JOURNAL OF MATERIALS SCIENCE **26** (1991) 3380–3385

# The combustion synthesis of refractory nitrides

## Part II *The synthesis of niobium nitride*

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The self-sustaining combustion of niobium in a nitrogen atmosphere was investigated. The effect of initial porosity, nitrogen pressure, and the amount of added diluent on the combustion process and on the nature of the products of combustion was determined. Auxiliary investigations on the interaction between niobium and nitrogen were made under isothermal conditions. Results of X-ray analyses of these investigations are compared to those obtained under self-propagating reaction conditions.

## 1. Introduction

Over the past several years a variety of ceramic, metallic, and composite materials have been synthesized by the self-propagating high-temperature synthesis (SHS) method. Details of the nature of this method and its advantages and limitations have been given in two recent review articles [1, 2] and discussed in a recent symposium [3]. Although in most cases self-sustaining reactions are established between solids, they can also be obtained between a solid and a gas. Examples of the latter case include the synthesis of nitrides and hydrides. Recent investigations on the synthesis of nitrides by self-propagating reactions have been reported [4–8] and earlier accounts of the preparation of these materials have been discussed in the aforementioned reviews [1, 2]. Reactions between transition metals and nitrogen are so exothermic that a self-sustaining reaction front can be maintained at 1 atm gas pressure [6–8]. In contrast, reactions between other elements, such as silicon and nitrogen, cannot become self-sustaining unless the gas is maintained at high pressure ($\sim$ 500 atm) [5]. In part, the difference in behaviour between transition metals (e.g. Ti) and others (e.g. silicon) is related to the solubility of nitrogen in these materials. Unlike silicon, titanium can dissolve a significant amount of nitrogen ($\sim$ 24 at %). The exothermic dissolution of nitrogen facilitates the combustion process even at low gas pressure.

In a recent investigation on the combustion synthesis of titanium nitride, it was observed that the degree of conversion to the product depended on the initial density of the titanium samples [6]. This was shown to be the conseqence of melting of the titanium in the interior of the samples. Lower density samples exhibited more extensive melting and hence had a lower degree of conversion. Because niobium melts at a considerably higher temperature, it is anticipated that it will remain solid during combustion and thus the effect of density should be different than that of titanium. In this paper we report the results of the effect of reactant (Nb) density, nitrogen pressure, and level of dilution on the combustion synthesis of NbN.

## 2. Experimental materials and methods

In the experiments aimed at determining the effect of density of nitrogen pressure, the niobium powder used was obtained as a $-325$ mesh material. For the remaining experiments a 99.8% pure Nb powder was used. As in the first powder, the latter had a sieve classification of $-325$ mesh ($\leqslant 44$ μm). The nitrogen gas used in the present study had a 99.997% purity and reported levels of impurity of $O_2$, $H_2O$, and total hydrocarbons of 5, 3, and 0.5 p.p.m, respectively.

The interaction between Nb and $N_2$ was also investigated under isothermal conditions using a Cahn R-1000 continuous recording microbalance. In such experiments, 0.5 g loose niobium powder was placed in a 32 mm diameter quartz crucible and reacted isothermally with nitrogen gas at 1 atm pressure at a number of selected temperatures between 200 and 900 °C. The rate of heating (up to the desired temperature) was held constant at 10 °C $\min^{-1}$ for all experiments.

For combustion wave experiments, niobium powders were pressed into cylindrical compacts of diameter 19 mm and length 25 mm. Samples with relative densities in the range 57%–61% were prepared by varying the pressure of compaction. The combustion

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temperature was measured using W–5% Re/W–26% Re thermocouples inserted into the side of the cylindrical samples, and the velocity of the combustion wave was determined from the measured time interval between two established locations along the side of the samples as observed visually or with a video camera and a time code generator. Combustion of Nb was carried out under nitrogen pressures ranging from about 1–14 atm.

The nature of the product of combustion and the lattice parameters of the nitride and solid solution phases were determined through X-ray diffraction analysis.

## 3. Results and discussion

### 3.1. Isothermal nitridation of Nb

Fig. 1a and b show the weight gain versus time for niobium powders heated at temperatures in the range 200–900 °C. No change in weight is observed at 200 °C even after nearly 15 h exposure and only a very small ( < 1 mg) weight gain is observed at 230 and 330 °C, as can be seen from the results plotted in Fig. 1a. At higher temperatures, significant weight gain is observed with the rate of weight gain decreasing with increasing time as seen in Fig. 1b. This is explicitly demonstrated by Fig. 2 in which the rate of weight gain is plotted against time for reactions at 330–900 °C. For the two highest temperatures the rate decreased dramatically in the first 3 h and then became linear, but with a small negative slope up to 15 h exposure. From the results of Fig. 1a, it can be concluded that within the limit of resolution of the electrobalance, 18 μg, the threshold temperature of interaction between Nb and $N_2$ is between 200 and 230 °C and that significant nitridation of this metal does not take place below about 500 °C.

X-ray diffraction analyses conducted on niobium samples exposed to nitrogen at various temperatures for up to 300 h gave the results shown in Table I. In all cases (except for the 200 °C samples where no reaction occurred) regardless of time and temperature, the product included a solid solution of nitrogen in niobium. At 330 °C (exposed for 13 h) niobium formed a solid solution only. At higher temperatures, NbN formed and at still higher temperatures ( $\geqslant$ 700 °C) the product also contained the phase $Nb_2N$. Additionally, the oxide $Nb_2O_5$ was observed in all products, presumably as a consequence of oxygen impurities in the combustion chamber.

The solubility of N in Nb to form a b c c solid solution is relatively limited with a maximum of 4.8 at % [9, 10]. The interstitial placing of nitrogen in the metal lattice is expected to increase the lattice parameter in a proportional way to the total amount of dissolved nitrogen. However, as will be seen below,

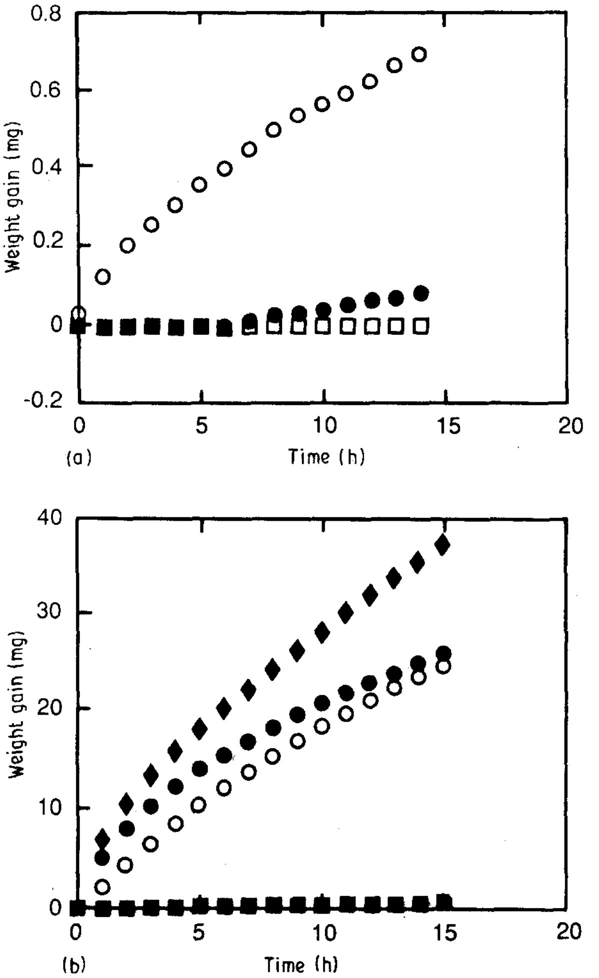

*Figure 1* Weight gain versus time for niobium in $N_2$ at 1 atm. Temperature (a) 200–330 °C, (○) 330 °C, (●) 230 °C, (□) 200 °C; (b) 330–900 °C, (◆) 900 °C, (●) 740 °C, (○) 560 °C, (■) 330 °C.

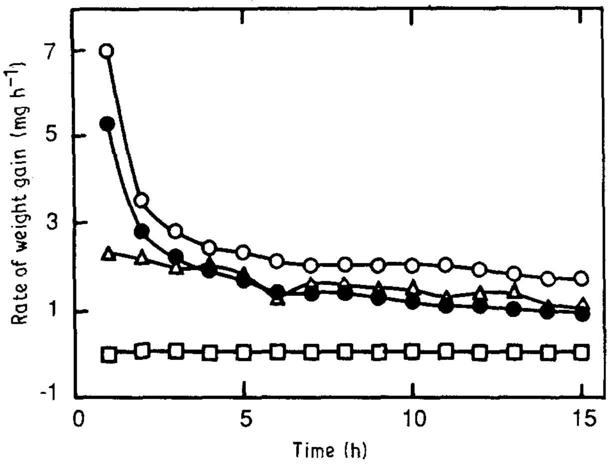

*Figure 2* The time dependence of the rate of weight gain of niobium in the range 330–900 °C. (○) 900 °C, (●) 740 °C, (△) 560 °C, (□) 330°C.

TABLE I Phase analysis of niobium samples reacted with $N_2$(g) (isothermal conditions)

| Temperature (°C) | Time (h) | Phase(s) |
|---|---|---|
| 200 | 20 | Nb |
| 330 | 17 | SS[a] |
| 560 | 17 | SS, NbN, $Nb_2O_5$ |
| 580 | 17 | SS, NbN, $Nb_2O_5$ |
| 700 | 292 | SS NbN, $Nb_2N$, $Nb_2O_5$ |
| 740 | 300 | SS, NbN, $Nb_2N$, $Nb_2O_5$ |
| 760 | 13 | SS, NbN, $Nb_2N$, $Nb_2O_5$ |
| 900 | 47 | SS, NbN, $Nb_2N$, $Nb_2O_5$ |

[a] SS, solid solution of nitrogen in niobium.

the dependence of the lattice parameter on concentration is more complex. Figs 3 and 4 show, respectively, the variation of the lattice parameter of the solid solution with reaction temperature at a constant time (13 h) and with time at a constant reaction temperature (760 °C). The parameter increases with increasing temperature between 400 and 580 °C and then decreases with further increase in temperature. It should be noted that below about 580 °C only a solid solution is observed and the recorded increase in the lattice parameter is consistent with general expectations. However, the decrease in the parameter at higher temperatures is related to another aspect of the interaction between nitrogen and niobium. It is reported that the formation of a niobium nitride phase from a solid solution involves the migration of Nb atoms and thus the creation of cation vacancies in the solid solution lattice [9]. The decrease in the lattice parameter is, therefore, believed to be the consequence of a nitride phase formation. As stated earlier, nitride phases were observed at temperature $\geqslant 680$ °C, a range in which the value of the parameter decreased, consistent with expectations. Fig. 4 shows the continuous decrease in the parameter with time of reaction at 760 °C, suggesting an increased nitride formation with exposure to a nitrogen atmosphere.

## 3.2. Interaction of Nb and $N_2$ through a self-propagating wave

### *3.2.1. Self-propagating reaction at 1 atm pressure of nitrogen*

A self-propagating wave can be initiated as a result of a reaction between niobium and nitrogen at 1 atm pressure. Under these conditions, the wave propagates in an oscillatory (non-steady state) mode and the product is only partially converted to the nitride. The effect of the initial sample density on the combustion velocity and degree of conversion to the nitride is shown in Fig. 5a and b, respectively. In Fig. 5b, the degree of conversion was calculated from the total weight gain assuming the product to be stoichiometric NbN. Although, as has been shown, the nature of the product is more complex, using this assumption facilitates comparisons. The decrease in velocity and the degree of conversion with increasing relative density of the reactant niobium compact is consistent with kinetic considerations of gas–solid reactions [6]. Because the melting point of niobium (2468 °C) is considerably higher than the highest measured combustion temperature ( < 2400 °C), no anomalous behaviour of these two parameters with density is expected, as was the case in the combustion synthesis of TiN [6].

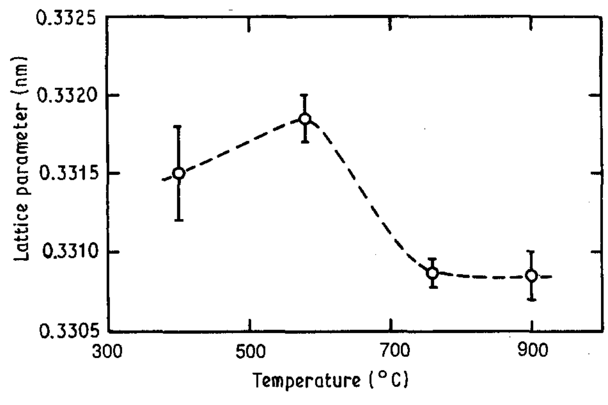

*Figure 3* The effect of reaction temperature on the lattice parameter of the solid solution of nitrogen in niobium. Heating time 13 h.

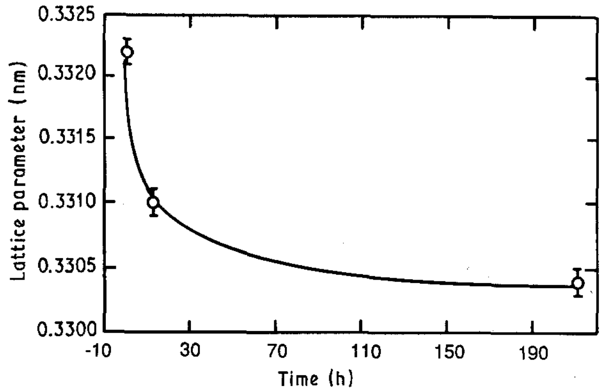

*Figure 4* The effect of reaction time on the lattice parameter of the solid solution of N in Nb. $T = 760$ °C.

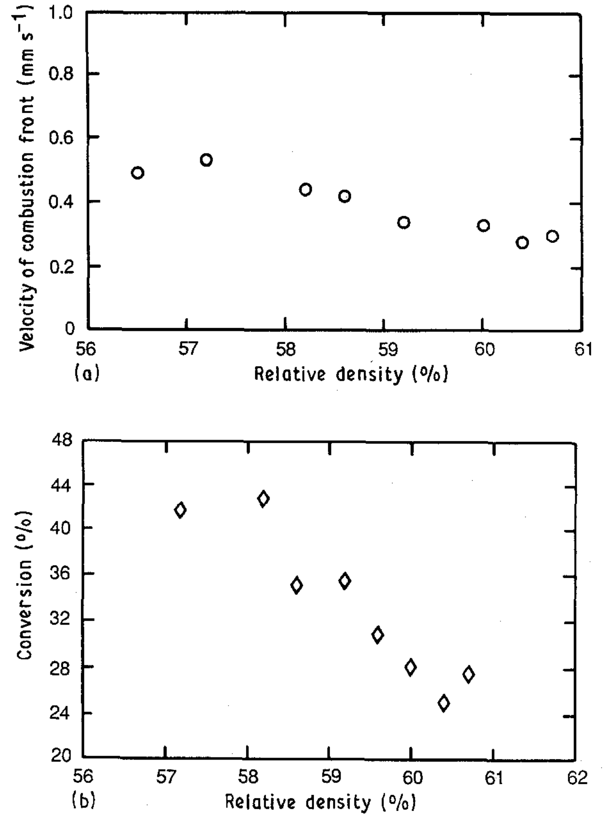

*Figure 5* The effect of the relative density of Nb compacts on (a) the combustion velocity, and (b) the degree of conversion to the nitride, NbN. $P_{N_2} = 1$ atm.

Visual observations of sectioned samples after the end of the combustion process showed the presence of a surface layer. This was found to be composed mainly of $Nb_4N_3$ (γ-phase) and a solid solution, with $Nb_2N$ (β-phase) as a secondary phase. In contrast, the interior of the sample was made up mainly of a solid solution with minor amounts of nitride phases ($Nb_2N$, $Nb_4N_3$, and NbN). From ten independent measurements, it was determined that the lattice parameter of the solid solution phase in the surface layer was smaller than that in the interior. The measured values are 0.331 87 and 0.332 15 ± 0.000 05 nm, respectively, and the difference between them is consistent with the explanation provided earlier regarding the role of niobium vacancies and their relationship to nitride phase formation [9].

### 3.2.2. *Effect of higher nitrogen pressure*

The influence of a change in nitrogen pressure on the combustion wave velocity and the degree of conversion is shown in Fig. 6a and b, respectively. The results shown in these figures were obtained with samples of a constant density of about 59%. In the cases of the velocity of propagation, the increase with increasing nitrogen pressure is nearly linear but the increase in the degree of conversion is more complex. As the pressure increased from about 1–3.4 atm, the conversion increased rapidly from about 35%–70%. However, with further increase in the pressure, the increase in conversion is much less significant, approaching an asymptotic value of 75% at the highest experimental pressure, 13.6 atm. As will be shown below, this observation is related to the formation of a surface layer.

Sectioned samples after combustion in nitrogen showed the presence of a well-defined surface layer with a distinct interface between it and the interior of each sample as shown in Fig. 7. The light-coloured region on the left-hand side of the figure is the surface layer and the grey region on the right is the interior of the sample. The white phase in the surface layer is a nitride of niobium and the grey phase in the interior is a solid solution. It was found that the composition and the relative thickness of the surface layer were dependent on the nitrogen pressure. Table II lists the compositions of the surface layer and the sample's interior for samples combusted at various gas pressures. Fig. 8 shows the dependence of the thickness of the surface layer (relative to the radius of the sample) on the pressure of nitrogen. Closer examination of the results of Table II and Fig. 8 offers an explanation for the unexpected dependence of conversion on pressure, Fig 6b. The increase in thickness of the surface layer with increasing pressure leads to expectations of increased conversion. However, as seen earlier (Fig. 6b), conversion is nearly at a maximum at as low a pressure as 3.4 atm. In contrast, the relative thickness of the surface layer continues to grow as the pressure increases beyond this value, ultimately increasing by a factor of three as the pressure reaches the maximum of 13.6 atm. Examination of the X-ray diffraction analyses, Table II, provides a possible explanation for these seemingly contradictory observations. At low pressures ( < 2.7 atm) the dominant nitride phase is $Nb_4N_3$ but at higher pressures the major phase in the surface layer is NbN (here observed as a solid solution with an impurity oxide phase resulting in the formula $NbN_{0.9}O_{0.1}$). As the pressure continues to increase,

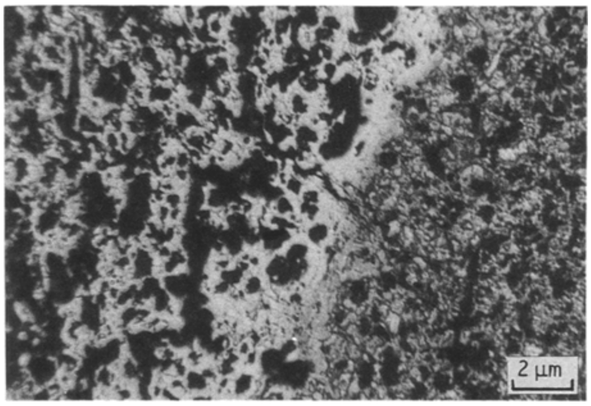

*Figure 7* Scanning electron micrograph showing the interface between the surface layer (left-hand side) and the interior of a combusted sample.

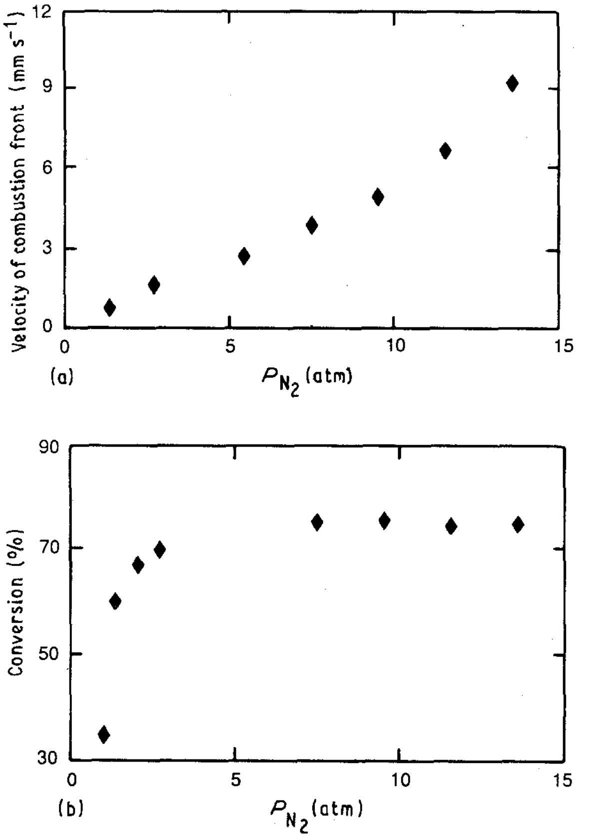

*Figure 6* The effect of nitrogen pressure on (a) the velocity of combustion, and (b) the degree of conversion to the nitride, NbN.

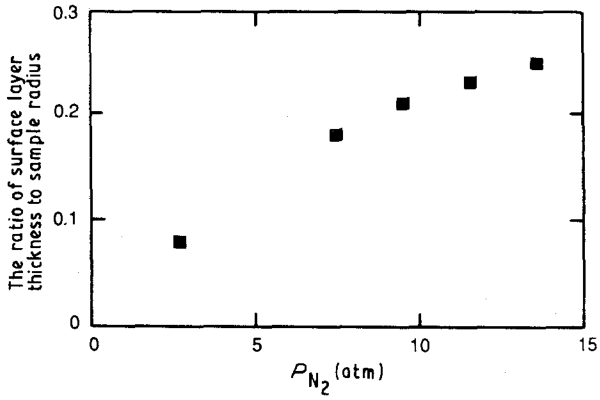

*Figure 8* The effect of nitrogen pressure on the relative thickness of the surface layer.

TABLE II. The phases produced at different nitrogen pressure

| Pressure (atm) | Phases in surface layer | Phases in interior |
|---|---|---|
| 1.0 | $Nb_4N_3$, SS[a], $Nb_2N$ | SS, $Nb_2N$, $Nb_4N_3$, NbN |
| 1.4 | $Nb_4N_3$, SS, $Nb_2N$ | SS, $Nb_2N$, $Nb_4N_3$, NbN |
| 2.0 | $Nb_4N_3$, SS, small amounts of $Nb_2N$ | SS, $Nb_2N$, $Nb_4N_3$, NbN |
| 2.7 | $NbN_{0.9}O_{0.1}$, $Nb_4N_3$, SS | SS, $Nb_4N_3$, $Nb_2N$ |
| 3.4 | $NbN_{0.9}$,$O_{0.1}$, small amounts of SS and $Nb_4N_3$ | SS, $Nb_4N_3$, $Nb_2N$ |
| 5.4 | $NbN_{0.9}O_{0.1}$ | SS, $Nb_2N$, $Nb_4N_3$ |
| 7.5 | $NbN_{0.9}O_{0.1}$ | SS, $Nb_2N$ |
| 9.5 | $NbN_{0.9}O_{0.1}$ | SS, $Nb_2N$ |
| 11.6 | $NbN_{0.9}O_{0.1}$ | SS, $Nb_2N$ |
| 13.6 | $NbN_{0.9}O_{0.1}$ | SS, $Nb_2N$ |

[a] SS, solid solution of nitrogen in niobium.

the surface layer becomes exclusively composed of this oxynitride. Presumably, in the absence of oxygen impurities, this layer would be the desired nitride, NbN. In view of these observations, we believe the dramatic decrease in the pressure dependence of conversion at $P_{N_2} \sim 3.4$ atm is a consequence of lower diffusivity of nitrogen in the oxynitride phase than in the precursor, $Nb_4N_3$. Such a proposal is supported by the decrease in the amount of nitrogen in the interior of the sample as seen from Table II. At higher pressures the only nitride observed in the interior is $Nb_2N$, the phase with the lowest N/Nb ratio observed. At lower pressures, the phases $Nb_4N_3$ and NbN are also observed. In addition, the lattice parameter of the solid solution in the interior shows a small decrease with increasing pressure as seen in Fig. 9, indicating a lower nitrogen content.

A typical approach to the determination of the mechanism of self-sustaining reactions is through a determination of the temperature dependence of the wave velocity. As has been previously reported [1, 2, 7], such a dependence has the following simplified general form

$$(v/T_c)^2 = K\left(\frac{R}{E}\right)\exp(-E/RT_c) \qquad (1)$$

where $v$ is the velocity, $T_c$ is the combustion temperature, $E$ is the activation energy of the process, $R$ is the gas constant, and $K$ is a constant which includes the heat capacity and density of the product and the heat of reaction.

The effect of a diluent on the combustion process of Nb in $N_2$ was also studied. Pure (99.9%) NbN ( − 100 mesh powder) was added as a diluent to the niobium reactant. The density of the samples was maintained at about 52% and the combustion was performed at $P_{N_2} = 3.4$ atm. The effect of the addition of a diluent on the temperature and velocity of combustion is shown in Fig. 10a and b, respectively. As expected, the temperature and velocity of combustion decreased with increasing amounts of diluent [11]. Such results are commonly used to calculate the activation energy of the combustion process. However, because the wave propagation was not in a steady-state mode for all levels of diluents, an activation energy cannot be calculated from the present investigation.

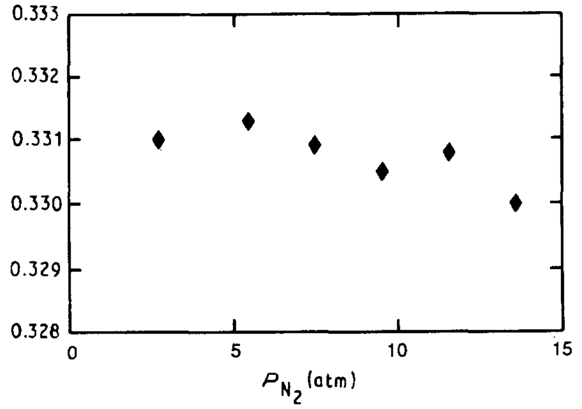

*Figure 9* The effect of nitrogen pressure on the lattice parameter of the solid solution phase in the interior of the sample.

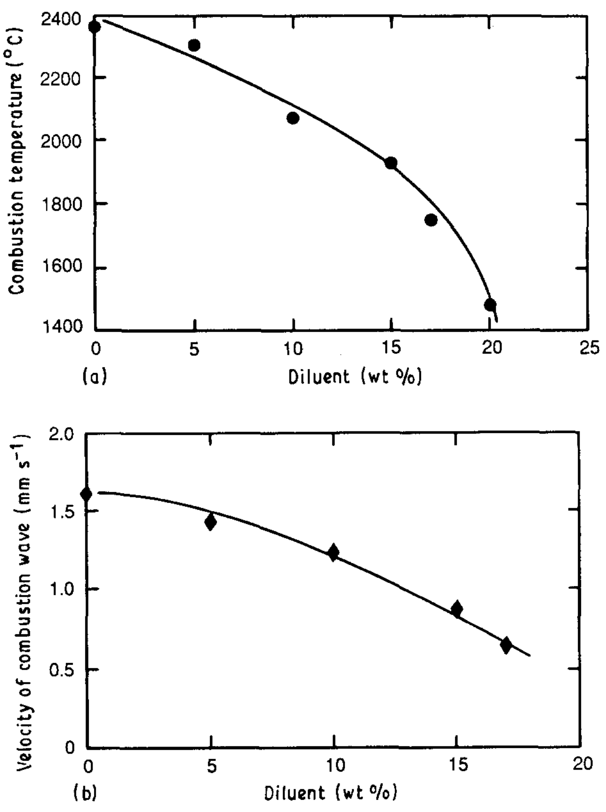

*Figure 10* The influence of a diluent on (a) the combustion temperature for Nb in $N_2$ at $P_{N_2} = 3.4$ atm, and (b) the combustion wave velocity for Nb in $N_2$ at $P_{N_2} = 3.4$ atm.

## Acknowledgement

This work was supported by a grant from the Office of Basic Energy Sciences of the Department of Energy.

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*Received 29 May*
*and accepted 26 June 1990*