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Phase relationships in the ternary systems (V, Cr, Mo, W, Mn, Re)–Al–N

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Phase equilibria in the ternary systems of aluminum and nitrogen with vanadium, chromium, molybdenum, tungsten, manganese and rhenium are investigated by X-ray diffraction of sintered alloys. No ternary phase is observed. AlN does not show solubility for these metals, and coexists either with the solid solution of these metals with aluminium (in the case of vanadium, chromium and manganese) or with the pure metal (for molybdenum, tungsten and rhenium). Isothermal sections are presented for 1073 K (Mn–Al–N), 1273 K (V–Al–N, Cr–Al–N, Mn–Al–N and Re–Al–N), 1573 K (V–Al–N) and 1773 K (Mo–Al–N, W–Al–N and Re–Al–N).

1. Introduction

Aluminium nitride is a candidate for a ceramic material to be used in high-temperature applications. One of its claimed advantages over Si_3N_4 is its chemical corrosion resistance against several transition metals [1, 2], but in fact very little information is found in the literature about phase equilibria between AlN and the transition metals vanadium, chromium, molybdenum, tungsten, manganese and rhenium. Aluminium does not attack CrN at 1173 K but reacts with Cr_2N under the same condition [3]. Samsonov and co-workers [4, 5] claim that AlN can be used for dispersion hardening and improvement of the oxidation resistance of chromium. AlN has been found to be chemically stable when in contact with molybdenum or tungsten up to 2273 K [6] and 2373 K respectively [7]. Huet and Vangeel [8] report compatibility at 2073 K for periods up to 1 year. AlN coatings can be deposited on molybdenum and tungsten at a temperature of 1373 K [9]. In the ternary system Mn–Al–N only the absence of ternary phases is stated [10]. Lack of further experimental information led to the present investigation of phase partition within the ternaries V–Al–N, Cr–Al–N, Mo–Al–N, W–Al–N, Mn–Al–N and Re–Al–N.

2. Experimental procedure

In each ternary system more than twenty compositions were prepared from the powders listed in Table I by mixing and cold pressing. In some cases binary master alloys were made first, and then used as starting material (e.g. $V_{0.50}Al_{0.50}$). Heat treatments between 1073 and 1273 K were conducted in molybdenum crucibles as well as boron nitride crucibles lined with zirconium foil. The crucibles were wrapped in tantalum foil and sealed in evaluated quartz tubes. Heat treatments between 1273 and 1773 K were made in molybdenum crucibles under 10^5 Pa of argon (purity better than 5 N, i.e. 99.999 wt %) by high-frequency heating. The duration of the heat treatments varied from 800 h (e.g. at 1273 K in the V–Al–N system) to 12 h (e.g. at 1773 K in the Cr–Al–N system). BN crucibles, initially used also at temperatures above 1273 K, tend to be attacked by the alloys at temperatures around 1500 K; their use was therefore abandonded in experiments above 1400 K. Except for this initial crucible material problem, no

TABLE I Ceramic and metallic powders used as starting materials

Material	Purity	Typical analytical characterization (impurities in ppm)	Supplier
AlN	m2N	h c p $a = 0.310\,80$ nm $c = 0.476\,62$ nm	Alpha Ventron GmbH, FRG
VN	2N	f c c $a = 0.412\,48$ nm	Materials Research Corporation, USA
CrN	2N	f c c $a = 0.412\,52$ nm	Materials Research Corporation, USA
MnN	3N	h c p $a = 0.278\,84$ nm $c = 0.452\,78$ nm	Alpha Ventron GmbH, FRG
Al	2N8	Fe < 100, Si 500, others < 200	Alpha Division, Ventron Corporation, USA
V	2N5	C 900, Si 800, Cr 600, Fe 500 Al 200, others < 100	Alpha Division, Ventron Corporation, USA
Cr	3N5	Fe, C, Al, Si < 100 each	Alpha Division, Ventron Corporation, USA
Mo	3N	–	Metallwerk Plansee, Austria
W	3N	–	Metallwerk Plansee, Austria
Mn	2N5	"puriss"	Fluka AG, Switzerland
Re	4N	–	Chase Brass and Copper, USA

reaction between specimen and contained was observed. All alloys were examined by X-ray powder diffraction (Cr*K*α, Cu*K*α). Since the AlN-containing specimens were not sintered to high density under these experimental conditions, only selected alloys were studied by optical microscopy.

In the ternaries V–Al–N and Cr–Al–N numerous alloys were also prepared by hot pressing, which was carried out at 1523 K under a pressure of 2.4×10^7 Pa for 2 h in a Centorr hot press. The graphite dies were lined with a thin layer of boron nitride as a lubricant. In addition alloys of the composition $V_{0.50}Al_{0.25}N_{0.25}$ and $Cr_{0.50}Al_{0.25}N_{0.25}$, prepared either from $Me_{0.50}Al_{0.50}$ + MeN (Me = metal) or 2 Me + AlN were heat treated at temperatures between 1073 and 1273 K under nitrogen pressures up to 3×10^6 Pa for 24 h in a high-pressure vessel.

3. Results

3.1. The ternary system V–Al–N

No ternary phase is observed within the temperature range between 1273 and 1773 K. Attempts to synthesize a ternary complex nitride V_2AlN having *H*-phase type structure by hot pressing from mixtures with the stoichiometric ratio of transition metal aluminides and transition metal nitrides occasionally yielded X-ray powder patterns resembling the characteristic *H*-phase pattern. However, the lattice parameters were close to those of the *H*-phase carbide V_2AlC and the specimen was not in equilibrium, as reflected by the presence of more than three phases in the X-ray powder pattern. It was not possible to synthesize sufficient amounts of this complex nitride by these preparation methods under the chosen conditions to permit unambiguous identification. Alloys of initially ideal composition $V_{0.50}Al_{0.25}N_{0.25}$ did not contain *H*-phase but rather VN_{1-x} (where x is variable) and AlN when heat-treated under N_2 pressures up to 3×10^6 Pa. It is therefore concluded that no *H*-phase V_2AlN exists within the experimental conditions of the present investigation.

At 1273 K, AlN is in equilibrium with the solid phases VAl_3, V_5Al_8, $V_{s.s.}$ (vanadium solid solution) and VN_{1-x}. The reaction proceeded very slowly, and annealing times up to 800 h were needed to obtain complete equilibrium. No solubility of the respective third element is observed in AlN, VN_{1-x}, VAl_3 or V_5Al_8 by lattice parameter measurements. Alloys of initial compositions AlN + 20 to 60 at % V consist after heat treatment of AlN + VN_{1-x} ($a = 0.4125$ nm, corresponding to 50 at % N) + $V_{s.s.}$ with a lattice parameter of $a = 0.3069$ nm. Assuming little or no nitrogen solubility in vanadium solid solutions rich in aluminium, this lattice parameter corresponds to about 40 at % Al in the vanadium solid solution. The isothermal section at 1273 K is presented in Fig. 1a. The binary homogeneity limits of the boundary phases are taken from literature data [11–18].

At 1573 K, AlN is in equilibrium with the solid phases VAl_3, V_5Al_8, $V_{s.s.}$ and V_9N_4. According to crystal structure analysis [15] V_9N_4 is the correct formula of the subnitride [16–18]. From lattice parameter measurements the compositions of $V_{s.s.}$ in equilibrium with AlN and V_9N_4 is found to be $V_{0.67}Al_{0.33}$. VN_{1-x} is not

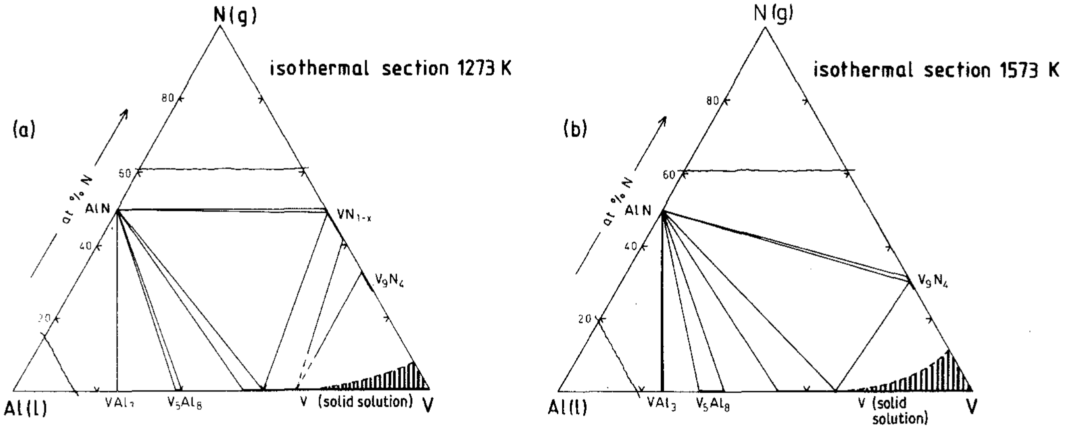

Figure 1 Isothermal sections of the system V–Al–N; (a) 1273 K, (b) 1573 K.

stable under its own vapour pressure at the chosen experimental conditions (1573 K, 10^5 Pa argon). The resulting isothermal section is shown in Fig. 1b.

At 1773 K the phase field AlN + V_9N_4 + $V_{s.s.}$ still dominates the ternary phase equilibria.

3.2. The ternary system Cr–Al–N

No ternary phase is observed between 1273 and 1773 K. As in the case of V_2AlN the existence of an *H*-phase type Cr_2AlN was indicated by X-ray diffraction, but it could not be established as in equilibrium phase in the Cr–Al–N system, even under external nitrogen pressures up to 3 x 10^6 Pa.

At 1273 K, solid-state equilibria are found between AlN and $Cr_{s.s.}$ (solid solution, s.s.), γ_2–Cr_5Al_8, γ_3–Cr_4Al_9 and ϵ-$CrAl_4$ respectively. Specimens with starting compositions $Cr_{0.50}Al_{0.25}N_{0.25}$ and $Cr_{0.25}Al_{0.25}N_{0.50}$ show after annealing (at 1273 K under 10^5 Pa argon) AlN and $Cr_{s.s.}$ with a lattice parameter a = 0.288 33 nm, but no Cr–N phase. Since the solubility of nitrogen in chromium at 1273 K is about 0.1 at% [16–19] the slight increase of the lattice parameter is due to aluminium solution in the $Cr_{s.s.}$ phase. Comparing this lattice parameter with literature data for the binary Cr–Al system [11, 20] yields a composition $Cr_{0.98}Al_{0.02}$ for the chromium-rich terminal solid solution in equilibrium with AlN. No Cr_2N was detected in these alloys. This is in agreement with thermochemical data (Table II) which indicates that Cr_2N is stable at 1273 K only if the N_2 partial pressure exceeds 1.4 x 10^3 Pa. Calculating the Gibbs free enthalpy of formation (ΔG) from chromium nitride and chromium aluminide for the pair AlN + $Cr_{s.s.}$ (Table III) shows that AlN coexists with $Cr_{s.s.}$ even under N_2 partial pressures at which Cr_2N is stable. An isothermal section of the Cr–Al–N system at 1273 K under argon is given in Fig. 2.

At 1473 K the phase equilibria remain unchanged except that ϵ-$CrAl_4$ is already liquid and the solubilites within the binary Cr–Al–system vary somewhat [16–18]. The composition of the vertix $Cr_{s.s.}$, $Cr_{s.s.}$ + AlN + N_2 (gas) is still 2 at% Al, but shifts to 16 at% Al at 1773 K (a = 0.291 75 nm). In this ternary alloy the lattice parameters of AlN do not deviate from binary values, indicating no solubility of chromium in aluminum nitride. X-ray analysis of an arc-melted alloy of the composition AlN + 50 at% Cr showed $Cr_{s.s.}$ with a = 0.298 47 nm and no AlN.

3.3. The ternary system Mo–Al–N

No ternary phase is observed between 1273 and

TABLE II Gibbs free enthalpy of formation (ΔG) for binary compounds and solid solutions of the boundary systems of Cr–Al–N [16–18, 23, 24, 26]

Reaction	ΔG (J)*
$2.64Cr + 0.5N_2(g) \rightleftharpoons 1.32Cr_2N_{0.76}$	$-26\,700 + 13.25\,T - 0.5\,RT\ln P_{N_2}$
$Al + 0.5\,N_2(g) \rightleftharpoons AlN$	$-320\,590 + 101.92\,T - 0.5\,RT\ln P_{N_2}$
$0.4Cr + 0.6Al \rightleftharpoons Cr_{0.4}Al_{0.6}$ (~ (1/13) γ-Cr_5Al_8)	$-22\,694 - 1.807\,T$
$(1-x)Cr + xAl \rightleftharpoons Cr_{s.s.}$ with x at% Al	$-60\,250x(1-x)$; x = 40.8 at 1273 K, 46.0 at 1673 K

*Temperatures in K.

TABLE III Gibbs free enthalpies (ΔG) for the equilibrium $Cr_2N + \gamma\text{-}Cr_5Al_8 \rightleftharpoons AlN + Cr_{s.s.}$

Temperature (K)	Reaction	ΔG (J)
1273	$1.32Cr_2N_{0.76} + 8.70Cr_{0.4}Al_{0.6}(\gamma\text{-}Cr_5Al_8) \rightleftharpoons AlN + 10.34Cr_{s.s.}$(40.8 at % Al)	− 113 543
1623*	$1.32Cr_2N_{0.76} + 12.54Cr_{0.4}Al_{0.6}(\gamma\text{-}Cr_5Al_8) \rightleftharpoons AlN + 14.19Cr_{s.s.}$(46 at % Al)	− 40 927

*Decompostion temperature of $\gamma\text{-}Cr_5Al_8(P_{N_2} = 1.013 \times 10^5$ Pa)

1773 K at the chosen external N_2 pressure. At both temperatures the three-phase fields (Mo_3Al_8 + Mo_3Al + AlN) and (Mo_3Al + $Mo_{s.s.}$ + AlN) exist. The high-temperature phases MoAl and $MoAl_2$, which should be stable at 1773 K according to the binary phase diagram of Mo–Al [21] could not be observed in the ternary (Fig. 3). Neither the molybdenum-containing constitutents nor AlN show solubility for the respective third element. In particular, molybdenum and $Mo_{s.s.}$ alloys do not alter their lattice parameters when equilibrated with AlN at elevated temperatures.

At lower temperatures or higher nitrogen partial pressures, Mo_2N becomes a stable phase [22] (e.g. 1273 K, 10^6 Pa N_2 or 1123 K, 10^5 Pa N_2). As can be calculated from thermochemical data [23, 24] Mo_2N is not in equilibrium with any molybdenum aluminide, but rather the tie-line AlN + Mo is stable up to high nitrogen pressures.

3.4. The ternary system W–Al–N

Three isothermal sections were investigated at 1273, 1373 and 1773 K (Fig. 4). No ternary phase is observed in this temperature range under the chosen nitrogen partial pressure. Since none of the high-temperature W–Al phases [16–18] are observed, and no tungsten nitride exists under ambient gas pressures [25], the three-phase-field (AlN + WAl_4 + $W_{s.s.}$) dominates the phase diagram at all temperatures investigated. The solid solubility of aluminium in tungsten is taken from binary phase diagram data [16–18]. The solubility of the respective third elements in binary $W_{s.s.}$, WAl_4 or AlN is virtually nil as concluded from lattice parameter measurements.

3.5. The ternary system Mn–Al–N

In agreement with Stadelmaier [10] no ternary phase is observed at temperatures up to 1273 K. At 1073 K, AlN is found coexisting with $MnAl_4$, Mn_4Al_{11} (*R*), $\gamma_2\text{-}Mn_5Al_8$, β-manganese (solid solution with aluminium), γ-manganese (solid solution with nitrogen and aluminum and hcp $\zeta\text{-}Mn_2N$. No solubility of the respective third element is detected in AlN or any of the Mn–Al phases, but $\gamma\text{-}Mn_{s.s.with\,N}$ dissolves at least 10 at % Al; for example alloys of initial composition AlN + *x* at % Mn (*x* = 20 to 80) consist of AlN (unchanged lattice parameter), hcp $\zeta\text{-}Mn_2N$ (a = 0.2766 nm and c = 0.4524 nm), and fcc $\gamma\text{-}Mn_{s.s.}$ with lattice parameter of a = 0.3864 nm. This lattice parameter is larger as compared to the binary fcc $\gamma\text{-}Mn_{s.s.}$ with a = 0.385 46 nm [27]. It is almost identical with the lattice parameter of $\epsilon\text{-}Mn_4N$ (a = 0.3863 nm [16–18]); but there is no doubt about the identification of this phase, since no

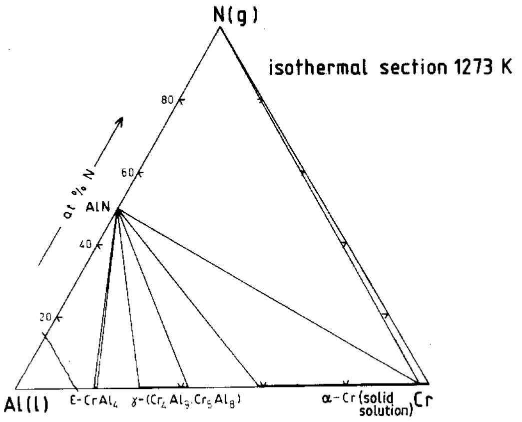

Figure 2 Isothermal section of the system Cr–Al–N at 1273 K.

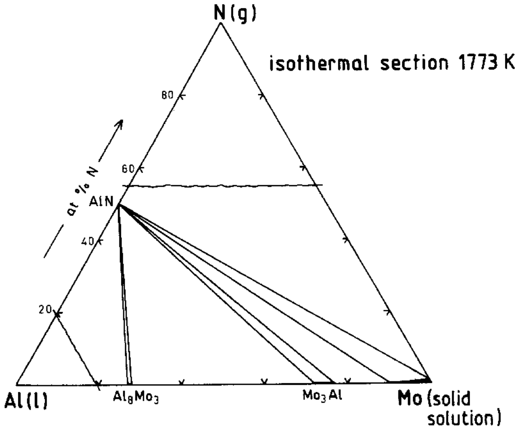

Figure 3 Isothermal section of the system Mo–Al–N at 1773 K.

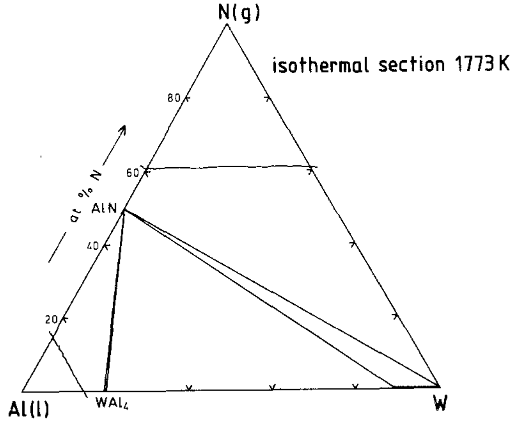

Figure 4 Isothermal section of the system W–Al–N at 1773 K.

superstructure reflections are observed and γ-manganese is known to dissolve considerable amounts of aluminium (e.g. in the presence of carbon [27]) which accounts for the lattice parameter increase. This is in agreement with results in the binary Mn–N system [28]. Above 1039 K the two phases fcc γ-$Mn_{s.s.}$ and ϵ-Mn_4N form at 13 at% by eutectoid reaction a hexagonal close-packed phase which forms continuous solid solutions with hcp ζ-Mn_2N at temperatures above 1173 K. The lattice parameters [28] are $a = 0.276\,73$ nm and $c = 0.452\,12$ nm (hcp ζ-Mn_2N, 13 at% N), and $a = 0.281\,98$ nm and $c = 0.457\,87$ nm (hcp ζ-Mn_2N, 25 at% N). Fig. 5a shows the phase equilibria at 1073 K.

At 1273 K only β-$Mn_{s.s.}$ is observed in solid equilibrium with AlN (Fig. 5b). The liquid region in the aluminium-rich corner increases considerably and participates in the phase equilibria to a wide extent. Since no alloys containing initially more nitrogen than aluminium were prepared the coexistence of AlN and γ-$Mn_{s.s.}$ can only be assumed, but no experimental data are available. hcp ζ-Mn_2N decomposes rapidly at this temperature [28].

3.6. The ternary system Re–Al–N

No ternary phase was found in the temperature interval between 1273 and 1773 K under the nitrogen partial pressure chosen in the experiment. At 1273 K four binary rhenium aluminides were found to be stable: $ReAl_4$, $ReAl_3$, ReAl and Re_2Al [29]. No rhenium nitride is reported to be stable at this temperature [16–18, 30]. In ternary compositions, AlN coexists with all binary rhenium aluminides and with rhenium without showing signs of mutual solubility (Fig. 6a). The only binary phases besides AlN that are stable at 1773 K are $ReAl_3$ and Re_2Al. The only solid-state three-phase fields existing at that temperature are therefore ($AlN + ReAl_3 + Re_2Al$) and ($AlN + Re_2Al + Re$) (Fig. 6b).

4. Discussion

The phase diagrams of Mo–Al–N, W–Al–N and Re–Al–N show AlN in equilibrium with all alloys of the respective ternary systems. There is very little change of binary solid solubilities with temperature on the nitrogen-rich phase boundary of the two-phase field AlN-transition metal. Composites prepared out of AlN with molybdenum, tungsten or rhenium are stable up to high temperatures and under thermal cycles. This is not the case with vanadium, chromium or manganese.

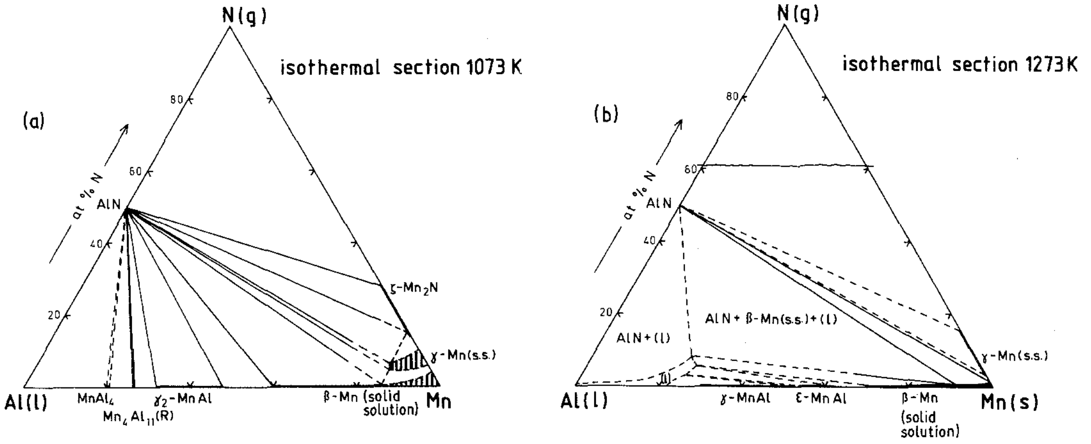

Figure 5 Isothermal sections of the system Mn–Al–N. (a) 1073 K; the phase relations near the binary Mn–N system between 13 and 25 at% N are not resolved. (b) 1273 K; schematic only.

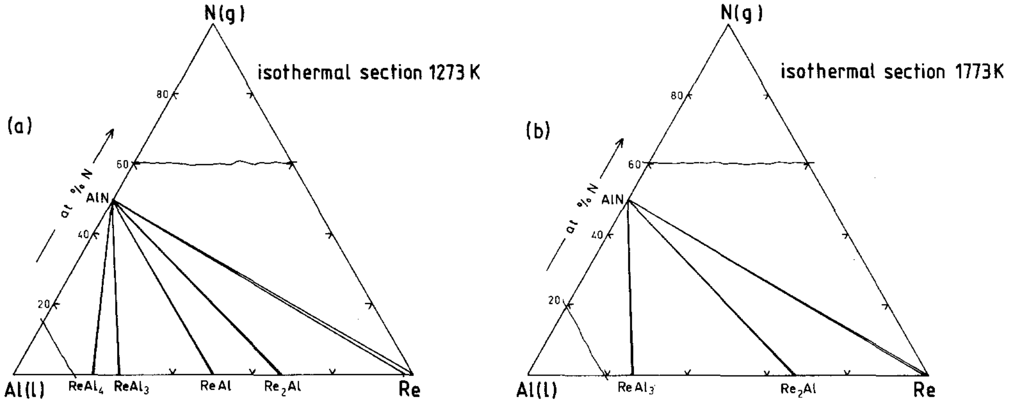

Figure 6 (a) Isothermal sections of the system Re–Al–N at (a) 1273 K; (b) 1773 K.

However, one cannot state simply that AlN is corroded by vanadium, chromium or manganese when in contact with these transition metals at elevated temperatures. All three elements lower the decomposition temperature of AlN in a eutectic type of reaction, but no tie-lines cut off the single-phase field of any of the elements from the phase fields in which AlN coexists.

At all temperatures AlN is in equilibrium with vanadium solid solution, but the homogeneity region with respect to aluminium content of this solid solution varies with temperature, leading to the formation of intermetallic compounds or binary vanadium nitrides. The intermetallic compounds do not corrode AlN. Small amounts of AlN will be completely dissolved by the vanadium solid solutions.

In the case of the couple Cr–AlN up to 1500 K the composition of the chromium-rich solid solution in equilibrium with AlN remains constant at a rather low solubility level.

There even exists a narrow composition range where AlN and manganese could be used in contact with each other if the temperature was kept constant. The composition of β-$\mathrm{Mn}_{\mathrm{s.s.}}$ coexisting with AlN is shifted to higher aluminium concentrations at lower temperatures, but at 1272 K the alloy system is to a large extent liquid. Similarly, γ-$\mathrm{Mn}_{\mathrm{s.s.}}$–AlN composites suffer from the strong temperature-dependence of the aluminium and nitrogen concentrations in the γ-Mn phase coexisting with AlN..

In conclusion, it is possible to find conditions of coexistence between AlN and the single-phase region of the transition metals vanadium, chromium and manganese, but the homogeneity limits of the single-phase field change considerably with temperature, and any thermal cycles will cause decomposition of the aluminium nitride/metal composites.

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