for molecular geometries. Chem Phys Lett 122(3):264–270
[36] Monkhorst HJ, Pack JD (1976) Special points for Brillouin-zone integrations. Phys Rev B 13(12):5188–5192
[37] Methfessel M, Paxton AT (1989) High-precision sampling for Brillouin-zone integration in Metals. Phys Rev B 40(6):3616–3621
[38] TCS Cemented Carbide Database 1.0, Thermo-Calc Software AB, 2015
[39] TCS Steels and Fe-alloys Database 9.1, Thermo-Calc Software AB, 2019
[40] Edtmayer C, Wolf M, de Oro Calderon R, Schubert W-D (2021) Effect of nickel on the formation of γ/γ' microstructures in WC/Co-Ni-Al-W. Int J Refract Met Hard Mater 100:105652
[41] Riley D (1944) Lattice constant of diamond and the C-C single bond. Nature 153(3889):587–588
[42] Davey WP (1925) Precision measurements of the lattice constants of twelve common metals. Phys Rev J1 PR 25(6):753–761
[43] Vincent F, Figlarz M (1967) Quelques precisions sur les paramètres cristallins et l'intensité des raies debye-scherrer du cobalt cubique et du cobalt hexagonal. Compt Rendus Hebdes Seances de L Acad des Sci Serie C 264(15):1270–2000
[44] Chen HL, Doernberg E, Svoboda P, Schmid-Fetzer R (2011) Thermodynamics of the Al3Ni phase and revision of the Al–Ni system. Thermochim Acta 512(1–2):189–195
[45] Bradley AJ, Taylor A (1937) XCIX The crystal structures of Ni2Al3 and NiAl3. Lond Edinb Dublin Philos Mag J Sci 23(158):1049–1067
[46] Ellner M, Kek S, Predel B (1992) Zur Existenz einer Phase Co3Al vom Cu3Au-Strukturtyp. J Alloys Compd 189(2):245–248
[47] Sato J, Omori T, Oikawa K, Ohnuma I, Kainuma R, Ishida K (2006) Cobalt-base high-temperature alloys. Science 312(5770):90–91
[48] Jia C, Ishida K, Nishizawa T (1994) Partition of alloying elements between γ (A1), γ’ (L1 2), and β (B2) phases in Ni-Al base systems. Metall Mater Trans A 25(3):473–485
[49] Kimura Y, Takahashi M, Hosoda H, Miura S, Mishima Y (2000) Compressive mechanical properties of multi-phase alloys based on B2 CoAl and E21 Co3AlC. Intermetallics 8(7):749–757
[50] Kimura Y, Sakai K, Mishima Y (2006) Revolutionary microstructure control with phase diagram evaluation for the design of E21 Co3AlC-based heat-resistant alloys. J Ph Equilib Diffus 27(1):14–21
[51] Pollock C, Stadelmaier H (1970) The eta carbides in the Fe–W–C and Co–W–C systems. Metall Trans 1(4):767–770
[52] Tracey VA (1992) Nickel in hardmetals. Int J Refract Met Hard Mater 11(3):137–149
[53] Ding EY (2000) Study on separation method of overlapped peaks in differential thermal analysis with computer simulation. J Therm Anal Calorim 63:517–523
[54] Gabriel A, Pastor H, Deo D, Basu S, Allibert C (1986) New experimental data in the C-Fe-W C-Co-W, C-Ni-W, C-Fe-Ni-W and C-Co-Ni-W cemented carbides systems and their application to sintering conditions. Int J refract hard Met 5(4):215–221
[55] Garcia I, ColladoCiprés V, Blomqvist A, Kaplan B (2019) Cemented carbide microstructures: a review. Int J Refract Met Hard Mater 80:40–68

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