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THE THERMAL POWER OF ALUMINUM NITRIDE AT TEMPERATURES BETWEEN 1350 AND 1650° C IN ARGON AND NITROGEN ATMOSPHERES

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THE THERMAL POWER OF ALUMINUM NITRIDE AT TEMPERATURES BETWEEN
1350 AND 1650° C IN ARGON AND NITROGEN ATMOSPHERES*

Wilhelm Anton Fischer and Bernd Schuh**

ABSTRACT. Description of the test apparatus for measuring the thermal voltage of the chain $Rh | AlN | Rh$ for temperature differences of up to $\pm 60^\circ C$ between 1350 and 1650° C. Determination of the thermal power and its homogeneous proportion. Calculation of the transfer heat of the migration ions resulting from the homogeneous thermal power. Discussion of the conduction mechanism in aluminum nitride AlN.

In an earlier paper [1], a report was given on the measurements of the electrical conductivity in aluminum nitride at high temperatures. On the basis of the results of these studies, the conclusion was drawn that, in AlN at temperatures between 1100 and 1700°C and nitrogen partial pressures of the argon-nitrogen atmosphere between $5 \cdot 10^{-5}$ and 1 atm, there is either predominant ion conduction or intrinsic semiconduction. For the purpose of further clarification, measurements of thermal power were conducted in aluminum nitride, by means of which information may be obtained on the conduction mechanism [2 - 5].

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**Duesseldorf.

***Numbers in the margin indicate pagination in original foreign text.

The test layout used is presented schematically in Figure 1. It corresponds to the earlier described arrangement [1] for the measurement of electrical conductivity. The heating unit used in these studies was a molybdenum wire resistance furnace with thyristor-controlled temperature regulation, sprayed with forming gas (95% N_2 , 5% H_2)

The measurements of thermal power were carried out in argon and nitrogen of high purity. The oxygen and water vapor content of the measurement gases were reduced through a purification plant to volumetric contents of 0.1 ppm each. Since no high differences were found between the two series of measurements, measurements in mixtures of these two gases were omitted.

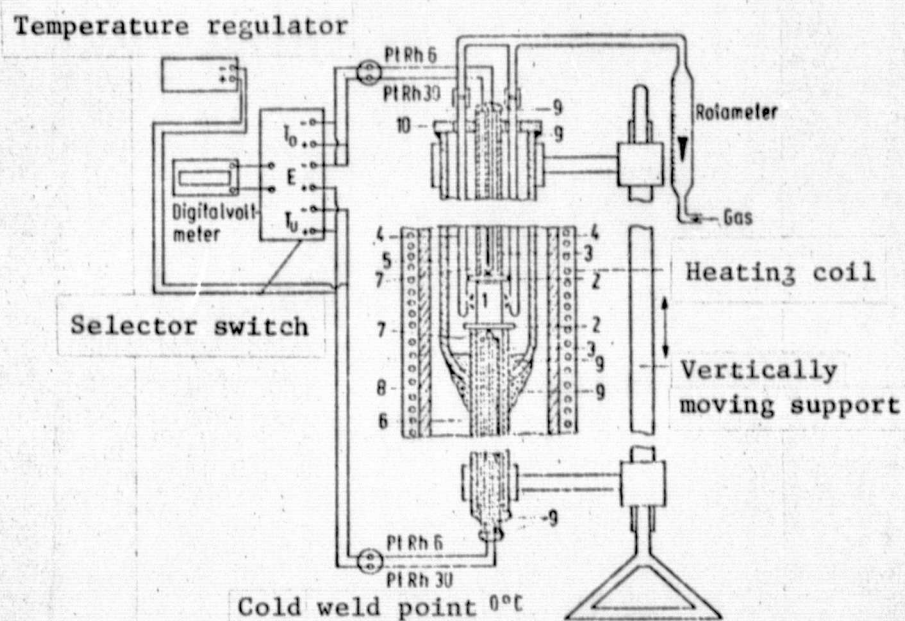


Figure 1. Test arrangement for measuring the thermal power of AlN

1 — sample; 2 — Rh disks; 3 — two-hole capillary (Al_2O_3); 4 — gas intake tubes (Al_2O_3); 5 — protective tube (Al_2O_3); 6 — support tube (Al_2O_3); 7 — hot weld point Pt-Rh18-Pt; 8 — carrier tube (Al_2O_3) for the heating coil; 9 — fireproof cement on Al_2O_3 base; 10 — cover plate (MgO).

The sample was heated for about 2 hours under nitrogen to the test temperature of 1650°C , and maintained for half an hour at this temperature. The thermal element on the lower rhodium disk was connected with the temperature regulator, so that the temperature occurring there was taken as constant reference temperature. By shifting vertically the protective tube and therefore the sample in the furnace space, it was possible to obtain temperature differences of up to $+60^{\circ}\text{C}$ between the upper and lower rhodium disks. After each adjustment, the measurement was carried out three times within 10 minutes with over current disconnected for a short time. The thermal voltage was measured between the positive sides of the thermo-elements which were welded on the rear sides of the lower and upper rhodium disks, with an automatic reversal of signs and a precision of 0.1 mV, /840 while the lower measurement point of the sample was connected with the positive pole of the instrument.

The reference temperature was reduced in intervals of about 80 to 1350°C . The measurements in the argon atmosphere were conducted in the same manner. The flow rate of the gases was in most cases 40 liters/h, occasionally also 20 liters/h.

Test results

The dependence of the thermal voltage of AlN on the difference in temperature is shown in Figure 2 for the measurements in the nitrogen atmosphere, and in Figure 3 for the argon atmosphere. The individual measurement points for different reference temperatures are located on straight lines which, however, do not pass through the origin of the coordinates which should be required. At the difference of temperature 0°C , a residual voltage occurs whose value increases with the increasing test temperature. Similar deviations were also observed in other ceramics in measurements of thermal power [6 - 7].

The next series of tests shows that this residual voltage is not the result of an error in temperature measurement, but is caused by an asymmetrical gas feed to the specimen. With a very careful

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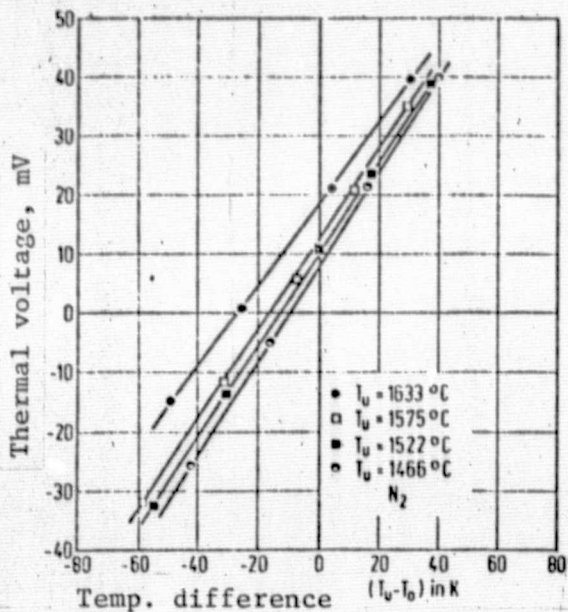


Figure 2. The thermal voltage of AlN as a function of the temperature difference over the specimen in nitrogen at temperatures of 1466 to 1633° C at the lower measuring point (with asymmetrical gas feed to the specimen)

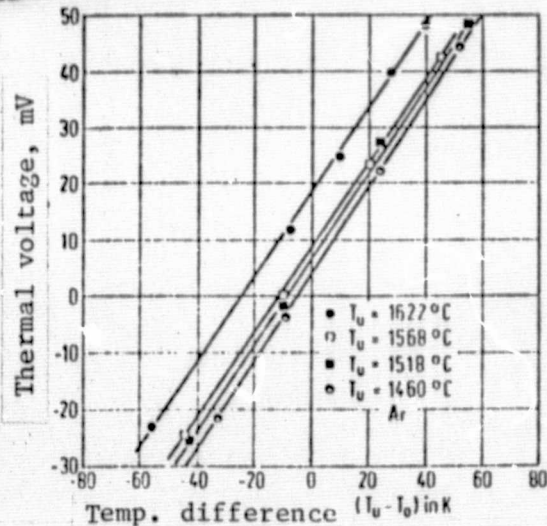


Figure 3. The thermal voltage of AlN as a function of the temperature difference over the specimen in argon at temperatures of 1460 to 1622° C at the lower measuring point (with asymmetrical gas feed to the specimen)

centering of both gas intake tubes 4 in Figure 1 in the center of the specimen, this residual voltage may be avoided in a great measure, as shown in Figures 4 and 5.

Independently of the value of the residual voltage, the values of the thermal power α may be calculated from the slope of the straight lines of Figures 2 to 5. The sign of the thermal power is established conventionally; it is chosen as positive when the two electrodes are charged negatively. In the present measurements, the hotter electrode has a positive charge, which gives a negative thermal power.

The temperature dependence of the thermal power of AlN in the nitrogen atmosphere is shown in Figure 6, while Figure 7 shows it in the argon atmosphere. The thermal power in argon is -0.78 mV/K in the studied temperature range of 1380 to 1650° C. In the nitrogen atmosphere it drops linearly from -0.85 mV/K to -73.0 mV/K at 1650° C.

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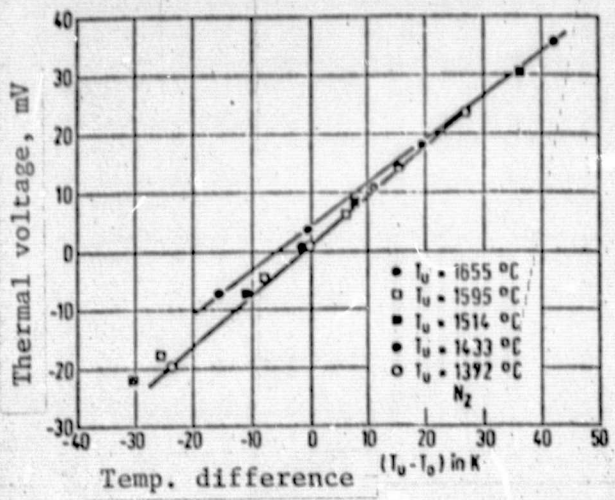


Figure 4. The thermal voltage of AlN as a function of the temperature difference over the specimen in nitrogen at temperatures of 1372 to 1655° C at the lower measuring point (with symmetrical gas feed to the specimen)

Unlike the conductivity measurements, in the measurements of thermal power, it was not possible to establish any effect of the rate of flow of the bases on the measured values.

In order to obtain indications regarding the conduction mechanism from measurements of the thermal power, its homogeneous component should be known [2, 3, 5]. The thermal power of an ion conductor consists basically of three elements [3]:

1. The homogeneous thermal power α_{hom} on the basis of the difference of potential forming inside the crystal.

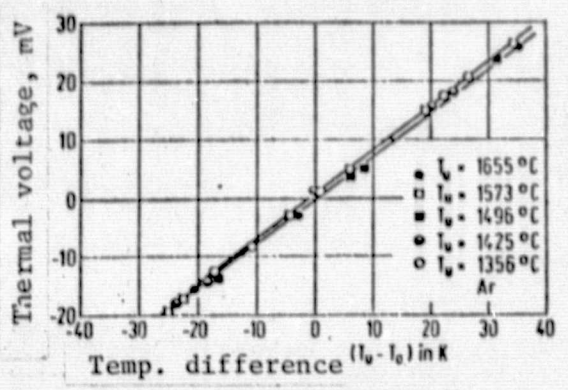


Figure 5. The thermal voltage of AlN as a function of the temperature difference over the specimen in argon at temperatures of 1356 to 1655° C at the lower measuring point (with symmetrical gas feed to the specimen)

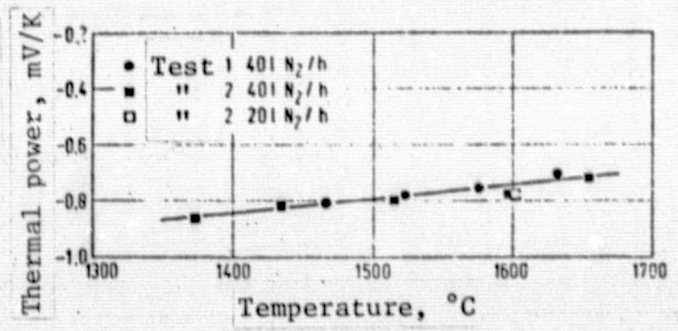


Figure 6. The thermal power of AlN as a function of temperature in a nitrogen atmosphere

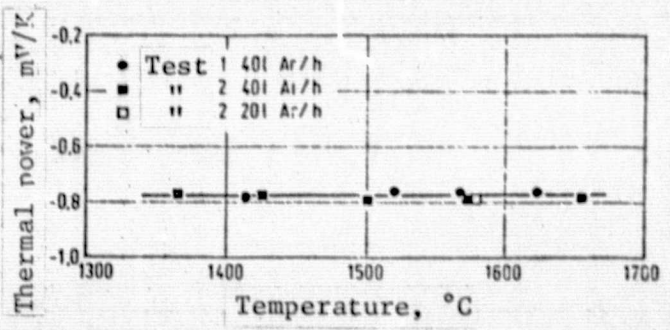


Figure 7. The thermal power of AlN as a function of temperature in an argon atmosphere

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2. The homogeneous thermal power α_{hom} of the metal leads, which is very small as compared with the total thermal power and may therefore be disregarded.

3. The heterogeneous thermal power α_{het} as a result of the difference of contact potential between the electrodes at different temperature and the semiconductor surface:

$$\alpha_{ges} = \alpha_{het} + \alpha_{hom} \quad (1)$$

Because of the layout of the AlN specimen, the following thermo-electric cell occurs between the two disk-shaped inert precious metal electrodes of rhodium:



through which the heterogeneous thermal power $\alpha_{(N_2)het}$ for the electrode reaction:



is established [5, 8, 9]:

$$\alpha_{(N_2)het} = - \frac{1}{3F} (\frac{1}{2} S_{N_2} - S_{N^{3-}}) \quad (4)$$

The molar entropy of gaseous nitrogen S_{N_2} may be calculated for a given temperature T and the pressure p_{N_2} according to the equation:

$$S_{N_2, T} = S_{N_2, T}^0 - R \cdot \ln p_{N_2} \quad (5)$$

In it, $S_{N_2, T}^0$ is the molar standard entropy tabulated [10] for the pressure $p_N^0 = 1$ atm and the temperature T of gaseous nitrogen. The partial molar entropy $\bar{S}_{N^{3-}}$ of the nitrogen ions in the solid electrolyte may be calculated approximately from the half-entropy of AlN, taking into account the relative atomic mass A of aluminum and nitrogen [11, 12]:

$$\bar{S}_{N^{3-}} = 0.5 \left(S_{AlN} - \frac{3}{2} R \ln \frac{A_{Al}}{A_{N^{3-}}} \right) \quad (6)$$

The molar entropy of aluminum nitride S_{AlN} is known for different temperatures [13].

Table 1 gives the heterogeneous thermal power calculated for the temperatures of 1700 K (1427° C) and 1900 K (1627° C) according to Equations (4) to (6). The homogeneous thermal power obtained after deducting these values from the thermal power α_{ges} measured at these temperatures is also indicated in Table 1.

TABLE 1. CALCULATED VALUES FOR HETEROGENEOUS AND HOMOGENEOUS THERMAL POWER

Temperature, °C	Heterogeneous thermal power, mV/K		Homogeneous thermal power, mV/K	
	Nitrogen	Argon*	Nitrogen	Argon*
1427	-0.27	-0.33	-0.55	-0.33
1627	-0.27	-0.44	-0.46	-0.34

* Argon with a volumetric nitrogen content of 5 ppm.

For the homogeneous thermal power, we have the equation [2, 5]:

$$\alpha_{hom} = \frac{Q}{T n F} \quad (7)$$

in which Q is the molar transfer heat of the wandering ions, and n is their valency.

Assuming a charge number $n = 3$, we calculate from the measurements the transfer heat of the ions in the nitrogen atmosphere as -64,700 cal/mol or -2.80 eV at 1427° C and as -60,479 cal/mol or -2.62 eV at 1627° C. In the argon atmosphere, the corresponding values are -38,820 cal/mol or -1.68 eV and -44,600 cal/mol or -1.93 eV.

Because of the temperature dependence of the transfer heat, Equation (7) is not satisfied exactly [5].

One should mention the fact that the values obtained from the thermoelectric measurements for the transfer heat of the ions do not differ much from the amounts calculated in the conductivity measurements [1] of the excitation energy of the charge carriers (2.19 at

temperatures below 1450° C and 2.7 eV at the higher temperatures), which was already indicated by Wagner [2] in anion conductive lead chloride. In the case of measurements in the nitrogen atmosphere, the amounts are very consistent at the higher temperatures.

Conclusion

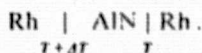
The measurements of electrical conductivity [1] described in the previous paper permitted no decision about whether, in the AlN at temperatures between 1450° C and 1700° C and nitrogen pressures between $5 \cdot 10^{-6}$ atm and 1 atm, there is intrinsic semiconduction or predominant ion conduction.

In the case of an intrinsic semiconduction, the thermal power should be equal to zero approximately for more or less the same mobility of the defect and excess electrons. As was shown by the measurements of the thermal power here, this is not correct. It may therefore be assumed with great probability that, in the studied range of temperature and pressure, AlN is predominantly ion-conductive. Further experimental and theoretical studies will furnish information regarding the occurrence and the type of this ion conduction.

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Summary

The thermal voltage of hot-pressed specimens of aluminum nitride was measured in the temperature range 1350 to 1650° C in both an argon and a nitrogen atmosphere. The hotter electrode was always the positive pole in the thermal chain



The thermal power values measured in the tests were -0.85 mV/K at 1380° C in a nitrogen atmosphere and -0.78 mV/K in an argon atmosphere for the same temperature. The homogeneous thermal power calculated from the measurements was -0.55 mV/K in a nitrogen atmosphere at 1427° C, -0.46 mV/K at 1627° C, and in an argon atmosphere with a volumetric content of 5 ppm N₂ — -0.33 mV/K.

The transfer heat calculated from the homogeneous thermal power agrees well for an assumed charge number of $n = 3$ for the migrating ions for the measurements in the nitrogen atmosphere with the activating energies established through the conductivity measurements. From the results of the thermal-power measurements, it was concluded that an ion conductivity predominates in AlN.

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