

# The influence of the various transport properties of the nitriding atmosphere on the formation of reaction-bonded $\text{Si}_3\text{N}_4$

## Part 2 *Thermal conductivity and thermal diffusivity*

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The thermal conductivities of nitrogen gas containing various second component gases have been calculated, and the importance of the gaseous phase in thermal conduction during nitridation has been described. Thermal segregations by thermal diffusion inside the nitriding furnace containing the various binary gas mixtures have also been calculated and the influence this effect has on the formation of reaction-bonded  $\text{Si}_3\text{N}_4$  is discussed. In  $\text{N}_2\text{-H}_2$  and  $\text{N}_2\text{-He}$  gas mixtures, nitrogen diffuses down the temperature gradient, leading to a lower concentration of nitrogen and a higher concentration of hydrogen or helium around the silicon compact than expected from the initial composition, whereas in  $\text{N}_2\text{-Ar}$  gas mixtures argon diffuses down the temperature gradient, leading to opposite results from the above; such phenomena affect the overall reaction rate and other transport properties. The conclusions obtained have been used in explaining previous experimental results obtained under various nitriding atmospheres.

### 1. Introduction

The variation in the diffusivity and viscosity of the nitriding atmosphere by addition of various second-component gases during the nitriding reaction between a silicon compact and nitrogen gas, and the influence of this variation on the formation of microstructures, were discussed in Part 1 [1] of this study. However, the question still remains, especially in Mangel's work [2], of why nitriding atmospheres containing helium had higher nitriding rates and resulted in more complete nitridation, in spite of the inert properties of helium gas. It was also unsatisfactory to explain the reports of Dagleish *et al.* [3] in which, despite the perfect removal of a silica film from the surface, the single crystal slices of silicon nitrided in a "flowing" atmosphere of  $\text{N}_2/\text{H}_2$  formed a deeper layer of nitride which was almost four times deeper than a layer of nitride formed in a "flowing" or "static" atmosphere of pure nitrogen. Therefore, among the various transport properties of a nitriding atmo-

sphere, consideration of only diffusivity and viscosity is not enough to explain perfectly all the phenomena occurring on addition of hydrogen and/or helium. Accordingly, in this study, the influence of the variation of thermal conductivity and thermal diffusivity in the nitriding atmosphere by addition of hydrogen, helium and argon on the formation of microstructures, has been considered. Particular emphasis has been placed on considering the nitrogen concentration distribution caused by the temperature gradient inside the nitriding furnace during the nitridation process and then discussing the effect these phenomena have on the overall rates and other transport properties. As far as we know, no consideration has been given to the influence of the nitrogen concentration gradient on the nitridation process.

### 2. Computation of thermal conductivities and segregations for binary gas mixtures

For the present purpose, thermal conductivities and segregations for binary gas mixtures containing

different proportions of nitrogen gas to second-component gases (hydrogen, helium and argon), were calculated using the basic equations, which were derived from the Chapman–Enskog theory [4–6].

Thermal conductivities of pure gases which are dilute gases, i.e. low density gases at normal pressure, were calculated using the following equations:

for monatomic gases,

$$\kappa = (15R/4M)\eta \quad (1)$$

and for polyatomic gases

$$\kappa = |C_p + (9R/4M)|\eta \quad (2)$$

where  $C_p$  is the specific heat capacity at constant pressure,  $R$  the gas constant,  $M$  the molecular weight of the gas, and  $\eta$  the viscosity of the gas which was calculated using Equation A3 in Part 1 [1] of this study. In order to compute the thermal conductivities of binary gas mixtures, the following equation was used:

$$\kappa_{\text{mix}} = \frac{\sum_i X_i \kappa_i M_i^{1/3}}{\sum_i X_i M_i^{1/3}} \quad (3)$$

where  $X_i$  is the mole fraction of component  $i$  having molecular weight  $M_i$  and intrinsic thermal conductivity  $\kappa_i$ .

The thermal segregations for the binary gas mixtures of various compositions in a closed furnace system over different temperature regions, i.e. the hottest region (1653 K) and coldest region (295 K), were computed using the same basic equations which have been outlined in Section 3, in order to explain thermal diffusion phenomena in the reaction furnace during nitridation.

### 3. Results and discussion

In a system with a temperature gradient, two types of flux are envisaged: (1) an energy flux (thermal conduction), (2) a mass flux (thermal diffusion). First of all, the importance and mechanism of thermal conduction by the gaseous phase in a silicon compact during nitridation are described and then the influence of the thermal segregation phenomena on the overall rates of the nitridation reaction, are discussed.

#### 3.1. Thermal conduction

The thermal conduction in the nitriding process plays a significant role since the large amount of

heat given off due to the highly exothermic nature of the nitriding reaction, makes close temperature control of the process difficult and the resultant temperature gradients influence the rate of reaction. Various investigators have studied this problem with the consensus of opinion [2] being that the strength-determining factor in RBSN is large pores which resulted from the melting of particles of unreacted silicon when the temperature of the body exceeded the melting point of silicon ( $\approx 1420^\circ\text{C}$ ) at some point, due to the exothermic nature of the nitridation process. Atkinson and Evans [7] have reported that temperature gradients as high as  $38^\circ\text{C}$  exist between the interiors of large silicon compacts and the ambient temperature of the furnace during nitriding, and that the size of the compact will determine the magnitude of the temperature excess over that of the surroundings. Other things being equal, the larger the compact the greater will be the excess. Therefore, rapid dissipation of the excess heat generated by the nitriding exotherm from the compact into the nitriding atmosphere is essential to the fabrication of high quality RBSN material.

The thermal conduction inside the silicon compact during the course of the nitriding run is expected to occur as follows. The pressed silicon compact consists of a gaseous continuous phase containing individual silicon particles which are in point contact with their nearest neighbours. Here the principal resistance to the overall rate at which heat, generated by the nitriding exotherm, is conducted through the matrix, is in the vicinity of the points of contact of silicon particles because heat is transferred from a particle to its neighbours by conduction through the gas adjacent to the point contacts. Under these conditions, the effective thermal conductivity of the porous silicon compact depends on the thermal conductivity of the gas but not on the thermal conductivity of the solid. Although, by sintering a pressed powder compact in argon before nitridation, silicon particles are joined by weak necks of silicon or silica derived from the oxide surface layer present on the original particles, the necks between the silicon particles are destroyed during the early stages of nitridation, resulting in the gaseous phase dependence of heat conduction.

On the basis of the above consideration, thermal conduction by a gaseous phase seems to be a major role in dissipating the heat generated by

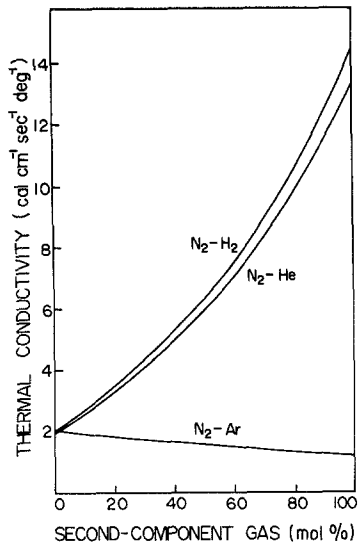


Figure 1 Variation of thermal conductivity of the nitriding atmosphere with additions of the various second-component gases at 1 atm and 1653 K.

the nitriding exotherm from the compact into the surrounding atmosphere, and this suggests that, in order to allow the heat to be dissipated rapidly, the nitriding atmosphere should contain a gaseous component which can increase the thermal conductivity of the nitriding atmosphere. Fig. 1 gives the calculated values of thermal conductivities of nitriding atmospheres which contain various mole fractions of nitrogen to hydrogen, helium and argon at 1 atm pressure and 1653 K. This figure shows that when hydrogen and helium are present in large concentrations, they can increase the thermal conductivity of the nitriding atmosphere, whereas the addition of argon would retard heat dissipation because it decreases the thermal conductivity of the atmosphere.

When present in small concentration, the second-component gases can also change the thermal conductivity of the nitriding atmosphere being inside the silicon compact, due to the pile up of second-component gases, which is the effect discussed in the Part 1 [1]. That is, when the initial reaction of silicon nitridation proceeds at a much too rapid rate, the resulting pressure gradient between the outside and inside of the compact causes viscous flow of the nitriding atmosphere through the pores into the silicon compact. The second-component gas, as well as nitrogen gas, then permeates into the compact but the consumption of only nitrogen gas builds up

the second-component gases inside the silicon compact until the resulting opposed concentration gradient is balanced by the diffusion which tends to equalize the composition. Since at a faster reaction rate the concentration of the second-component gas inside the compact can be increased far above the initially added composition, the thermal conductivity of the nitriding atmosphere being inside the silicon compact can be increased more than that expected from the amounts of hydrogen or helium added initially, and it can be decreased more than that expected from the added amount of argon.

Mangels [2] performed the nitrogen-demand nitriding runs in which as the nitriding reaction proceeds, nitrogen is consumed and the nitriding gas is then allowed to enter the furnace to regain the constant control pressure, and the furnace temperature is increased until another pressure drop is detected and nitriding gas is again allowed to enter the furnace. This sequence will repeat itself until the maximum programmed temperature is reached.

Mangels [2] has reported that the microstructure of RBSN prepared using the variable H<sub>2</sub>/N<sub>2</sub> and the variable He/N<sub>2</sub> atmospheres are uniform with no evidence of uncontrolled nitriding, whereas the 100% nitrogen and variable argon atmospheres result in structures which have a large porosity surrounded by large grains of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, which are the typical features of silicon meltout resulting from uncontrolled nitriding. Mangels has explained that the H<sub>2</sub>/N<sub>2</sub> and He/N<sub>2</sub> mixtures would allow the heat generated by the nitriding exotherm to be dissipated from the compact into the nitriding atmosphere, and that the more complete nitridation and generally higher nitriding rate obtained by using the variable atmosphere are attributable to more reduced partial pressures of nitrogen, which has been noted earlier by Atkinson *et al.* [8].

Despite all the above explanations, however, an important question still remains in Mangels's work. For example, the variable helium atmosphere has the highest nitriding rate and the highest strength was obtained in all the various nitrogen-demand nitriding runs. Moreover, despite the fact that helium does not have the function of aiding the removal of the reaction-inhibiting silica film which hydrogen has, even the constant helium atmosphere has a high nitriding rate. That is, the higher nitriding rates and more complete

nitridations were obtained by using helium rather than other gases as the variable atmosphere. Accordingly, the given results cannot be explained solely by the early notes of Atkinson *et al.* [8] who found that, using isothermal nitriding runs, more complete nitridation was obtained with reduced partial pressures of nitrogen.

Furthermore, since the higher the reaction temperature the higher the nitriding rate becomes [8], the presence of lower thermal conductivity gases than nitrogen gas in the nitriding atmosphere would retard the dissipation of the heat generated by the exothermic nitriding reaction, and this would increase the temperature of the compact, hence resulting in a higher nitriding rate. However, Fig. 1 shows that the thermal conductivity of argon is less than that of nitrogen, which in turn is less than that of helium, which is slightly less than that of hydrogen. Therefore, this can explain the formation of RBSN with uniform microstructure but cannot explain the reason for the increase in nitridation rates when using helium.

On the other hand, this question can be solved if a more reduced partial pressure of nitrogen around the silicon compact is obtained with additions of helium compared to other gases of the same composition. Therefore, the thermal diffusion effect inside the nitriding furnace during nitridation has been considered.

### 3.2. Thermal diffusion

Diffusion is most frequently associated with a nonuniformity of composition, but it can also arise from nonuniformity of other properties, in particular that of temperature and pressure. Enskog and Chapman [4], independently developed the kinetic theory of gases in nonuniform states, and showed that in general a temperature gradient should cause diffusion. Because of thermal diffusion, when a temperature gradient is set up in a mixture which is initially uniform in composition, a concentration gradient develops, and this increases until the separating effect of thermal diffusion is balanced by the diffusion which tends to equalize the composition. Thus, in the steady state where there is nonuniformity of temperature, there is nonuniformity of composition. In gas mixtures at normal temperatures the heavier molecules usually diffuse down the temperature gradient, leading to a higher concentration in the colder region than in the warmer.

For example, when the nitridation of a silicon

compact is performed at 1653 K in a closed tube or cold wall furnace, whose coldest regions are maintained at 295 K, and which contains nitrogen of  $X_A^0$  mole fraction and a second component gas of  $(1 - X_A^0)$  mole fraction, there will be a mass flux of gas inside the tube due to the temperature gradient, resulting in a concentration gradient. Then a mass flux of nitrogen gas is given by

$$J_A^T = -cD_A^T(d\ln T/dz) \quad (4)$$

where  $c$  is the gas concentration,  $D_A^T$  the thermal diffusivity of component A which is nitrogen here, and  $z$  the diffusion distance. The thermal diffusivity of the second-component as B (hydrogen, helium and argon) is numerically the same but of opposite sign to component A:

$$D_B^T = -D_A^T. \quad (5)$$

However, the resulting concentration gradient is opposed by the ordinary diffusion which tends to equalize composition. The opposed mass flux of nitrogen gas due to the concentration gradient is

$$J_A^D = -cD_{AB}dx_A/dz \quad (6)$$

where  $D_{AB}$  is the interdiffusion coefficient, and  $D_{AB} = D_{BA}$ . The values of  $D_{AB}$  for various binary gas mixtures were calculated using Equation A2 in Part 1 [1]. Now, when a steady state is reached, there will be no net flux; hence

$$J_A^T + J_A^D = -cD_{AB}[(D_A^T/D_{AB})(d\ln T/dz) + (dx_A/dz)] = 0. \quad (7)$$

Here the ratio  $D_A^T/D_{AB}$  is known as the thermal diffusion ratio,  $k_T$ ; inserting this into Equation 7 gives, for the thermal diffusion ratio,

$$k_T = -(dx_A/dz)/(d\ln T/dz) \quad (8)$$

Since the thermal diffusion ratio,  $k_T$ , is a very complex function of temperature, concentration and molecular weight, and depends parametrically on the force law of the molecules, the computational procedure is cumbersome. In this study, the higher approximation to  $k_T$  given by Hirschfelder *et al.* [5] was used for computation, and  $D_A^T$  can be estimated from the relation  $D_A^T = k_T D_{AB}$ ; the introduction of the equations is omitted here because of its complexity. The computed values of the thermal diffusion ratio have been plotted in Fig. 2 for binary gas mixtures (nitrogen, hydrogen helium and argon) as a function of composition. It can be found from this figure that in  $N_2-H_2$

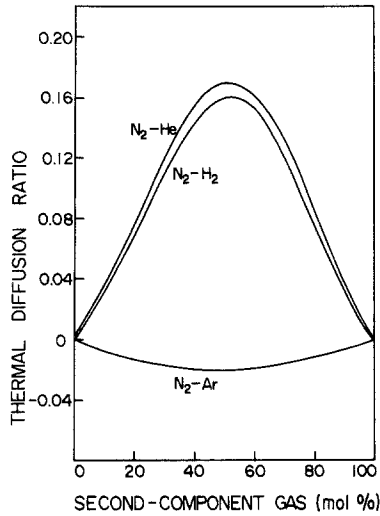


Figure 2 Thermal diffusion ratio as a function of composition for the various nitriding atmospheres of a binary gas mixture at  $\bar{T} = 620$  K.

and  $N_2$ -He mixtures,  $k_T$  is positive, and increases with additions of up to 50 mol% hydrogen or helium, then decreases above 50 mol%, and helium increases  $k_T$  slightly more than hydrogen, whereas in the  $N_2$ -Ar mixture,  $k_T$  is negative, and increases negatively with the amount of argon, then decreases above 50 mol%, and the degree of change of  $k_T$  with addition of argon is smaller than that on addition of helium or hydrogen. The meaning of the sign of  $k_T$  is as follows. The generally adopted convention [4-6] is that when  $k_T$  is positive, component A migrates to the cold region; when  $k_T$  is negative component A moves to the hot region. Therefore, in  $N_2$ - $H_2$  and  $N_2$ -He mixtures, nitrogen gas migrates to the hot region, whereas in  $N_2$ -Ar mixtures nitrogen moves to the cold region. These results are consistent with the fact [4-6] that the heavier molecules usually diffuse down the temperature gradient. The resultant steady state difference in composition between the two regions may be obtained by integrating Equation 8 for a mean temperature of  $\bar{T}$ .

$$\Delta x_A = x_A(T'') - x_A(T') = -k_T(\bar{T}) \ln(T''/T'), \quad (9)$$

where  $T''$  and  $T'$  are, respectively, the temperature of the hot and cold regions of the furnace. Usually the mean temperature is calculated from Equation 5:

$$\bar{T} = |T''T'/(T'' - T')| \ln(T''/T'). \quad (10)$$

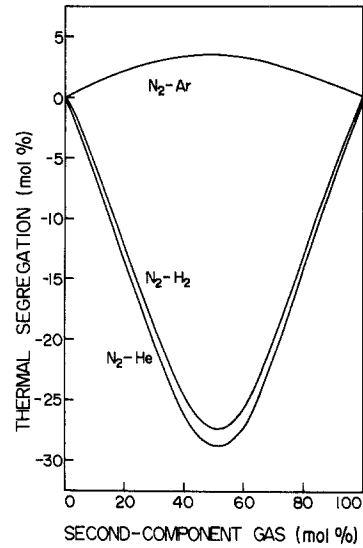


Figure 3 The order of magnitude of thermal segregation as a function of composition of the second-component gas in the various nitriding atmospheres at  $T' = 295$  K and  $T'' = 1653$  K.

For present interest, inserting  $T'' = 1653$  K and  $T' = 295$  K, yields  $\bar{T} = \sim 620$  K.

Finally, the estimated order of magnitude of thermal diffusion, calculated for various binary gas mixtures from Equation 9, are shown in Fig. 3. This figure shows that, during the nitriding reaction in the tube furnace, the steady state difference in nitrogen concentration between the hot and cold regions increases with addition of up to 50 mol% second component gas, and then decreases with above 50 mol%, and the situation in the  $N_2$ -Ar mixture is contrary to that in  $N_2$ - $H_2$  and  $N_2$ -He mixtures. Of course, the calculated order of magnitude of thermal segregation is incorrect in several respects and may be different from the real values. First of all, the calculation was made using equations which were derived from the ideal model, considering a binary gas mixture contained in two large vessels connected to each other with a narrow tube which had a diameter small enough to eliminate convection currents substantially. Accordingly, the real phenomena occurring inside the reaction furnace are too complex to analyse correctly and the degree of change in concentration around the silicon compact caused by the thermal diffusion effect will be very different according to the temperature distribution in the furnace used. For example, the magnitude of change in concentration of the hot region depends on the volume

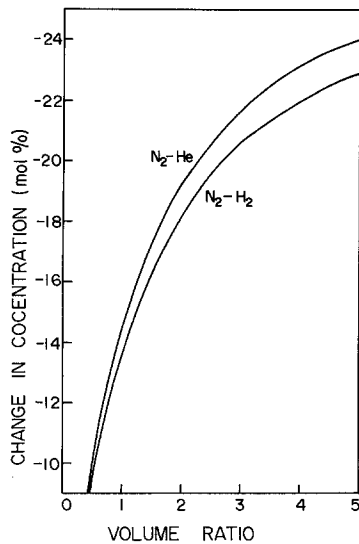


Figure 4 Change in nitrogen concentration around the hot region as a function of the volume ratio of the cold region to the hot region for 1:1  $N_2$ -He and  $N_2$ - $H_2$  mixtures at  $T' = 295$  K and  $T'' = 1653$  K.

ratio of the cold and hot regions. If the volumes of the cold and hot regions are respectively,  $V'$  and  $V''$ , and  $x_A^0$  is the initial mole fraction of nitrogen before thermal segregation occurs, the following equation is established.

$$x_A^0 V' + x_A^0 V'' = x_A(T') V' + x_A(T'') V'' \quad (11)$$

From this equation and Equation 9, the change in concentration of the hot region can be deduced as follows:

$$x_A(T'') - x_A^0 = \Delta x_A V' / (V'' + V'). \quad (12)$$

The changes in concentration as a function of  $V'/V''$  for 1:1  $N_2$ -He and  $N_2$ - $H_2$  mixtures calculated using Equation 12 are shown in Fig. 4.

Since the degree of change in concentration caused by thermal diffusion is also affected by the condition of temperature distribution inside the nitriding furnace, thermal diffusion may be a disturbing factor, needing consideration in the comparison of the experimental results obtained from the nitriding furnace with different temperature distributions. In addition, only binary gas mixtures are considered in this study to avoid the complexity of further problems, but ternary gas mixtures can be also considered on the same basis.

On the other hand, Atkinson *et al.* [8] have

noted earlier the formation of different structures in RBSN with different nitrogen partial pressures. They found that the lower the nitrogen pressure the greater the mass of nitride eventually formed. They explained this behaviour with a nucleation and growth model, where the concentration of nuclei and their growth both depend on the nitrogen pressure. Therefore, the thermal diffusion effect predicts that, on addition of hydrogen or helium to nitrogen, more complete nitridation will be obtained from a more reduced nitrogen partial pressure around the silicon compact than that expected from the initial added composition. Because the thermal diffusion ratio of helium is greater than that of other gases, the reason why the nitriding runs with addition of helium have higher reaction rates and more complete nitridation than those with other gases of the same composition, is attributable to a greater fall in the partial pressures of nitrogen around the compact caused by the addition of helium rather than other gases. Since the steady state difference in concentration between the hot and cold regions depends on the temperature difference between the two regions and the gas composition of the nitriding atmosphere as shown in Fig. 3, thermal diffusion seems to have a significant effect on the nitriding runs in which large amounts of second-component gases are used.

Furthermore, an increase in the concentration of hydrogen and helium above the initially added composition, around the silicon compact makes the effects on viscosity and thermal conductivity more significant than those expected from the initially added amounts, whereas in the nitriding atmosphere containing argon, the decrease below the initial composition in the concentration of argon around the compact yields a less significant effect than that expected from the amount added.

All the above results explain Mangels' [2] experimental results, which showed that the variables helium atmosphere nitriding run had the highest nitriding rate and showed a more complete nitridation, and even the constant helium atmosphere had a high nitriding rate. However, despite the fact that the order of magnitude of the thermal diffusion in the  $N_2$ -He mixture is nearly the same as that in the  $N_2$ - $H_2$  mixture (as shown in Figs. 3 and 4), the constant helium atmosphere had a nitriding rate ( $28.69 \text{ g Si h}^{-1}$ ) surprisingly higher than that ( $17.6 \text{ g Si h}^{-1}$ ) of the variable hydrogen atmosphere (final gas composition 25%

H<sub>2</sub>/N<sub>2</sub>). This result can be explained by considering the starting composition of the variable hydrogen atmosphere (4% H<sub>2</sub>/N<sub>2</sub>) which is smaller than the starting composition for constant helium (7% He/N<sub>2</sub>). It seems, therefore, that for an understanding of the adding effect of the second component gas on the morphology formation of RBSN, attention must be focused on the first few minutes in which the rapid reactions take place; this attention was also emphasized in Part 1. In addition, particular consideration has to be given to the function of hydrogen in enhancing the rate of nitridation by assisting removal of the reaction-inhibiting silica film, and also the influence of the resultant reaction products on the nitridation process.

On the other hand, noticing that Mangels used a cold wall vacuum furnace for nitriding, a high concentration of nitrogen around a cold wall is expected to take place during the nitriding run. Accordingly, the nitriding atmosphere should contain a large amount of helium which can increase the molecular diffusivity, thermal diffusivity and conductivity, and contain a small amount of hydrogen which can assist in the removal of a reaction-inhibiting oxide film on the silicon surface.

The results reported by Dagleish *et al.* [3] can be explained as follows; they nitrided silicon single crystal slices free of native surface oxide under a "flowing" nitrogen + 12% hydrogen atmosphere, but the real concentration of hydrogen around the silicon slices may be far above 12% due to the thermal diffusion effect. Hence, the greatly increased partial pressure of hydrogen around the specimen decreases the viscosity and increases the thermal conductivity of the atmosphere more than expected, from the 12% hydrogen added, and this leads to the formation of a Si<sub>3</sub>N<sub>4</sub> layer with a more uniform microstructure, and a greater reduced partial pressure of nitrogen around the specimen results in the formation of a deeper layer of the nitride.

#### 4. Conclusion

When nitridation of a silicon compact is performed under a binary gas mixture, even when the added gas is inert relative to the nitriding reaction, this inert component gas plays an important role in the thermal conduction during nitridation when its thermal conductivity is different from that of nitrogen, and the concentration gradient of nitro-

gen is increased due to the temperature gradient in the nitriding furnace. Because of the thermal diffusion, nitrogen diffuses down the temperature gradient in the binary gaseous mixture containing helium or hydrogen, leading to a lower concentration of nitrogen within the uniform hot zone than in the cold zone; hence the increase in the rates of reaction on addition of hydrogen and/or helium is a greater fall in nitrogen partial pressure around the compact than expected from the initial composition, and then the relative increase in hydrogen or helium concentration above amount added around the silicon compact, will affect other transport properties of the nitriding atmosphere more effectively than expected from the added amount. However, since nitrogen diffuses up the temperature gradient in the binary gaseous mixture containing argon, leading to a higher concentration of nitrogen around the silicon compact than expected from the original composition, all phenomena occurring on addition of argon are, therefore, contrary to those occurring on addition of hydrogen or helium. All the above results are similarly applicable to the ternary gas mixtures.

Accordingly, such changes in the concentration of nitrogen have an important effect on the formation of the microstructure in RBSN, as illustrated in Atkinson's report, which described the final thickness or nitriding rate of the nitride was a function of the nitrogen pressure at which it was grown; the thick layers growing and the greater mass of nitride formed at low pressure. The above results, therefore, explain well the results of Mangel's work, that is, why the variable helium atmosphere exhibited the highest nitriding rate and uniform structure with optimum strength.

In addition, since the change in concentration around the silicon compact due to thermal diffusion depends on the volume ratio of the cold and hot regions, and the temperature distribution inside the furnace, thermal segregation may be a disturbing factor, needing consideration in the comparison of experimental results obtained in the nitriding furnaces with the different conditions. Since it also depends on the gas composition of the nitriding atmosphere, the effect of thermal segregation may be significant on the nitriding runs in which large amounts of second-component gases are used.

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