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The Ternary System Nickel—Aluminum—Carbon

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Phase equilibria in the ternary system nickel—aluminum—carbon were determined. The phase boundaries are given for an isothermal section at 1000 °C. No ternary phase occurs, but $Ni_3Al(\gamma')$ exhibits a solubility for carbon up to 7-8 at%. NiAl(β) also dissolves carbon (ca. 3 at%).

(Keywords: Carbides, ternary; Phase diagram, Al—Ni—C*)*

Das ternäre System Nickel—Aluminium—Kohlenstoff

Die Phasengleichgewichte im ternären System Nickel—Aluminium—Kohlenstoff wurden für den isothermen Schnitt bei 1000 °C bestimmt. Die Löslichkeiten und Phasengrenzen werden angegeben. Es tritt keine ternäre Phase auf, aber $Ni_3Al(\gamma')$ löst bis zu 7—8 at% Kohlenstoff. NiAl(β) löst ebenfalls Kohlenstoff (ca. 3 at%).

Introduction

The phase relationships in several transition metal—aluminum—carbon systems have recently been investigated[1]. There are only a few data for the ternary nickel—aluminum—carbon system although it is of considerable interest with regard to Ni-based superalloys. In this context it was to clarify whether Ni_3AlC_{1-x} is a distinct ternary phase or a solid solution of carbon in the binary $Ni_3Al(\gamma')$-phase, with partially filled $L1_2$ type structure.

The binary systems nickel—aluminum, nickel—carbon and aluminium—carbon are well established[2]. *Hütter* and *Stadelmaier*[3] found that Ni_3Al dissolves up to 5.8 at% carbon. They reported a lattice parameter of 0.3603 nm for Ni_3AlC_{1-x} as compared to 0.3573 nm for the binary $Ni_3Al(\gamma')$-phase. No data on the temperature of the alloy

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preparation were given and it was not stated, if Ni_3AlC_{1-x} is an isotypic, but separate ternary phase as indicated by *Fritscher*[4] in a melting-surface diagram, or if Ni_3AlC_{1-x} is an extended carbon solution in the binary $Ni_3Al(\gamma')$. $Ni_3Al(\gamma')$ and Ni_3AlC_{1-x} were never observed simultaneously in molten specimens[4].

Experimental

Seventy alloys were made from nickel powder (3 N, Alpha Ventron Corp.), aluminum powder (3 N 8, Alpha Ventron Corp.) and graphite (pure by emission spectrograph, Le Carbone Lorraine). Appropriate mixtures were cold pressed and arc melted under purified argon. From these alloy buttons thin pellets were cut which were annealed either in a vacuum furnace ($p \leq 10^{-6}$ Torr) at 1 000 °C for 170 h or in sealed, evacuated quartz tubes at 700 °C for 340 h. The surface of the annealed specimens were cleaned, polished, etched (echant 1 part HNO_3 + 2 parts HCl + 3 parts lactic acid) and examined by metallography and X-ray-diffractometry. Hardness measurements were made using the *Vickers*-technique.

Results and Discussion

No ternary phase has been found, however, γ' dissolves carbon, forming a structure arrangement such as a defect perovskite carbide. The homogeneous range of the γ'-phase field was determined by lattice parameter measurements (Tables 1 and 2). The increase of the γ'-lattice parameter in the binary system Ni—Al with decreasing Ni/Al ratio is fairly regular. The lattice parameters for the vertices $[\gamma'(\gamma' + \gamma + C)]$ and $[\gamma'(\gamma' + \beta + C)]$ were taken from alloys in the resp. three phase fields (Table 2). The increase of the lattice parameter of the γ'-phase with the carbon content was determined, considering the fact that an alloy $Ni_{.785}Al_{.165}C_{.05}$ does not contain free graphite (see Table 2) and by

Table 1. *Lattice parameter of binary* Ni—Al-*alloys in the* Ni *rich region*

Ni	Al (At%)	a [nm]
70	30	0.3566 + NiAl(β)
72	28	0.3564
73	27	0.3561
74	26	0.3560
75	25	0.3557
76	24	0.3555
77	23	0.3553
88	12	0.3533
100	0	0.3516

Table 2. *Results of X-ray and metallographic analysis of* Ni*-rich alloys and lattice parameters of* $Ni_3Al(\gamma')$*-phase and* Ni *(s.s.)* (γ)*-phase*

a) 700 °C

Composition (At%) Ni	Al	C	X-ray results a [nm]	a [nm]		Metallographic results
75	25		0.3557			(prim. β decomp.)
67.5	27.5	5	0.3577			mainly γ' + trace prim. β
70	25	5	0.3578			single phase γ'
75	20	5	0.3589	0.3544		two phase; peritect. prim γ'
78.5	16.5	5	0.3589	0.3543		two phase; peritect. prim. γ'
90	5	5		0.3524		single phase γ (porous)
65	25	10	0.3577		+ C	mainly γ' + trace β + graphite
67.5	22.5	10	0.3590		+ C	mainly γ' + trace graphite
72.5	17.5	10	0.3589	0.3546	+ C	$\gamma' + \gamma$ + graphite
56	29	15	0.3575		+ β + C	β-lamellae, + γ' + graphite
60	25	15	0.3573		+ β + C	γ' + trace β + graphite
62	23	15	0.3579		+ C	γ' + graphite
64	21	15	0.3585		+ C	γ' + graphite
66	19	15				$\gamma' + \gamma$ + graphite
66	22.5	17.5	0.3583		+ C	γ' + graphite
55	25	20	0.3573		+ β + C	
60	20	20	0.3583		+ C	γ' + graphite
72	8	20		0.3517		γ (porous) + graphite
57.5	18.5	25	0.3581		+ C	γ' + graphite
50	15	35	0.3588	0.3544	+ C	$\gamma' + \gamma$ + graphite
b) 1000 °C						
75	25		0.3557			(prim. β decomp.)
67.5	27.5	5	0.3575			mainly γ' + trace prim. β
70	25	5	0.3582			γ' single phase
78.5	16.5	5	0.3582	0.3547		$\gamma' + \gamma$
90	5	5		0.3533		γ single phase (porous)
65	25	10	0.3578		+ β + C	prim. graphite + γ' + β
67.5	22.5	10	0.3581			prim. graphite + γ'
72.5	17.5	10	0.3583	0.3546	+ C	
81	9	10		0.3537	+ C	γ (porous) + graphite
56	29	15	0.3578		+ β + C	prim. graphite + β dendrites in γ'
58	27	15	0.3580		+ β + C	prim. graphite + β dendrites in γ'
60	25	15	0.3578		+ β + C	prim. graphite + β dendrites in γ'

Table 2 (continued)

Composition (At%) Ni	Al	C	X-ray results a [nm]	a [nm]		Metallographic results
62	23	15	0.3580		+ C	γ' + graphite
64	21	15	0.3579		+ C	γ' + graphite
66	19	15	0.3582	0.3545	+ C	$\gamma' + \gamma$ + graphite
60	20	20	0.3583		+ C	γ' + graphite
72	8	20		0.3547	+ C	γ + graphite
50	25	25	0.3579		+ β + C	prim. graphite in sek. β-matrix
57.5	18.5	25	0.3581		+ C	γ' + graphite
63	7	30		0.3543	+ C	γ + graphite
50	15	35	0.3582	0.3546	+ C	

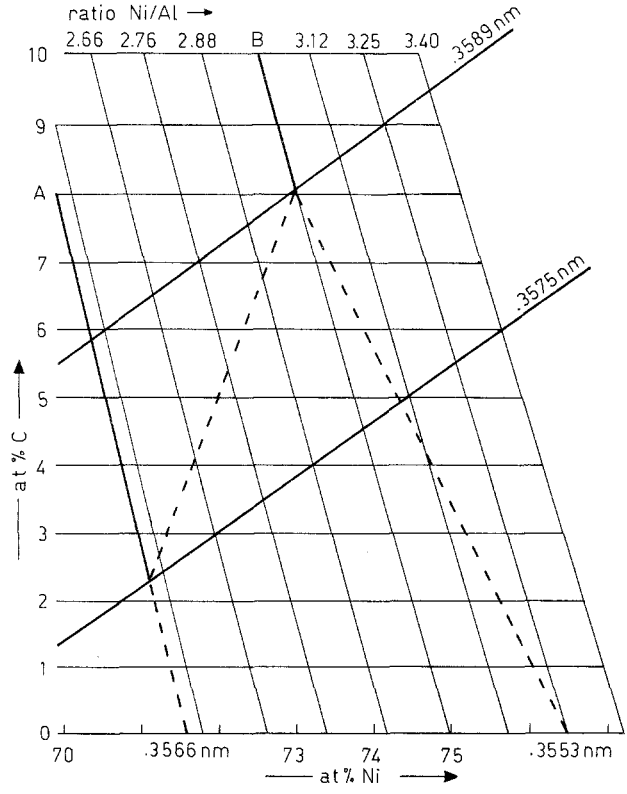

Fig. 1. γ'-Phase field as determined by the binary data and the intersection of isoparametric curves with [$(\beta + \gamma' + C)$, $(\gamma' + C)$] and [$(\gamma' + C)$, $(\gamma' + \gamma + C)$]-phase boundaries at 1000 °C

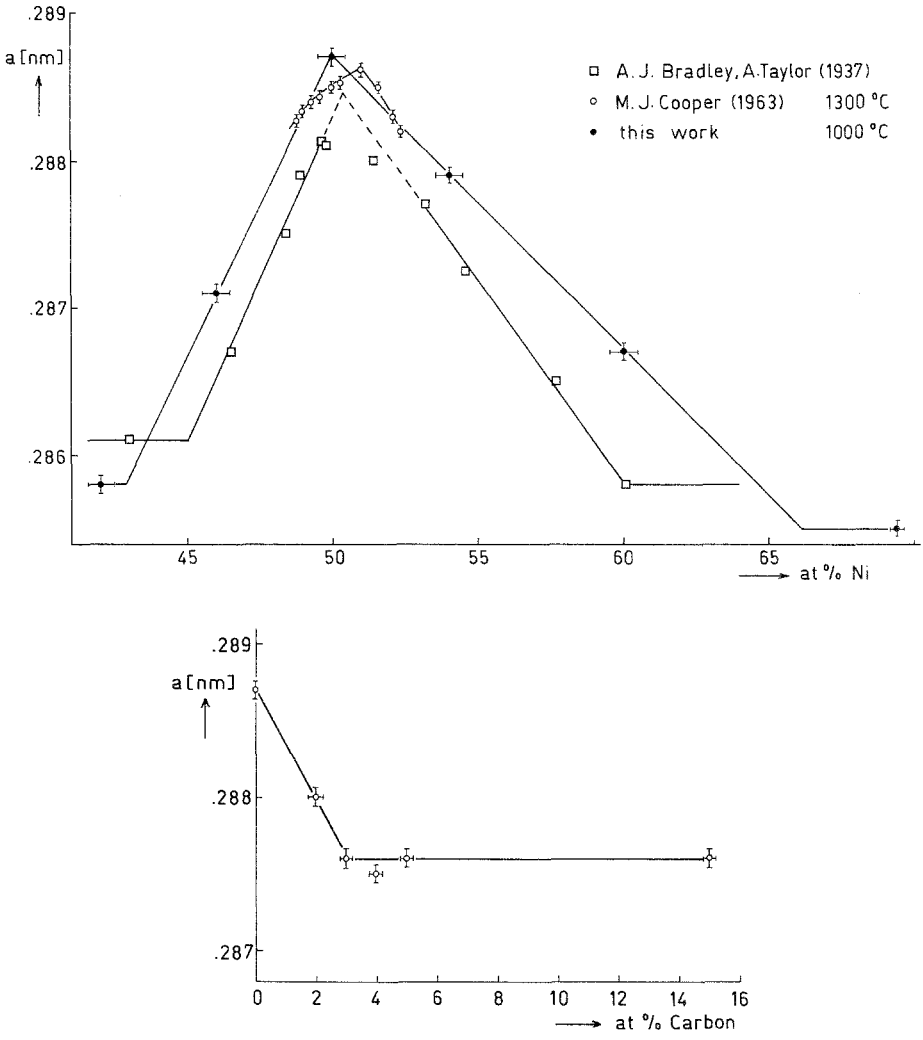

Fig. 2. Lattice parameter dependency of NiAl(β)-phase with Ni/Al-ratio (a) and carbon content (b) at 1 000 °C

the assumption that the variation of the lattice parameter with increasing carbon content is about the same for the $Ni_3Al(\gamma')$-phase and the Ni(s.s.)(γ)-phase. From these data one can construct isoparametric lines for the various compositions in the $Ni_3Al(\gamma')$-phase field (Fig. 1). The intersection of the isoparametric curves for the appropriate lattice parameters with the phase boundary tie lines, determined by X-ray and metallographic analysis, yield the composition of the vertices

Table 3. *Results of X-ray analysis of* Al-*rich alloys and lattice parameter of* NiAl(β)-*phase containing alloys*

a) 700 °C

Composition (At%) Ni	Al	C	Phases detected (lattice parameters in nm)	a			
25	75		$NiAl_3$				
30	70		$NiAl_3$		$+ Ni_2Al_3$		
38	62				Ni_2Al_3		
42	58		NiAl	0.2860	$+ Ni_2Al_3$		
46	54		NiAl	0.2863			
50	50		NiAl	0.2887			
54	46		NiAl	0.2877			
60	40		NiAl	0.2863			
19.5	58.5	22	$NiAl_3$		$+ Ni_2Al_3$	+ C	
15.8	47.2	37	$NiAl_3$		$+ Ni_2Al_3$	+ C	
49.5	49.5	1	NiAl	0.2884			
49	49	2	NiAl	0.2879			
48	48	4	NiAl	0.2878		+ C	
38	57	5	NiAl	0.2872		+ C	
42.8	52.2	5	NiAl	0.2885		+ C	
47.5	47.5	5	NiAl	0.2880		+ C	
57	38	5	NiAl	0.2863		+ C	
40.5	49.5	10	NiAl	0.2883		+ C	
45	45	10	NiAl	0.2879		+ C	
54	36	10	NiAl	0.2864		+ C	
56	29	15	NiAl	0.2858	$+ Ni_3Al$	+ C	

b) 1 000 °C

38	62				Ni_2Al_3	$a = 0.4036$	$c = 0.4876$
42	58		NiAl	0.2858	$+ Ni_3Al$		
46	54		NiAl	0.2871			
50	50		NiAl	0.2887			
54	46		NiAl	0.2879			
60	40		NiAl	0.2867			
70	30		NiAl	0.2855	$+ Ni_3Al$		
15.6	46.9	37.5	Al_4C_3		$+ Ni_2Al_3$	+ C	
49.5	49.5	1	NiAl	0.2884			
49	49	2	NiAl	0.2880			
48.5	48.5	3	NiAl	0.2876			
48	48	4	NiAl	0.2875		+ C	
38	57	5	NiAl	0.2876		+ C	
47.5	47.5	5	NiAl	0.2876		+ C	
57	38	5	NiAl	0.2864		+ C	
36	54	10	NiAl	0.2865		+ C	
42.5	42.5	15	NiAl	0.2876		+ C	
65	25	10	NiAl	0.2856	$+ Ni_3Al$	+ C	
56	29	15	NiAl	0.2855	$+ Ni_3Al$	+ C	
58	27	15	NiAl	0.2856	$+ Ni_3Al$	+ C	
50	25	25	NiAl	0.2856	$+ Ni_3Al$	+ C	

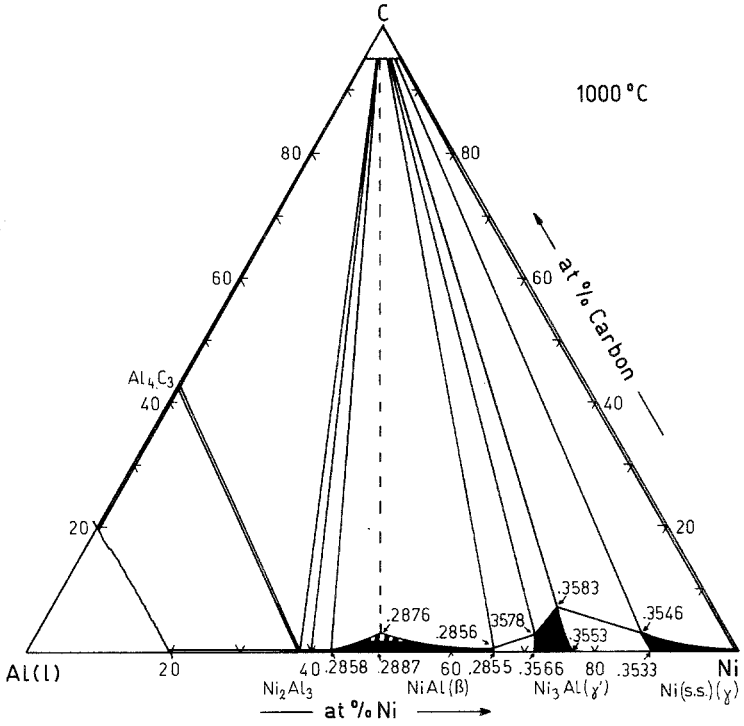

Fig. 3. Isothermal section Ni—Al—C at 1000 °C

$[\gamma'(\gamma' + \beta + C)]$ at 700 °C $Ni_{.70}Al_{.28}C_{.02}$ at 1000 °C $Ni_{.695}Al_{.275}C_{.03}$ and $[\gamma'(\gamma' + \gamma + C)]$ at 700 °C $Ni_{.69}Al_{.23}C_{0.08}$ and at 1000 °C $Ni_{.705}Al_{.22}C_{.075}$.

The intensity data of the X-ray diffractograms were not accurate enough to decide whether all carbon atoms are positioned in the octahedral voids of the γ'-phase or if there is a more complex filling type not excluding partial substitution as indicated by the relatively constant ratio Ni/(Al + C).

The solubility of carbon in the NiAl(β)-phase, is of particular interest (Fig. 2 a, b) because of the anomalous behavior of the lattice parameter in the β-phase NiAl. The maximum (or peak) of lattice parameter in the β-phase was reported to be at 50.8 at% Al by *Cooper*[5], who explained the peculiar dependency of the lattice parameter on the Ni/Al ratio by partial substitution and creation of vacancies on the atomic sites.

With increasing amount of carbon the corresponding lattice parameters decrease. As the voids in the β-NiAl phase are small, substitution on the metal sites is likely. If the singularity (peak instead of a maxi-

mum) would be real, a split of the two phase area [NiAl(C) solid solution + graphite] has to be assumed. This point needs more exploration. Lattice parameters of alloys in the three-phase field ($Ni_2Al_3 + \beta + C$) and ($\beta + \gamma' + C$) are presented in Table 3.

Although according to literature[2] Ni_2Al_3 exhibits a composition range of several at% in the binary NiAl system, no lattice parameter variations were detected. Also carbon containing specimens did not show any change in the lattice parameter compared to the binary alloy.

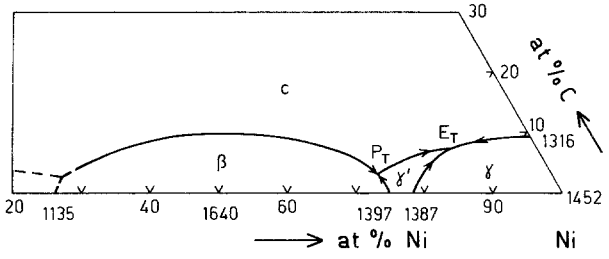

Fig. 4. Melting surface of the Ni-rich corner of the system Ni—Al—C

Analogous results were found for $NiAl_3$ and Al_4C_3. The isothermal section incorporating all these data is shown in Fig. 3. Having shown, that Ni_3AlC_x does not exist as a distinct ternary phase a modified melting surface diagram of the Ni-rich corner of the Ni—Al—C system is proposed (Fig. 4).

Hardness measurements in the γ'-phase region gave HV_{50}-values of 300-350 kg/mm² for binary alloys and 440-480 kg/mm² for ternary alloys, which is somewhat lower than the hardness values given by *Inoue*[6] for nonequilibrium FeNiAlC-alloys with partially filled $L1_2$-structure.

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