

SELF-PROPAGATING HIGH-TEMPERATURE
SYNTHESIS OF TITANIUM NITRIDES UNDER
HIGH NITROGEN PRESSURES

I. P. Borovinskaya and V. É. Loryan

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In recent years the self-propagating high-temperature synthesis (SHS) process has found extensive application for the production of various refractory inorganic compounds [1]. The process, as is well known, is based on the utilization for synthesis of the internal energy resources of reacting systems, so that no special heating devices are required, and can readily be combined with high-pressure processes. In [2, 3] studies were made of the effect of high pressures on the formation of products in SHS processes occurring in the zirconium-nitrogen system. The object of the work described below was to investigate the conditions of formation of nitrides and nitrogen solid solutions during the combustion of porous metallic titanium specimens in nitrogen gas at pressures $P_{N_2} = 5-4500$ atm.

Experiments were conducted with PTS titanium powder and "extra pure" nitrogen (containing not more than 0.001% oxygen). Specimens of 10-, 20-, and 30-mm diameters were pressed to relative densities $\Delta = 0.5-0.77$. For quenching combustion products, in a number of experiments the pressure in the reactor was rapidly released, and the reactor was evacuated. After combustion some specimens were vacuum-annealed for 4-8 in an SShVL 062/25 furnace at a temperature of 700°C. The combustion products obtained were analyzed for nitrogen and titanium by standard methods [5].

According to literature data, the following phases may be present in the titanium-nitrogen system: an α solid solution of nitrogen in titanium, having a composition ranging from Ti to $TiN_{0.25}$; materials of compositions ranging from $TiN_{0.25}$ to $TiN_{0.45}$ contain an ϵ phase together with a nitride or an α solid solution; materials ranging in composition from $TiN_{0.45}$ to $TiN_{0.98}$ contain cubic titanium nitride [4].

The maximum calculated adiabatic temperature of combustion in the titanium-nitrogen system with the formation of a nitride but without its dissociation is $\sim 4900^\circ K$. Although the real temperature of combustion in this system is lower than the maximum adiabatic temperature, during combustion sintering and partial melting of the reaction mass take place, hindering filtration of nitrogen toward the combustion front. In the earlier investigations reported in the literature it proved possible to obtain approximately stoichiometric nitrides by reducing the intensity of combustion through the use of inert additions. Single-phase nonstoichio-

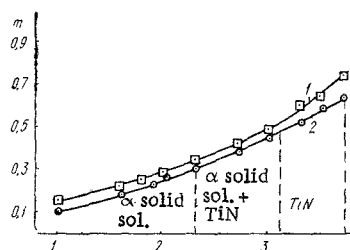


Fig. 1

Fig. 1. Variation of depth of nitriding of specimens [$m = (\% N/A_N)/(\% Me/A_{Me})$] with nitrogen pressure ($\log P_{N_2}$): 1) $\Delta = 0.6$; 2) $\Delta = 0.77$.

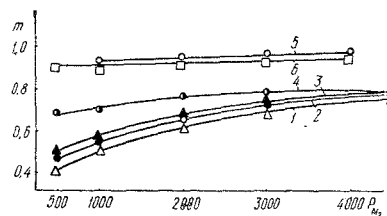


Fig. 2

Fig. 2. Variation of depth of nitriding of specimens (m) with nitrogen pressure ($\log P_{N_2}$) and amount of nitride addition: 1) without addition; 2) 5; 3) 15; 4) 30; 5) 40 (starting mixture was burnt in packing material); 6) 50% of addition.

TABLE 1

Exp. No.	Chem. composition	Lattice parameters of α solid solns.		Latt. param. of nitrides	Conditions of preparation	
		<i>a</i>	<i>c</i>	<i>a</i>	N ₂ pressure, atm	rel. density
1	TiN _{0,08}	—	—	—	5	0,5
2	TiN _{0,11}	2,934	4,734	—	10	0,77
3	TiN _{0,19}	2,969	4,765	—	40	0,77
4	TiN _{0,24}	2,981	4,805	—	80	0,77
5	TiN _{0,32}	2,988	4,810	—	200	0,77
6	TiN _{0,15}	—	—	—	10	0,6
7	TiN _{0,26}	2,986	4,807	—	80	0,6
8	TiN _{0,27}	2,987	4,809	—	100	0,6
9	TiN _{0,5}	—	—	4,218	1000	0,6
10	TiN _{0,57}	—	—	4,219	1500	0,6
11	TiN _{0,59}	—	—	4,221	2000	0,6
12	TiN _{0,66}	—	—	4,224	3000	0,6
13	TiN _{0,78}	—	—	4,227	4500	0,6
14*	TiN _{0,9}	—	—	4,231	1000	—
15	TiN _{0,94}	—	—	4,233	3000	—
16	TiN _{0,99}	—	—	4,234	4000	—

*In the preparation of nitrides in experiments 14-16, the starting metal was diluted by 40-50% by weight with titanium nitride of composition TiN_{0,94}.

metric nitrides and α solid solutions could not be obtained. In the present work solutions of nitrogen in titanium ranging in composition from TiN_{0,08} to TiN_{0,32} and nonstoichiometric nitrides ranging in composition from TiN_{0,5} to TiN_{0,99} were prepared by synthesis. Some characteristics of the combustion products obtained are given in Table 1.

As can be seen from Table 1 and Fig. 1,* single-phase solid solutions can be obtained on specimens with a relative density $\Delta = 0.77$ at pressures $P_{N_2} = 10-200$ atm and on specimens with a relative density $\Delta = 0.6$ at pressures $P_{N_2} = 10-100$ atm. In our work some unusual combustion phenomena were observed. In experiments with $\Delta = 0.77$ combustion occurred in a single stage, without the "recombustion" stage characteristic of the majority of metal-nitrogen systems and which is linked with additional volume nitration of specimens heated up by the combustion front. Similar single-stage processes were observed during the combustion of specimens with a relative density $\Delta = 0.6$ at a pressure $P_{N_2} = 60$ atm. All specimens with $\Delta = 0.77$ were nonporous, with a metallic luster, and unchanged in shape and size. Specimens with $\Delta = 0.5-0.6$ burnt at $P_{N_2} = 60$ atm, too, were nonporous and had a metallic luster, but were slightly changed in shape. During combustion at up to $P_{N_2} = 60$ atm specimens with a relative density $\Delta = 0.5-0.6$ remained porous, and could continue to burn, with the formation of heterogeneous products. A rapid release of pressure and removal of nitrogen from the reaction volume enabled combustion products to be obtained at various pressures without the recombustion stage.

Immediately after the passage of the combustion front, however, pressure was released and the reaction volume evacuated, which practically ruled out the possibility of additional volume nitration occurring after the passage of the front. On the resultant specimens could clearly be seen two zones: a 1.5- to 2-mm-thick surface layer, which, according to the results of chemical and x-ray phase analyses, consisted of a nonstoichiometric nitride, and a central part consisting of an α solid solution. The formation of the surface nitride layer was a result of recombustion occurring during the passage of the front, and could not be prevented, because during combustion the specimen did not melt, but remained porous. The only product in this case was a molten α solid solution of nitrogen in titanium. The lowest nitrogen content attained during combustion was 2.55 wt.%, corresponding to the composition TiN_{0,08}.

The upper limit of the homogeneity range of the α solid solution of nitrogen in titanium was found to correspond to the composition TiN_{0,32}. This value is slightly higher than those reported in the literature. Investigations revealed that the α solid solutions of compositions higher than TiN_{0,27} obtained in this work were unstable. During vacuum annealing for 4-8 h at a temperature of 700°C they decomposed with the forma-

*In Fig. 1 the ranges of the different phases are shown for $\Delta = 0.77$.

tion of an α solid solution of a lower composition and the ε phase. It is interesting to note that the ε phase had never before been detected in combustion products.

Raising the pressure from 200 to 1100 atm for specimens with $\Delta = 0.77$ and from 100 to 1000 atm for specimens with $\Delta = 0.6$ led to the formation of two-phase products (Fig. 1) consisting of α solid solutions and titanium nitrides of varying compositions. The nitrogen content of the two-phase zone products ranged from 8.5 to 12.95%. Raising the nitrogen pressure still further, from 1100 to 4500 atm at $\Delta = 0.77$ and from 1000 to 4500 atm at $\Delta = 0.6$, brought about the appearance of single-phase nonstoichiometric cubic nitrides (Fig. 1). The chemical compositions and lattice parameters of nitrides of various compositions obtained in this work are given in Table 1.

In high-pressure synthesis experiments the highest nitrogen concentration that could be attained in products was 18.45 wt.%, corresponding to the composition $\text{TiN}_{0.78}$. The reason why the use of such high nitrogen pressures in synthesis did not bring about the formation of nitrides of stoichiometric composition was that it caused partial melting of the reaction products, which prevented nitrogen from penetrating the specimens. A similar situation has been observed in the nitration of zirconium [3]. In the present work nitrides of higher degrees of nitration were obtained in combustion experiments with mixtures of titanium and a titanium nitride (not more than 50 wt.%).

The variation of the composition of reaction products with pressure for mixtures of various degrees of dilution is depicted in Fig. 2. Nitride specimens of compositions ranging from $\text{TiN}_{0.9}$ to $\text{TiN}_{0.99}$ were found to be unsintered homogeneous products which had retained their original shape. Unlike that of specimens burnt without dilution, the nitriding of these specimens occurred through a solid-phase mechanism. At lower diluent contents (5, 15, and 30 wt.%) sintered products with a metallic luster were obtained.

CONCLUSIONS

Experiments on the high-pressure combustion of metal specimens in nitrogen yielded α solid solutions of nitrogen in titanium of various compositions lying within the homogeneity range and nonstoichiometric titanium nitrides ranging in composition from $\text{TiN}_{0.5}$ to $\text{TiN}_{0.99}$.

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