



The influence of the in-situ formed and added carbon on the formation of metastable Ni-based phases during detonation spraying



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ARTICLE INFO

Article history:

Received 11 March 2016

Accepted 5 June 2016

Available online 7 June 2016

Keywords:

A. Metals, carbides

B. Coatings

C. Electron microscopy

ABSTRACT

Detonation (D-gun) spraying uses detonation of hydrocarbon fuel to heat and accelerate the powder particles. Spraying using incomplete combustion can lead to changes in the composition of the sprayed material due to the presence of the in-situ formed carbon particles in the spraying atmosphere. In this work, we have studied the phase formation of the deposits obtained by D-gun spraying of Ni and “Ni-amorphous carbon mixtures”. It was found that solid solutions based on metastable hcp-Ni and fcc-Ni form in detonation deposits at $O_2/C_2H_2=0.7$ and explosive charges of 50–70%. No metastable phases were found in the coatings sprayed at O_2/C_2H_2 greater than 1.1. Microstructural and elemental analyses confirmed that the in-situ formed carbon is preferentially incorporated in molten Ni particles. Carbon ex-situ introduced into the feedstock powder changes the sprinkling conditions of the melt over the substrate surface and lowers the cooling rate of the molten particles. As a result, deposits obtained at an explosive charge of 60% and 70% from powders containing added carbon tend to show lower concentrations of the hcp phase compared with deposits obtained from Ni.

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1. Introduction

Detonation spraying, or D-gun spraying, was developed several decades ago and since then has transformed into a powerful and flexible coating deposition technology [1,2]. The design of the modern detonation spraying facilities allows obtaining coatings in a wide range of conditions differing in the composition and temperature of the detonation products and their quantity per single shot of the gun. It was shown that significant compositional changes of the coating relative to the feedstock powder can occur during detonation spraying depending on several parameters, including the oxygen/fuel ratio [2–5]. Acetylene is commonly used as a fuel in detonation spraying and practically significant materials are usually sprayed at molar ratios $O_2/C_2H_2 \geq 1$. However, deposition of the coatings is also possible at lower oxygen contents. Incomplete combustion of acetylene results in the formation of solid carbon particles [6]. When metals are sprayed in such conditions, the presence of the in-situ formed carbon can affect the phase composition of the sprayed metal-based deposits. As

detonation spraying is a fast non-equilibrium high-temperature process, in which the physical and chemical events are inter-related, the exact path of the material formation and evolution of the composition will depend on many factors.

Herein, we present a study of the carbon incorporation in nickel during detonation spraying. The behavior of nickel and “Ni-amorphous carbon mixtures” (Ni-C_{am}) was investigated at $O_2/C_2H_2=0.7$ to track the influence of the in-situ formed and ex-situ added carbon on the phase composition of the deposited material.

2. Experimental

Carbonyl nickel (99.9% purity, Norilsk Nickel, Russia) and amorphous carbon C_{am} (95% purity, PM-15, Omsk, Russia, globule size 100–200 nm) powders were taken to prepare the feedstock powders. The Ni powder was sprayed without any pre-treatment. The details of the ball milling procedure to prepare Ni-50 vol% C_{am} composite feedstock can be found in Ref. [7]. A detonation spraying was conducted using Computer-Controlled Detonation Spraying facility CCDS2000. The detailed technical description of this equipment and its design can be found in Ref. [2]. The explosive charge was 40–70% of the barrel volume and different

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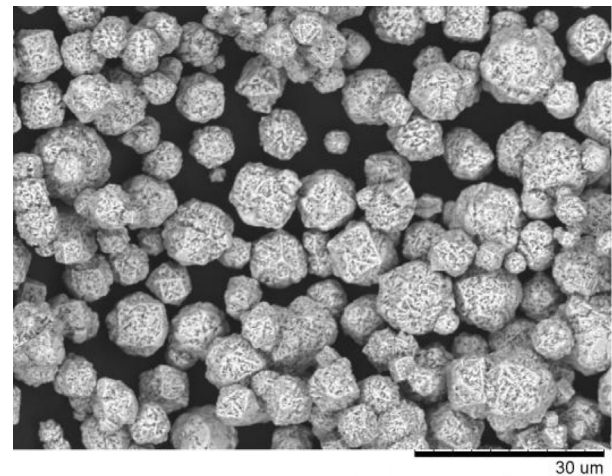
O_2/C_2H_2 ratios (0.7; 1.1; 2.0) were used in comparative experiments. Nitrogen was used as a carrier gas. The spraying distance was 100 mm. The powders were deposited on steel substrates. X-ray diffraction (XRD) patterns of the feedstock powders and detonation deposits were recorded using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with $Cu\ K\alpha$ radiation. XRD patterns were collected in the interval $10^\circ < 2\Theta < 90^\circ$ with a step size of $\Delta 2\Theta = 0.0195^\circ$ and a counting time of 35.4 s per step. Several scans were recorded with a counting time of 708 s per step. Refinement of the lattice parameters from the XRD patterns and quantitative analysis were carried out using TOPAS 4.2 software (Bruker AXS, Germany). The morphology of the powders and detonation deposits was studied by Scanning Electron Microscopy using a Hitachi Tabletop TM-1000 and a Hitachi-3400S microscopes. Energy-dispersive spectroscopy (EDS) was conducted using NORAN Spectral System 7 (Thermo Fisher Scientific Inc.) attached to the Hitachi-3400S microscope.

3. Results and discussion

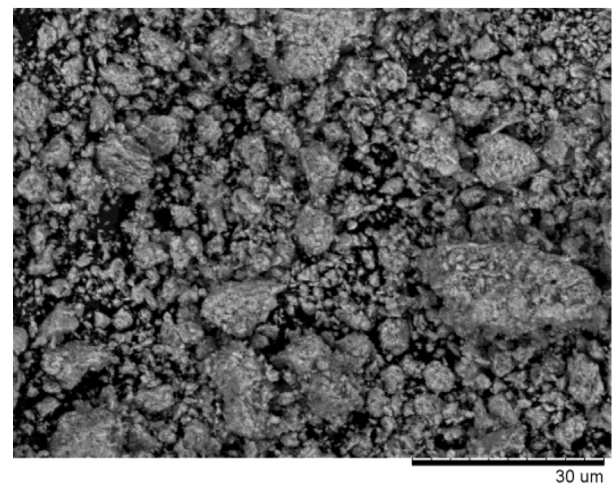
Fig. 1(a)–(b) shows the morphology of the Ni powder and the powder prepared by ball milling of Ni-50 vol% C_{am} mixtures. In the ball milled powders, along with thorough mixing of nickel and amorphous carbon, dissolution of carbon into nickel occurs, which explains the asymmetric shape of the peaks of the face-centered cubic (fcc) structure of Ni (Fig. 1(c)). Indeed, it was shown that carbon solubility in nickel can be extended by non-equilibrium treatments, such as splat quenching [8] or mechanical alloying [9,10].

Carbon forming as a result of incomplete combustion of acetylene is always in excess relative to the amount of metallic powder injected into the gun barrel in a single shot. However, only a fraction of the in-situ formed carbon will incorporate in the deposits. Fig. 2(a)–(b) shows the XRD patterns of the deposits obtained from the Ni powder and Ni- C_{am} mixtures at $O_2/C_2H_2 = 0.7$ and explosive charges of 50–70%. The patterns show reflections of fcc Ni-based solid solutions with varying lattice parameters (Table 1) marked as (1) and (2). The patterns also show reflections with positions close to those of hexagonal close-packed (hcp) Ni. With increasing explosive charge for both Ni and Ni- C_{am} , the total of the two fcc solid solutions in the deposited layers decreases, while the content of the hcp phase increases (Table 1). An increase in the lattice parameters of solid solutions observed with increasing explosive charge indicates higher carbon contents in the Ni lattices. It should be noted that reflections of the graphite phase were absent in the XRD patterns of the coatings obtained at $O_2/C_2H_2 = 0.7$. While graphitization of amorphous carbon readily occurs during sintering of its mixtures with nickel [7], the duration of the detonation spraying process appears to be too short for the graphitization transformation to take place in the coatings.

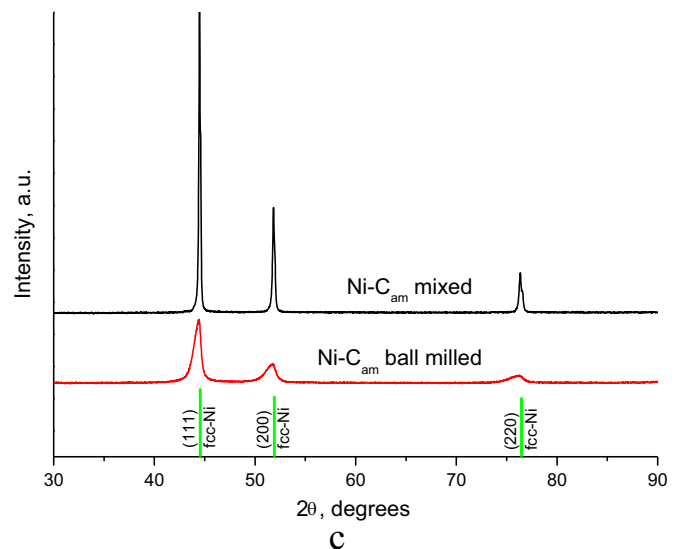
Hcp-Ni is metastable and was observed by Bolokang and Phasha [11] in Ni water-quenched from 1100 °C. It has been shown that hcp-Ni can be stabilized by carbon layers covering the surface of nanoparticles [12] and carbon incorporated into the lattice [13]. In our experiments, in the conditions of incomplete combustion and the in-situ formation of carbon both stabilization mechanisms can be involved. Lattice parameters of nominally pure hcp-Ni determined by different authors for materials produced by different methods have been summarized in Refs. [11,12]. As was pointed out in Ref. [11], a scatter in the lattice parameters can be due to the influence of impurities stabilizing the hcp structure. The values that have been reported previously are either smaller or larger than the lattice parameters calculated in this work. This allowed us to assign the observed XRD reflections to a carbon-containing Ni-based solid solution of hcp structure. Worth noting is a study by



a



b



c

Fig. 1. Morphology of the Ni powder (a) and the composite powder prepared by ball milling of Ni-50 vol% C_{am} mixtures (b) and XRD patterns of the Ni-50 vol% C_{am} mixtures before and after ball milling (c).

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