

## Thermodynamical consideration of the synthesis of solid AlN from thermal plasma

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The synthesis process of solid AlN in thermal plasmas was investigated theoretically by computing the equilibrium composition of the gas mixture involving nitrogen and various amounts of aluminum, oxygen and hydrogen for the temperature range between 1000 and 5500 K. The results obtained by treating the plasma as a single-gas system were combined with those which take into account the presence of solid AlN and liquid Al, to find the optimal conditions for the deposition of solid AlN. The factors determining the efficiency of this process are discussed.

*Keywords:* plasma synthesis, AlN synthesis, thermodynamics of AlN.

### INTRODUCTION

Thermal plasmas, as high-temperature mixtures of atoms, molecules, ions and electrons, are nowadays widely used for the synthesis of high-purity ultrafine powders (in the size range 10–100 nm) of silicon, aluminum and boron oxides, nitrides and carbides. A substance introduced into a thermal plasma evaporates and, depending on the temperature, partially dissociates into atoms and ionizes, producing ions and electrons. The formation of molecules and radicals stable at higher temperatures also occurs. By rapid cooling (quenching) of this system under controlled conditions, a saturated or supersaturated vapor is formed and the formation of ultrafine (solid) particles can be achieved.

AlN ceramics have high thermal (up to 320 W/mK at room temperature<sup>1</sup>), but very low electrical conductivity<sup>2</sup> ( $> 10^{14} \Omega \text{ cm}$ ). The very low coefficient of thermal expansion ( $4.1 \times 10^{-6}/^\circ\text{C}$ , similar to that of silicon) provides high thermal shock resistance. These properties make this material very appropriate for the use in the electronic industry. Conventional methods for aluminum nitride powder synthesis are *via* carbothermal reduction of either aluminum or aluminum hydroxide and by the direct nitridation of aluminum metal with nitrogen or ammonia. However, AlN prepared by

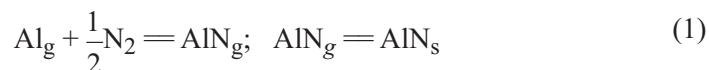
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these routes has the disadvantage of containing a high level of both metallic and oxygen impurities. Measurements indicate that the residual impurities in commercial AlN, particularly oxygen, are responsible for lowering its thermal conductivity.

The first attempt to produce AlN utilizing a plasma was reported by Long and Foster<sup>3</sup> in 1959. They used an electric arc between aluminum rods as electrodes in a nitrogen atmosphere. A very hard AlN lump (containing 92.1 % AlN) was formed. In the last decade, aluminum nitride of high purity in the form of an ultrafine powder has been synthesized by injecting pure aluminum powder<sup>4</sup> or evaporating an Al anode<sup>1</sup> into a Ar + N<sub>2</sub> or N<sub>2</sub> + NH<sub>3</sub> plasma.

In previous papers<sup>1-4</sup> it was pointed out that the probable mechanism for the deposition of solid AlN involves the formation of oversaturated AlN vapor in the plasma. In this paper a systematic thermodynamical consideration of this process is presented. Use was made of the fact that a thermal plasma is a plasma in local thermodynamical equilibrium, which makes possible the theoretical determination (by employing free energy data for the compounds present in it) of its composition, and from this information the temperature, pressure and relative amounts of their components optimal for a particular synthesis. In order to examine the reactivity of aluminum towards nitrogen, oxygen and hydrogen and the possibility of the formation of AlN in plasma, the equilibrium composition of the gas systems Al/N, Al/N/O and Al/N/H in the temperature range 1000–5500 K was calculated. From these data, the temperature zones (for a certain Al/N gas system) with saturated and/or oversaturated AlN and Al vapor were determined and the possibility of the formation of AlN in the solid state form *via* two different reactions routes:



and



was analyzed [the subscripts g, s and l in Eqs. (1) and (2) indicate gas, solid and liquid phase, respectively].

#### METHOD OF CALCULATION OF EQUILIBRIUM COMPOSITION

The calculation of the equilibrium gas mixture compositions under condition of constant pressure was carried out using the method developed by White *et al.*<sup>5</sup> It is based on the fact that the equilibrium of the system corresponds to its minimum energy state. The free energy,  $G$ , of the system is the sum of the chemical potentials,  $\mu_i$ , multiplied by the mole fractions,  $x_i$ , of its components,

$$G = \sum_{i=1}^n x_i \mu_i \quad (3)$$

where  $n$  is the number of chemical species and  $x_i$  their mole fractions to be determined. The set of  $x_i$  values leading to the equilibrium can be obtained by solving the equation

$$\delta G = 0 \quad (4)$$

under the fulfilled mass balance condition

$$\sum_{i=1}^n a_i x_i = b_j; \quad j = 1, 2, \dots, m \quad (5)$$

where  $m$  represents the number of elements in the system,  $a_i$  is the number of atoms of element  $j$  in the molecule  $i$ , and  $b_j$  is a coefficient proportional to the percentage of the element  $j$  in the system. The quasi-neutrality of a system also containing charged species is ensured by the condition

$$\sum_{i=1}^n q_i x_i = 0 \quad (6)$$

where  $q_i$  represents the charge of species  $i$ . According to the method of White *et al.*,<sup>5</sup> the mole fractions  $x_i$  are calculated by an iterative procedure. One starts with any set of positive numbers  $x_{i0}$  which satisfy Eqs. (5) and (6) and builds the zeroth-order approximation for  $G$ . The free energy is then expanded into a Taylor series up to the quadratic terms in  $x_i - x_{i0}$ . The conditions (5) and (6) are taken into account with the help of Lagrange multipliers  $\pi_j$ . A minimization of the free energy leads to a system of linear equations which determine the improved values for  $x_i$  and thus a new approximation for  $G$ . The procedure is repeated until convergence is achieved. It should be noticed that the dimension of the system is  $(m + 1)$ , *i.e.*, it depends only on the number of elements in the system. The concentrations of the species present in traces can be calculated using the equation:

$$z_i = \exp [ - (G/RT)_i - \ln p + \sum_i a_i \pi_j ] \quad (7)$$

where  $p$  is the total pressure in the system.

The compositions of the Al/N, Al/N/O and Al/N/H gas systems were calculated under the assumption of local thermal equilibrium in the temperature range between 1000–5500 K and at a total pressure of 1 atm. The calculations were carried out for nitrogen to aluminum mole ratios [ $b_j$  from Eq. (5)] of N:Al = 0.999:0.001, N:Al = 0.99:0.01 and N:Al = 0.95:0.05. These mole ratios were chosen in order to simulate the nitrogen (or nitrogen plus ammonia) plasma in presence of aluminum used for the synthesis of solid AlN. Besides, the composition of the Al/N/O and Al/N/H single phase (gas) systems were computed at a constant nitrogen to aluminum mole ratio, N:Al = 0.999:0.001. These calculations were performed for Al:O = 1:10 and Al:O = 1:0.1 mole ratios (system Al/N/O), and for Al:H = 1:3 and Al:H = 1:0.03 mole ratios (system Al/N/H). Finally, two other sets of calculations were also carried out: in the first ones, the Al/N gas mixture was treated in equilibrium with solid AlN (there is no AlN liquid phase<sup>4,6</sup>), *i.e.*, as a two-phase system; additionally, the Al/N gas system in equilibrium with liquid aluminum was considered.

The equilibrium partial pressures of up to 43 species (atoms, ions, electrons, molecules, radicals; see Table I), whose Gibbs (free) energy data were available<sup>6</sup> (or were calculated using *ab initio* data, such as those for  $\text{Al}_2$ ,  $\text{Al}_2^+$ ,  $\text{Al}_2^-$ ,  $\text{Al}^{-7}$ ), were calculated in the temperature range between 1000–5500 K for the single phase system, and in the range 500–2700 K for the two-phase system.<sup>8</sup>

#### RESULTS OF THE CALCULATIONS

The equilibrium partial pressures of aluminum-containing compounds for the Al/N/O (gas) system with Al:O mole ratios of 1:10 and 1:0.1, as a function of temperature are shown in Figs. 1 and 2, respectively. In excess of oxygen (to aluminum), oxides of aluminum (predominantly  $\text{AlO}_2$ ) stable at higher temperatures are formed. At nearly 3000 K, the partial pressures of AlO and Al (in atomic form) become equal. At temperatures  $T > 3500$  K, the dominate forms are aluminum in atomic and ionic forms (Al,  $\text{Al}^+$ ). At relatively low temperatures, AlN appears in the plasma with a very low partial pressure, *e.g.*, of  $10^{-9}$  atm at 3750 K. The partial pressure of AlN increases with temperature and reaches a maximum at 5500 K ( $\approx 2 \times 10^{-7}$  atm, which is about 0.01 % of the total amount of aluminum present in the system). With an excess of aluminum (to oxygen) (Fig. 2) at temperatures  $T < 5500$  K, aluminum is present in the plasma predominantly in the atomic form, and at  $T = 5000$  K, the partial pressures of aluminum in atomic and ionic forms become nearly equal. AlN molecules appear with a partial pressure of  $10^{-9}$  atm at 1600 K, *i.e.*, at a lower temperature compared to the case when oxygen is in excess. The AlN partial pressure increases with temperature and reaches a maximum at 5500 K ( $\approx 2 \times 10^{-7}$  atm).

The equilibrium partial pressures of aluminum-containing compounds of Al/N/H system with Al:H molar ratios of 1:3 and 1:0.03 are shown in Figs. 3 and 4, respectively. In both cases, in the temperature range between 1000 and 5500 K, aluminum is present in the system predominantly as atomic aluminum. Molecules of AlN appear at about 1700 K with a partial pressure of  $1 \times 10^{-9}$  atm. The partial pressure of AlN increases with temperature achieving a maximum value of  $\approx 2 \times 10^{-7}$  atm at 5000 K.

Lastly, the partial pressures of aluminum-containing compounds in the Al/N system with Al:N = 0.001:0.999, Al:N = 0.01:0.99 and Al:N = 0.05:0.95 mole ratios are shown in Fig. 5. In these cases aluminum at temperatures  $1000 < T < 5500$  K is mostly present in the atomic form. As in the Al/N/O and Al/N/H systems, AlN reaches a maximum partial pressure at 5500 K.

Equilibrium pressures for saturated vapors of the molecules of AlN and the Al atom, corresponding to heterogeneous equilibrium (at  $p = 1$  atm):



are presented in Fig. 6. The equilibrium pressures of the saturated vapors ( $p^s_{\text{AlN}}$  and  $p^s_{\text{Al}}$ ) are functions of temperature only and can be obtained by means of the formulae:

$$\ln p^s_{\text{AlN}} = \frac{G^0_{\text{AlN}(s)} - G^0_{\text{AlN}(g)}}{RT}; \quad \ln p^s_{\text{Al}} = \frac{G^0_{\text{AlN}(l)} - G^0_{\text{Al}(g)}}{RT} \quad (9)$$

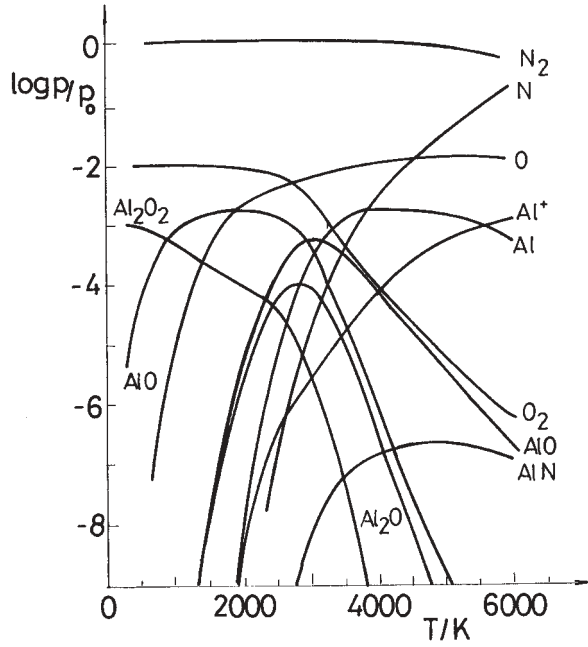


Fig. 1. Equilibrium partial pressures of aluminum, oxygen and nitrogen containing species in the N:Al:O = 0.989:0.001:0.01 gas system, as a function of temperature.

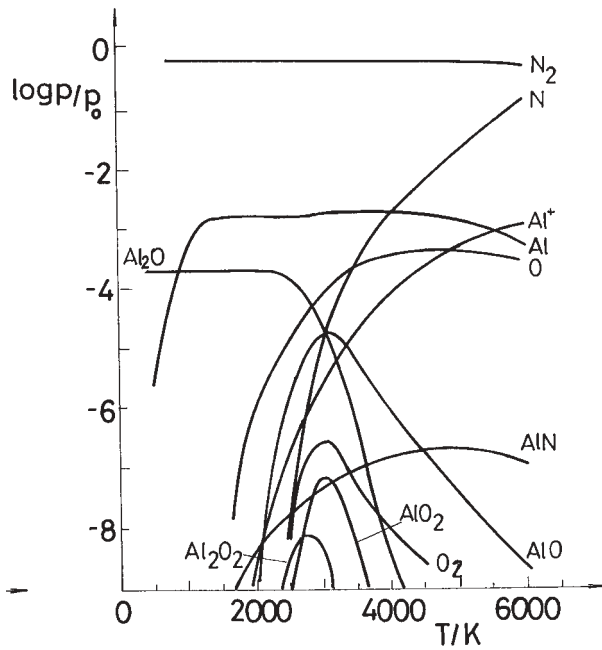


Fig. 2. Equilibrium partial pressures of aluminum, oxygen and nitrogen containing species in the N:Al:O = 0.9889:0.001:0.0001 gas system, as a function of temperature.

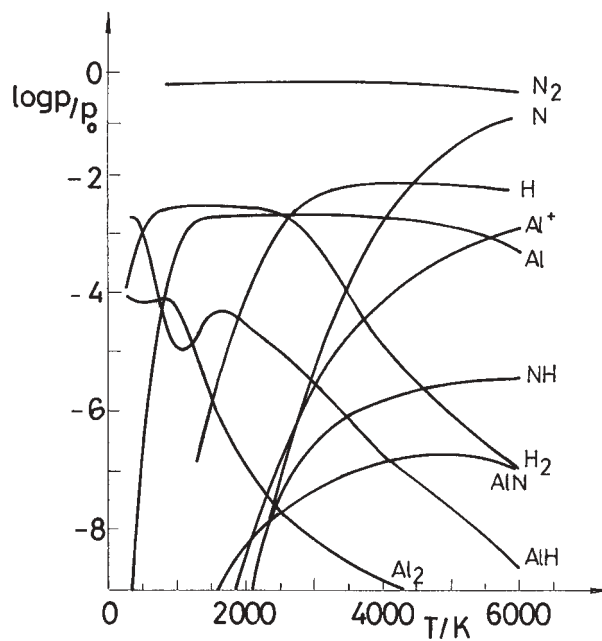


Fig. 3. Equilibrium partial pressures of aluminum, hydrogen and nitrogen containing species in the N:Al:H = 0.996:0.001:0.003 gas system, as a function of temperature.

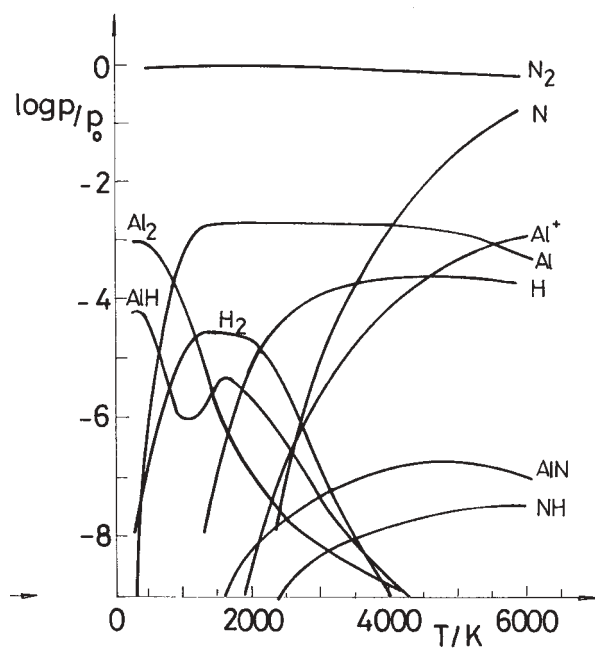


Fig. 4. Equilibrium partial pressures of aluminum, hydrogen and nitrogen containing species in the N:Al:H = 0.99897:0.001:0.00003 gas system, as a function of temperature.

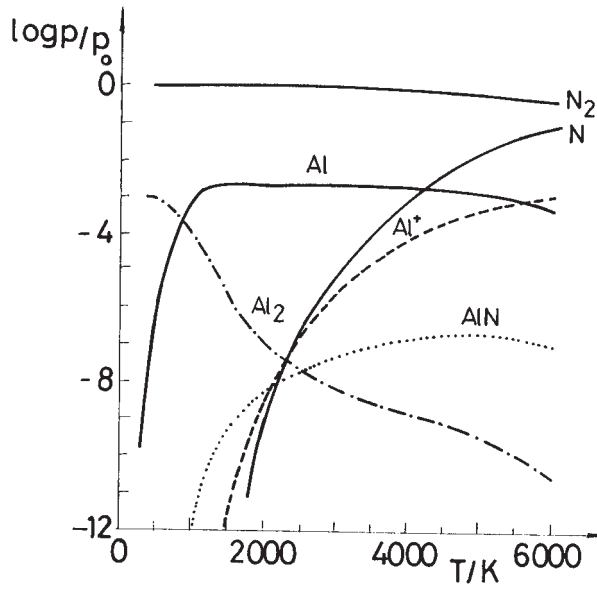


Fig. 5. Equilibrium partial pressures of aluminum and nitrogen containing species in the N:Al = 0.999:0.001 gas system, as a function of temperature.

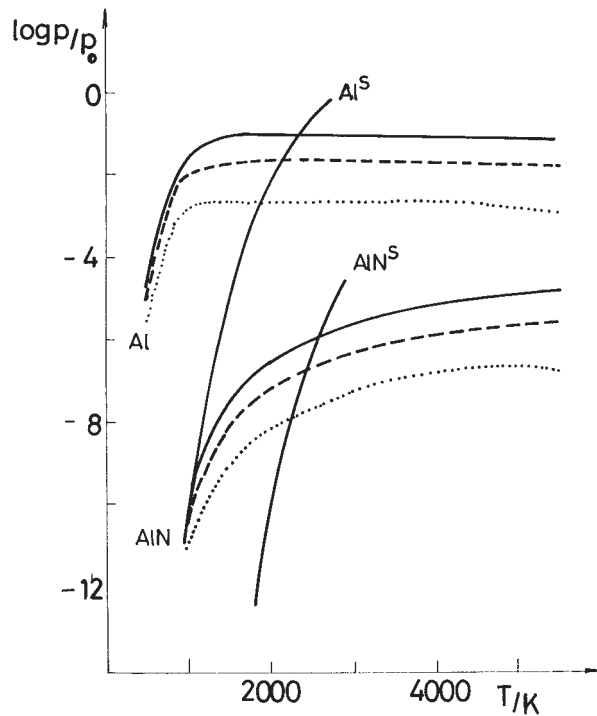


Fig. 6. Equilibrium partial pressures of Al and AlN in the N:Al = 0.95:0.05 (solid lines), N:Al = 0.99:0.01 (dashed lines) and N:Al = 0.999:0.001 (dotted lines) gas systems as a function of temperature; equilibrium pressures for saturated vapors of the AlN molecule ( $AlN^S$ ) and the Al atom ( $Al^S$ ), corresponding to the heterogeneous equilibria,  $AlN_g = AlN_s$  and  $Al_g = Al_l$  (at  $p = 1$  atm), as a function of temperature.

TABLE I. Species considered in the computations

Al; N; e <sup>-</sup>	Al; Al <sup>+</sup> ; Al <sup>-</sup> ; Al <sub>2</sub> ; Al <sub>2</sub> <sup>-</sup> ; Al <sub>2</sub> <sup>+</sup> ; N; N <sub>2</sub> ; N <sup>+</sup> ; N <sup>-</sup> ; N <sub>2</sub> <sup>+</sup> ; e <sup>-</sup> ; AlN
Al; N; H; e <sup>-</sup>	Al; Al <sup>+</sup> ; Al <sup>-</sup> ; Al <sub>2</sub> ; Al <sub>2</sub> <sup>+</sup> ; Al <sub>2</sub> <sup>-</sup> ; N; N <sub>2</sub> ; N <sup>+</sup> ; N <sup>-</sup> ; N <sub>2</sub> <sup>+</sup> ; e <sup>-</sup> ; AlN; H; H <sub>2</sub> ; NH <sub>3</sub> ; N <sub>2</sub> H <sub>2</sub> ; NH; NH <sub>2</sub> ; N <sub>2</sub> H <sub>4</sub> ; H <sup>+</sup> ; H <sup>-</sup> ; H <sub>2</sub> <sup>+</sup> ; AlH; AlH <sup>+</sup>
Al; N; O; e <sup>-</sup>	Al; Al <sup>+</sup> ; Al <sup>-</sup> ; Al <sub>2</sub> ; Al <sub>2</sub> <sup>+</sup> ; Al <sub>2</sub> <sup>-</sup> ; N; N <sub>2</sub> ; N <sup>+</sup> ; N <sup>-</sup> ; N <sub>2</sub> <sup>+</sup> ; e <sup>-</sup> ; AlN; O; O <sub>2</sub> ; NO; O <sub>3</sub> ; NO <sub>2</sub> ; O <sup>+</sup> ; O <sub>2</sub> <sup>+</sup> ; NO <sup>+</sup> ; O <sup>-</sup> ; O <sub>2</sub> <sup>-</sup> ; AlO; AlO <sub>2</sub> ; AlO <sup>+</sup> ; AlO <sub>2</sub> <sup>-</sup> ; Al <sub>2</sub> O; Al <sub>2</sub> O <sup>+</sup> ; Al <sub>2</sub> O <sub>2</sub> ; Al <sub>2</sub> O <sub>2</sub> <sup>+</sup>

TABLE II. Saturation temperatures for Al and AlN in Al/N systems

Al:N	$T_{\text{Al}}^{\text{s}}/\text{K}$	$T_{\text{AlN}}^{\text{s}}/\text{K}$
0.001 : 0.999	1840	2260
0.01 : 0.99	2080	2420
0.05 : 0.95	2340	2540

$G_{\text{AlN(s)}}$ ,  $G_{\text{AlN(g)}}$ ,  $G_{\text{Al(l)}}$ , and  $G_{\text{Al(g)}}$  are standard Gibbs energies corresponding to solid AlN, AlN in gas phase, liquid Al and Al in gas phase respectively.  $R$  is the gas constant,  $T$  temperature and  $\ln$  natural logarithm. In the same figure (Fig. 6) the equilibrium partial pressures of Al ( $p_{\text{Al}}$ ) and AlN ( $p_{\text{AlN}}$ ) computed for the Al/N gas phase systems are also presented. The curves corresponding to  $p_{\text{Al}}^{\text{s}}$  and  $p_{\text{Al}}$ , as well as those for  $p_{\text{AlN}}^{\text{s}}$  and  $p_{\text{AlN}}$  intersect each other, indicating the temperatures  $T_{\text{AlN}}^{\text{s}}$  and  $T_{\text{Al}}^{\text{s}}$  (presented in Table II) at which the partial pressures of Al and AlN for a specific (with respect to the Al/N mole ratio) Al/N system become equal to the pressures of the saturated vapors of the corresponding species (Al or AlN). At temperatures left of the intersection points  $T < T_{\text{AlN}}^{\text{s}}$  and  $T < T_{\text{Al}}^{\text{s}}$ , the partial pressures of AlN and Al are higher than the pressures of the corresponding saturated vapors, indicating the temperature region with oversaturated vapors. At temperatures between the intersection points corresponding to Al and AlN,  $T_{\text{Al}}^{\text{s}} < T < T_{\text{AlN}}^{\text{s}}$ , the only existing oversaturated vapor is that of AlN. The oversaturation ratios  $\gamma_{\text{Al}} = p_{\text{Al}}/p_{\text{Al}}^{\text{s}}$  and  $\gamma_{\text{AlN}} = p_{\text{AlN}}/p_{\text{AlN}}^{\text{s}}$  for Al:N molar ratios of 0.001:0.999, 0.01:0.99 and 0.05:0.95 as a function of temperature are presented in Fig. 7.

## DISCUSSION

By rapid cooling of plasma with high contents of AlN to a temperature  $T$  from a temperature in the range between 2340 K and 2520 K (at an Al:N = 0.05:0.95 mole ratio), 2080 K  $< T < 2420$  K (at Al:N = 0.01:0.99), and 1840 K  $< T < 2260$  K (at Al:N = 0.001:0.999), the systems become oversaturated with respect to the AlN vapor pressures. If the oversaturation ratio  $\gamma$  is high enough, a transformation of AlN vapor into solid AlN (crystal) can occur. As a consequence of the formation of solid AlN, the amount of AlN in the gas phase is lowered and the equilibrium ratio between Al, AlN and/or N<sub>2</sub> (N) corresponding to the gas phase reactions:



and





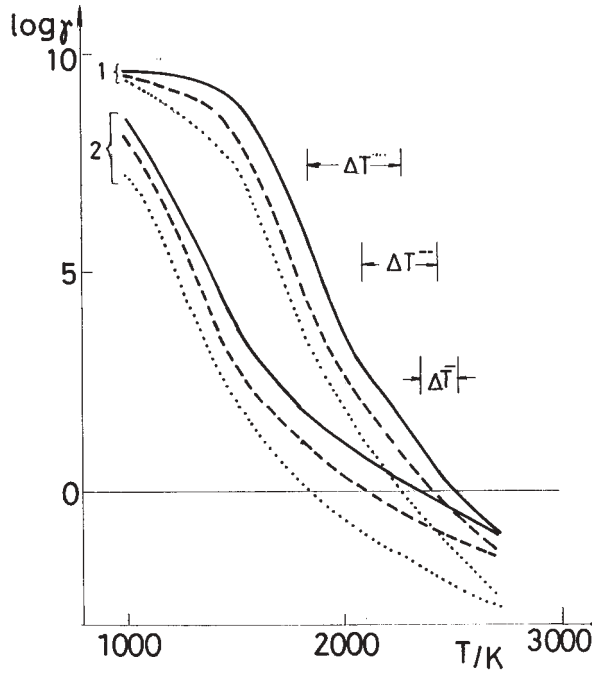


Fig. 7. The oversaturation ratios  $\gamma = p/p^s$  (1: AlN, 2: Al) for mole ratios Al:N = 0.05:0.95 (solid line), Al:N = 0.01:0.99 (dashed line) and Al:N = 0.001:0.999 (dotted line), as a function of temperature.

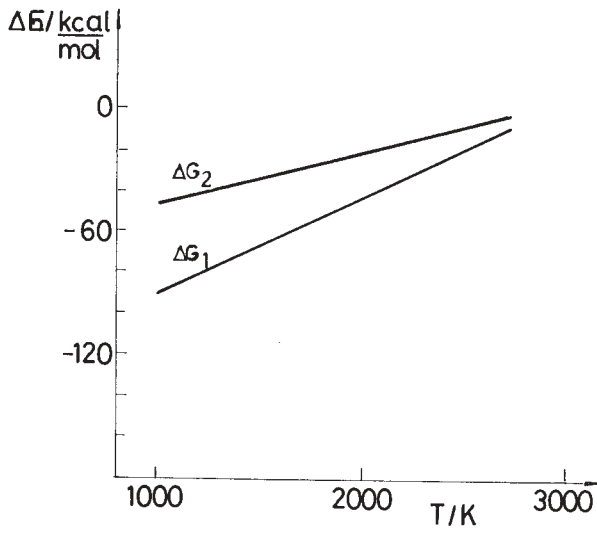


Fig. 8. Standard Gibbs energy for the reactions  $Al_g + 1/2 N_2 = AlN_s$  ( $\Delta G_1$ ) and  $Al_l + 1/2 N_2 = AlN_s$  ( $\Delta G_2$ ) as a function of temperature.

is disturbed. To reestablish these equilibriums, the reactions (10) and (11) are shifted to the right, leading to the deposition of solid AlN until the heterogeneous equilibrium (at a definite temperature) is completed:



The overall reaction is then:



The partial pressures of other aluminum species (Al, Al<sub>2</sub>, etc.) in the gas phase are now determined by the partial pressures of AlN arising from the heterogeneous equilibrium and the content of nitrogen (under constant pressure of 1 atm). As a consequence, the amount of aluminum in the gas phase is drastically lowered (to ≈ 0.2 % of the total amount present) on account of the formation of solid AlN (Table III). Thus, practically all aluminum introduced into the system will be converted into solid AlN.

TABLE III. Partial pressures (atm) of aluminum containing species in the Al/N system determined by the heterogeneous equilibrium  $\text{AlN}_g = \text{AlN}_s$

T/K	AlN	Al	Al <sub>2</sub>
1000	$3.1 \times 10^{-20}$	$6.0 \times 10^{-20}$	$1.5 \times 10^{-37}$
1500	$3.1 \times 10^{-17}$	$8.0 \times 10^{-11}$	$1.8 \times 10^{-21}$
1800	$6.0 \times 10^{-13}$	$1.2 \times 10^{-6}$	$1.0 \times 10^{-12}$
2000	$8.3 \times 10^{-11}$	$2.5 \times 10^{-5}$	$1.0 \times 10^{-10}$
2300	$2.6 \times 10^{-8}$	$3.1 \times 10^{-3}$	$3.9 \times 10^{-7}$
2500	$4.8 \times 10^{-7}$	$3.2 \times 10^{-2}$	$1.0 \times 10^{-5}$

At temperatures  $T < 2340$  K (Al:N = 0.05:0.95 mole ratio),  $T < 2080$  K (Al:N = 0.01:0.99), and  $T < 1840$  K (Al:N = 0.001:0.999 mole ratio) not only AlN, but also Al vapor is oversaturated and the formation of aluminum in the liquid form should be taken into consideration:



Due to the formation of liquid aluminum and according to the Le Chatelier's principle, the reactions (10) and (11) in the gas phase should be shifted now to the left and, as a consequence, the AlN molecules dissociate.

Alternatively, AlN as solid could be formed<sup>1</sup> via the route:



However, this reaction does not seem to be probable. First, the standard Gibbs energy for reaction (15) is less negative than that for reaction (13), as it is shown in Fig. 8. On the other hand, reaction (15) implies the existence of the heterogeneous equilibrium presented by Eq. (8), which completely determines the composition of the gas system at

definite temperature (non-variant system, according to the Gibbs phase rule). In the systems considered in the present calculations (excess of nitrogen), which correspond to the usual experimental conditions, such conditions can not be fulfilled.

#### CONCLUSION

The most important results of the present study are contained in Fig. 7. They support the assumption that the probable mechanism governing the conversion of AlN out of a plasma into the solid phase is the formation of oversaturated AlN vapor by rapid cooling of the sample (see, *e.g.*, Ref. 4). Moreover, the computed temperature range in which this process begins (between 2300 and 2500 K, depending on the ratio of aluminum and nitrogen considered) agrees well with the results of previous investigations. Fig. 7 shows that three factors favor the efficiency of this conversion: i) a larger relative amount of aluminum; ii) in the range up to 5500 K, higher temperature from which the sample is to be cooled; at  $T > 5500$  K the efficiency decreases with increasing temperature, because the partial pressure of AlN becomes increasingly smaller; iii) larger difference between the temperature of the sample before and after cooling. On the other hand, the appearance of liquid aluminum is a process which competes with the deposition of solid AlN and diminishes its purity. All three factors listed above, (i-iii), also favor the transformation of oversaturated aluminum vapor into liquid aluminum. On the other hand, the indirect formation of solid AlN *via* the reaction of liquid Al with nitrogen seems to be improbable. The relative probability for the formation of solid AlN compared to that for the appearance of liquid Al is determined by the difference in the corresponding oversaturation ratios at a given Al/N ratio and the temperature in question. In Fig. 7 the intervals  $\Delta T$  between the lowest temperatures at which oversaturated AlN and Al appear are indicated. This temperature interval increases continuously with decreasing Al/N ratio. If a sample is cooled to a temperature within  $\Delta T$ , only solid AlN is formed. The temperature at which (for a given Al/N ratio) the maximal amount of *pure* solid AlN is formed corresponds, thus, to the appearance temperatures of liquid Al, given in Table II. The optimal ratio of aluminum and nitrogen and the temperatures for the synthesis of AlN in the plasma is determined by a compromise between the above tendencies. They should be chosen by also taking into consideration the experimental conditions [*e.g.*, the influence of the added substance (Al in the case in question) on various parameters and processes (*e.g.*, thermal and electrical conductivity, mass transport), stability of plasma etc.

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## ИЗВОД

## ТЕРМОДИНАМИЧКО РАЗМАТРАЊЕ СИНТЕЗЕ КРИСТАЛНОГ АЛУМИНИЈУМ НИТРИДА ИЗ ТЕРМАЛНЕ ПЛАЗМЕ

ЈЕЛЕНА РАДИЋ-ПЕРИЋ и НИКОЛА ПЕКАС

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Теоријски је проучаван процес синтезе чврстог AlN у термалној плазми. У том циљу израчунат је равнотежни састав гасне смеше која садржи азот и различите количине алуминијума, кисеоника и водоника у интервалу температура од 1000 до 5500 К. Резултати добивени при третирању плазме као једнофазног гасног система упоређени су са онима у којима је узето у обзир присуство чврстог AlN и течног Al, да би се пронашли оптимални услови за депоновање чврстог (кристалног) AlN. Дискутовани су фактори који утичу на ефикасност овог процеса.

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