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Detonation spraying of titanium and formation of coatings with spraying atmosphere-dependent phase composition

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ABSTRACT

The phase development in the coatings formed by detonation spraying of titanium in a wide range of compositions of the spraying atmosphere is reported. The phase composition of the coatings was found to be very sensitive to the O_2/C_2H_2 ratio and the nature of the powder carrier gas. Using $O_2/C_2H_2 = 1.1$ and air as a carrier gas, titanium oxynitride-containing coatings were obtained, while at $O_2/C_2H_2 = 2.5$, titanium oxides were the reaction products. In highly reducing conditions at $O_2/C_2H_2 = 0.7$ and with the use of nitrogen as a carrier gas, titanium carbide and carbonitride formed. Higher contents of nitrides in the coatings were found when nitrogen was added into the $O_2 + C_2H_2$ mixture. Metal-ceramic coatings formed at high transformation degrees of titanium were either composed of metallic titanium-rich particulate agglomerates distributed in a ceramic-rich matrix or contained alternating layers rich in metallic titanium and rich in ceramic compounds.

1. Introduction

Thermal spraying processes of coating manufacturing are based on heating and acceleration of powder particles by high-temperature gaseous flows [1–5]. For many materials, the action of hot gases during thermal spraying induces chemical reactions and leads to the formation of new phases in the coatings [6–17]. Interaction of particles of reactive metals (titanium, chromium or aluminum) with oxygen and nitrogen during thermal spraying presents an opportunity to form ceramic inclusions distributed in metal matrices [6,8–10]. Thermal spraying associated with chemical reactions offers new possibilities of coating design in terms of new phase compositions and microstructures that cannot be obtained by spraying of pre-mixed powders [13].

For a fast and highly non-equilibrium process of detonation spraying, it is very difficult to predict the extent of chemical reactions that occur between the powders and the gaseous phase [12]. The temperatures of the detonation products and the powder carrier gas heated by the shock wave are 3500–4500 K and 1000–1500 K, respectively. As the particles leave the barrel, they enter the surrounding atmosphere, and the interaction with air cannot be excluded. To a certain extent, the particles are "protected" by a cloud of the detonation products and the carrier gas. When the sprayed particles reach the substrate, they additionally heat, as the kinetic energy transforms into thermal energy. Calculations show that this temperature increase is of the order of 100–150 K. While the splats formed by the particles are still hot, the material is capable of interacting with oxygen and nitrogen of ambient air.

In this work, titanium was selected as a model material to study chemical effects involved in the coating formation, as metallic titanium is very reactive and can form oxides, nitrides, and carbides when allowed to react with the spraying atmosphere. In order to gain knowledge of the basic character, we varied the spraying parameters in a wide range (used different O_2/C_2H_2 ratios, different powder carrier gases, and different explosive charges—amounts of the explosive mixture). In our previous studies, it was found that even titanium-containing intermetallics, which are much less reactive than pure titanium, tend to react with nitrogen contained in the powder carrier gas [12,17] during detonation spraying. Changes in the phase composition of the coatings caused by the reactivity of titanium during thermal spraying were reported in refs.[14,15]. Kovaleva et al. [14] observed the formation of titanium oxide TiO and titanium carbide TiC during cumulative-detonation spraying of titanium. In their experiments, they used a constant oxygen/propane ratio. Kawakita et al. [15] showed that oxidation of titanium during the high-velocity oxy-fuel (HVOF) spraying can be controlled by reducing the temperature of the combustion products through the addition of nitrogen. Titanium can react with other species present in the feedstock. As was demonstrated by Zhu et al. [16], titanium of a Fe-Ti alloy can form carbides during detonation spraying reacting with carbon contained in the feedstock powder. Due to the short spraying time, the reactions between solid components of the feedstock powder may not occur or will occur only partially. Röttger et al. [18] produced coatings by HVOF using a blend of a gas-atomized

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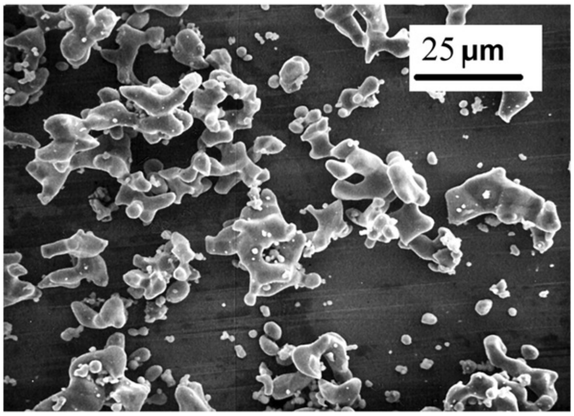

Fig. 1. Morphology of the titanium powder used in the present study.

high-carbon high-boron steel powder and a Fe-Ti alloy powder and did not observe any carbide phases in the as-sprayed coatings. The in situ formation of TiC in a steel matrix occurred during post-spray treatment by hot isostatic pressing at 1000 °C for 2 h, which provided sufficient time for the diffusion processes.

To our best knowledge, no report has presented *systematic* studies of the in situ phase formation and microstructure development of the coatings produced by detonation spraying of metallic titanium powders containing no additives. Such information is important for a deeper understanding of the nature and mechanisms of the physical and chemical processes involved in the detonation spraying of metal-containing materials. Therefore, the goal of this work was to investigate the detonation spraying behavior of titanium in a wide range of compositions of the spraying atmosphere—from highly reducing to highly oxidizing conditions created by changing the O_2/C_2H_2 ratio and with nitrogen or air used as powder carrier gases. Experiments were conducted with varied amounts of explosive charge. Special conditions presumably favoring titanium nitride formation were created by introducing nitrogen into the explosive $O_2 + C_2H_2$ mixture. It was shown that the in situ formed titanium-containing ceramic phases can become the major constituents of the coatings as a result of chemical reactions.

2. Materials and methods

2.1. Detonation spraying conditions

Titanium (99% purity, average particle size 15 μm, PTOM-2, Russia) was used as a feedstock powder. The morphology of the powder is shown in Fig. 1. The coatings were deposited using a computer-controlled detonation spraying (CCDS2000) facility, detailed description of which can be found in refs. [4,12]. The barrel of the detonation gun was 1000 mm long and 20 mm in diameter. The spraying distance was normally 10 or 100 mm. The spraying frequency was 5 Hz. The quantity of the powder sprayed per pulse was 40 mg. Air or nitrogen was used as a powder carrier gas. Spraying was performed using

Table 1
Detonation spraying conditions of the titanium powder.

Sample	O_2/C_2H_2	Spraying distance, mm	Explosive charge, %	Carrier gas
Ti-1	1.1	100	30	air
Ti-2	2.5	100	30	air
Ti-3	1.1	10	30	N_2
Ti-4	1.1	10	40	N_2
Ti-5	1.1 + 33vol.%N_2*	10	60	N_2
Ti-6	0.7	10	40	N_2
Ti-7	0.7	10	50	N_2
Ti-8	0.7	100	50	N_2

* N_2 was added into the mixture of $O_2 + C_2H_2$, the volume content of N_2 in the mixture was 33 %.

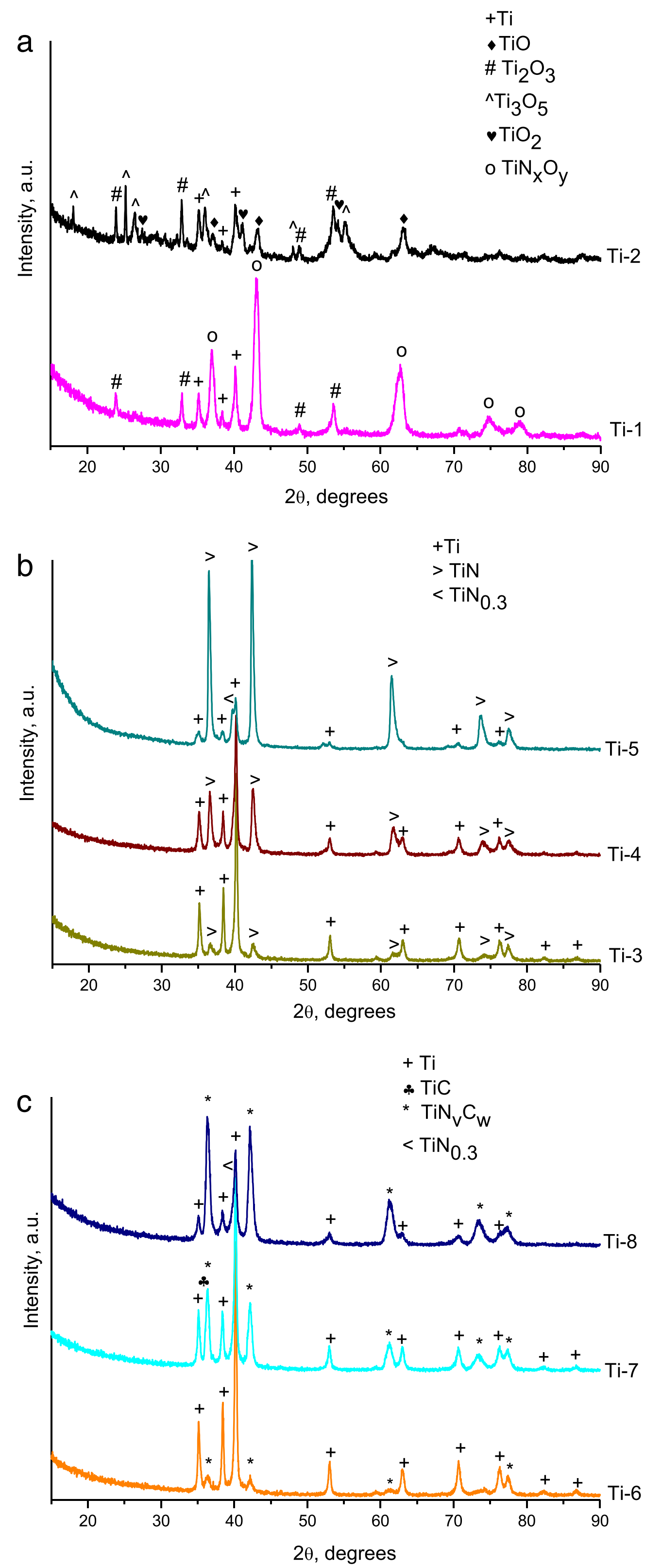

Fig. 2. XRD patterns of the coatings produced by detonation spraying of titanium: (a) Ti-1 and Ti-2; (b) Ti-3, Ti-4 and Ti-5; (c) Ti-6, Ti-7, and Ti-8.