SHS Powders for Thermal Spray Coating†

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Abstract
The possibilities of preparing advanced powders for thermal spraying functional coatings by the method of self-propagating high-temperature synthesis are discussed in this review. Besides important economical and ecological benefits, the method allows the formation of powders with improved or unique structure and properties in size ranges and with an external morphology suitable for different thermal spray processes. A number of novel powders and recent achievements are presented.

Keywords: self-propagating high-temperature synthesis, powder, thermal spray coating

Introduction
Modern industrial technologies call for the development of novel materials with improved properties, lower costs and environmentally suitable processes. Surface engineering that attempts to create functional layers on the surface is obviously the most economical way to provide high performance to machinery and equipment. Among the wide range of available methods (including varieties of atomistic and particulate deposition, bulk coatings wetting processes and surface modification), thermal spray coatings offer the most versatile solutions. Thermal spray processes form a continuous coating by melting the consumable material (feedstock) to form droplets and impinging these droplets on the substrate. The mechanism of bonding to the substrate in thermal sprayings (TS) is the same as plating, both mechanical interlocking and atomic interaction, with the shear strength around 7 MPa\(^1\). The thickness of the coatings can range from 10 µm to a few millimeters\(^2\). Other advantages of thermal spraying include a practically unlimited assortment of powders to be sprayed, high efficiency and relatively low substrate temperature (373-583 K), thus minimizing shape distortion, oxidation and phase transformations in the near-surface layer. Demanded characteristics for thermal spray feedstock powders can be very different, depending on the spraying process, the operating conditions, the desired properties of the final coating, etc. Besides the intrinsic material properties, the technical requirements for the TS feedstock powders include good flowability and sprayability. They are greatly affected by the particle size, shape and morphology as well as particle size distribution. That is why thermal spray feedstock powder production processes must be reliable and flexible, while remaining as inexpensive as possible.

Self-propagating high-temperature synthesis (SHS) or combustion synthesis, discovered by A.G. Merzhanov and colleagues in 1967, is known as a very promising technique for processing materials (ceramics, intermetallics, cermets, etc.) with good physical and chemical properties at relatively low costs\(^3,4\). The main point of the process is that after localized initiation, the reaction propagates as a narrow zone – combustion wave – along a sample driven by the exothermic reaction between components of the charge mixture without the application of external heating (furnaces, etc.). Because of the extreme conditions in the SHS wave (high temperature of up to 3500°C, fast heating of up to 10\(^6\) K/s, steep temperature gradient of up to 10\(^5\) K/cm, rapid cooling in the after-burn zone of up to 100 K/s, and fast accomplishment of reaction, 0.5 s to 1 min), chemical interaction mechanisms during the SHS are often non-equilibrium, resulting in the formation of materials with improved structure and properties, especially in multi-component composite systems\(^5,6\). Moreover, a product with increased purity can be obtained due to evaporation of volatile impurities at the high temperatures of the

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process. Besides the important economical benefits connected with low energy requirements and short reaction times, the method is promising from an environmental point of view. Two ecological aspects related to SHS are usually considered: ecological cleanness of the SHS technologies and possibilities of industrial waste inertation, minimization and reuse in SHS reactions. Generally, the SHS process is believed to be ecologically clean. However, for some large-scale production, gas emission of volatile impurities during synthesis can be an environmental threat. The major achievements in the exploitation of SHS for environmental protection include: the fixation and consolidation of high-level radioactive wastes; the treating and recycling of a highly toxic solid waste from electrolytic zinc plants; the recycling of silicon sludge from semiconductor industries, aluminum dross produced by aluminum foundries, nonferrous metal cutting and grinding waste, Fe₃O₄ dross and dead catalysts; the degradation of chlorinated aromatics. The first works available in the literature that take into account SHS as compared with conventional methods of powders preparation. Since then, a great number of researchers have been engaged in investigating thermal spray coatings from SHS powders. Most of them dealt with wear-resistant coatings formed by different thermal spray methods from “titanium carbide/metal binder” compositions. It was conditioned by the high exothermal effect of TiC formation (giving full scope for the choice of binder material acting as diluents in the synthesis process) and good coating properties (comparable with or even better than that of conventionally used WC/Co and Cr₃C₂/NiCr coatings). The chemical and morphological features of different SHS powders were described, and their technical characteristics of flowability and sprayability were outlined. Wear performance and hardness test results for various TS coatings were also reported. Further progress was connected with widening sprayed materials including improvement of TiC-based powders (forming double (Ti, Cr)C, (Ti, W)C and (Ti, Mo)C carbides, complex alloyed binders, introducing additional solid lubricant phases, etc.), as well as the development of other compositions. At present, more than 90 different SHS powders have been investigated as feedstock materials for TS coatings. Different kinds of plasma spraying methods (air plasma spraying (APS), supersonic air plasma spraying (SAPS), low-pressure plasma spraying (LPPS), underwater plasma spraying (UPS)), as well as detonation spraying (DS), flame spraying (FS) and high-velocity oxygen-fuel spraying (HVOF) are in common use for depositing protective coatings from SHS powders. The first attempt to systematize results on using self-propagating high-temperature synthesis for thermal spraying was made recently by A.L. Borisova and Yu.S. Borisov. The compositions of the most widely reported thermal sprayed SHS powders as well as methods of their deposition and properties of the coatings have been listed. However, only general information about some of the SHS powders and their processing is presented in this review, while some promising powders and recent achievements were not mentioned. The aim of this work is to summarize relevant up-to-date literature and results of the author’s research on producing advanced SHS powders for thermal spraying functional coatings.

1. Fundamentals of Powder SHS Technology

As stated above, the main condition for implementation of the SHS process is a high enough exothermicity of the charge mixture. According to experimental data, SHS normally takes place when the adiabatic temperature is higher than 1800 K or at a ratio of reaction heat to a specific thermal capacity of a product at room temperature ∆H₂₉₈/ C₂₉₈ > 2000 K.

The powder SHS technology is based on burning green powder mixtures in special reactors in the environment of an inert or reacting gas, and also in vacuum or in the open air. The chemistry of the SHS process is versatile. Materials can be produced from elements and using compounds, mineral raw materials and industrial waste as reactants. Combustion products are usually porous sinters which are exposed to subsequent processing to produce powders of a different function. The general technological configuration of SHS powder production includes the following operations: (1) preparation of a green mixture: sieving, milling, drying of components (if necessary) and mixing; (2) filling of a reactor with a green mixture and gases; (3) synthesis after a short-term thermal initiation and (4) subsequent processing of the synthesized products. In the case of synthesis from elemental powders, the subsequent processing of the synthesized product includes only mechanical treatment: scraping, crushing, milling and classification.
Some additional operations can be necessary in the case of the more complicated routes. For example, magnesiothermy synthesized product after crushing is exposed to acid enrichment to remove magnesium oxide, and is then dried and mechanically processed.

The main parameters to control the synthesis process are composition and structure of the charge mixture (including type and amount of additives and fillers); reactant’s dispersion; relative density and charge volume; initial temperature of the sample; composition and pressure of ambient gases; external influences (preliminary mechanical activation of charge mixtures, electric and magnetic fields, ultrasonic, centrifugal and gravitation forces, shock waves, etc.). Detailed information about the relationships between SHS process parameters and combustion product structure and properties can be found elsewhere. In this review, we summarize the main approaches to the synthesis of powders for thermal spraying. A number of novel powders and recent achievements are presented.

2. Thermal Sprayed Powders

All the powders that have proven themselves for thermal spraying can be divided into two main groups: refractory compounds and composite powders. The most representative powders and characteristic features of their processing are given below.

2.1. Refractory compounds

The most common route for manufacturing powders of carbides, borides, silicides, etc. is conventional synthesis from elemental powders (Ti+C=TiC; Ti+2B=TiB2; Mo+2Si=MoSi2) in a pressure-defined reactor. High-caloric mixtures (for example, Ti+C and Ti+2B) are normally diluted with 15-20% wt. % of combustion product. To provide stoichiometric composition of titanium carbide, 1-1.5% carbon excess is usually required. Other details of manufacturing techniques for TiC, TaC, NbC, TiB2 and MoSi2 powders can be found in.

For low-caloric mixtures (for example, Cr+C), liquid-phase processes with aluminothermic reactions can be used. This process is called SHS with reducing stage. Two competitive reactions MoO3+Al→Me3Al2O3 and MeO2+Cr→Me+CO proceed simultaneously in the first stage of the process. The SHS proper, i.e. synthesis of carbide from the metal and carbon, takes place in the second stage. A two-phased melt consisting of carbide and alumina is finally formed. Phase separation resulting from differences in carbide and oxide density occurs under gravitational or centrifugal forces. A chromium carbide powder is hereby produced from a mixture containing 37 wt.% CrO3, 27 wt.% Cr2O3, 27.5 wt.% Al and 8.5 wt.% graphite. The respective technology is described in.

Nitride powders (TiN, ZrN, etc.) are usually formed by the combustion of metal powders in gaseous nitrogen spontaneously entering into the reaction zone after being “filtered” through the pores. One of the critical parameters for this route is careful control of the reacting gas pressure. A 40-70% dilution with coarse-grained combustion product powder is also necessary to provide the filtration processes.

In open (continuous-flow) reactors with a directed flow of the reacting or doped gas through the loose powder, so-called “Filtration SHS Technology” is implemented. The main advantages of the process include the possibility of synthesizing titanium nitride at a low pressure of supplied nitrogen (less than 5 MPa) without charge mixture dilution. Moreover, it is possible to remove emitted gases, thus increasing the purity of the product, and allows cutting wastes and sludge to be used as reactants without precleaning.

So-called azide technology is based on using solid azide powder as the nitriding reactant instead of gaseous or liquid nitrogen. The chemical equation of TiN synthesis is written as follows: 4Ti+NaN3+NH4C l=4TiN+NaCl+2H2↑. As compared to systems with gaseous nitrogen, this route allows increasing the reactant concentration in the synthesis zone, eliminating filtration problems and producing more fine-grained powder (because of the lower combustion temperature) at high efficiency (no charge dilution is used). However, NaN3 is toxic and more expensive than gaseous nitrogen.

Complex refractory compounds such as double carbides, carbonitrides, etc., can be produced using three- and more-component charge mixtures. For example, the production route for double titanium-chromium carbide Ti8Cr5C is similar to TiC synthesis process except for the addition of chromium powder into the powder mixture and 2% carbon excess. SHS of titanium carbonitride TiC0.5N0.5 is formed by combustion of the powder mixture comprising titanium and carbon-blake with 30% diluent of carbonitride powder in nitrogen media.

SHS powders of carbides, nitrides and silicides are intended for wear-resistant and high-temperature TS-coatings. Among the developed thermal sprayed powders worthy of note are powders of molybdenum disilicide (for high-temperature oxidation-resistant
coatings, chromium and double titanium-chromium carbides (for wear-protective coatings).

Another class of refractory compounds showing growing interest for thermal spray applications is intermetallics. The general chemical equation of intermetallics combustion synthesis can be written as follows: \( \text{Me}^+ + \text{Me}^{-} \rightarrow \text{Me}^{+} \text{Me}^{-} \).

Due to the fact that the exothermal effect of most intermetallic compound formation from elemental powders is not high enough\(^{11}\), preheating of the charge mixture before ignition is normally used. Preliminary mechanical activation (MA) of the reacting mixtures allows synthesis to be performed without heating at higher conversion completeness. Single-phase equilibrium and ultrafine (nanocrystalline) intermetallic compounds were reported to be formed through the mechanically activated self-propagating high-temperature synthesis (MASHS) route\(^{87,88}\).

Of the intermetallics, nickel, iron and titanium aluminate-based powders are currently in use for thermal spray protective coatings. Some examples of novel SHS powders developed in the Powder Metallurgy Institute are presented below.

**NiAl powders modified with nanoadditives.**

Due to the high melting temperature, good high-temperature strength, low density, high thermal conductivity and excellent oxidation resistance\(^{89,90}\), NiAl protective coatings can be used effectively for high-temperature applications.

As was mentioned before, the powder for thermal spraying has to have good flowability and this property is greatly affected by the particle size distribution and particle morphology. The best flowability is achieved for particles of spherical shape. While particle size requirements vary for different TS methods, the particle size distribution is a critical parameter for thermal sprayed powders. Powder particles that are too coarse cannot be heated sufficiently during spraying to deposit on the substrate. Conversely, particles that are too fine can be overheated and suffer thermal degradation (decomposition) during spraying. That is why precise control of formation of the necessary particle size distribution is a very important task of the TS feedstock powder production process.

Interesting results have been obtained when adding nanoadditives (nanopowders of ultradispersed diamond (UDD) and SiO\(_2\)) to the charge mixture for the synthesis of NiAl powders\(^{11}\). The as-synthesized powder particle size appeared to be strongly dependent on the nanoadditive aggregate size (the less the nanoadditive aggregate size, the finer the powders that can be formed). **Fig. 1** represents cross-sections of conventional SHS (a) and modified with 5 vol.% UDD (200-nm sized aggregates consisting of particles of about 20-40 nm) NiAl SHS powder (d). As can be seen from the figure, the modified powder has a more uniform particle size distribution with 4-8-fold smaller particles. Close to spherical shape is kept in the powder. This dispersive effect can be explained by the fact that nanoadditives, being the nucleus of heterogeneous crystallization, promote quicker and more uniform intermetallic phase formation in the early stage of SHS, meanwhile preventing intensive sintering and grain growth processes because of lower combustion temperature. Nanoadditives can also essentially improve internal oxidation behavior of the material: an intergranular oxidation resulting in material fracture has been observed in the conventional NiAl SHS-powder (Fig. 1b). In contrast, fine oxide inclusions sufficiently uniformly distributed in the material are formed in the modified powder (Fig. 1e). Finally, modification of powders with nanoadditives results in an increase of the powder’s deposition efficiency. For example, the thickness of detonation spray coatings from the modified NiAl SHS powder is 1.5-2.5 times higher than that of the unmodified one at the same spraying conditions (compare Fig. 1e and f). It seems to be connected with a more even particle size distribution and a more fine-grained structure\(^{90}\).

**Ni-Al-Cr powder.** It is known that chromium is one of the most widely used alloying elements to improve properties of nickel aluminides\(^{89}\). It increases the oxidation resistance of NiAl, suppressing the formation of metastable aluminum oxides in a temperature range of 900-1000°C and promoting the formation of a dense fine-grained \( \alpha - \text{Al}_2\text{O}_3 \) protective film, providing high corrosion resistance\(^{90}\), and also improves the mechanical properties of NiAl by solid solution hardening and hardening by thin inclusions of \( \alpha - \text{Cr} \)\(^{90}\).

Recently, we have developed a novel SHS powder based on nickel monoaluminide alloyed with chromium and strengthened with dispersed inclusions of chromium-based solid solution (Fig. 2a)\(^{94}\). The powder is produced using preliminary mechanical activation of the reacting mixture of Ni-20 wt.% Cr alloy with aluminum before synthesis. In the developed powder, the NiAl phase contains 3-6 wt.% Cr and secondary inclusions on the basis of chromium up to 25 wt.% of nickel and up to 15 wt.% of aluminum. The increased content of chromium dissolved in NiAl is evidently connected with the fact that chromium substitutes not only for nickel but also for aluminum sites in a B2 lattice. The powder microhardness is 320-550.
The high-velocity oxy-fuel flame (HVOF) spray coating from the developed NiAlCr powder (Fig. 2b) demonstrates good mechanical properties and excellent oxidation behavior up to 1300 K.

FeAl-FeAl powder. Due to the high Young’s modulus, high elevated temperature strength retention, excellent corrosion resistance in oxidizing, sulfiding or carburizing environments up to 1000°C, relatively low density as compared with stainless steels and nickel superalloys, and low price of raw materials, FeAl intermetallic alloys based on the ordered B2 structure are very attractive materials for medium-temperature applications. However, poor room temperature ductility, low creep resistance and sensibility to environmental embrittlement restrict their industrial applications as structural parts.

Recently, a new FeAl-FexAly powder with improved characteristics and low cost has been developed. Creation of the powder was based on the idea of strengthening the material with inclusions of secondary precipitates of other iron aluminides formed during synthesis. The powder was prepared through the MASHS route. Fig. 3a,b shows the morphology and cross-section of the developed powder. The powder is characterized by the typical eutectoid structure with lamellar morphology of aluminum-enriched crystals. According to energy dispersive X-ray analysis (EDX) results, the light-gray contrast of matrix phase corresponds to the composition of B2 FeAl with some aluminum excess. The composition of the lamellae crystals with dark-gray contrast is close to that of the FeAl2 compound. However, the X-ray diffraction pattern (Fig. 4) clearly shows the evidence of a three-phased composition: Fe2Al3, typical reflexes

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are also found in the spectrum. An Fe$_3$Al$_5$ phase is likely to be located on the particle surface and is presented as fine inclusions within the lamellae crystals' volume (see Transmission Electron Microscopy (TEM) micrograph, Fig. 3c). The phase mixture formation evident in the TEM micrograph and identified as FeAl$_3$+Fe$_3$Al$_5$ is probably from the result of the non-equilibrium conditions of structure formation during synthesis, similar to that described in.

The microhardness of the powder is about 500-850 HV$_{50}$. It is significantly higher than the typical microhardness of B2 alloys (250-450 HV$_{50}$). It should be noted that no cracks were observed in the material even after microindentation tests in spite of the fact that the structure consists completely of intermetallic phases. It is likely that the increased mechanical properties of the powder are provided by the eutectoid structure of multiphased composition of iron aluminitides similar to a Ti-Al system, for which superplasticity was observed in the two-phase area ($\gamma$ + $\alpha_2$). Nanoprecipitates of the Fe$_3$Al$_5$ phase can also contribute to the increased crack resistance.

High-quality coatings from the FeAl-Fe$_3$Al$_5$ powder can be obtained using detonation and high-velocity oxy-fuel flame spraying techniques with a porosity of less than 1% and microhardness of 834 and 831 HV200, respectively. Material peculiarities (high aluminum content and fine-grained structure of multiphased intermetallic composition) provide the coatings with good corrosion- and wear-resistance. The tribological performance of the coatings (abrasion, sliding and erosion behavior) is close to that of composites based on alloyed iron and nickel aluminitides with oxide and carbide strengthening. The oxidation resistance of the FeAl-Fe$_3$Al$_5$ coating is comparable with that of NiCrAl-Al$_2$O$_3$: dense and protective alumina film is formed during oxidation tests.

**Ti-Al-Cr powder.** Titanium aluminitides alloys are known as a promising material for structural use in automotive and aerospace applications due to their low density, relatively high strength and low creep properties even at 1200 K. However, they are limited by the poor oxidation resistance at elevated temperatures (>1000K) and poor toughness at ambient temperature. The addition of suitable alloying elements can improve the above characteristics. Fig. 6 shows the morphology and cross-section of the novel Ti - 46at.%Al - 8 at.% Cr powder produced using the MASHS route. The powder is characterized by the multiphase dispersed strengthened structure with coherent precipitates/matrix bonding. The main structural constituents of the powder are titanium aluminitides alloyed with chromium: ($\gamma$-TiAl(Cr), $\alpha_2$-TiAl(Cr) and Al$_{0.67}$Cr$_{0.08}$Ti$_{0.25}$) (Fig. 7). In spite of the high total intermetallic content of the synthesized powder (about 95%), no cracks are observed in the material, even during microhardness tests. The
powder is characterized by the higher hardness as compared to known gamma-alloys (average microhardness value was 313 HV0.25) and improved oxidation resistance.

High-quality detonation spray coatings with high hardness (940-1100 HV) and low porosity (less than 1%) have been obtained from the developed powder (Fig. 6c). The coatings exhibit good oxidation behavior up to 1173 K. The main phases identified in the oxide scale are (Al0.94Cr0.05)2O3 with corundum structure and TiO2 (rutile) alloyed with some aluminum.

Over the last years, there has been much interest in producing thick ferrite films for electromagnetic applications. Ferrites are iron-containing nonconducting ceramic materials with special magnetic properties. Traditionally, ferrites have been manufactured by conventional ceramic powder processing routes which involve milling the component oxides (in the correct proportions) with an organic binder in a ball mill, compacting, drying, pre-firing to burn out the binder and then sintering to form the ferrite crystal structure. Self-propagating high-temperature synthesis provides the important economical benefit connected with substitution of the rather long and expensive furnace ferritization stage for the fast and energy-efficient combustion process. The characteristic of an SHS process is that it requires the presence, in the initial mixture, of a combustible and an oxidant to implement the combustion reaction. Iron is usually used as a combustible, which is incorporated into the composition of the ferrite. Oxygen is used as the oxidant, obtained from one of two sources: an internal source, for example due to the oxygen evolution during decomposition of NaClO4 added to the reactive mixture, or an external source, for example oxygen in the air or bottled oxygen. Combined sources can be also used. Preliminary MA of a charge mixture in

Fig. 5 Comparative oxidation behavior of HVOF coatings (a) and cross-section of HVOF coating from FeAl-Fe0.8Al powder after 48 hour duration in air at 950°C (b).

Fig. 6 Morphology (a) and cross-section (b) of TiAlCr powder; cross-section of detonation spray coating from the powder (c).

Fig. 7 X-ray diffraction pattern of TiAlCr powder.
high-energy mills has a strong influence on the combustion parameters as well as on the structure and phase-formation mechanisms during SHS, resulting in improved conversion completeness and the formation of a fine homogeneous structure with uniform elemental distribution within the ferrite powder particles.

Recently, novel Ni,Zn-ferrite SHS powders with additions of Co and Mn have been developed for thermal spraying. The ferrite powder is manufactured via the MASHS route from reactive mixtures consisting of the constituent oxides and NaClO₄ as an oxidant. The investigation results have shown that the as-synthesized powder can be produced in size ranges and with an external morphology suitable for both high-velocity oxy-fuel flame and atmospheric plasma spraying. The powder has a single-phase spinel crystal structure and powder particles comprise sintered sub-micron grains. The spinel crystal structure of the original feedstock powder can be wholly or largely retained in the sprayed deposit, providing the necessary electromagnetic properties. The composition can be adjusted to match special requirements.

2.2. Composite powders

Composite powders are the most widely used for thermal spraying group of SHS powders. Self-propagating high-temperature synthesis provides an opportunity to produce composites via a single-stage process even in systems of materials with significantly different properties (for example, melting temperatures) as well as compositions that cannot be formed by the other methods.

Composite powders of the type “refractory compound / metallic binder” are produced by the synthesis of a refractory compound in the presence of metal binders, so-called “diluent”, using a high-temperature exothermal reaction of refractory compound formation. A wide range of compositions for wear-resistant coatings has been developed.

The most popular powders becoming widespread for thermal spray applications are titanium- and chromium carbide-based powders as well as titanium diboride-containing composites. Iron, nickel, cobalt, aluminum, copper and their alloys can be used as binders. A typical structure of a titanium carbide-based powder is presented in Fig. 9a. The principal advantages of the synthesized powders were fine distribution of carbide grains in the material volume and high cohesive bond strength between components of the composite (due to melting of metal binder during synthesis). The structure peculiarities of SHS powders provided the good coating properties. In general, the deposition efficiency, density, hardness and wear-resistance of TS coatings from the composite SHS powders were higher than that from plated or agglomerated ones (Table 1, 2).

![Fig.8 Cross-sections of (Ni,Zn,Co,Mn)Fe₂O₄ powder (a) and HVOF coating from it (b)](image)

![Fig.9 Cross-sections of NiCr / TiC powder (a) and LPPS coating from it (b).](image)
Further improvement can be achieved with the formation of complex compounds. A typical example is powder based on double chromium and titanium carbides. The idea of creating such a composition was based on the attempt to combine the excellent wear-resistance and extreme high hardness of titanium carbide with the high corrosion-resistance of chromium carbide. The powder was obtained by the simultaneous synthesis of chromium and titanium carbides in the presence of a nickel-chromium binder. To provide conversion completeness in systems with a high chromium carbide content, preheating as well as mechanical and chemical activation of the process were applied.

SHS yielded a fine-grained product with a composite structure. X-ray analysis identified three phases: titanium carbide, chromium carbide and a solid solution based on gamma-nickel. Depending on the TiC/Cr-C ratio in the charge mixture and the synthesis conditions, chromium can be mostly dissolved in titanium carbide, forming titanium-chromium carbide solid solution (double titanium-chromium carbide) or can make up its proper carbides.

Table 3 represents the oxidation resistance of the SHS composite powder 75 wt.% (Cr$_7$C$_3$) / 25 wt.% (Ni$_2$0Cr) - depending on the carbide phase composition. To control the content of chromium dissolved in the double carbide solid solution, titanium carbide lattice parameter measurements are presented (chromium is known to occupy titanium sites in TiC, decreasing its lattice parameter). In general, dissolving chromium in the titanium carbide lattice during synthesis ensures a higher oxidation resistance of the material. For the composition with 30 wt.% Cr$_7$C$_3$, in spite of significantly lower weight gain, the oxidation kinetics is still controlled by the formation of titanium oxides that do not exhibit a high protective ability. A protective chromia layer is formed at a titanium-to-chromium carbide ratio of 30:70 (see Table 3, line 6). The material oxidation behavior is practically the same as that of the composite with pure chromium carbide. Interestingly, when the synthesis conditions assist chromium to form its proper carbide, leading to a lower Cr content in titanium-chromium solid solution, the oxidation resistance of the composition drops again (compare line 5 and 6, Table 3).

Fig. 10a illustrates the structure of the developed powder. Gray fields consist of double carbide grains that are round in shape of up to 0.5-1 µm in size surrounded by the very thin layers of nickel solid solution (light in color). The chromium content is practically constant through the crystals. It was evaluated as about 3 wt.% based on the electron probe micro-analysis results. The microhardness of these areas is 766-1449 H.V50. The material also contains Cr$_2$ polyhedral crystals (light-gray) of 5-10 µm in size and a microhardness of 1449-1648 HV50. There are some
fine inclusions of nickel solid solution in chromium carbide areas, too.

HVOF coatings from the synthesized (Cr$_3$C$_2$-TiC)/NiCr powder (Fig. 10 (b)) demonstrate an extremely high thermal cycling lifetime (8-10 times higher than that of HVOF coatings from conventionally used WC-17%Co and 25NiCr-75Cr$_3$C$_2$ powders (Praxair Specialty)\textsuperscript{57}). Elevated temperature erosion in a wide range of test conditions did not reveal any signs of the material corrosion\textsuperscript{57}. The main mechanism of the surface degradation is mechanical wear caused by the impacting particles. The surface morphology of the erosion grooves is indicative of a ductile wear mechanism.

The industrial-scale production of the developed (Cr$_3$C$_2$-TiC)/NiCr powder has been approved in PMI with a deviation of the titanium carbide lattice parameter less than ±0.0001 nm. Since 1996, the powder has been employed in coal-fired boilers of energy plants and also in waste-incinerating systems as well as in the paper and chemical industries in the USA, Sweden, Germany and Poland.

Another approach to improvement of metal/ceramic composite powders is the development of binder materials. A big advance was achieved with complex binders\textsuperscript{35, 37, 42, 54, 73} and the introduction of solid lubricant phases such as graphite, calcium fluoride and molybdenum disilicide\textsuperscript{44, 48, 60, 65, 75} (by adding corresponding powders to the charge mixture). For example, SHS powders with solid lubricants (TiC/NiCr/MoS$_2$, TiC/NiCr/CaF$_2$, TiC/FeCr/graphite, TiC/Fe-CrMo/graphite and Cr$_2$O$_3$/TiO$_2$/CaF$_2$) provide good coating performance under dry or limited lubricated friction conditions and at high temperatures\textsuperscript{65}.

One more class of composite powders showing promise for TS applications is lightweight high-performance intermetallic-oxide composites which enable a significant decrease in weight whilst providing top performance as compared to existing materials.

In general, SHS intermetallic/oxide powders can be produced using two main approaches: (1) synthesis of intermetallics from the corresponding metal powders in the presence of dispersed alumina particles and (2) formation of necessary compositions using aluminothermal reduction of metal oxides. Both routes have some limitations connected with too low (in the first case) and too high (in the second one) exothermal reaction effects. In both cases, preliminary mechanical activation provides for the efficient solution of the problems and results in the formation of homogeneous fine-grained materials.

Fig. 11a represents the microstructure of a NiAl/Al$_2$O$_3$ composite powder produced by the synthesis of nickel monoaluminide from elemental powders in the presence of dispersed alumina particles\textsuperscript{45}. The powder microhardness is 350-650 HV$_{50}$. The amount of alumina is optimized in such a way that the mate-
rial’s thermal expansion coefficient is close to that of a carbon steel substrate, providing high performance of the coatings under thermal shock conditions. Plasma coatings from the powder (Fig. 11b) also exhibit good wear-resistance.\textsuperscript{45} Nanocomposite powders. The processing of nanostructured materials has attracted more attention in recent years due to the fact that the nanometer size scale brings substantial changes into physico-chemical and mechanical properties, in comparison with bulk properties.\textsuperscript{108} To produce nanostructural feedstock from micron- and submicron-grained composite powders, the post-synthesis treatment of SHS powders in attrition mills and high-energy mills is used.\textsuperscript{77-79} Nanocomposite coatings have been obtained from these feedstocks.

Recently, together with our colleagues from the Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia, we have developed a new approach to produce SHS nanocomposite powders using mechanocomposite precursors.\textsuperscript{109-111} It can be illustrated by the example of producing intermetallic/oxide powders in systems with aluminothermal reactions. The point of the process is that the aluminothermal reduction of metal oxides, fully or partially completed during the mechanical activation step, forms nanocomposite precursors containing nanosized alumina inclusions. In the second step, SHS proceeded in the precursors thus formed. The as-synthesized powders completely inherit the pre-

![Fig. 11 Cross-sections of NiAl / Al$_2$O$_3$ powder (a) and high-velocity plasma spray coating from it (b).](image)

![Fig. 12 Microstructure of nanocomposite SHS powders (a-b, d-e) and detonation spray coatings from them (c, f): a-c – FeAl / Al$_2$O$_3$ powder; d-f – FeAl(Cr) / Al$_2$O$_3$ powder.](image)
cursor’s structural morphology \(^{10,11}\). It is probably connected with the high rate of chemical reactions in the nanocomposite precursors and implementation of non-equilibrium phase formation mechanisms at the lowered temperatures \(^{11}\).

This approach was used to develop nanocomposite powders FeAl/Al\(_2\)O\(_3\) and FeAl(Cr)/Al\(_2\)O\(_3\) with so-called interpenetrating structure with improved interfacial strength \(^{12}\) (Fig. 12 a, b, d, e). Detonation spray coatings from the powders (Fig. 12c, f) also have a nanocomposite structure with average crystallite size of the intermetallic phase 15-57 nm, porosity less than 1%, microhardness 750-850 Hv200 and high antifriction properties at conditions of lubricated friction of sliding and rolling (friction ratio of coatings FeAl/Al\(_2\)O\(_3\) and FeAl(Cr)/Al\(_2\)O\(_3\) at loading of 5 MPa, sliding velocity 4.2 m/s and use of samples of hardened steel 45 subjected to nitrocementation as a counterbody is 0.05 and 0.045, respectively) \(^{11}\).

Thus, the SHS method opens up a great deal of opportunities for creating advanced powders for thermal spraying. A summarized list of thermal sprayed powders, methods of their deposition and coating properties is given in Table 4. At present, SHS powders for thermal spraying are developed and produced by the Institute of Structural Macrometallurgy (Russia), Powder Metallurgy Institute (Belarus), London & Scandinavian Metallurgy Co., Ltd. (Great Britain), Exotherm Co. (USA), Xform Inc. (USA) and Kyoritsu Ceramic Co. Ltd. (Japan).

**Summary**

From the results obtained it is evident that self-propagating high-temperature synthesis is a promising method for the preparation of advanced powders for thermal spraying functional coatings. Besides important economical and ecological benefits, the method allows the formation of powders with improved or non-stoichiometric TiN, NiAl modified with nano SiO\(_2\) and UDD PS, DS Wear protection, erosion- and corrosion-resistant coatings \(^{8, 13, 85}\).

<table>
<thead>
<tr>
<th>Powder composition</th>
<th>Spraying method</th>
<th>Coating function (properties)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSi(_2)</td>
<td>PS, HVOF</td>
<td>High-temperature oxidation-resistant coating</td>
<td>21, 24</td>
</tr>
<tr>
<td>Cr(_2)C(_2); (Ti, Cr)C; Cr(_2)C/Ti(<em>x)Cr(</em>{1-x})</td>
<td>PS</td>
<td>Wear protection</td>
<td>17, 51, 85</td>
</tr>
<tr>
<td>TiC-TiC(_2): (clad with nickel)</td>
<td>PS</td>
<td>Long-term oxidation resistance at 500°C</td>
<td>14, 17</td>
</tr>
<tr>
<td>TiB(_2): (SHS) + MoSi(_2)</td>
<td>APS</td>
<td>Composite-coated cathodes for aluminum electrolysis process</td>
<td>76</td>
</tr>
<tr>
<td>TiN, ZrN</td>
<td>PS</td>
<td>Coatings on carbon fibers</td>
<td>86</td>
</tr>
<tr>
<td>non-stoichiometric TiN(_x)</td>
<td>TS</td>
<td>Wear-resistant coating</td>
<td>85</td>
</tr>
<tr>
<td>NiAl; NiAl; NiAlCr; NiAl modified with nano SiO(_2) and UDD</td>
<td>PS, DS</td>
<td>High-temperature applications, high oxidation resistance</td>
<td>29, 94, 91-92</td>
</tr>
<tr>
<td>TIAI; TiAl</td>
<td>PS, DS</td>
<td>Lightweight, oxidation- and corrosion-resistant, Aircraft fuel coupling</td>
<td>8, 27, 81</td>
</tr>
<tr>
<td>TiAlCr</td>
<td>DS</td>
<td>Oxidation-resistant up to 900°C</td>
<td>102</td>
</tr>
<tr>
<td>FeAl-FeAl(_2)</td>
<td>HVOF, DS, PS</td>
<td>Wear and corrosion protection</td>
<td>64, 67</td>
</tr>
<tr>
<td>(Ni, Zn, Co, Mn) FeCo(_x)</td>
<td>HVOF, APS</td>
<td>Electromagnetic applications</td>
<td>105</td>
</tr>
<tr>
<td>TiC/Al SiC/Al, SiC/Al-Si</td>
<td>UPS, APS, LPPS</td>
<td>Wear protection of Al alloys</td>
<td>25, 31</td>
</tr>
<tr>
<td>TiC/Ni</td>
<td>PS</td>
<td>Modifying additive for CoNiCrAlY intermediate layer for thermal-barrier coating</td>
<td>78</td>
</tr>
<tr>
<td>TiC/Co/Ni</td>
<td>TS</td>
<td>Wear-resistant coating</td>
<td>85</td>
</tr>
<tr>
<td>(Ti, Cr)C/Ni; TiCr decency coated with Ni</td>
<td>PS</td>
<td>Wear protection, erosion- and corrosion-resistant coatings</td>
<td>8, 13, 85</td>
</tr>
<tr>
<td>TiC/NiCr</td>
<td>PS</td>
<td>Wear protection</td>
<td>15</td>
</tr>
<tr>
<td>TiC/Fe; TiC/Co; TiC/Al; TiC/Fe/C/Fe; TiC/FeCr/TiC/ NiCr; TiC/FeCu; TiC/FeCrNi; TiC/FeCrMoC; TiC/FeCrMnO; TiC/ CrNiMo; TiC/FeNiCrMo; TiC/ NiCr; TiC/ NiCrMo; TiC/ NiTiCrAl</td>
<td>HVOF, PS, UPS, LPPS</td>
<td>Wear protection</td>
<td>23, 31, 34, 42, 46, 52-56, 58, 66, 73</td>
</tr>
<tr>
<td>(Ti, W)C/Ni; TiC/NiCr; Cr/NiCr; (Mo, Ti)/C/ NiCr; (W, Ti)/C/ NiCr; (Ti, W)/C/ NiCr; TiC/ NiTiCrAl</td>
<td>PS, HVOF</td>
<td>Protection against corrosion and wear</td>
<td>35, 53, 56, 63</td>
</tr>
<tr>
<td>TiC/NiCr</td>
<td>PS</td>
<td>High sliding wear resistance</td>
<td>32</td>
</tr>
<tr>
<td>TiC/NiAl</td>
<td>TS</td>
<td>Protection against oxidation and wear in sulfur-containing area</td>
<td>28</td>
</tr>
<tr>
<td>TiC/NiCr; TiC/FeCr; Cr-Cr/CrN</td>
<td>LPPS, HVOF</td>
<td>Protection against erosion at temperatures up to 400°C for TiC-based powders; up to 600°C for Cr-Cr-based powder</td>
<td>30, 32</td>
</tr>
</tbody>
</table>
unique structure and properties in size ranges and with an external morphology suitable for different thermal spray processes. Usage of different kinds of the SHS process activation plays an important role in structure and phase-formation mechanisms, providing good flexibility and reliability even for industrial-scale powder production.

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