Possibilities of the Computer-Controlled Detonation Spraying method: A chemistry viewpoint

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Abstract

This article is aimed to discuss the chemical aspects of detonation spraying of powder materials. In this method of coating deposition, ceramic, metallic or composite powders are injected into the barrel of a detonation gun filled with an explosive gaseous mixture. When the latter is ignited, the powders are heated and accelerated toward the substrate. Subjected to high temperatures, the powders are prone to chemical reactions, the reaction products possibly becoming the major phase constituents of the coatings. What types of reactions are possible? Can these reactions be carried out in a controlled manner? We answer these questions considering the interactions of the sprayed powders with the gaseous environment of the barrel as well as those between the phases of a composite feedstock powder. In Computer-Controlled Detonation Spraying (CCDS), the explosive charge and stoichiometry of the fuel-oxygen mixtures are precisely measured and can be flexibly changed. Our studies demonstrate that with the introduction of a highly flexible process of CCDS, detonation spraying has entered a new development stage, at which it can be considered as a powerful method of composition and microstructure tailoring of thermally sprayed coatings. During CCDS of TiO_2-containing powders, chemical reduction of titanium dioxide can be carried out to different levels to form either oxygen-deficient TiO_{2-x} or Ti_3O_5 suboxide. CCDS of Ti_3Al can produce titanium oxide coatings when oxidation by the detonation products dominates or titanium nitride-titanium aluminide coatings when oxidation is hindered but the interaction of the powders with nitrogen—a carrier gas component—is favored. During detonation spraying of Ti_3SiC_2–Cu composites, the Ti_3SiC_2 phase is preserved only in cold conditions; otherwise, Si de-intercalates from the Ti_3SiC_2 phase and dissolves in Cu resulting in the formation of the TiC_x–Cu(Si) composite coatings.
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1. Introduction

Detonation spraying is a variation of thermal spraying, in which the feedstock powder particles are heated and accelerated toward the substrate by the products of gaseous detonation. Depending on the conditions of spraying, the powder particles partially or fully melt and form coatings of low porosity and good adhesion characteristics [1,2]. During heating, the sprayed particles also experience chemical action of the gaseous species, which are the detonation products of the fuel-oxygen mixtures or the carrier gas components. Indeed, the oxidation of the sprayed material has been observed to accompany the thermal spraying processes [3–5].

In order to tackle this issue, explosive mixtures rich in fuel were used to yield the detonation products of reducing chemical nature [6,7].

Next-generation detonation spraying facilities using computer control of the process appeared in 2005 [2] and since that time have been evaluated for several material systems [7–13]. A key advantage of the Computer-Controlled Detonation Spraying (CCDS) method is the possibility of precisely controlling the quantity of the explosive gaseous mixture used for each shot of the detonation gun and the oxygen to fuel ratio of the explosive mixtures. The carrier gas used to inject the powders into the barrel of the detonation gun and clean the system after each shot can be chosen based on its chemical properties.

A schematic of a CCDS2000 facility is presented in Fig. 1. A distinctive feature of detonation spraying is a pulsed character of the process enabled by the procedure described below. A channel inside gun barrel 1 850–1000 mm long and 20 mm

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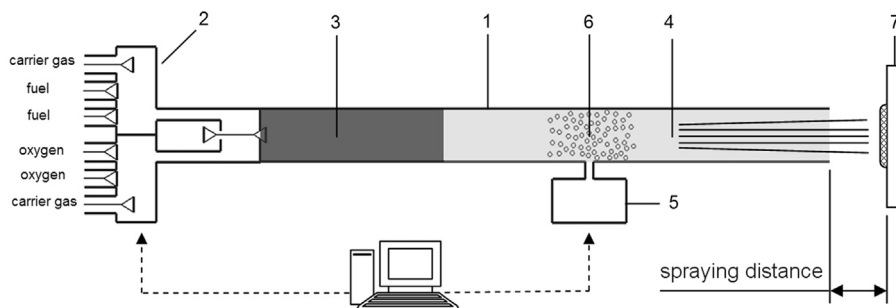*E-mail address:* dina1807@gmail.com (D.V. Dudina).

Fig. 1. A schematic of a CCDS2000 facility: 1 – gun barrel, 2 – computer-controlled precision gas distribution system, 3 – explosive charge, 4 – carrier gas, 5 – computer-controlled powder feeder, 6 – cloud of injected powder, 7 – substrate.

in diameter is filled with gases by a computer-controlled precision gas distribution system 2; first, it is filled with a carrier gas, then with a certain portion of an explosive mixture, which results in the formation of a stratified gas medium consisting of explosive charge 3 and carrier gas 4. Then a certain amount of the feedstock powder is injected into the barrel through an orifice by a computer-controlled feeder 5 with the help of the carrier gas flow. The powder injected into the barrel forms cloud 6, which for the taken barrel diameters and injection conditions can be considered uniform in density across the barrel cross-section. The cloud extends over a distance of up to 2–3 barrel diameters from the injection point having a concentration gradient along the barrel axis. The spraying distance is measured as a distance from the exit of barrel 1 to the surface of substrate 7. Once the powder is injected, the computer gives a signal to initiate detonation, which is done by an electric spark. An explosive combustion of the charge occurs within a time of the order of 1 ms such that a detonation wave forms in the explosive mixture transforming into a shock wave in the carrier gas. The detonation products heated up to 3500–4500 K and the carrier gas heated by the shock wave up to 1000–1500 K move at a supersonic speed and exchange heat and interact with the powder during 2–5 ms. In this process, the powder particles can be heated up to the material's melting temperature and accelerated up to velocities as high as $500 \text{ m} \cdot \text{s}^{-1}$. Here, depending on the initial composition of the explosive mixture and the nature of the carrier gas, certain chemical reactions are possible causing changes in the phase composition of the sprayed powder. A CCDS facility is thus a dynamic reactor, in which, using controllable flows of chemically active gases, it is possible to induce chemical reactions in the sprayed powder materials and synthesize coatings containing newly formed phases—reaction products.

The explosive charge measured as a fraction of the barrel volume that is filled with an explosive mixture and the oxygen to fuel ratio both influence the particle temperatures and velocities, and, therefore, the coating structure, adhesion, remaining porosity and other characteristics [2]. Along with physical and mechanical property tailoring of the coatings, variable spraying parameters help control the chemical processes during spraying. In this context, a distinct study has been conducted by Shtertser et al. [7], who evaluated CCDS conditions differing in the value of explosive charge for obtaining WC-Co-based coatings with an acceptable porosity and at the same time preserving an additive MoS₂, which

tends to decompose at temperatures normally required to produce dense WC-Co-based coatings.

Conducting experiments on a CCDS2000 facility, we have found that as the spraying conditions are varied—flexibly and in a wide range allowed by the technical capabilities of the facility—new phases can appear in the coatings in substantial quantities as a result of chemical reactions of reduction or oxidation [10–13]. Chemical sensitivity of the powders to the spraying atmosphere and interaction between the phases of composite powders at high temperatures are extremely important for the phase and microstructure development of the coatings. Due to the pulsed nature of the detonation spraying process, chemical interactions take place in highly non-equilibrium conditions as hot gases attack the powder particles. The reaction products may be metastable in terms of phase and crystalline structure due to fast reaction and rapid cooling of the splats upon deposition on the substrate. The goal of this article is to analyze the potential of the CCDS method for controlling the extent of chemical reactions in different material systems. We have investigated CCDS processes for an oxide-based material (TiO₂–Ag), an intermetallic compound (Ti₃Al) and a metal–ceramic composite (Ti₃SiC₂–Cu).

2. Experimental details

2.1. Detonation spraying conditions

A Computer Controlled Detonation Spraying (CCDS) facility [2] was used to deposit the coatings. Acetylene C_2H_2 was used as a fuel and oxygen was used as an oxidizer. The explosive charge was varied from 30 to 60% of the total barrel volume; several O_2/C_2H_2 molar ratios were used (1.05, 1.07; 1.48, 1.50; 2.00, 2.04).

2.1.1. TiO₂–Ag

The barrel of the detonation gun was 850 mm long and 20 mm in diameter. Air was used to purge the system before each shot and to inject the feedstock powders through the powder feeder. The spraying distance was set at 150 mm. The coatings were deposited on copper substrates 1 mm thick.

2.1.2. Ti₃Al

In one set of experiments, the barrel of the detonation gun was 800 mm long and 26 mm in diameter. Nitrogen was used to purge the system and as carrier gas. The spraying distance was 150 mm. The coatings were deposited on steel substrates 1 mm thick. In another set of experiments, the barrel of the detonation gun was 1000 mm long and 20 mm in diameter. Air was used to purge the system and as carrier gas. The coatings were deposited on steel substrates 3 mm thick. Several experiments were conducted with the same barrel geometry and argon as carrier gas. The spraying distance was set at 100 mm.

2.1.3. Ti₃SiC₂–Cu

The barrel of the detonation gun was 1000 mm long and 20 mm in diameter. Air was used to purge the system and inject the feedstock powders. The coatings were deposited on copper substrates 3 mm thick. The spraying distance was set at 100 mm.

2.2. Synthesis and preparation of the feedstock powders

2.2.1. TiO₂–Ag

Titanium dioxide (rutile, 99.999%) and silver (99.99%) powders were used to prepare the powders mixtures for the detonation spraying. The mixtures corresponding to the TiO_2-2.5 vol% Ag composition were ball milled in a high energy ball mill. The milled TiO_2-2.5 vol% Ag powders contained a large fraction of very fine particles (less than 5 μm in size). Particles in this size range are unsuitable for the detonation spraying as they tend to lose their velocity in the reflected shock waves. In addition, fine powders usually suffer from poor flowability and are difficult to efficiently inject in the barrel by the feeder. Therefore, agglomeration of the milled powders using a polyvinyl alcohol water solution was carried out. The dried product was sieved through a 71 μm-sieve.

2.2.2. Ti₃Al

Ti₃Al single-phase powders were synthesized by an exothermic reaction between titanium and aluminum in a thermal explosion mode in a mechanically milled 3Ti–1.15Al (at.) mixture following the processing route elaborated by Filimonov et al. [14]. Ti (98.5%) and Al (98%) powders were used as reactants. The experimental parameters were found in order to synthesize single-phase Ti₃Al. The product of thermal explosion was obtained in a powder form and was sieved through a 71 μm-sieve. For certain experiments, the 40–71 μm fraction was separated.

2.2.3. Ti₃SiC₂–Cu

Titanium silicon carbide Ti₃SiC₂ was synthesized from elements in the powder mixtures of Ti (99%), Si of semiconductor purity and amorphous carbon (lampblack, PM-15) mechanically milled and ignited to initiate a reaction of self-propagating high-temperature synthesis (SHS). Prior to mixing with copper, the synthesized Ti₃SiC₂ was milled to reduce its particle size and sieved through a 40 μm-sieve. The 20 vol% Ti₃SiC₂-Cu composite powders were prepared by mixing Cu (PMS-1, 99.7%) and Ti₃SiC₂ powders a planetary ball mill. The obtained composite agglomerates were sieved through a 71 μm-sieve.

2.3. Feedstock powder and coating characterization

The X-ray diffraction (XRD) patterns of the powders and coatings were recorded using a D8 ADVANCE diffractometer (Bruker AXS) with Cu Kα radiation. XRD phase analysis was performed using ICDD PDF-4+ database (Release 2011). The feedstock powder morphology and microstructure of the coatings were studied using Scanning Electron Microscopy by means of a Hitachi-Tabletop TM-1000 Scanning Electron Microscope with a back-scattered electron detector. For metallographic investigations, cross-sections of the coatings were prepared by cutting, mounting and polishing. Chemical etching was used to reveal the microstructural features of the coating obtained by spraying of the Ti₃SiC₂–Cu composite powders. The etching solution was prepared by mixing 10 g FeCl₃·6H₂O, 3 ml concentrated HCl and 100 ml H₂O.

3. Results and discussion

In the general form, the reaction occurring during detonation of a hydrocarbon fuel mixed with oxygen can be presented by the following scheme [2]:
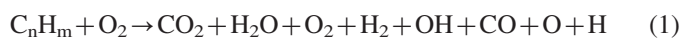
$$C_nH_m + O_2 \rightarrow CO_2 + H_2O + O_2 + H_2 + OH + CO + O + H \quad (1)$$

Molar fractions of the major components of the detonation products of acetylene–oxygen mixtures of different stoichiometry are shown in Table 1. The detonation products can possess a very high oxidizing activity due to the presence of atomic oxygen. In the detonation products of the $C_2H_2 + 2.04O_2$ mixtures, the content of atomic oxygen is about 11 mol.% [2]. As the explosive charge increases (in a CCDS facility normally from 30 to 60%), the temperatures up to which the particles heat during their flight inside the barrel increase [10,11]. The highest temperature of the detonation products is reached in acetylene–oxygen mixtures containing about 50 vol% of C_2H_2. As the oxygen content in the explosive mixture increases, the temperature of the detonation products decreases. However, due to reduced particle velocities observed when higher oxygen contents in the acetylene–oxygen

Table 1

Molar fractions of the major components of the detonation products of acetylene–oxygen mixtures of different stoichiometry.

Components	Molar fraction		
	$O_2/C_2H_2 = 1.07$	$O_2/C_2H_2 = 1.48$	$O_2/C_2H_2 = 2.04$
O	0.009	0.064	0.112
O_2	–	0.015	0.065
H	0.215	0.160	0.102
H_2	0.165	0.094	0.053
OH	0.013	0.070	0.106
H_2O	0.014	0.060	0.083
CO	0.579	0.503	0.411
CO_2	0.005	0.033	0.069

mixtures are used, the sprayed particles are heated up to higher temperatures before exiting the barrel.

3.1. Chemical interaction of the sprayed powders with the detonation products of acetylene–oxygen mixtures

3.1.1. Reduction

Although reduction of titanium dioxide is frequently encountered in thermal spraying, the products of reduction are usually only minor phase constituents of the coatings. Worth noting is research presented by Berger [15], who observed Magnéli phases as the major components in the vacuum plasma sprayed coatings obtained from commercial titanium dioxide. Reduction of titanium dioxide was due to the presence of hydrogen in the plasma. However, possibilities of controlling the phase composition of the coatings and the content of the products of chemical reduction of titanium dioxide have not been addressed in detail.

We conducted detonation spraying of the TiO_2-2.5 vol%Ag powders with rutile as the major phase (Fig. 2(a)) in both reducing and oxidizing atmospheres created by the detonation products of acetylene–oxygen mixtures of different stoichiometry [10,11]. At an O_2/C_2H_2 ratio of 1.05 and a low value of

Fig. 2. XRD patterns of the TiO_2–Ag composite powder (a) and the coatings produced by detonation spraying at $O_2/C_2H_2 = 1.05$, explosive charge 30% and 60% (b).

explosive charge (30%), rutile was preserved in the sprayed coatings; however, as was concluded from an observed change in its lattice parameter, it lost some oxygen (Fig. 2(b)). Further reduction of TiO_2 to an oxygen-deficient phase and titanium suboxide Ti_3O_5 was observed in the coating sprayed in reducing conditions at a higher explosive charge (60%) and, consequently, at higher particle temperatures. Reduction of titanium dioxide can occur owing to the following reactions

$$3TiO_2 + CO = Ti_3O_5 + CO_2 \qquad (2)$$

and

$$3TiO_2 + H_2 = Ti_3O_5 + H_2O \qquad (3)$$

Owing to highly non-equilibrium conditions of splat cooling in detonation spraying, the Ti_3O_5 phase that formed in the coatings was λ-phase, which is metastable at room temperature.

3.1.2. Oxidation

XRD pattern of the synthesized titanium aluminide Ti_3Al powder confirmed that the product of thermal explosion is a single-phase intermetallic compound (Fig. 3(a)). Conducting detonation spraying of the Ti_3Al powder, we have noticed that in oxidizing conditions of spraying, it can fully transform into titanium oxides (Fig. 3(b)). In these experiments, a barrel 800 mm long was used (see Section 2). Coatings produced by detonation spraying at $O_2/C_2H_2 = 1.05$ do not contain any oxides. In oxidizing conditions at $O_2/C_2H_2 = 2.00$, the coating is composed of 3 titanium oxides, while the Al/Ti at. ratio decreases to 0.057 as was determined by the EDS analysis in our previous study [12]. The observed loss of Al can be explained by the mechanical instability of particles having an Al_2O_3 scale on its surface during the flight and impact upon the substrate and by the formation of aluminum monoxide AlO, which is known to form during combustion of Al at low oxygen contents [16].

The presence of nitride phases in the coating sprayed at $O_2/C_2H_2 = 1.05$ is due to the interaction of the powders with nitrogen used as carrier gas. Coatings sprayed from the Ti_3Al powder at $O_2/C_2H_2 = 1.05$ and $O_2/C_2H_2 = 2.00$ and an explosive charge of 50% demonstrate an example of how the chemical processes affect the coating microstructure (Fig. 4). Both coatings possess a layered structure; however, the Ti_3Al–TiN coating has thicker layers than the titanium oxide coating. This difference can be explained by the occurrence of only partial transformation of Ti_3Al into TiN taking place on the particle surface in the former case and complete transformation of the initial Ti_3Al into titanium oxides in the latter case.

3.2. Chemical interaction with the carrier gas

The detonation spraying experiments with the Ti_3Al powder described in this subsection were conducted using air as carrier gas. In these experiments, a barrel 1000 mm long was used (see Section 2). The characteristic feature of the obtained coatings was the presence of titanium nitrides Ti_2N and TiN,
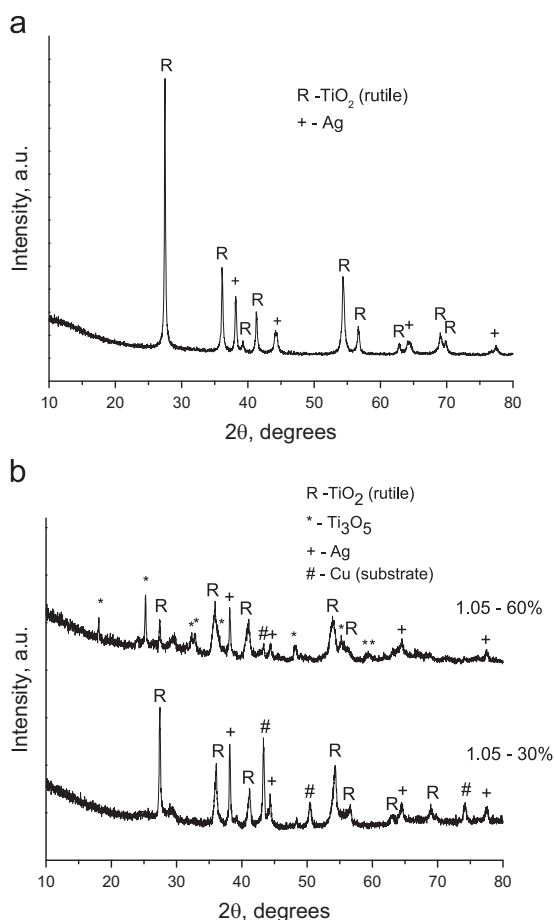
a

b
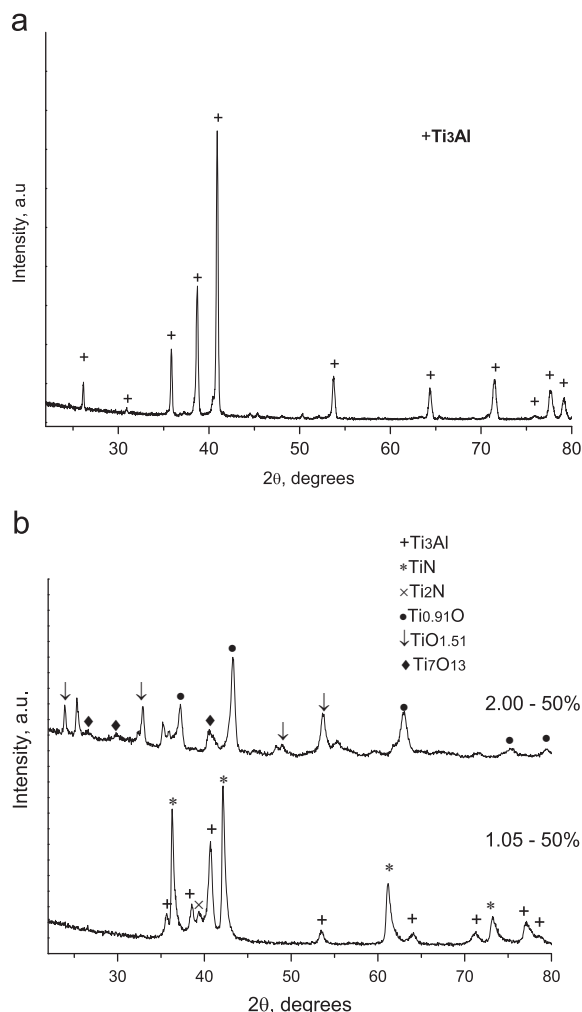

Fig. 3. XRD patterns of the Ti₃Al powder (a) and the coatings produced by detonation spraying of the Ti₃Al powder, fraction < 71 μm at $O_2/C_2H_2 = 1.05$ and 2.00, explosive charge 50% (b).

a

b

Fig. 4. Microstructure of the coatings produced by detonation spraying of Ti₃Al, fraction < 71 μm (cross-section of the coating; the coating/substrate boundary is horizontal): $O_2/C_2H_2 = 1.05$, explosive charge 50% (a); $O_2/C_2H_2 = 2.00$, explosive charge 50% (b).

whose relative contents changed with increasing explosive charge or oxygen content in the acetylene–oxygen mixtures. The presence of a nitride layer adherent to the base Ti₃Al during its oxidation in air at 900 °C has been confirmed by Dettenwanger and Schütze [17]. The source of nitrogen in the detonation sprayed coatings was air used as carrier gas while the exact phase composition of the coatings was affected by the particle temperatures. In coatings sprayed at $O_2/C_2H_2 = 1.48$ and explosive charges of 30% and 40%, both nitrides were present (Fig. 5(a)), the content of TiN being slightly higher in the coating sprayed at an explosive charge of 40% due to a higher temperature of the particles as is seen by the increased intensities of the reflections of the TiN phase in the XRD pattern. At higher temperatures reached at $O_2/C_2H_2 = 2.04$, the Ti₂N phase was not found in the coatings sprayed at an explosive charge of 40% (Fig. 5(b)). These observations indicate that temperature is an important factor in the interaction of Ti₃Al with nitrogen of air. A mixture of Ti₂N and TiN forms at low temperatures; at higher temperatures, the only nitride phase in the coatings is TiN. Substituting argon for air helped reduce the content of nitrides in the deposited layers; however, they were not fully eliminated. Indeed, nitrogen uptake could also occur during
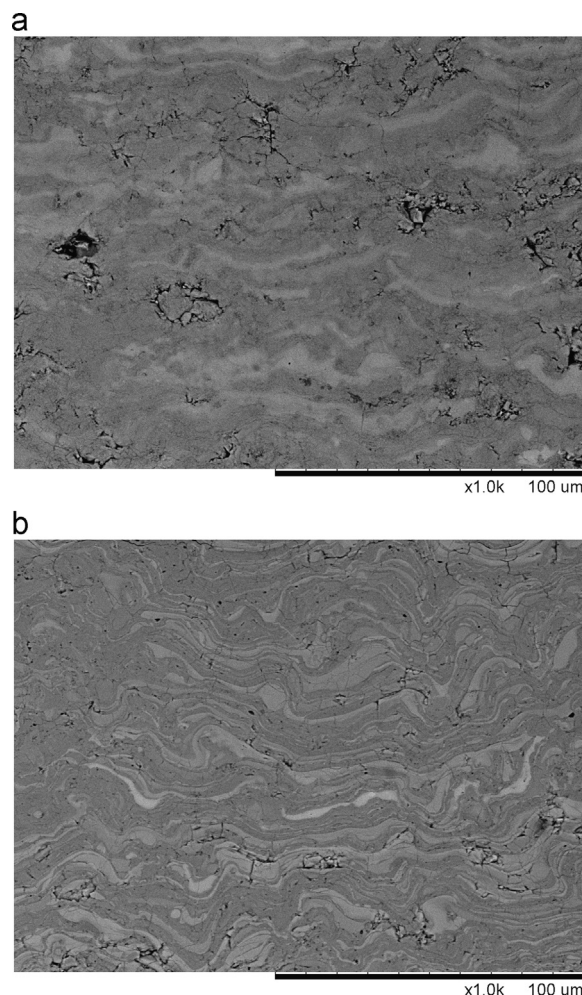
the particle flight to the substrate upon exit from the barrel, which cannot be ruled out in the detonation gun-substrate set-up of the selected geometry.

3.3. Interfacial reactions between the components of the composite feedstock powders

We have studied an interfacial reaction between titanium silicon carbide and copper in Ti₃SiC₂–Cu composites during detonation spraying under varied conditions. Ti₃SiC₂ belongs to the class of MAX-phases, which are hexagonal-structure ternary carbides and nitrides with a formula $M_{n+1}AX_n$, where $n = 1, 2, 3$ and M is an early transition metal, A is an A-group element and X is carbon or nitrogen [18]. The main challenge in thermal spraying of MAX-phases is to preserve the phase in the coating after it has been subjected to high temperatures and possibly an environment containing strong oxidizers [19]. When a MAX-phase is a component of a multiphase system, its possible interactions with other components should be addressed as well. A MAX-phase can experience decomposition leading to de-intercalation of A-element from its crystalline structure. In detonation spraying of Ti₃SiC₂–Cu

a

b
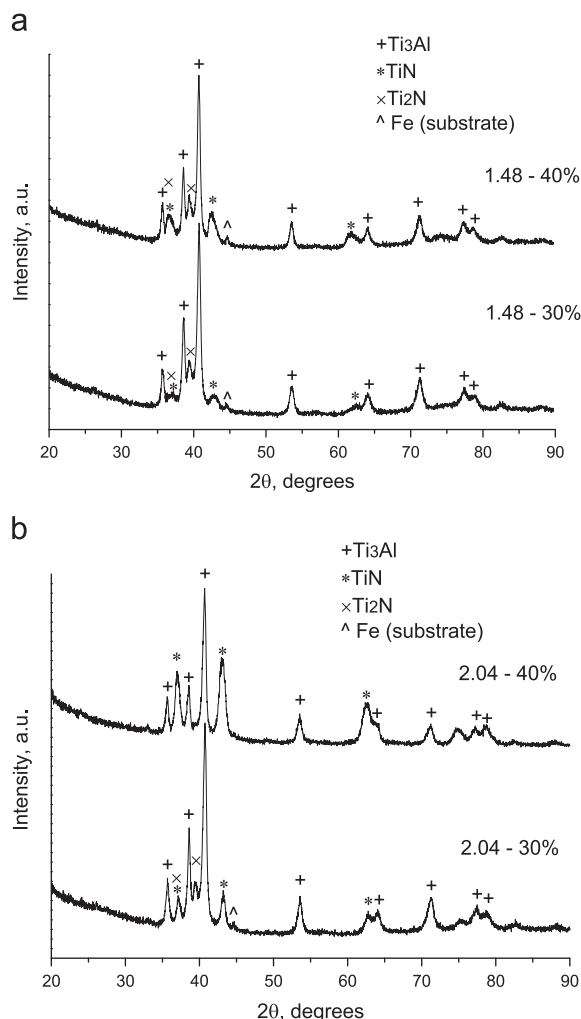

Fig. 5. XRD patterns of the coatings produced by detonation spraying of Ti_3Al, fraction 40–71 μm at $O_2/C_2H_2 = 1.48$, explosive charge 30% and 40% (a) and $O_2/C_2H_2 = 2.04$, explosive charge 30% and 40% (b).

Fig. 6. XRD patterns of the Ti_3SiC_2–Cu composite powder and the coatings produced by detonation spraying at $O_2/C_2H_2 = 1.07$, explosive charge 30% and $O_2/C_2H_2 = 1.07$, explosive charge 40%.

composites, particular attention should be directed to chemical interactions between the Ti_3SiC_2 and Cu phases, as Si has been shown to de-intercalate from Ti_3SiC_2 at temperatures above 900 °C in the presence of metallic Cu [20]. At the same time, in order to produce dense coatings well adhered to substrates, the sprayed powders have to be heated sufficiently to establish strong bonding with the substrate and cohesion between the layers of the coatings.

We have shown that it is possible to preserve the Ti_3SiC_2–Cu phase composition in the sprayed coatings only in cold conditions of detonation spraying—at an explosive charge of 30% and $O_2/C_2H_2 = 1.07$ (Fig. 6). As the particle temperature increased with increasing oxygen content in the acetylene–oxygen mixtures or with increasing explosive charge, even slightly—from 30 to 40% —keeping the same O_2/C_2H_2 ratio, Ti_3SiC_2 reacted with Cu according to the following scheme

$$Ti_3SiC_2 + Cu \rightarrow TiC_x + Cu(Si) \qquad (4)$$

which resulted in the formation of the TiC_x–Cu(Si) composite coatings.

Chemical etching of the polished surface of the cross-sections of the coatings helped making an interesting
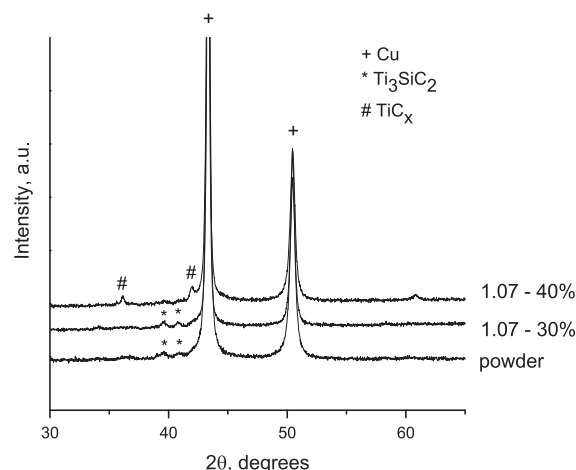
observation. In the coating deposited at $O_2/C_2H_2 = 1.07$ and an explosive charge of 30%, the lines reflecting the micro-structural features of the Ti_3SiC_2–Cu powder agglomerates produced by mechanical milling show random orientation (Fig. 7(a)). This indicates solid-state deposition of the Ti_3SiC_2–Cu composite particles. In the coating deposited at a higher temperature reached at an explosive charge of 40%, these lines have preferential orientation parallel to the coating/ substrate interface (Fig. 7(b)) indicating the presence of a characteristic layered structure formed by partially molten composite particles. The coating deposited at an explosive charge of 40% is denser than that deposited at an explosive charge of 30% but in terms of mutual distribution of the two phases (Ti_3SiC_2–Cu and TiC_x–Cu(Si)), no noticeable differences can be found in spite of the occurrence of the chemical reaction. The Ti_3SiC_2–Cu system is an example of a composite system that is very sensitive to the conditions of spraying. The behavior of this system during detonation spraying directly points to the advantages of CCDS with its flexibly changeable and adjustable spraying parameters.

3.4. Potential applications of detonation sprayed coatings of controlled chemical and phase composition produced by CCDS

As was seen from the above discussed examples, CCDS offers possibilities of producing coatings with the targeted phase composition, which is highly desirable for practical applications. Chemical reduction of TiO_2 to oxygen-deficient phases and suboxides is interesting form the viewpoint of making catalytically active materials and antibacterial surfaces. Ti_3Al–TiN coatings can protect titanium from oxidation. Ti_3SiC_2–Cu composites can find applications in the design of sliding contacts and electric switches. The reaction between Ti_3SiC_2 and Cu should be prevented to fully benefit from the properties of Ti_3SiC_2 and high electrical conductivity of the copper matrix. However, if higher temperatures are required to
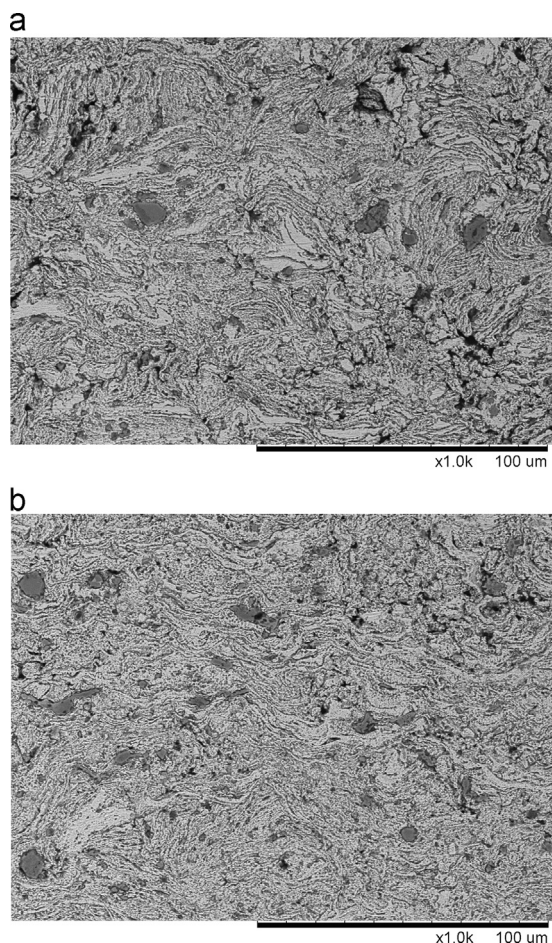
Fig. 7. Microstructure of the coatings produced by detonation spraying of the Ti$_3$SiC$_2$–Cu composite powder (cross-section of the coatings, etched in FeCl$_3$ solution; the coating/substrate boundary is horizontal): O$_2$/C$_2$H$_2$ = 1.07, explosive charge 30% (a); O$_2$/C$_2$H$_2$ = 1.07, explosive charge 40% (b).

improve adhesion of the coatings, a certain loss in electrical conductivity can be tolerated in the TiC$_x$–Cu(Si) composites, which gain additional mechanical strength due to solid solution strengthening of the copper matrix upon dissolution of silicon.

Further research on the possibilities of the detonation spraying for producing coatings of tailored phase composition and microstructure will benefit from involving Transmission Electron Microscopy to analyze the grain structure, as was done in our previous work [12], and detect poorly crystallized phases, if those are present in the coatings.

4. Conclusions

Our studies have shown that with the introduction of CCDS facilities, in which careful adjustment of the spraying parameters is made possible, detonation spraying has entered a new development stage, at which it can be considered as a powerful method of depositing coatings of tailored phase composition and microstructure. In CCDS, chemical reactions involving powders can be prevented or allowed to proceed to a chosen extent.

In reducing conditions, as the explosive charge is increased, TiO$_2$ is first reduced to an oxygen-deficient phase and then deeper to titanium suboxide Ti$_3$O$_5$. Ti$_3$Al is chemically sensitive to the atmosphere of spraying and easily transforms into titanium nitrides and oxides. Its oxidation can be prevented by creating reducing conditions of spraying; however, the use of nitrogen or air as carrier gases induces the formation of Ti$_2$N and TiN. As the explosive charge increases leading to an increase in the particle temperature, the Ti$_2$N phase disappears and the content of the TiN phase increases. In oxidizing conditions, complete oxidation of Ti$_3$Al can occur resulting in the formation of a mixture of titanium oxides. The formation of new phases in the coatings affects their microstructure development and results in the new microstructural features. Using detonation spraying of the Ti$_3$SiC$_2$–Cu composite powders, an interfacial reaction between the phases of the feedstock powders has been studied. In cold conditions of spraying, de-intercalation of Si can be prevented and the Ti$_3$SiC$_2$–Cu coatings form. At higher temperatures of spraying, the phases interact to form the TiC$_x$–Cu(Si) composite coatings.

References

[1] Y.A. Nikolaev, A.A. Vasiliev, V.Yu. Ulianitsky, Gas detonation and its application in engineering and technologies (Review), Combustion, Explosion and Shock Waves 39 (2003) 382–410.

[2] V. Ulianitsky, V. Shtertser, S. Zlobin, I. Smurov, Computer-controlled detonation spraying: from process fundamentals toward advanced applications, Journal of Thermal Spray Technology 20 (2011) 791–801.

[3] V.E. Oliker, V.L. Sirovatka, I.I. Timofeeva, E.F. Grechishkin, T.Ya. Gridasova, Effect of properties of titanium aluminide powders and detonation spraying conditions on phase and structure formation in coatings, Powder Metallurgy and Metal Ceramics 44 (2005) 472–480.

[4] V.E. Oliker, V.L. Sirovatka, I.I. Timofeeva, T.Ya. Gridasova, Ye.F. Hrechyshkin, Formation of detonation coatings based in titanium aluminide alloys and aluminum titanate ceramic sprayed from mechanically milled powders Ti-Al, Surface and Coatings Technology 200 (2006) 3573–3581.

[5] C. Senderowski, Z. Bojar, W. Wolczynski, A. Pawlowski, Microstructure characterization of D-gun sprayed Fe–Al intermetallic coatings, Intermetallics 18 (2010) 1405–1409.

[6] G. Sundarajan, G. Sivakumar, D. Sen, D. Rao Srinivasa, G. Ravichandra, The tribological behaviour of detonation sprayed TiMo(CN) based cermet coatings, International Journal of Refractory Metals and Hard Materials 28 (2010) 71–81.

[7] A. Shtertser, C. Muders, S. Veselov, S. Zlobin, V. Ulianitsky, X. Jiang, V. Bataev, Computer controlled detonation spraying of WC/Co coatings containing MoS$_2$ solid lubricant, Surface and Coatings Technology 206 (2012) 4763–4770.

[8] A. Sova, D. Pervushin, I. Smurov, Development of multimaterial coatings by cold spray and gas detonation spraying, Surface and Coatings Technology 205 (2010) 1108–1114.

[9] O.I. Lomovsky, D.V. Dudina, V.Yu. Ulianitsky, S.B. Zlobin, V.F. Kosarev, S.V. Klinkov, M.A. Korchagin, D.-H. Kwon, J.-S. Kim, Y.-S. Kwon, Cold

and detonation spraying of TiB$_2$–Cu nanocomposites, Materials Science Forum 534–536 (2007) 1373–1376.

[10] D.V. Dudina, S.B. Zlobin, N.V. Bulina, A.L. Bychkov, V.N. Korolyuk, V.Yu. Ulianitsky, O.I. Lomovsky, Detonation spraying of TiO$_2$–2.5 vol% Ag powders in a reducing atmosphere, Journal of the European Ceramic Society 32 (2012) 815–821.

[11] D.V. Dudina, S.B. Zlobin, V.Yu. Ulianitsky, O.I. Lomovsky, N. V. Bulina, I.A. Bataev, V.A. Bataev, Detonation spraying of TiO$_2$–Ag: controlling the phase composition and microstructure of the coatings, Ceramic Transactions 237 (2012) 161–169.

[12] D.V. Dudina, M.A. Korchagin, S.B. Zlobin, V.Yu. Ulianitsky, O. I. Lomovsky, N.V. Bulina, I.A. Bataev, V.A. Bataev, Compositional variations in the coatings formed by detonation spraying of Ti$_3$Al at different O$_2$/C$_2$H$_2$ ratios, Intermetallics 29 (2012) 140–146.

[13] D.V. Dudina, V.Yu. Ulianitsky, S.B. Zlobin, N.V. Bulina, O.I. Lomovsky, Detonation sprayed coatings: tailored phase composition and new microstructural features, in: T.S. Sudarshan, M. Jeandin, V. Fridrici (Eds.), Surface Modification Technologies, XXVI, Valardocs, India, 2013, pp. 377–384.

[14] V.Yu. Filimonov, M.A. Korchagin, I.A. Dietenberg, A.N. Tyumentsev, N.Z. Lyakhov, High temperature synthesis of single-phase Ti$_3$Al intermetallic compound in mechanically activated powder mixture, Powder Technology 235 (2013) 606–613.

[15] L.M. Berger. Titanium oxides—new opportunities for en established coating material, in: Proceedings of the ASM International Thermal Spray Conference, 2004, pp. 934–945.

[16] J.R. Carney, J. Scott Miller, J.C. Gump, G.I. Pangilinan, Atmospheric effects on the combustion of detonating aluminized explosives, AIP Conference Proceedings 845 (2005) 948–951.

[17] F. Dettenwanger, M. Schütze, Isothermal oxidation of α$_2$-Ti$_3$Al, Oxidation of Metals 54 (2000) 121–138.

[18] M.W. Barsoum, The M$_{N+1}$AX$_N$ phases: a new class of solids; thermodynamically stable nanolaminates, Progress in Solid State Chemistry 28 (2000) 201–281.

[19] M. Sonestedt, J. Frodelius, J.-P. Palmquist, H. Högberg, L. Hultman, K. Stiller, Microstructure of high velocity oxy-fuel sprayed Ti$_2$AlC coatings, Journal of Materials Science 45 (2010) 2760–2769.

[20] Y. Zhou, W. Gu, Chemical reaction and stability of Ti$_3$SiC$_2$ in Cu during high-temperature processing of Cu/Ti$_3$SiC$_2$ composites, Zeitschrift für Metallkunde 95 (2004) 50–56.