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Investigations Within the Quaternary System Titanium—Nickel—Aluminium—Carbon*

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The phase relationship within the quaternary system: titanium—nickel—aluminium—carbon was established for 1100 °C (quench). A quaternary η-carbide with a lattice parameter of $a = 11.40$-11.46_3 Å was found to exist. The H-phase Ti_2AlC and the perovskite phase Ti_3AlC are no longer stable in the presence of minor amounts of nickel.

[Keywords: Quaternary System (Ti, Ni, Al, C); η*-Carbides]*

Untersuchungen im System Titan—Nickel—Aluminium—Kohlenstoff

Die Phasenbeziehungen im Vierstoff-System Ti—Ni—Al—C wurden für 1100 °C (abgeschreckt) ermittelt. Die Existenz eines quaternären Carbids (η-Carbid) mit dem Gitterparameter $a = 11{,}40$—$11{,}46_3$ Å wurde nachgewiesen. Die H-Phase Ti_2AlC und die Perowskit-Phase Ti_3AlC sind in Gegenwart von bereits geringen Mengen an Nickel nicht stabil.

Introduction

Complex carbides of formula Ti_2AlC and Ti_3AlC have been reported[1] to be of considerable efficiency, when used as abrasives for glass polishing. With nickel proposed as a possible binder, a study of the quaternary system titanium—nickel—aluminium—carbon was of interest. Out of the four ternary systems, namely, Ti—Al—C[2], Ni—Al—C[3], Ti—Ni—Al[4] and Ti—Ni—C[5, 6] which are building up the quaternary, the two first named ternary combinations have extensively

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* Dedicated to Professor *Otto Kratky*.

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been studied only recently. The two latter ternaries are comparatively well known from literature data. The Ni—Al—C and Ti—Ni—C systems display a relatively simple constitution, inasfar as no ternary phase occurs. It has been found[3] that no true ternary Ni—Al-carbide exists, but an appreciable amount of carbon dissolves in the γ'-phase (Ni_3Al). At 1000 °C, all stable Ni aluminides are in equilibrium with carbon, and Ni_2Al_3 forms a two-phase field with Al_4C_3. Within the Ti—Ni—C system the binary carbide TiC_{1-x} dominates the equilibria, which are determined by two-phase areas TiC and the Ti—Ni intermetallics besides the components. No solubility of carbon in the binary Ti—Ni phases, except for Ti_2Ni, has been reported[6].

Different from these ternaries, the combination Ti—Ni—Al, which has first been examined by *Taylor* et al.[7] exhibits ternary aluminides; among these the *Heusler*-phase $TiNi_2Al$ is the most stable compound. Two more Ti—Ni aluminides are described as a *Laves*-phase TiNiAl and a μ-phase $NiAl_2Ti$, while still another has not been explored in detail. Except for the *Heusler*-phase, all other ternary aluminides decompose above 800 °C. In connection with Ni-base alloys the ternary system Ti—Ni—Al was also studied by Hughes[8], focusing on the mutual behaviour of the *Heusler*-phase and the intermetallics TiNi and NiAl. It was shown, furthermore, the strong coupling of the Ti—Ni—Al phases with TiC_{1-x} in the precipitates of Cr—Ni ferritic steels. Thus the presence of mixtures of TiC_{1-x} with NiAl, Ni_3Al and/or $TiNi_2Al$ were observed.

Sample Preparation

Sample preparation was made by sintering the powder mixtures of the components as well as by arc melting and annealing, as described previously[2], where the materials used are specified. Nickel powder (m3N) was from Alpha Div. Ventron Corp. For sintering the powders of the components in evacuated quartz tubes the pressed pellets were wrapped into a tantalum foil to avoid reaction with the quartz. In general there was no attack of the pressed specimens on the tantalum foil observed at 1100 °C.

Results

The equilibria for isothermal sections have been worked out by x-ray diffraction techniques. Pertinent data for the powder patterns of the observed phases are listed in Table 1. With regard to the observed binary and ternary phases there is good agreement of the lattice parameters determined in this work and those reported in literature. As can be seen from Table 1 all existing solid phases (1100 °C, quench)

Table 1. *Binary, ternary and quaternary phases, observed in* Ti—Ni—Al—C *alloys*

Binary Phases	Lattice Parameters (in Å) observed in this work	 literature data
Ti—Ni:		
Ti_2Ni	11.30_7	11.27_8 (11.315)
TiNi		3.01_5
$TiNi_3$	5.102_8; 8.271_9	5.1089; 8.3188
Ti—Al:		
Ti_3Al	5.79_3; 4.62_3	5.77_5; 4.63_8 (25 at%)
TiAl	4.00_1; 4.07_1	4.00_5; 4.07_1 (50 at%)
$TiAl_3$	3.84_6; 8.59_4	3.85_0; 8.59_6
Ti—C:		
TiC_{1-x}	4.31_7 (average)	4.326-4.296 x = 0.04-0.52
Ni—Al:		
Ni_3Al	3.55_3 (Ni-rich)	3.55_3-3.566
NiAl	2.87_7 (55 at% Ni)	2.855-2.887-2.858
Ni_2Al_3	4.039_3; 4.902_7	4.03_6; 4.90_1
Ni—C:		
None		
Al—C		
Al_4C_3	3.33_8; 25.11_7	3.33_2; 24.99_0
Ternary Phases		
Ni_2AlTi	5.865—5.886	5.87 or 2 × 2.92
Ti_3AlC (P)	4.150	4.156
Ti_2AlC (H)	3.056; 13.62_3	3.040; 13.60_0
Quaternary Phase		
Ti_3NiAl_2C	11.46_3	—

have been corroborated so far. The lattice parameter of the *Heusler*-phase $TiNi_2Al$ has been found to be between 5.86_5 and 5.88_6 Å. The average value compares well with literature data of $a = 5.87$[9] or 2 × 2.92 Å[10]. This value (2.92 Å) is due to the assumption that $TiNi_2Al$ is to be crystallizing with a CsCl type structure of composition Ni(Ti, Al). The slight variation of the cell parameter indicates the presence of a small range of homogeneity[7], which also was adopted by *Kaufman* et al.[4].

Discussion

The Ti—Ni—Al-η *Carbide*

According to *Stover* et al.[6], the phase Ti_2Ni appears to dissolve a measurable amount of carbon. These authors confirm the findings by *Kuo*[11], as they were unable to prepare solid solutions of composition "Ti_4Ni_2C" analogous to Ti_4Ni_2O which crystallizes with a filled up Ti_2Ni type structure, a so-called η-oxide. The largest lattice parameter found for a ternary alloy Ti—Ni—C was: $a = 11.365$ Å, while for pure Ti_2Ni a cell parameter of $a = 11.315$ Å has been given. This value is somewhat larger than that listed by *Pearson*[9] (11.278 Å). It is of interest to note, that another early study[12] of the ternary system Ti—Al—C indicates the possible formation of an η-carbide with an a-parameter of approximately 11.2 Å. Such a carbide has not been corroborated later on[2].

Several samples of the quaternary system Ti—Ni—Al—C, however, were found to contain a phase closely related to Ti_2Ni. This is proven by the powder pattern of a sample of composition Ti_3NiAl_2C, evaluated in Table 2. Complete indexing based on a cubic face centered cell (Fd3m) leads to a lattice parameter of $a = 11.46_3$ Å. The line intensities of these powder patterns correspond virtually to those of Ti_2Ni or to the characteristic patterns of η-carbides (nitrides or oxides). The cell parameter of the newly observed phase is considerably larger than the parameters found and reported for Ti_2Ni (see Table 1), $Ti_2Ni(C)$ solid solution[6] or Ti_4Ni_2O. Only few Ti—Ni— Al—C-specimens have been detected having a cell parameter between 11.40 Å and that for Ti_2Ni or $Ti_2Ni(C)$. Thus the conclusion can be made that a quaternary (Ti—Ni—Al) η-carbide occurs that structurally derives from Ti_2Ni. It is known, that aluminium acts as a stabilizer for carbides e.g. in niobium or tantalum containing compounds[13]. Such carbides are Nb_3NiAl_2C, Nb_3Ni_2AlC or Ta_3CrAl_2C, where the parent lattice in sites 48f and 32e is of the formula $[Nb_3Ni_2]$ or $[Nb_3Al_2]$ respectively with aluminium or nickel in the icosahedron center and carbon filling the voids in site 16c leaving the site 8a empty[14]. In the case of the (Ti—Ni—Al) η-carbide it appears that more nickel is substituted by aluminum and less voids being filled by carbon. The mode of carbon filling can not be decided from the present data. As a formula for the (Ti—Ni—Al) η-carbide the composition Ti_3NiAl_2C seems to be adequate, also comparing the lattice parameters of quaternary η-carbides consisting of niobium or tantalum, nickel, aluminum, and carbon. As the radii of titanium and tantalum are not far apart the cell parameter for Ta_3NiAl_2C (11.4_5 Å) is close to that for "Ti_3NiAl_2C". In fact, samples of this composition only contain traces of TiC_{1-x} and NiAl. With the parameters given in Table 2, an

Table 2. *Powder Data for* η*-phase*-Ti_3NiAl_2C (Co- *and* Cu Kα)

$Int._{obs.}$	$Int._{meas.}$ (Cu Kα)	$Int._{calc.}$	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	Indices
—	—	8.1*	—	0.0183	(111)
—	—	0.8	—	0.0488	(220)
—	—	1.3	—	0.0671	(311)
w	10.4	14.3	0.0730	0.0731	(222)
vw	5.2	0.7	0.0958	0.0975	(400) C
m	22.1	37.2	0.1160	0.1158	(331)
m$^+$	27.4	38.9	0.1462	0.1463	(422)
vst	100.0	100.0	0.1651	0.1646	(333) (511)
m$^+$	29.1	47.7	0.1950	0.1951	(440)
vw	4.2	3.5	0.2131	0.2134	(531)
vw	4.8	6.7	0.2196	0.2195	(442) (600)
—	—	0.1	—	0.2438	(620)
—	—	2.2	—	0.2621	(533)
w$^+$	10.7	19.4	0.2685	0.2682	(622)
vw	4.6	2.0	0.2924	0.2926	(444) C
vw	4.6	3.6	0.3116	0.3109	(555) (711)
vw	8.4	0.1	0.3432	0.3414	(642) C
vw	4.7	3.0	0.3588	0.3597	(553) (731)
vw	3.2	2.1	0.3904	0.3902	(800) C
w	8.7	13.6	0.4081	0.4084	(733)
st	30.5	35.3	0.4393	0.4389	(660) (822)
w	5.0	11.1	0.4571	0.4572	(555) (751)
vw	2.9	5.1	0.4637	0.4633	(662)
—	—	2.4	—	0.4877	(840)
vw	3.7	7.2	0.5060	0.5060	(753) (911)
—	—	0.1	—	0.5120	(842)
—	—	1.6	—	0.5365	(664)
—	—	1.5	—	0.5547	(931)
—	—	1.3	—	0.5847	(844)
st$^-$	21.2	22.5	0.6038	0.6035	(771) (755) (933)
vw	5.1	4.5	0.6338	0.6340	(862) (10.20)
w	5.0	6.5	0.6526	0.6522	(773) (951)
w$^+$	11.0	12.0	0.6591	0.6584	(666) (10.22)
—	—	0.0	—	0.7011	(953)
—	—	0.2	—	0.7072	(864)
—	—	0.5	—	0.7315	(10.42)
vw	4.0	6.2	0.7485	0.7498	(775) (11.11)
—	—	2.2	—	0.7803	(880)
w	6.0	10.0	0.7967	0.7986	(971) (11.31)
—	—	2.8	—	0.8047	(882) (10.44)
w	6.8	15.1	0.8295	0.8291	(10.60)
—	—	1.7	—	0.8474	(973) (11.33)
w$^+$	6.0	8.2	0.8536	0.8535	(10.62)
m$^+$	20.3	36.8	0.8783	0.8778	(884) (12.00)
m$^-$	13.2	12.3	0.8961	0.8961	(777) (11.51)
m	16.8	31.1	0.9264	0.9266	(10.64) (12.22)
—	—	4.0	—	0.9449	(11.53)

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* Not observable; C coincidence; $a = 11.46_3$ Å; $I_{calc.}$ for Ti in 48f) ($x = 0.194$), Al in 32e) ($x = 0.825$), Ni in 16 d), C in 16 c).

excellent fit for the intensity calculations can be obtained. A more statistical distribution such as 16 Ni + 16 Al in 32 e) and 16 Al in 16 d) positions is unlikely.

The Constitution of the Quaternary System Ti—Ni—Al—C

In an exploratory way the phase distribution of the above named combination was clarified for 1 100 °C. The results are presented in Figs.

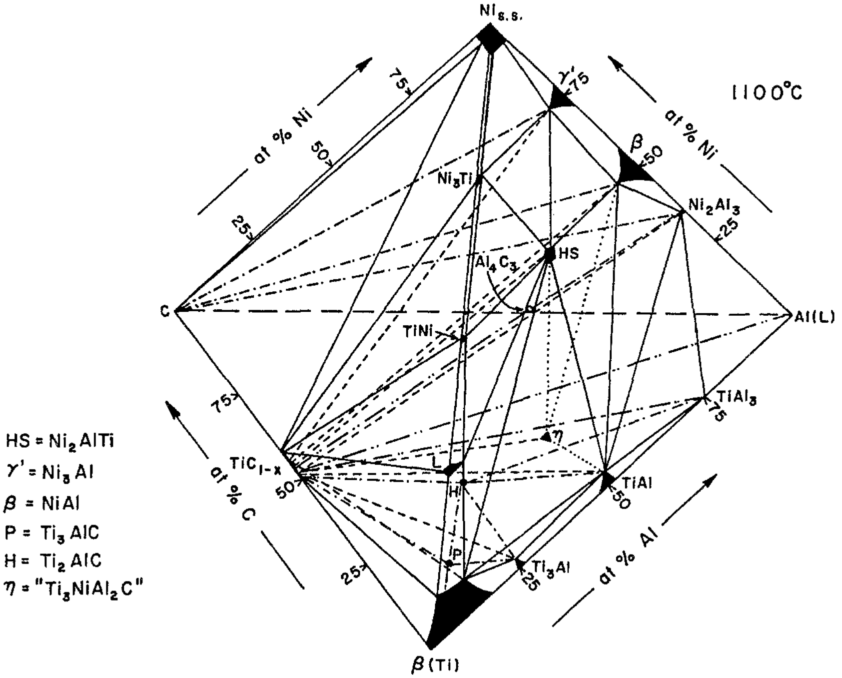

Fig. 1. Schematic representation of an isothermic and isobaric space of the quaternary system Ti—Ni—Al—C

1 and 2 as well as in Table 3. Fig. 1 represents an overall (isothermal) view of the four component system and Fig. 2 an isothermal section at 50 at % Ni, while the nonvariant four-phase equilibria are listed in Table 3. There are a total of 24 four-phase equilibria with titanium carbide TiC_{1-x}, as the most dominant participant. It should be mentioned however that only a few 4-phase equilibria have experimentally been observed by x-ray diffraction techniques, i.e. where all four phases could unambiguously be distinguished by their characteristic patterns. Nevertheless from the presence of the monovariant 3-phase regions a complete phase diagram can be derived[15]. Although the main objective for studying this quaternary system was related to

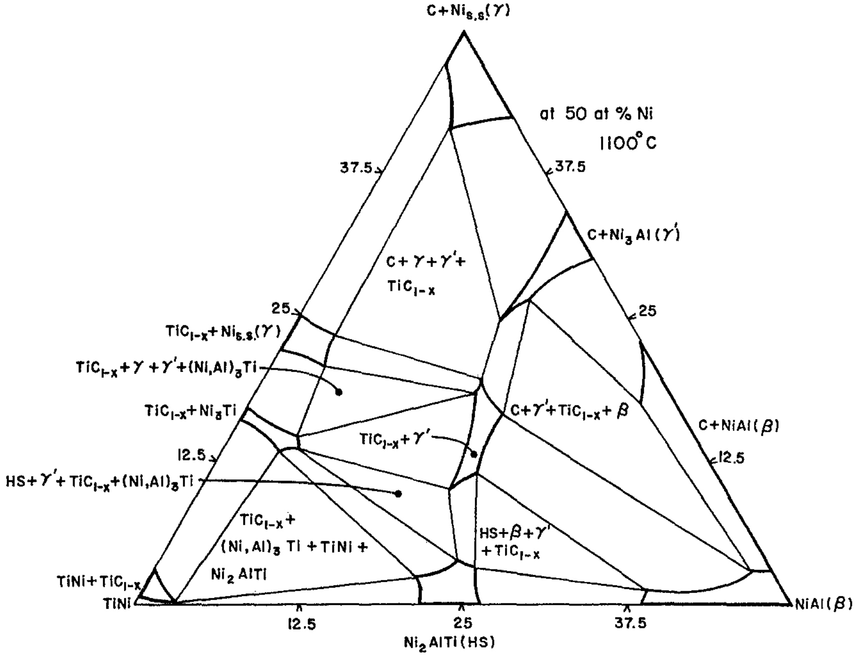

Fig. 2. Isothermic section at 50 at% Ni

Table 3. *Nonvariant 4-phase equilibria of the quaternary system* Ti—Ni—Al—C *at 1100 °C*

TiC_{1-x} + HS ($TiNi_2Al$) + γ' $(Ni, Ti)_3Al$ + Ni_3Ti
TiC_{1-x} + HS + γ' + NiAl
TiC_{1-x} + η + NiAl (β) + HS
TiC_{1-x} + γ' + γ ($Ni_{s.s}$) + Ni_3Ti
TiC_{1-x} + γ' + γ + C
NiAl + γ' + TiC + C
TiC_{1-x} + NiAl (β) + Ni_2Al_3 + C
TiC_{1-x} + C + Al_4C_3 + Ni_2Al_3
TiC_{1-x} + η + HS + TiAl (Ni)
TiC_{1-x} + Al (L) + Al_4C_3 + Ni_2Al_3
TiAl (Ni) + η + HS + NiAl (β)
TiC_{1-x} + Ni_2Al_3 + TiAl (Ni) + $TiAl_3$
TiC_{1-x} + $TiAl_3$ + Al (L) + Ni_2Al_3
TiC_{1-x} + HS + NiTi + Ni_3Ti
β-Ti + TiC_{1-x} + Ti_2Ni (L) + HS
TiC_{1-x} + NiTi + Ti_2Ni (L) + HS
TiC_{1-x} + HS + TiAl (Ni) + β-Ti
TiC_{1-x} + β-Ti + Ti_3Al (Ni) + TiAl (Ni)
TiC_{1-x} + H + TiAl (Ni) + $TiAl_3$
TiAl (Ni) + H + Ti_3Al (Ni) + TiC_{1-x}
P + β-Ti + Ti_3Al (Ni) + TiC_{1-x}
H + P + TiC_{1-x} + Ti_3Al (Ni)
TiAl (Ni) + η + NiAl (β) + TiC_{1-x}
TiAl (Ni) + NiAl (β) + Ni_2Al_3 + TiC_{1-x}

the problem of finding a suitable binder for the H-phase Ti_2AlC and the perovskite phase Ti_3AlC, there are other reasons too, for a more detailed study. In particular, the behaviour of combinations of titanium carbide and γ' is of major interest, inasfar as composite hard materials such as WC-(Ni, Al) cermets have recently been proposed[16].

Fig. 1 demonstrates the complexity of phase equilibria despite the fact that only one quaternary compound (η) has been observed. It is obvious that isothermal sections at temperatures below 1100 °C (quench) do involve more compounds. Besides the Ti—Ni—Al intermetallics, Ti_2Ni is, at the chosen temperature, just melted[17] and no solid Al and $NiAl_3$ are present. From the full and differently dashed lines (tie lines) the 4-phase spaces can be recognized. The extension of the respective homogeneous regions (singlephase) is based on an estimate, that is to say the nonvariant points and the univariant saturation lines are close to those for the saturation of the corresponding ternary systems. The large homogeneous range of β-Ti solid solutions (at 1100 °C, quench), for e.g. exhibits a small solubility for carbon only; similarly TiC_{1-x} does not take up an appreciable amount of nickel or aluminum. In contrast, γ' and NiAl(β) dissolve titanium and carbon as well. There is, however, no indication for carbon solubility in the Heusler-phase or in the nickel containing TiAl. Interestingly, at already low concentrations of nickel both the complex Ti—Al—C carbides become suppressed. Nickel soaks up the aluminum from these complex carbides, which is understandable considering the high stability (heat of formation) of TiC_{1-x} on the one hand and of NiAl (and Ni-aluminides) on the other. Thus it is not very likely that additions of nickel exert a suitable effect as binder in an equilibrium state. The precise amount of nickel which dissolves in TiAl and Ti_3Al has, however, not been determined as yet.

The aspect dealing with higher nickel concentration, as shown in Fig. 2 for 50 at% Ni, is connected with the presence of the duplex alloys consisting of TiC_{1-x} and γ'[Ni_3(Al, Ti)] as a possible cermet combination.

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