Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 3253–3260

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

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

Dina V. Dudina[a,*], Igor S. Batraev[b], Vladimir Yu. Ulianitsky[b], Michail A. Korchagin[a]

[a]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk 630128, Russian Federation
[b]Lavrentiev Institute of Hydrodynamics SB RAS, Novosibirsk, 630090, Russian Federation

Received 23 August 2013; received in revised form 16 September 2013; accepted 24 September 2013
Available online 2 October 2013

## 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.


*Keywords:* Detonation spraying; Coatings; Oxides; Intermetallics; Metal–ceramic composite

## 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

*Correspondence to: Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Kutateladze str. 18, Novosibirsk 630128, Russian Federation. Tel.: +7 383 233 24 10; fax: +7 383 332 28 47.
*E-mail address:* dina1807@gmail.com (D.V. Dudina).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.09.111

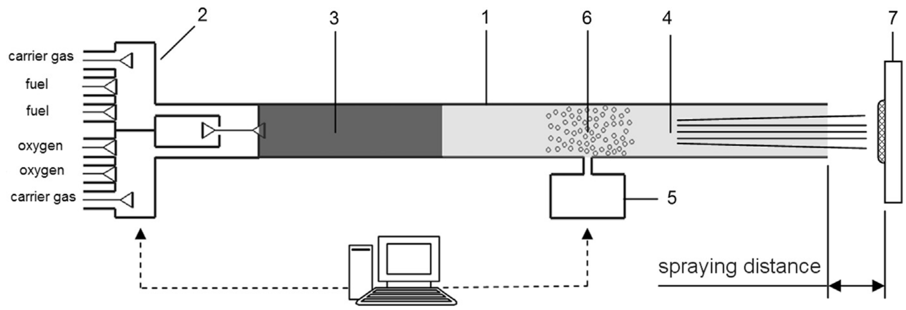


Fig. 1. A schematic of a CCDS2000 facility: 1 – gun barrel, 2 – computer-controlled precision gas distribution system, 3 – explosive charge, 4 – carrier gas, 5 – computer-controlled powder feeder, 6 – cloud of injected powder, 7 – substrate.

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 $500\ m \cdot s^{-1}$. 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 $MoS_2$, 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 ($TiO_2$–Ag), an intermetallic compound ($Ti_3Al$) and a metal–ceramic composite ($Ti_3SiC_2$–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. $TiO_2$–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.