

# Fabrication, microstructure and properties of chemical vapour deposited AlN/Mo laminated composites

V. P. KOPYAKOV

*Russian Academy of Sciences, Institute of Structural Macrokinetics, Chernogolovka, Moscow Region, 142432, Russia*

The synthesis of AlN/Mo multilayer composites was investigated. Laminates of this type are used as ceramic–metal units in electrical and vacuum devices. Appropriate chemical vapour deposition (CVD) technologies have been developed for AlN/Mo laminated composites. The extreme behaviour of the thermodynamic and technological parameters as a function of CVD reactor temperature was studied and several types of AlN coating microstructures were observed. The highest AlN crystallization rate and the best properties were obtained in the “bimodal” type microstructure. The mechanisms for the different types of deposited microstructures are discussed. The temperature dependence of the thermal resistance and the long-term thermal stability in a vacuum and in caesium vapour media were studied for AlN/Mo three-layer laminates. Only the laminates with a “bimodal” type AlN microstructure were found to be satisfactory. Fully dense laminates of this type were characterized by high electrical and corrosion resistance for a minimum of 5000 h. It was concluded that the laminated composite based on molybdenum/aluminium nitride is an excellent alternative to the presently existing niobium/corundum laminates.

## 1. Introduction

Laminated ceramics–metal composites are used as multilayer ceramics–metal units for electrical and vacuum devices (for example, the collector and insulating sleeves of thermionic energy converters). Hot isostatic pressing is commonly used for manufacturing of Al<sub>2</sub>O<sub>3</sub>/Nb laminated composites [1, 2], but this type of composite has serious disadvantages. Firstly, corundum ceramics are not characterized by a sufficiently high thermal conductivity and by both long-term corrosion and radiation resistance [3, 4]. Secondly, among all the refractory metals, only niobium is compatible with corundum ceramics in respect to the thermal expansion coefficient. So, only on the basis of multilayer structures of Al<sub>2</sub>O<sub>3</sub>/Nb is it possible to manufacture collector units with satisfactory characteristics and acceptable service life. However, in this case, it is necessary to consider the problems of rather low niobium thermo-emission effectivity and electroconductivity and also its tendency to corrosion in liquid-metal heat carriers.

These problems can be solved partly by the replacement of corundum ceramics with ceramics based on scandium and yttrium oxides. In this case it is possible to solve the problems of long-term corrosion and radiation resistance [4, 5], but new problems appear which are connected with rather low electrical resistance, low strength, thermal conductivity, and less close values of the thermal expansion coefficient of niobium and these oxides. In addition, the

disadvantages of the niobium metallic material still remain.

Our attempts to solve all these problems allow us to suggest a new electroinsulating material: aluminium nitride. Aluminium nitride-based ceramics can be compared with corundum ceramics in electrical resistance and strength characteristics, but it is characterized by higher radiation and corrosion resistance than that of beryllium and aluminium oxides and can be compared with beryllium oxide by its specific thermal conductivity [6, 7]. AlN ceramics is also known to have a sufficiently high temperature compatibility with refractory metals [8]. Finally, AlN is an ecologically safe material.

AlN has been rather poorly studied as a coating material and as a ceramics layer in the multilayer ceramics–metal composites. The problems of creating such laminates based on aluminum nitride have not been solved. This is complicated by the necessity of creating high-quality vacuum-tight ceramics–metal laminates with low thermal resistance for operation under conditions of high temperature, active corrosion media and high radiation flows. This paper deals with the solution of this problem.

## 2. Synthesis of AlN/Mo laminated composites

CVD of AlN layers on plane and pipe substrates was carried out in an apparatus with a flow of the reacting

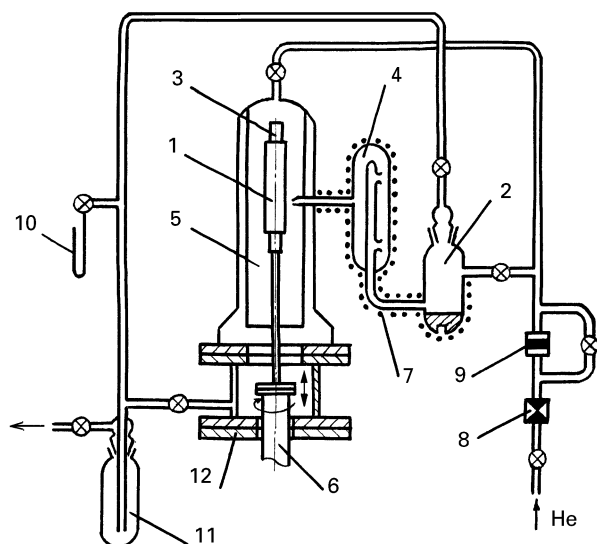


Figure 1 Diagram of the apparatus used for deposition of AlN coatings: (1) substrate; (2) evaporator; (3) internal tungsten heater; (4) gas mixer; (5) reactor-crystallizer; (6) sample rotation and axial displacement feed-through; (7) nichrome heaters; (8) feeder valve; (9) gas flowmeter; (10) manometer; (11) liquid nitrogen trap; (12) flanges.

vapour mixture (Fig. 1). We considered two synthesis schemes of AlN with its simultaneous deposition as a layer on the surface of refractory metal: with a starting agent of  $\text{AlCl}_3/\text{NH}_3$  gas mixture or a vapour of aluminium chloride monoammoniate,  $\text{AlCl}_3\text{NH}_3$ . In the latter case the deposits were of higher quality and did not peel off the substrate [9]. Molybdenum was selected as the most favourable substrate material because it has a best match with aluminium nitride with respect to both lattice parameter and thermal expansion coefficient.

The deposition rate is known to depend, in the general case, on both substrate temperature and reagent concentration in the vapour mixture. The reagent concentration is determined by the temperature in the evaporator and the flow rate of the transporting inert gas. We studied the dependence of AlN depos-

ition rate on the main technological parameters: Table I partially summarizes the results of the study. The data show that the deposition rate increases from  $3.3 \times 10^{-6}$  to  $5.0 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$  within the substrate temperature range 1400–1570 K. When the temperature is further raised, the deposition rate begins to decrease, probably, as a result of dissociation of monoammoniate in the gas phase.

The exterior appearance of the coatings unambiguously depends on the deposition temperature. Visual evaluation shows that coatings deposited in the temperature range 1400–1500 K are glass-like, colourless, transparent and lustrous. In the deposition temperature range of 1530–1570 K, coatings remain transparent but becomes lustreless, and at 1600–1700 K they lose their transparency and acquire a greyish-brown colour but retain the same crystallinity.

The data on the effect of the substrate temperature on pycnometric density of the coatings (Table I) show that dense compact (i.e. virtually poreless) coatings are obtained at a temperature of about 1560 K. This agrees well with the fact that the coatings formed at this temperature are vacuum tight.

To form tubular ceramic-metal laminates, CVD molybdenum coatings were used as the external metal layers (jackets). The existence of the appropriate conditions of epitaxial crystallization provided high contact strength and vacuum tightness between aluminium nitride and molybdenum layers. The molybdenum coatings were applied directly on to the aluminium nitride layer in a CVD apparatus with a flow of reacting vapour mixture (Fig. 2). The pressure of molybdenum pentachloride (a starting reagent) was maintained within the 1.5–1.8 kPa range. The chloride-nitrogen mixture was diluted with a dry and pure helium flow, additionally warmed and blown through a nozzle on to the substrate surface. The substrate temperature was maintained at 1200–1400 K. The total pressure in the CVD apparatus was maintained at 2.5–3.0 kPa using a rotary pump. The rate of deposition of the perfect molybdenum coating was  $100\text{--}200 \mu\text{m h}^{-1}$ .

TABLE I Temperature and kinetic conditions of CVD of AlN layers

$T_{\text{substr}}(\text{K})$	Crystallization rate, $U$ ( $10^6 \text{ g cm}^{-2} \text{ s}^{-1}$ )	Pycnometric density, $d$ ( $\text{g cm}^{-3}$ )	Content (mass %)				
			Main components <sup>a</sup>		Impurities <sup>b</sup>		
			[Al]	[N]	[C]	[O] ( $\times 10^2$ )	
			Total	Unbonded			
1400	3.3	2.80	73.2	20.8	26.9	0.07	1.80
1500	4.2	2.82	72.3	18.1	27.9	0.09	2.80
1530	4.8	3.05	68.0	4.5	32.9	0.09	1.15
1550	5.0	3.14	66.1	0.5	34.0	0.08	1.80
1570	5.0	3.14	67.8	4.9	32.6	0.06	1.90
1650	4.5	3.12	69.2	10.0	30.4	0.10	2.10
1700	4.2	3.12	72.1	18.2	28.2	0.07	1.75

<sup>a</sup> Stoichiometric composition is 65.8 mass % Al and 34.2 mass % N.

<sup>b</sup> Molybdenum and silicon impurities are not more than  $10^{-2}$  and  $10^{-3}$  mass %, respectively, in each specimen.

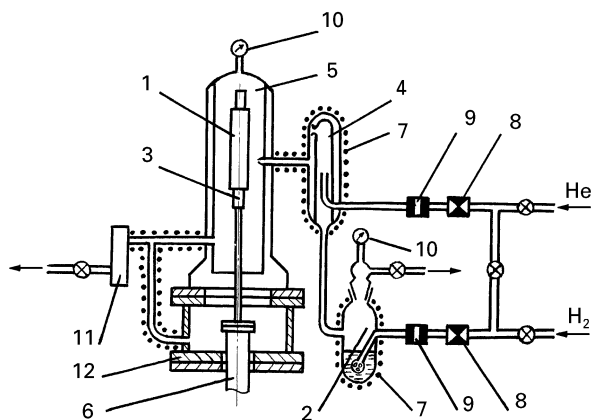


Figure 2 Diagram of the apparatus used for deposition of molybdenum coatings (see Fig. 1 for designations).

### 3. Results and discussion

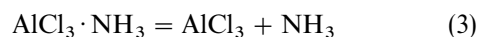
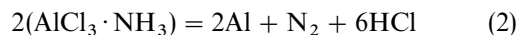
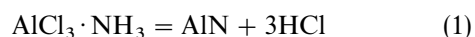
#### 3.1. Microstructural analysis

The AlN coating microstructure was studied by light microscopy [9, 10]. Metallographic specimens (across the coating) were prepared in the conventional way. The micrographs presented in Fig. 3 show that the coating structure changes substantially within the temperature range studied. In the range 1400–1500 K, a coating grew with a layered structure (Fig. 3a and b), while the coating obtained at  $T > 1650$  K consisted of large grains, which were not in close contact with each other (Fig. 3c and d). In the intermediate narrow temperature range (near 1550 K), the layered structure was not formed and the bulk of the coating (the matrix) was threaded with crystalline fibres (whiskers), which grew in a statistical direction from the substrate to the external surface of a coating (Fig. 3e and f), so that whiskers grew somewhat faster than the matrix. The layered structure has already been found in AlN coatings by other researchers (and also the coarse-grained structure) [11–14], but its origin was not explained (as in [11]), or was simply ignored. The bimodal structure was not investigated earlier. Thus, three structure types are observed in the AlN coating within the temperature range studied: layered, bimodal and coarse-grained.

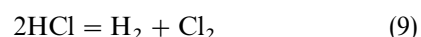
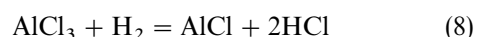
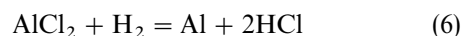
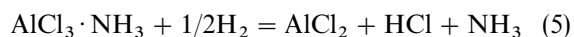
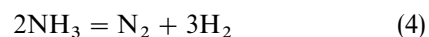
It can be seen at high magnification that layered coatings deposited at 1500 K and below have a complicated layered structure (Fig. 3b). Thick layers, which are made up of thin ones, are seen at the edge of the resolution limit of the light microscope. Note that not only thick layers but also the thin ones located within the thick ones manifest a periodical arrangement. This allows us to speculate a kind of regular pulsation during the AlN deposition process, as has been established for several other systems (e.g. the SiC system [15]). It should also be noted that layered and coarse-grained AlN coatings contain pores and cavities, both at their boundary with the substrate and in their bulk, while bimodal coatings are more dense and adhere tightly to the substrate.

In relation to the probable mechanisms that operate on the substrate surface and in ambient media, the thermodynamic representation of the Al–N–H–C system (Fig. 4, curve 1, AlCl<sub>3</sub>; 2, NH<sub>3</sub>; 3, H<sub>2</sub>; 4, Cl; 5,

AlCl<sub>2</sub> and AlCl; 6, Cl<sub>2</sub>; 7, N<sub>2</sub>; 8, HCl) allows us to assume that, being in contact with the heated surface of a sample, the starting reagent, (aluminium chloride monoammoniate) undergoes the following changes at low (below 1500 K) temperature



In addition, the following reactions can proceed in the vapour phase adjacent to the sample surface



Thus, the efficiency of the AlN deposition process cannot be very high in the low-temperature region because of the side reactions which occur; in particular, the partial reduction of aluminium trichloride to dichloride and monochloride should be kept in mind.

According to the calculations, the concentration of subchloride decreases when the substrate temperature is higher than 1600 K; this indicates that the reduction reaction by hydrogen (Reaction 6) proceeds to a greater extent [12]. In addition, direct synthesis of aluminium nitride becomes possible above 1500 K [13, 14]



Reactions 6 and 10 furnish an additional mechanism for the AlN deposit to grow and the possibility of its realization increases with temperature.

Thus, the thermodynamic analysis data show that there is a region of threshold temperatures (1500–1600 K) in the system: above these temperatures the efficiency of AlN formation increases and at least two chemical mechanisms of AlN crystallization on a heated substrate become possible.

It was noted that the composition of bimodal-type coatings is very close to the stoichiometric one, while layered and coarse-grained deposits contained an excess of aluminium (see Table I). Consequently, the development of a particular morphology of a deposit is connected with the ratio of its main components and depends on the pyrolysis temperature of the starting reagent.

Based on the experimental and thermodynamic data, we suggest the following mechanisms for the formation of different types of AlN coatings. With the deposition of the first thin AlN layer, the blackness and emissivity of molybdenum substrate increase drastically. The result is that the substrate temperature is reduced at constant power supply to the heater. Then the efficiency of the main pyrolysis Reaction 1, taking place on the substrate surface, should also be reduced while the contribution of side

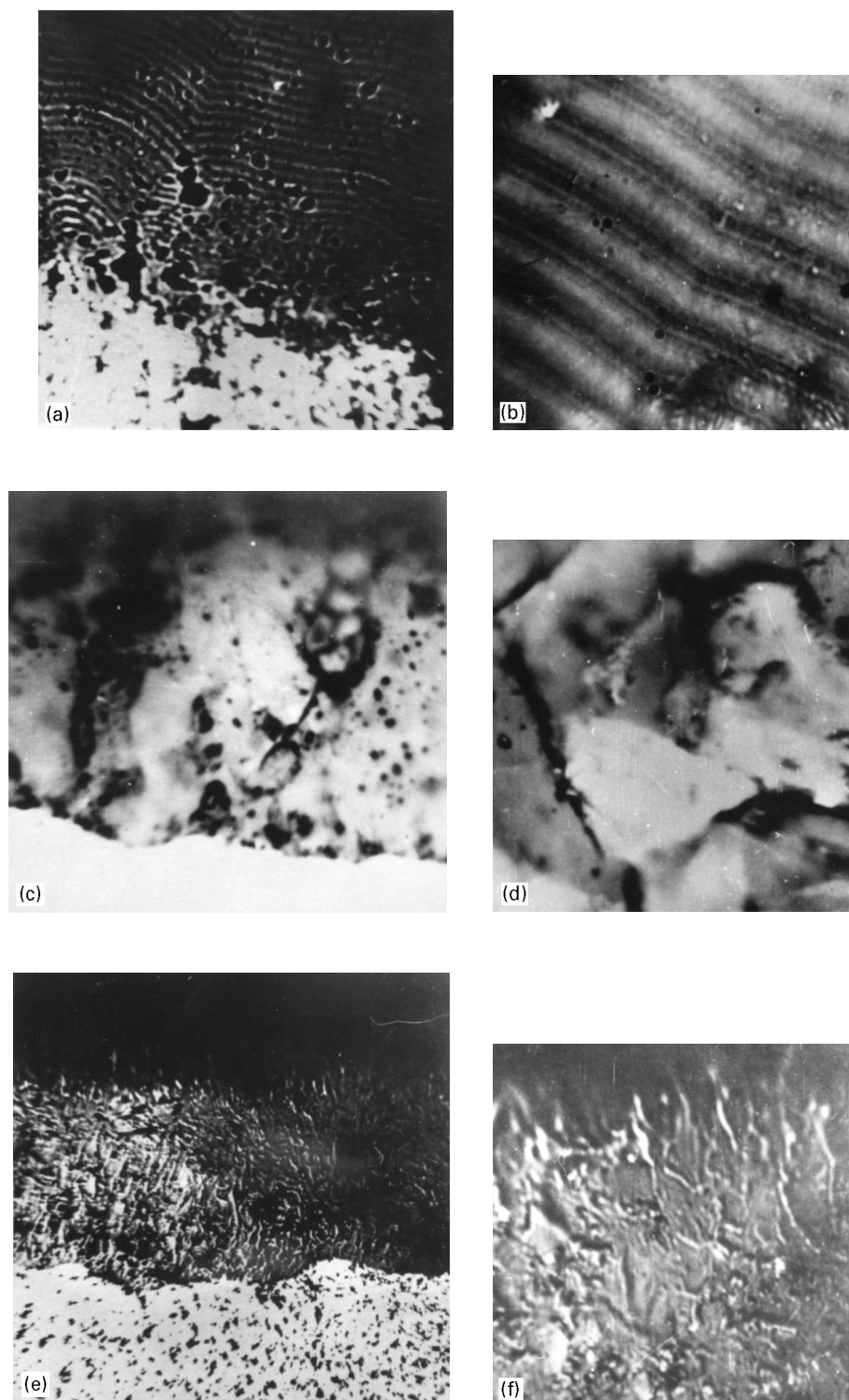


Figure 3 Micrographs of AlN coatings deposited at various temperatures: (a) 1370 K ( $\times 960$ ); (b) 1370 K ( $\times 1350$ ); (c) 1670 K ( $\times 960$ ); (d) 1670 K ( $\times 1350$ ); (e) 1570 K ( $\times 450$ ); (f) 1570 K ( $\times 1850$ ).

reactions and, in particular, of Reaction 2, should be increased, and an aluminium excess should arise in the deposit. A chemical test showed up to 20 mass % free aluminium in the layered deposits.

Owing to the presence of free aluminium, the emissivity of the coating is reduced and its temperature is somewhat increased. As a result, two lower contributions (of side Reaction 2 and the higher efficiency of Reaction 1) are provided until a high-emissivity layer is formed. In this way, self-regulation of AlN deposition is exerted with a particular opera-

tion cycle. The stoichiometry of the deposit is then kept practically unchanged but the concentration of free aluminium experiences periodical oscillations, resulting in a layered coating morphology (Fig. 3a and b).

Such a situation is characteristic if the temperature is near the lower limit of the pyrolysis temperature range of the starting reagent. Side reactions at higher temperatures are obviously less effective, and the yield of the main pyrolysis product increases. Thus, temperature oscillations are eliminated, as well as the layer-type morphology of the coatings.

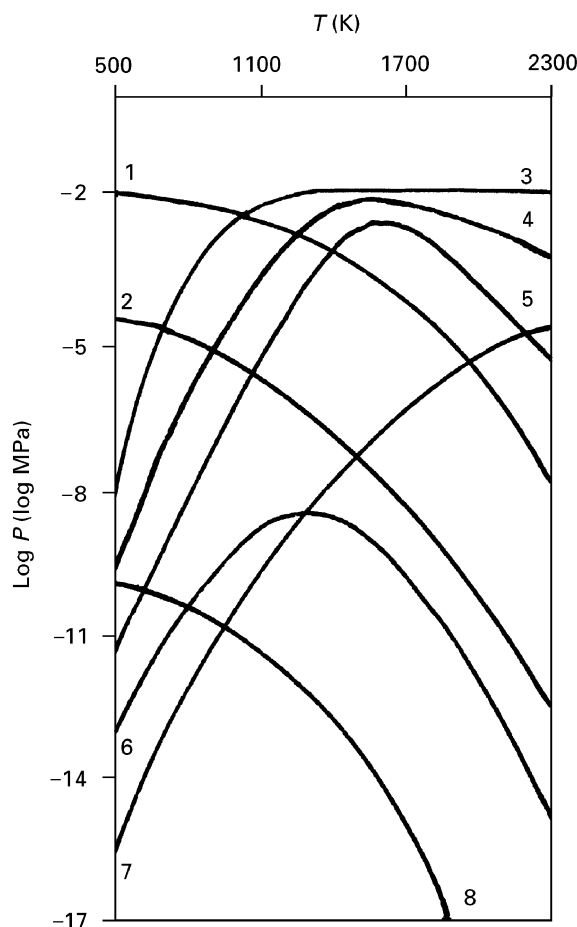
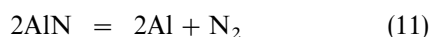


Figure 4 Calculated equilibrium composition of the vapour phase in the AlN–N–H–Cl system ( $P_{\Sigma} = 0.1$  MPa): 1, AlCl<sub>3</sub>; 2, NH<sub>3</sub>; 3, H<sub>2</sub>; 4, Cl; 5, AlCl<sub>2</sub> (AlCl); 6, Cl<sub>2</sub>; 7, N<sub>2</sub>; 8, HCl.

We note that at higher temperatures (in the range of coarse-grained coating morphology), free aluminium appears in the coating because of partial thermal dissociation of AlN



but not via the pyrolysis of the starting reagent upon the side Reaction 2.

At relatively low temperatures, the only means of AlN formation in monoammoniate pyrolysis is obviously by Reaction 1. The direct AlN synthesis from the elements (Reaction 10) will be more pronounced at  $T > 1500$  K [13, 14]. Furthermore, close to the upper limit of the temperature range studied, there is also a contribution of starting reagent pyrolysis in the vapour phase adjacent to the substrate surface. All these processes, together with the sintering of the coating material, which is also more effective at higher temperatures ( $T > 1570$  K), result in the formation of coarse-grained-type coatings.

A narrow temperature range exists at about 1550 K, where both AlN synthesis reactions (Reactions 1 and 10), are obviously effective, but the contributions of the vapour bulk pyrolysis and solid sintering are not yet sufficiently large. In this range, bimodal-type coatings are deposited similar to that shown in Figs 3c and 4c. As mentioned above, such a coating appears as a matrix (consisting of fine crystal particles)

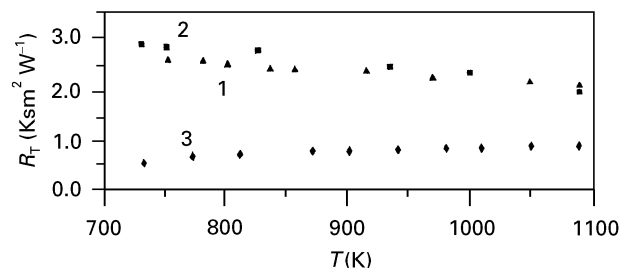


Figure 5 Thermal resistance of three-layered packs with nitride ceramics versus temperature. Morphological types of ceramics: 1, layered; 2, coarse-grained; 3, bimodal.

pierced by whisker-like crystals. X-ray phase analysis of such a coating showed that it was single-phase wurtzite-type AlN in spite of the diversity in its morphology.

The same phase composition was observed in most specimens of different morphological types. This is possibly an indication of very high dispersity of the aluminium phase. Only a substantial content of free aluminium will give rise to more intense reflections due to this phase in the X-ray diffraction patterns. In order to obtain an independent argument for the assumptions made above, direct synthesis of AlN on a heated molybdenum substrate was attempted. The experiments were eventually successful, although at 1600 K, whiskers grew only if high-purity aluminium pellets were used as a source of aluminium vapour and dissociated ammonia was the vapour medium.

### 3.2. Ceramics/metal laminates properties

The results of tests on three-layer tubular laminates are presented. The extreme behaviour of the physical and service properties was found to be characteristic of Mo/AlN/Mo composites with aluminium nitride of different morphologies. Preliminary thermal tests on Mo/AlN laminates with no jackets were performed in a vacuum and in caesium vapour, both at temperatures increasing up to 1300 K and thermocycling. The specimens with only bimodal-type nitride ceramics showed no substantial variation of the structure during the tests. The occurrence of porosity was observed in specimens with layered-type nitride ceramics because of the interaction of the unbound aluminium with caesium vapour. The bimodal-type nitride ceramics remained poreless. The nitride whiskers were divided into short fragments because of the diffusion sintering processes. These fragments were tightly bound to the matrix. The main feature of the thermal processes was the conversion of the fibrous AlN composite into the dispersed one.

The temperature dependence of the thermal resistance,  $R_T$ , of Mo/AlN/Mo tubular laminates with aluminium nitride of three morphological types was studied (Fig. 5) [16, 17]. Thermal resistance is a reciprocal value of the thermal transfer coefficient ( $R_T = 1/k \text{ K m}^2 \text{ W}^{-1}$ ). It can be seen that the laminates with layered or coarse-grained type ceramics are characterized by a higher thermal resistance (about  $2.0 \text{ K cm}^2 \text{ W}^{-1}$ ). An abnormal type of temperature

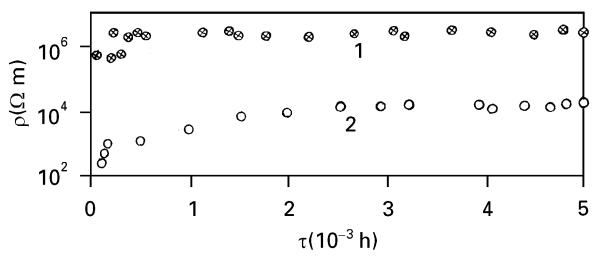


Figure 6 Electrical resistivity of laminates with bimodal-type nitride ceramics (1) in vacuum and (2) caesium vapour, versus the exposure time (see the text for details).

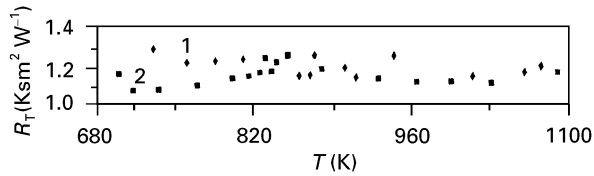


Figure 7 Thermal resistance of laminates with bimodal-type nitride ceramics (1) before and (2) after the tests in vacuum and caesium vapour (see the text for details).

dependence of thermal resistance proves the significant contribution of contact resistance in the general thermal resistance of the laminates. Bimodal-type ceramics allow the thermal resistance of the laminates to be reduced to  $< 1.0 \text{ K cm}^2 \text{ W}^{-1}$ . In this case, the temperature-dependence appearance proves to be a negligible contribution of the contact resistance in the general thermal resistance of the laminates. The behaviour is determined by the temperature dependence of the thermal conductivity of nitride ceramics.

Fig. 6 shows the results of long-term thermal tests in caesium vapour of laminates with bimodal-type nitride ceramics. During the test, the caesium vapour pressure was 120–140 Pa and the laminate temperature was  $1000 \pm 10 \text{ K}$ . Specific volume electrical resistance was measured periodically. For 5000 h the value of the electrical resistance remained stable. Fig. 7 shows the results of thermal resistance measurements for laminates with bimodal-type ceramics before and after the long-term tests in caesium vapour. The results of the measurements before and after the test are practically the same. This proves the high

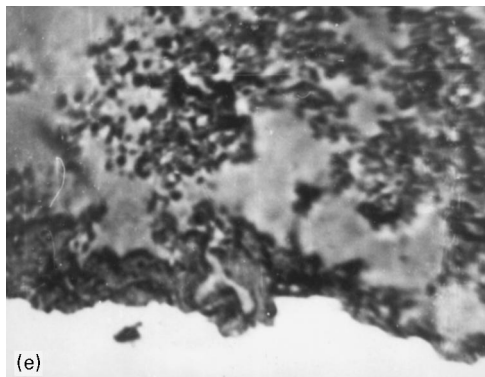
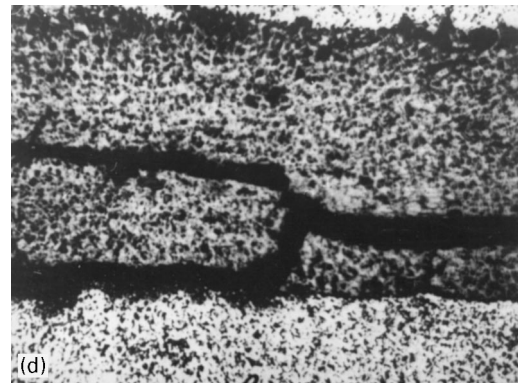
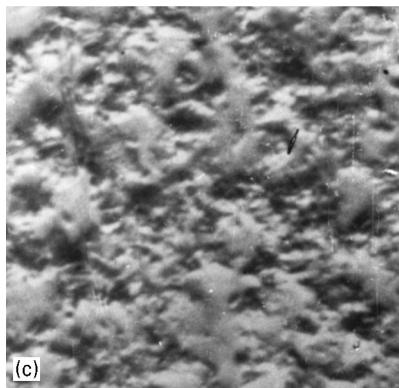
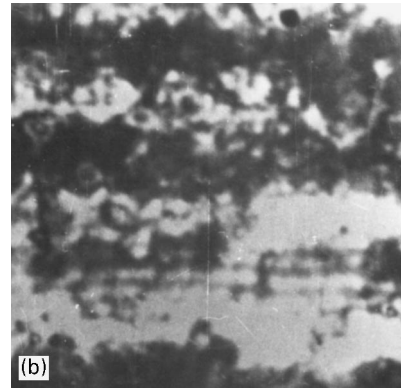
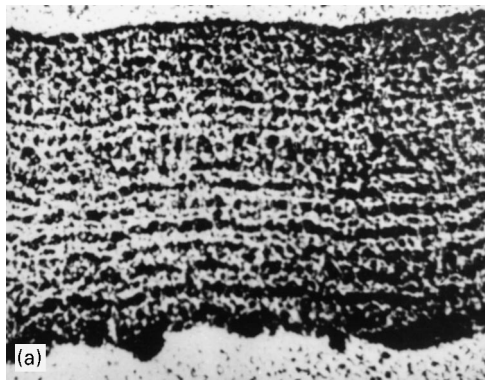


Figure 8 Nitride ceramics microstructure after testing the laminates: (a, b, d) layered type; (a, d)  $\times 170$ ; (b)  $\times 2400$ ; (c, e) bimodal type ( $\times 960$ ); (a, c) *in vacuo*, 1200 K, 5 h; (b, d) caesium vapour, 1200 K, 100 h; (e) *in vacuo*, 1200 K, 5000 h, and caesium vapour, 1000 K, 5000 h, and double measurements of the thermal resistance.

thermal and corrosion stability of laminates with bimodal-type nitride ceramics.

Microstructure investigations of laminates with ceramics of several morphological types after thermal and caesium tests of various durations, allowed determination of differences in ceramic structure evolution. In laminates with layered-type ceramics, homogenization of the ceramic layer composition occurs due to the diffusive dispersal of excess aluminium, and as the result, pore chains are formed in the layers of increased excess aluminium (Fig. 8a, b).

Sintering of the fibres with the matrix takes place in the laminates with bimodal-type ceramics. It can be seen that fibres are divided into short fragments (Fig. 8c), but porosity is not in evidence. This fact can be explained by the closeness of such ceramics composition to the stoichiometric one. Prolonged annealing intensifies the ceramic sintering processes (Fig. 8d and e). The rough cracks appear in the laminates with layered-type ceramics (Fig. 8d). The good features are found in the laminates with bimodal-type ceramics. The ceramic/metal interface remains dense and there is a good adherence between the ceramics and the metal layers (Fig. 8e). The main service properties remain unchanged in this instance.

#### 4. Conclusion

Both thermodynamic estimation and an experimental study of the Al–N–H–Cl system allowed the extreme behaviour of the temperature dependences of composition, structure and properties of the reaction products to be studied. The highest CVD rate of AlN was observed within the narrow temperature range 1550–1570 K. Single-phase layers with bimodal-type morphology, closest to AlN in stoichiometric composition, and of maximum density, are formed at these temperatures. We can conclude, that only ceramics of bimodal-type are satisfactory. Vacuum-tight tubular laminates, with such ceramics, are characterized by high electrical and corrosion resistance and low thermal resistance. These properties remain unchanged during thermal vacuum and caesium tests for at least 5000 h.

Thus we can conclude that the conception of tubular laminates based on molybdenum metal and aluminium nitride ceramics is an excellent alternative to the

existing laminates conception, based on niobium metal and corundum ceramics.

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