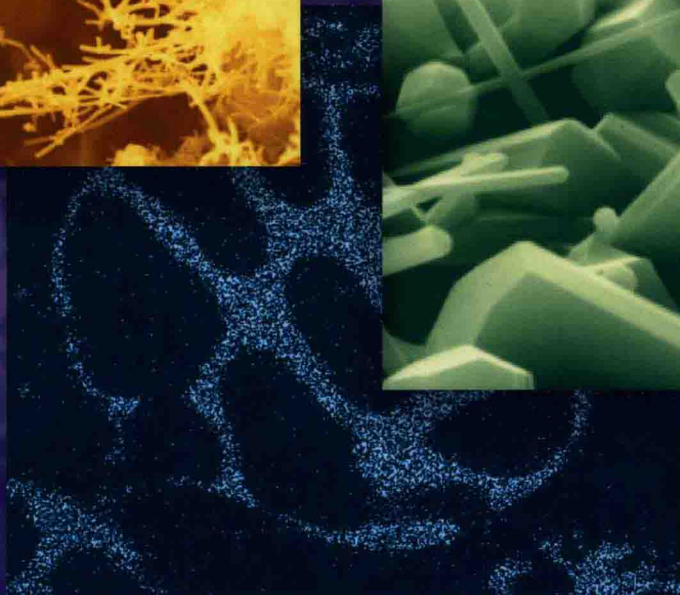
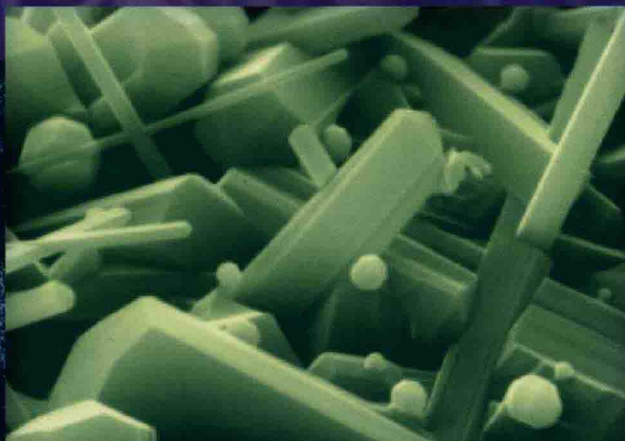
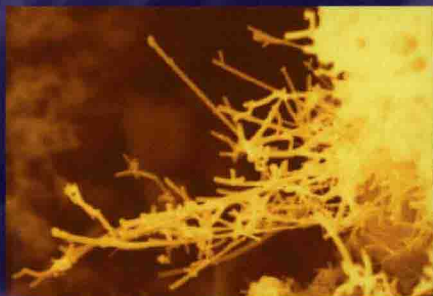


Edited by

Alexander A. Gromov and Liudmila N. Chukhlomina

# Nitride Ceramics

Combustion Synthesis, Properties,  
and Applications



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## **Nitride Ceramics**

Combustion Synthesis, Properties, and Applications



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## Foreword

Although we live in a world filled with nitrogen, that is, the main constituents of our atmosphere are nitrogen with 78% and oxygen with about 21%, nitrides or nitridic minerals are very rare in nature. This is caused by the fact that nitrogen is much less reactive than oxygen and even lesser than carbon. So, most of the natural minerals are more or less of oxidic nature. Nevertheless, a broad range of nitrogen compounds or nitrides exist. An overview on existing nitrogen compounds was compiled by Kieffer and Benesovsky [1] and is given in Table 1.

The positions of the most interesting nitrides are accentuated in Table 1. These are the *metallic nitrides* of the group 4B to 6B and also the so-called *diamond-like* or nonmetallic nitrides of the group 3A and 4A. The nitrides of the group nos. 1–3 are salt-like, while those of the groups 7B and 8 are metallic. The nitrides of the Lanthanides and Actinides have a transitional position; the actinide nitrides in Table 1 can be numbered among the metallic species. The majority of the remaining nitrogen compounds of the groups 5A–7A is gaseous.

Of great technical interest are the nitrides in the accentuated fields in Table 1. The metallic nitrides, especially those of the 4B and 6B groups show very high hardness, high abrasion resistance, and are characterized by very high melting temperatures. The stability of these nitrides decreases from group 4B to 6B and within the 6B group from the relatively stable chromium nitrides via molybdenum nitride to tungsten nitride. Furthermore, it is important to state that the stability of these nitrides, especially at higher temperatures up to the melting point, is strongly dependent on the nitrogen pressure.

The mononitrides of the 4B and 5B metals crystallize in an fcc lattice with one exception: TaN at ambient conditions shows an hcp lattice. Only at enhanced temperatures (>about 1500 °C) and enhanced nitrogen pressures (>about 5 bar), TaN is transferred into an fcc lattice.

Other interesting properties of these metallic nitrides are their excellent electrical and thermal conductivity as well as in the case of TiN, the gold-like color. So TiN coatings are used not only on cutting tools to enhance the abrasion resistance but also for decorative – and scratch-resistant – surfaces of various metallic articles.

**Table 1** Nitrogen compounds in the periodic table of elements according to Kieffer and Benesovsky [1].

1A	2A	3B	4B	5B	6B	7B	8				1B	2B	3A	4A	5A	6A	7A
H <sub>3</sub> N																	
Li <sub>3</sub> N	Be <sub>3</sub> N <sub>3</sub>											BN			N	O <sub>x</sub> N	F <sub>3</sub> N
Na <sub>3</sub> N	Mg <sub>3</sub> N <sub>2</sub>											AlN	Si <sub>3</sub> N <sub>4</sub>	P <sub>x</sub> N	S <sub>x</sub> N		
K <sub>3</sub> N	Ca <sub>3</sub> N <sub>2</sub>	ScN	Ti <sub>2</sub> N TiN	V <sub>2</sub> N VN	Cr <sub>2</sub> N CrN	Mn <sub>4</sub> N Mn <sub>2</sub> N Mn <sub>3</sub> N <sub>2</sub>	Fe <sub>4</sub> N Fe <sub>2</sub> N	Co <sub>3</sub> N Co <sub>2</sub> N	Ni <sub>3</sub> N Ni <sub>3</sub> N <sub>2</sub>	Cu <sub>3</sub> N Ag <sub>2</sub> N	Zn <sub>3</sub> N <sub>2</sub>	GaN	Ge <sub>3</sub> N <sub>4</sub>	AsN	SeN	Cl <sub>3</sub> N	
Rb <sub>3</sub> N	Sr <sub>3</sub> N <sub>2</sub>	YN	ZrN	Nb <sub>2</sub> N Nb <sub>4</sub> N <sub>3</sub> NbN	Mo <sub>2</sub> N MoN							Cd <sub>3</sub> N <sub>2</sub>	InN	Sn <sub>3</sub> N <sub>4</sub>	SbN	TeN	Br <sub>3</sub> N
Cs <sub>3</sub> N	Ba <sub>2</sub> N Ba <sub>3</sub> N <sub>2</sub>	LaN	Hf <sub>2</sub> N HfN	Ta <sub>2</sub> N TaN	W <sub>2</sub> N WN	Re <sub>2</sub> N						Hg <sub>3</sub> N <sub>2</sub>	TiN	Pb <sub>3</sub> N <sub>4</sub>	BiN		J <sub>3</sub> N
Lanthanides																	

Regarding the three nonmetallic nitrides in Table 1, the technical importance of these is partly similar to that of the metallic nitrides but partly quite different.

Boron nitride (BN) exists in two modifications with completely different properties. The hexagonal  $\alpha$ -boron nitride is according to its crystal lattice and its properties very similar to graphite, that is, it crystallizes in a hexagonal lattice and consists of layers of a planar, hexagonal honeycomb structure with alternating B- and N-atoms. This BN modification is also called “white graphite.” It is, for example, used as a solid lubricant as well as a material for high-temperature and oxidation-resistant crucibles. Cubic boron nitride (CBN) is the second hardest material behind diamond. So CBN is predominantly used as material for cutting tools or as grinding material.

The outstanding property of AlN is its high thermal conductivity up to 180–220 W m<sup>-1</sup> K<sup>-1</sup> and it is an electrical insulator. So AlN is used as a ceramic heat sink in microelectronics.

The last of the mentioned nonmetallic nitrides is silicon nitride (Si<sub>3</sub>N<sub>4</sub>). Since about 50 years, the importance of Si<sub>3</sub>N<sub>4</sub> as a technical ceramic increased permanently. Si<sub>3</sub>N<sub>4</sub> combines high hardness and abrasion resistance with a relatively low density of about 3.24 g cm<sup>-3</sup> and good oxidation resistance up to



high temperatures. These properties led to the application of  $\text{Si}_3\text{N}_4$  as material for ball bearings, nozzles, valves in automotive engines, and many more.

For all the nitrides mentioned here, there are – besides or because of their outstanding properties – two main challenges:

- Synthesis of pure materials.
- Processing and shaping to technical components.

The classical ways of nitride synthesis are the following:

- Nitriding of metals or of hydrides.
- Nitriding of metal oxides in the presence of carbon.
- Conversion of metal chlorides and metal oxychlorides with ammonia.
- Decomposition of ammonia compounds.
- Conversion of oxides with calcium nitride.
- Gas-phase deposition of metal halides.

The classical processing path of shaping these refractory materials to bulk bodies is sintering. This means the conversion of a more or less porous structure into a dense body. During normal sintering, the driving force for the densification is the reduction of the surface energy. This process is initiated by applying a sufficient amount of activation energy, mainly by heating from an external source (sintering furnace) up to the sintering temperature. But especially regarding refractory materials like nitrides, the necessary temperatures are very high and require rather expensive processing equipment. One way out of this problem is to implement a process, where the necessary heat of reaction is generated by an intrinsic chemical reaction. This is performed by using special precursors as starting materials, which have a lower level of activation energy combined with an exothermic reaction, which leads to the desired material or the desired shape. The generic term for this processing method is “reaction bonding.” Within reaction bonding, one of the most interesting processes is combustion synthesis (CS), also called *self-propagating high-temperature synthesis* (SHS). As can be seen from the wording within this process, the main emphasis is laid on material synthesis, but it may also be used to produce bulk shapes.

The characteristic feature of CS is, after initiation locally, the self-sustained propagation of a reaction wave through the heterogeneous mixture of reactants [2]. Since the process occurs at high temperatures, the method is ideally suited for the production of refractory materials with unusual properties such as advanced nitrides and nitrogen compounds.

In its usual form, SHS is conducted starting from finely powdered reactants that are intimately mixed. The synthesis is initiated by local heating of one preferred end of the sample. Usually, heating is started from the top of the sample. After starting a wave of exothermic reaction runs through the sample. Thus, the SHS mode of reaction can be considered to be a well-organized wavelike propagation of the exothermic chemical reaction through a heterogeneous medium, followed by the synthesis of the desired condensed product. Regarding the synthesis or processing of nitrides or nitrogen compounds, the atmosphere during the CS process

plays an important role. By adjusting composition and pressure of the sample-surrounding atmosphere, the products' shape and properties can be targeted and controlled.

In the present book, the material's spectrum concentrates on new or advanced synthesis methods for metallic nitrides and nitrogen compounds – TiN, VN, NbN, TaN, and CrN, as well as on the nonmetallic species – AlN, BN, and SiAlONs.

Up to now, CS or SHS has become a promising choice for industrial fabrication because of its relatively low processing costs, high energy efficiency, and short processing time. These technologies shall update or extend the classical technologies and they shall lead to new materials with technologically important properties combined with more simple and more economic processing technologies

*Dr. Hans-Joachim Ritzhaupt-Kleissl*

## References

1. Kieffer, R. and Benesovsky, B. (1963) *Hartstoffe*, Springer-Verlag, Wien, p. 287.
2. Varma, A., Rogachev, A.S., Mukasyan, A.S., and Hwang, S. (1998) Combustion synthesis of advanced materials: principles and applications. *Adv. Chem. Eng.*, **24**, 79–227.

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## Preface

Widely used oxides for the production of technical ceramics are rooted in the past. In twenty-first century, non-oxide materials will play a decisive role in technical ceramics production, in particular materials based on nitrides. Nitride ceramic is characterized by stability of dielectric properties, high mechanical strength, heat resistance, chemical resistance in different environments, and so on. Oxynitride ceramics is an intermediary between the nitride and oxide ceramics, which is a cheaper and affordable technological solution. Combustion synthesis (CS) or self-propagated high-temperature synthesis (SHS), discovered in USSR, is a simple method used for nitrides and oxynitrides production because of their non-expensive facility, high-rate exothermic reaction, and wide range of synthesized products. The cost of CS ceramic products is much lower than that of the products synthesized by “furnace” technologies. The rate of nitrides phase formation in the combustion wave “metal-nitrogen” is very fast (up to several moles per second).

Chapter	Nitrides of element											Oxynitrides		Chapter describe		
	B	Al	Si	Ti	V	Cr	Zr	Nb	Hf	Ta	Other	SiAlON	AlON	CS <sup>a</sup>	Pr <sup>a</sup>	Ap <sup>a</sup>
1.	+	+	+	+			+	+	+	+		+		+	+	+
2.	+													+	+	+
3.		+												+	+	
4.												+		+	+	
5.	+	+		+			+						+	+	+	+
6.					+			+		+				+	+	
7.	+		+	+	+	+		+						+	+	+
8.		+	+	+			+				+			+	+	
9.		+												+	+	+
10.	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+

a) CS = combustion synthesis, Pr = properties of nitrides, Ap = application.

The formation mechanism, properties, and application of the nitrides and oxynitrides produced by CS are comprehensively studied in this book. The majority of industrially important nitrides are represented by all authors (table).

October 2014

*Alexander A. Gromov*  
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