

THE EFFECT OF NITROGEN PRESSURE ON NITRIDATION OF SILICON

Boris Kurtev

Research Institute of Electrotechnical Ceramics, Pospíšilova 281, 500 64 Hradec Králové

Received 20. 9. 1979

The effect of nitrogen pressure on the final stage of nitridation of silicon powder compacts at temperatures above the melting point of silicon was studied. On the basis of the time course of the process established, as well as on that of the dependence of the kinetic constant on nitrogen pressure, and of the phase composition of the products, it is suggested that under the given conditions the nitrogen pressure affects in particular the rate of formation of β - Si_3N_4 and that above the melting point of silicon the formation of β - Si_3N_4 is controlled by the process on the reaction boundary.

INTRODUCTION

Silicon nitride-based ceramics, prepared by reaction sintering of silicon powder compacts in nitrogen atmosphere, exhibits a comparatively high mechanical strength, which, in contrast to that of oxidic ceramics, is stable up to about 1400 °C. It shows an outstanding resistance to abrupt changes of temperature, to oxidation and corrosion by melts of most non-ferrous metals. These properties make silicon nitride a promising engineering material for machine components exposed to dynamic stressing at high temperatures.

The necessary reliability of such components requires among others also maintenance of reproducible material properties. In this connection, a detailed knowledge of the reaction sintering process is of primary significance. The mechanism and the kinetics involved in the formation of both silicon nitride modifications in this process are affected by a number of variables and for this reason the concepts of the process have till recently been quite incomplete and contradictory. Only the results of some more recent experimental studies [1], [2], [3] allowed to formulate a more satisfactory description of the system of mechanisms involved in the nitridation of silicon [4], [5], [11].

On the basis of these studies it may be assumed that the following three main mechanisms probably take place in the nitridation of technical-grade purity silicon containing admixtures of iron and oxygen:

1. The mechanism of transport in gaseous phase involving the formation of gaseous SiO which, with participation of the liquid phase arising in the presence of iron and other impurities, reacts further with nitrogen producing α - Si_3N_4 whiskers (the so-called V-L-S mechanism) [2] [6].

2. The mechanism of surface nucleation and growth during which a compact layer of α - Si_3N_4 gradually grows over the silicon surface [1]. This mechanism plays a primary part only when the conditions for mechanism 1. cease to exist. Nitridation of high-purity silicon therefore starts with this second mechanism.

3. The mechanism involving transport via a compact Si_3N_4 layer, yielding primarily β - Si_3N_4 . Below the melting point of silicon (1410 °C) the process is probably controlled by diffusion of silicon to the surface of the Si_3N_4 layer [3] and therefore

proceeds very slowly. According to some authors [7] the presence of iron has an accelerating effect. The nitridation is considerably promoted above the melting point of silicon, which indicates to a change in the rate-controlling step.

Of considerable significance in the establishment of mechanisms of heterogeneous reactions between solids and gases is the study of the relationship between the kinetics and the partial pressure of the reacting gaseous component. This relationship is usually pronounced in cases when a boundary process is the rate-controlling one (sorption, chemical reaction). Very few such measurements have so far been carried out in the study of nitridation of silicon.

Atkinson [1] found that the rate of nitridation of pure silicon in the initial stage of the growth of nuclei is a linear function of nitrogen pressure which implies that physical adsorption of nitrogen is the rate-controlling step under these conditions. Also in the initial stages of nitridation of technical-grade silicon the nitridation rate can be influenced within certain limits by nitrogen pressure, which is made use of in practice for slowing down the exothermic reaction in this stage [8]. Guzman [9] has described acceleration of the reaction sintering of silicon nitride by raising the nitrogen pressure up to 1 MPa.

Preliminary experiments by the present author [4] indicated that in the progressed stage of silicon nitridation at temperatures below its melting point the effect of nitrogen pressure on the nitridation rate and on the ratio of α/β -Si₃N₄ in the product was within the range of 0.1 to 5 MPa indistinct, whereas above the melting point an increase in nitrogen pressure was responsible for accelerating the reaction and for increasing the proportion of β -Si₃N₄. No difference between the behaviour of pure and technical-grade silicon has been established in this case.

On the basis of these results a more detailed investigation of the kinetics of the final stage of nitridation of silicon at temperatures above its melting point and of the relationship between the kinetic constant and nitrogen pressure was undertaken with the aim of verifying the existing conceptions of the mechanism involved under these conditions, in particular with respect to the nature of the rate-controlling step.

EXPERIMENTAL

The method

The technical-grade silicon employed in the experiments was treated by dry grinding to a specific surface of 1.15×10^3 m²/kg (measured by nitrogen adsorption) which corresponds to a mean particle size of about 2 μ m. In the ground state the silicon contained about 3.5% impurities (Table I).

Under a pressure of 105 MPa the powder was pressed into pellets weighing about 1 g, which had an apparent density of 1.50×10^3 kg/m³. The pellets were

Table I - Chemical composition of powdered silicon

SiO ₂	96.49 %	MnO	0.020 %
Fe ₂ O ₃	1.06	CaO	0.081
Al ₂ O ₃	1.68	MgO	0.020
TiO ₂	0.380	Na ₂ O	traces
CuO	0.008	K ₂ O	0.010

brought into the final reaction stage by preliminary nitridation at 1300 °C under atmospheric pressure in nitrogen which contained 5% by vol. H₂, 6 ppm O₂, 100 ppm H₂O and at a linear rate of gas flow of about 1.5 cm/min through the furnace. The furnace was of all-metal design provided with molybdenum heating elements. The nitridation was carried out up to a mean weight gain $\varphi_0 = 34.4\%$, which corresponds to transformation degree $x_0 = 0.517$.

The final nitridation was carried out in an autoclave using induction heating. The pre-nitrided pellets were nitrided at 1440 °C in a static atmosphere of nitrogen of 99.999% N₂ purity under a pressure of 0.1 to 2.1 MPa for periods of 10 to 90

Table II

The effect of nitrogen pressure on the kinetics of nitridation of technical-grade silicon at 1440 °C

Pressure [MPa]	Time [min]	φ [%]	x	\bar{x}	$(1 - \bar{x})^{\frac{1}{3}} - 1$	$3R_0^2 k$	$\log 3R_0^2 k$
0.1	10	38.2	0.575	0.120	-0.0417	3.80×10^{-3}	-2.4202
	20	41.4	0.619	0.211	-0.0760		
	30	—	—	—	—		
	40	46.9	0.705	0.390	-0.1520		
	60	—	—	—	—		
	90	57.3	0.862	0.715	-0.3420		
0.2	10	39.5	0.595	0.163	-0.0574	5.58×10^{-3}	-2.2534
	20	—	—	—	—		
	30	48.1	0.724	0.430	-0.1706		
	40	15.2	0.771	0.526	-0.2202		
	60	56.5	0.850	0.669	-0.3222		
	90	61.4	0.924	0.842	-0.4596		
0.4	10	41.5	0.624	0.221	-0.0799	7.83×10^{-3}	-2.1062
	20	47.2	0.710	0.400	-0.1567		
	30	51.7	0.778	0.540	-0.2280		
	40	55.6	0.837	0.663	-0.3040		
	60	61.0	0.918	0.831	-0.4473		
	90	63.7	0.959	0.915	-0.5610		
0.6	10	—	—	—	—	9.31×10^{-3}	-2.0310
	20	49.2	0.740	0.461	-0.1862		
	30	—	—	—	—		
	40	58.5	0.881	0.753	-0.3724		
	60	62.9	0.946	0.888	-0.5187		
	90	64.8	0.975	0.948	-0.6270		
1.1	10	45.3	0.682	0.342	-0.1300	12.6×10^{-3}	-1.8996
	20	53.0	0.798	0.581	-0.2520		
	30	58.7	0.884	0.795	-0.3780		
	40	62.0	0.933	0.862	-0.4832		
	60	64.2	0.956	0.930	-0.5880		
	90	64.9	0.978	0.955	-0.6450		
2.1	10	47.6	0.716	0.413	-0.1620	14.4×10^{-3}	-1.8408
	20	55.6	0.837	0.662	-0.3025		
	30	60.1	0.916	0.826	-0.4425		
	40	63.5	0.956	0.909	-0.5500		
	60	64.9	0.977	0.951	-0.6305		
	90	—	—	—	—		
Initial state		34.4	0.517	0.0	0.0		

minutes. In each experiment 8 pellets were nitrided in a graphite crucible the inside of which was coated with boron nitride.

The total weight gain of the individual pellets was determined and in selected cases the morphology was examined on polished sections and the α - and β - Si_3N_4 contents were determined semiquantitatively by X-ray diffraction [4].

The total weight gain φ established was expressed for the individual pellets as the normalized conversion degree \bar{x} which specifies the conversion with respect to the prenitrided state as the initial one and which is defined by the formula (1)

$$\bar{x} = \frac{\varphi - \varphi_0}{\varphi_{\text{th}} - \varphi_0} \quad (1)$$

where φ_{th} is the theoretical weight gain corresponding to total conversion of silicon to silicon nitride (66.46%).

The time dependence of \bar{x} measured at 1440 °C and under various nitrogen pressures was evaluated according to equations for reaction on spherical reaction boundaries on the assumption that the process is rate-controlled by

- transport through a layer of products (parabolic kinetics)
- a process on the reaction boundary (linear kinetics).

In the first case one may assume the validity of the Carter's equation, while for the latter case, equation [4] has been derived in the form

$$(1 - \bar{x})^{1/3} - 1 = 3R_0^2kt \quad (2)$$

which is similar to the Jander's equation; k is a rate constant and R_0 is a constant characterizing the particle size.

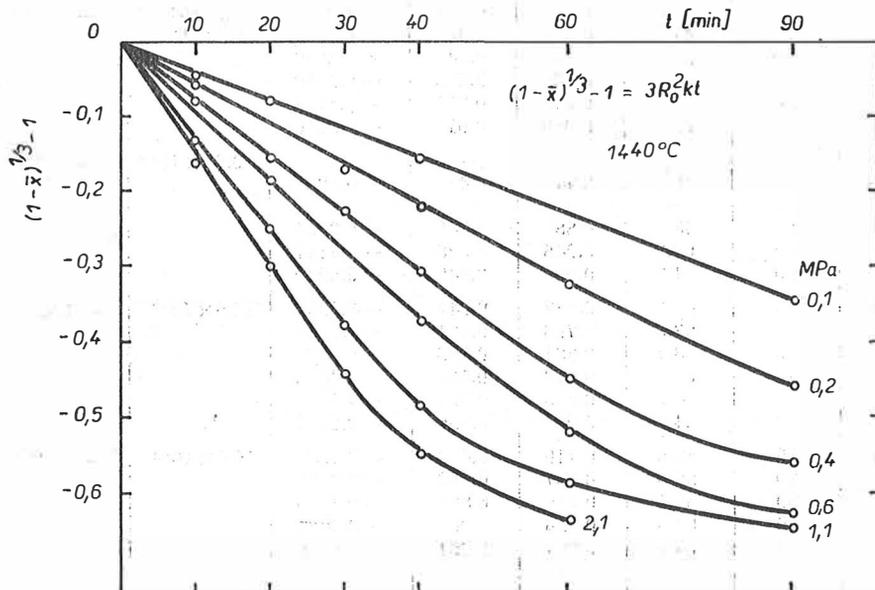


Fig. 1. The presentation of the experimental data from Table II constructed by means of the kinetic equation (2).

From the slope of isobars satisfying the respective kinetic equation, the dependence of the rate constant k on nitrogen pressure can be evaluated even in the case when the rate constant itself cannot be calculated because the multiplying constant R_0 is unknown. In the case of equation (2) the slopes have the value $3R_0^2k$ and therefrom

$$3R_0^2k = ap_{N_2}^n \quad (3)$$

or in a logarithmic form

$$\log 3R_0^2k = n \log p_{N_2} + \log a \quad (4)$$

where n is a constant characterizing the dependence of the rate constant on nitrogen pressure and can be evaluated graphically.

The results

The experimental data are summarized in Table II listing the mean weight gains obtained in the individual experiments, and the corresponding \bar{x} values. For the individual \bar{x} also the corresponding values of the left-hand side of equation (2) (which fits best to the experimental data) are given in Table II, as well as the values of slopes of the individual isobars and of their logarithms.

The experimental data from Table II are plotted in the diagram in Fig. 1. Fig. 2 shows the dependence of the rate constant on nitrogen pressure according to equation (4). Fig. 3 shows the content of α - and β - Si_3N_4 vs. nitrogen pressure during nitridation. Fig. 4 a-f are micrographs of polished sections illustrating the effect of nitrogen pressure on the course of nitridation.

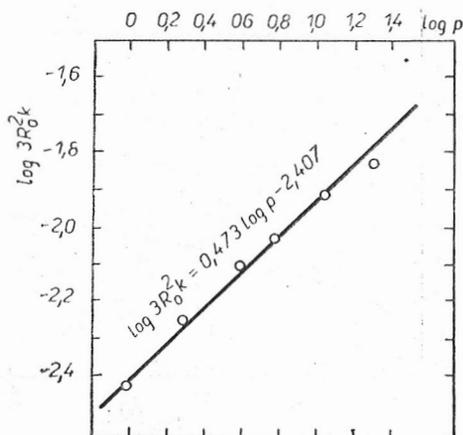


Fig. 2. Linear kinetic constant vs. nitrogen pressure.

CONCLUSION

Investigation of the time course of the final stage of silicon nitridation above its melting point and of the relationship between this process and the nitrogen pressure has allowed the following conclusions to be made:

1. The kinetics of the process is approximately linear.
2. Within the range being studied, the rate constant is a function of the square root of nitrogen partial pressure.
3. The content of β - Si_3N_4 being formed increases with increasing nitrogen pressure, while the content of α - Si_3N_4 remains constant.

These findings indicate above all that the effect of nitrogen pressure under these conditions is restricted to the dominating mechanism of β - Si_3N_4 formation and that the mechanism of α - Si_3N_4 formation is therefore different (Fig. 3).

The linear kinetics of nitridation above the melting point of silicon indicates that under these conditions the nitridation is controlled by the process on the reaction boundary. The layer of reaction products coating the reacting silicon grains in the final stage of nitridation (Fig. 4) therefore does not act as a diffusion barrier under these conditions.

The deviation of the linear course, apparent as a slow-down of the process at its end (Fig. 1) is caused by the presence of coarse silicon grains.

Since, according to Sieverts [10], the solubility of biatomic gases in molten metals is directly proportional to $p^{1/2}$, the established direct proportionality of the kinetic constant to the square root of the nitrogen partial pressure allows to assume that under the given conditions the reaction is controlled by dissolution of nitrogen in liquid silicon, which is accompanied by dissociation of the molecular nitrogen. The decreasing dependence of the process rate on nitrogen pressure, observed in the region above 1 MPa, probably indicates that the chemical reaction takes over the control of the process.

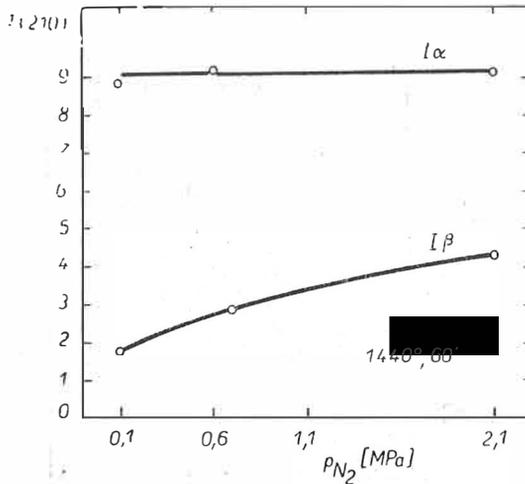


Fig. 3. The effect of nitrogen pressure on the phase composition of Si_3N_4 .

Acknowledgement

The author wishes to express his gratitude to the Institute of Metallic Materials of the Slovak Academy of Sciences in Bratislava, in particular to Ing. A. Schweighofer, CSc., and to Ing. S. Kúdela, CSc., for their co-operation in the experiments.

References

- [1] Atkinson A. et al.: J. Amer. Soc. 59, 285 (1976).
- [2] Elias D. P., Lindley M. W.: Powder Metallurgy Internat. 8, 162 (1976).
- [3] Jennings H. M.: Thesis, Brown University, 1975.
- [4] Kurtev B.: Thesis, VÚEK, Hradec Králové 1978.
- [5] Gugel E. et al.: Ber. Dt. Keram. Ges. 56, 10 (1979).
- [6] Gribkov et al.: Kristallografia 16, 982 (1971).
- [7] Horsley R. F.: Thesis, University of Leeds 1971.
- [8] Kurtev B., Tláškal M.: Czechoslovak Patent 175124 (1976).
- [9] Guzman I. Ja.: Ogněupory [7] 34 (1975).
- [10] Sieverts A.: Z. Metallkunde, 21, 37 (1929).
- [11] Riley F. L. in: Nitrogen Ceramics (red. F. L. Riley), p. 265, Noordhoff, Leyden 1977.

VLIV TLAKU DUSÍKU NA NITRIDACI KŘEMÍKU

Boris Kurtev

Výzkumný ústav elektrotechnické keramiky, Hradec Králové

Práce se zabývá studiem vlivu tlaku dusíku na závěrečné stadium nitridace výlisků z práškového křemíku technické čistoty při teplotách nad bodem tání křemíku.

Výlisky, přednitridované při 1300 °C na stupeň přeměny 0,5, byly nitridovány při 1440 °C v rozmezí tlaků 0,1 až 2,1 MPa po dobu 10 až 90 min. Analýza fázového složení, mikroskopické vyšetření a vyhodnocení přírůstků hmotnosti podle parabolických a lineárních kinetických rovnic pro kulovou symetrii reakčního rozhraní vedlo ke zjištěním:

1. Kinetika nitridace je za těchto podmínek lineární.

2. Rychlostní konstanta je ve sledovaném rozmezí funkcí druhé odmocniny parciálního tlaku dusíku.

3. S rostoucím tlakem se zvyšuje podíl vznikajícího β -Si₃N₄, zatímco obsah α -Si₃N₄ zůstává stálý.

Z toho vyplývá, že vliv tlaku dusíku je za těchto podmínek omezen jen na dominující mechanismus vzniku α -Si₃N₄ a že mechanismus vzniku α -Si₃N₄ je odlišný (obr. 3). Lineární kinetika nitridace nad bodem tání křemíku (obr. 1) naznačuje, že řídicí úlohu má za těchto podmínek proces na reakčním rozhraní.

Jelikož podle Sievertse [10] je rozpustnost dvouatomových plynů v roztavených kovech přímo úměrná $p^{1/2}$, lze ze zjištěné přímé úměrnosti kinetické konstanty a $p_{N_2}^{1/2}$ (obr. 2) usoudit, že řídicím dějem reakce je za těchto podmínek rozpouštění dusíku v kapalném křemíku, spojené s disociaí. Snížení závislosti rychlosti děje na tlaku dusíku, které lze pozorovat v oblasti nad 1 MPa, pravděpodobně znamená, že řídicí úlohu začíná přebírat chemická reakce.

Obr. 1. Vyjádření experimentálních dat z tabulky II pomocí kinetické rovnice (2).

Obr. 2. Závislost lineární kinetické konstanty na tlaku dusíku.

Obr. 3. Vliv tlaku dusíku na fázové složení Si₃N₄.

Obr. 4. Vliv tlaku dusíku na nitridaci křemíku při 1440 °C. Leštěné nábrusy, 250 ×.

a) atmosférický tlak, 10 min., b) atmosférický tlak, 60 min., c) 0,6 MPa, 10 min., d) 0,6 MPa, 60 min., e) 2,1 MPa, 10 min., f) 2,1 MPa, 60 min.

ВЛИЯНИЕ ДАВЛЕНИЯ НА АЗОТИЗАЦИЮ КРЕМНИЯ

Борис Куртев

Научно-исследовательский институт электротехнической керамики, Гradeц Кралове

Автором проводится исследование влияния давления азота на заключительную стадию азотирования прессаготовок из порошкообразного кремния технической чистоты при температурах выше температуры плавления кремния.

Прессаготовки, азотированные предварительно при температуре 1300 °C до степени превращения 0,5, азотировали при 1440 °C в пределах давлений 0,1—2,1 МПа во время 10—90 минут. На основании анализа фазового состава, микроскопического исследования и оценки прироста веса согласно параболическим и линейным кинетическим уравнениям для шаровой симметрии реакционного раздела установили:

1. Кинетика азотирования является при таких условиях линейной.

2. Константа скорости в исследуемом диапазоне является функцией второго корня парциального давления азота.

3. С растущим давлением повышается доля образующегося β - Si_3N_4 , в то время как количество α - Si_3N_4 остается постоянным. Из этого следует, что влияние давления азота при таких условиях касается только преобладающего механизма образования β - Si_3N_4 и что механизм образования α - Si_3N_4 является разным (рис. 3).

Линейная кинетика азотирования выше температуры плавления кремния (рис. 1) показывает, что ведущую роль при таких условиях играет процесс на реакционном разделе.

Так как согласно Сивертсу [10] растворимость двухатомных газов в расплавленных металлах прямо пропорциональна $p^{1/2}$, можно на основании установленной пропорциональности кинетической константы и $p_{\text{N}_2}^{1/2}$ (рис. 2) выводить, что управляющим процессом реакции при таких условиях является растворение азота в жидком кремнии, связанное с диссоциацией. Понижение зависимости скорости процесса от давления азота, которое можно заметить в области выше 1 МПа, со всей правдоподобностью значит, что управляющая роль процессом начинает переходить к химической реакции.

Рис. 1. Выражение экспериментальных данных из таблицы II при помощи кинетического уравнения (2).

Рис. 2. Зависимость линейной кинетической константы от давления азота.

Рис. 3. Влияние давления азота на фазовый состав Si_3N_4 .

Рис. 4. Влияние давления азота на азотирование кремния при 1440 °С. Полирование анилифы, увеличение в 250 раз; а) атмосферное давление, 10 мин.; б) атмосферное давление, 60 мин.; в) 0,6 МПа, 10 мин.; д) 0,6 МПа, 60 мин.; е) 2,1 МПа, 10 мин.; ф) 2,1 МПа, 60 мин.

The Effect of Nitrogen Pressure on Nitridation of Silicon

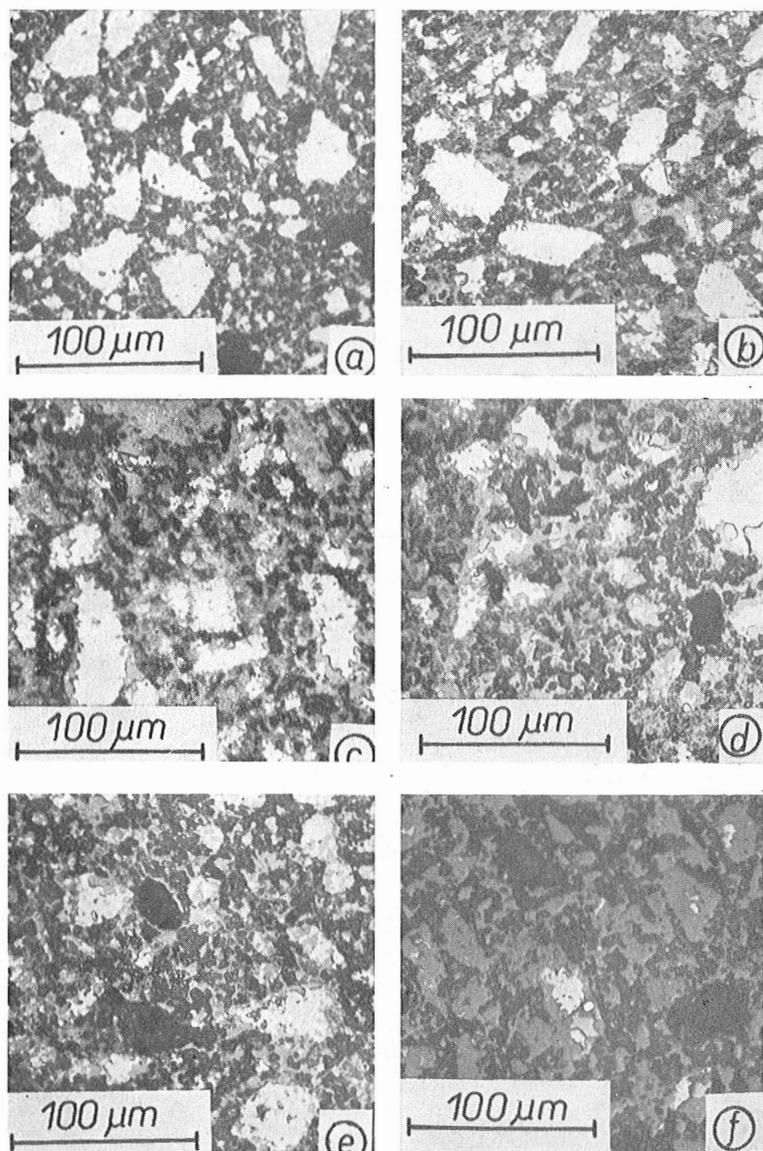


Fig. 4. The effect of nitrogen pressure on nitridation of silicon at 1440 °C. Polished sections, 250×; a) atmospheric pressure, 10 min., b) atmospheric pressure, 60 min., c) 0.6 MPa, 10 min., d) 0.6 MPa, 60 min., e) 2.1 MPa, 10 min., f) 2.1 MPa, 60 min.