



USE OF COLD GAS DYNAMIC SPRAYING OF BI-METALLIC POWDER MIXTURES AS ALTERNATIVE TO CLASSIC POWDER METALLURGY ROUTE FOR PRODUCING INTERMETALLIC MATERIALS

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Resume

The paper presents cold gas dynamic spraying (or Cold Spray) as a novel surface treatment technology capable not only of surface modifications but also being used as bulk creating technology. This is demonstrated on numerous samples where bi-metallic powder feedstock is deposited into bulk, self-standing pieces of material that does not need the support of substrate. Mixtures from the group of Fe, Al, Ti, Ni, Cu were used for the initial bi-metallic mixtures. The deposited samples were then subjected to annealing at temperatures ranging from 300 to 1100°C in protective atmosphere and resulting morphologies and microstructures were analysed. Generally materials with high proportion of intermetallic phase content were obtained. These are discussed as potential scaffolds for metal or polymer matrix composites or as hi temperature resistive supports for catalysts with filter functions.

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1. Introduction

Due to the similarities, the innovative low-temperature cold gas dynamic spray process (cold spray, CGDS, CS) [1] is regarded as one of the thermal spray techniques (Fig. 1). It is a novel surface treatment technology whereby protective or function performing coatings are readily applied onto prepared substrates. The coating is not formed by means of thermal input but high kinetic energy impingement and corresponding severe plastic deformation. The resulting material exhibits practically zero oxidation, extremely low porosity and excellent machinability among other interesting features. As such the cold spray process is also suitable for producing self-supporting (bulk) material

by depositing thick coatings onto disposable substrate.

In thermal spray processes finely divided metal or non-metal material is deposited in a molten or semi-molten state onto a prepared substrate to form a spray deposit ("coating") [2]. The material is inserted in various forms, heated in gaseous medium and propelled towards the substrate surface [3]. Depending on the technology, the high velocities of acting gases cause acceleration of the small particles of the material up to 1400 m.s⁻¹ [1]. Eventual heating can cause further increase in the particles kinetic energy and likely cause partial or full-scale melting of the particles [4]. The immense kinetic energies stored in particles account for the large

amount of both elastic and plastic deformation of the molten or semi-molten particles during the process of its solidification at the surface. The solidified particles are called 'splats' and due to common concurrence of acting temperature and velocity, their resulting shape is far from ideal spheres, with their shape best described as lamella [4]. A synchronous relative movement of the thermal spray source against the substrate enables covering the substrate in individually deposited layers, each consisting of millions of the solidified splats. The final coating thickness is influenced by a number of spray gun passes, relative speed of the gun towards the surface, the efficiency of the deposition process and material deposition rate (indicated in kg.s^{-1} and proportional to the number of particles entering the jet) and could generally vary from 5 μm (a single layer coating) up to several mm (usually a coating with graded or sandwich layer structure). However, vast amounts of oxidation is typically present in the thermally sprayed deposit, which is the effect of inevitable presence of oxygen either from the fuel or from surrounding atmosphere, which takes part in the stream of semi-molten particles transported to the substrate. This means that it is quite difficult to create metallurgically clean deposit consisting only of metallic phases. The coatings exhibit inimitable, messy structure consisting of the solidified splats, unmolten or partly molten particles, both amorphous and recrystallized phases, voids, micro-cracks, and various impurities such as oxide inclusions [7]. As such, the properties of the final coatings may vary significantly from those of the feedstock material, often resulting in deterioration in the targeted performance.

1.1 Cold gas dynamic spray process

The newest of all the thermal spray processes, cold spray is the next progressive step in the development of high kinetic energy coating processes, following the trend of increasing particle spray velocity and reducing particle temperature (Fig. 1). In the process,

a compressed gas such as helium, nitrogen or air is divided into pressure gas (pressures up to 5 MPa, flow rates up to 90 $\text{m}^3.\text{hr}^{-1}$) and a feeder gas. The pressure gas is moderately heated and exits the spray gun via a conical convergent-divergent Laval nozzle [5] accelerated to supersonic velocities. The feedstock powder is injected axially into the feeder gas flow at the gun nozzle intake and accelerated to velocities of 300-1500 m.s^{-1} [5] (Fig. 2). Contrary to its high-temperature counterparts, cold sprayed coating is not built up by means of melting and solidifying of impinging particles. Instead, bonding in cold spray is associated with a solid-state plastic deformation, namely adiabatic shear instabilities caused by high strain deformation rate during impingement, thereby producing dense coatings without the feed-stock material being significantly heated [1].

Cold spray has some unique features as compared to other thermal deposition techniques. Bonding of particles occurs solely when the impact velocities of particles exceed a critical value, v_{critical} [6]. This critical velocity depends on the type of spray material, the powder quality, particle size and the particle impact temperature. Particles cold sprayed below the threshold value merely act as abrasives, a process similar to grit-blasting. The nozzle exhaust gas velocity propelling the particles is given as:

$$v = \sqrt{\frac{TR}{m_a(\text{gas})} \cdot \frac{2k}{k-1} \cdot \left[1 - \left(\frac{P_e}{P} \right)^{\frac{k-1}{k}} \right]} \geq v_{\text{critical}} \quad (1)$$

where $k = \frac{c_p}{c_v}$ is the isotropic expansion factor, c_p and c_v are the specific heats of the gas at constant pressure or volume, respectively, T is the absolute temperature of the inlet gas, R is the ideal gas constant ($8.314 \text{ J.mol}^{-1}\text{K}^{-1}$), $m_a(\text{gas})$ is the molecular weight of the used pressure gas and P_e and P are the absolute pressures of the exhaust gas at the nozzle exit and the inlet gas, respectively. Arising from equation 1, the ideal solution for fabricating cold sprayed coatings is the usage of helium as the propellant

gas, due to its inert character, viscosity, and the velocities attained by the particles in the jet. Due to the He production costs, helium recuperation

systems were recently introduced. However, majority of the nowadays CGDS production uses N_2 or N_2/He mixtures.

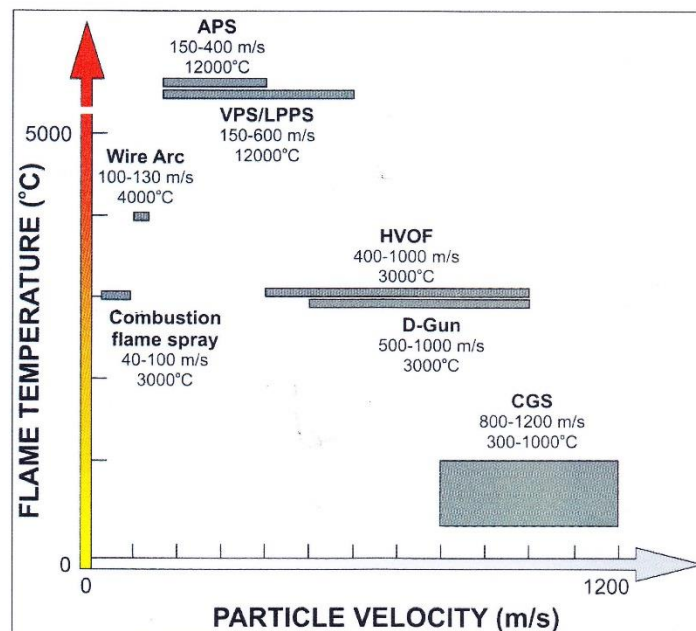


Fig. 1. In flight temperatures and velocities of the feedstock material in various thermal spray processes. (full colour version available online)

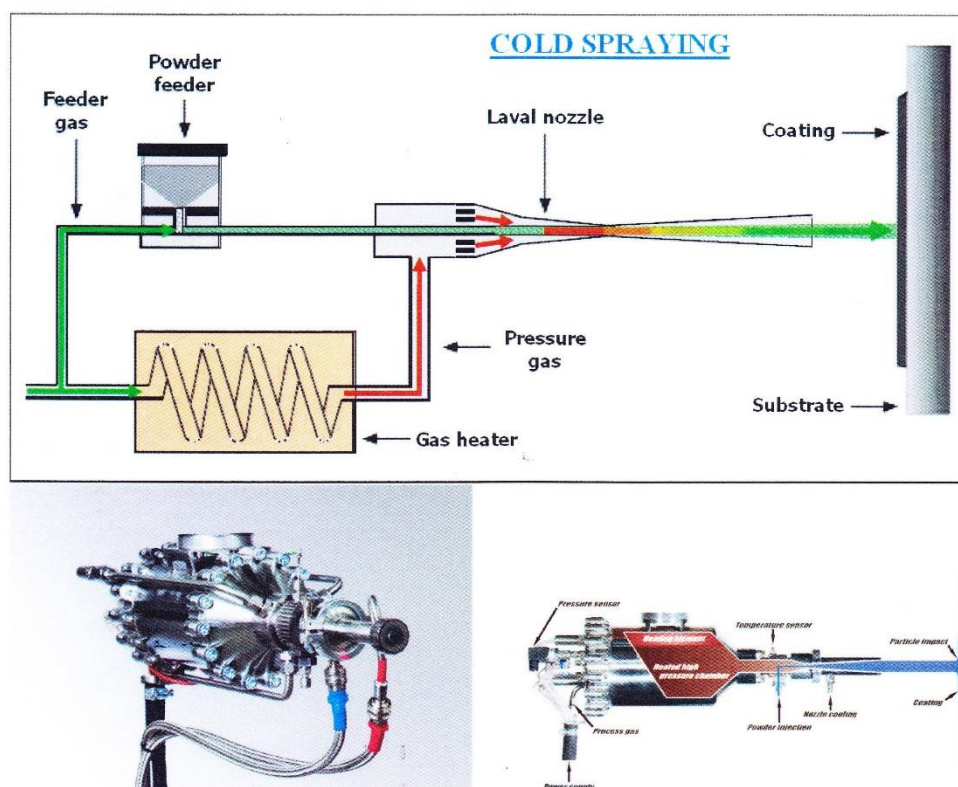


Fig. 2. Schematics of cold spray process and commercial high-pressure gun (image courtesy of Impact Innovation GmbH). (full colour version available online)

1.2 Properties of coatings prepared by CGDS

Due to its ambient-temperature character (Fig. 1), cold spraying eliminates the detrimental effects of high temperatures experienced with other thermal spray techniques. Phase and composition changes of the original feedstock are negligible and the substantial reduction of material oxidation in cold-sprayed coatings results in dramatic increase of thermal and electrical conductivities of metallic coatings. Further, the absence of oxides improves the intrinsic bonding strength, resulting in superior adhesion strengths among the thermal spray processes. Also the contact between individual particles is direct metallic without any oxide separation. Coating hardness is also improved. It was shown that cold spray coatings exhibit strict isotropy of their intrinsic mechanical properties in the elastic range [8] that could eventually open up a whole new range of possibilities. Other advantages of cold spray technique include extended components lifetime [9, 10], reduced material loss by vaporization, low gas entrapment (in voids) and insignificant grain growth and recrystallization. High spray rates (up to 10 kg.hr⁻¹) and deposition efficiency (up to 99 %) allow fast coating build-ups of about 250 µm per pass. The inherent residual stresses induced by cold spray are of compressive nature, allowing production of thicker coatings, even production of bulk materials which is later shown in this study.

1.3 CGDS coatings applications

Typical applications of cold spray technology include coatings with increased thermal conductivity, wear and fatigue resistant coatings on biomedical implants [11], deposition of electrical conductors in electronics industry [12], corrosion protection coatings with enhanced performance due to low oxide content and deposition onto glass or aluminium and other comparatively low-temperature melting substrate materials to locally increase hardness or wear resistance. CS coatings are frequently used as oxidation or corrosion protection [13].

Furthermore, cold spray allows spraying materials with low decomposition temperatures, e.g. polymers. Combining the advantages, CS can produce composite coatings of highly dissimilar materials, such as metal-matrix composites [14] or small-grain intermetallic alloys [15].

The thermal load on the substrate and preceding layers from consecutive nozzle passes is minimal as opposed to high-temperature spray processes. Therefore, the resulting stresses are of compressive nature [16] and the coating delamination and decohesion is restrained. Thereby, the overall coating adhesion is significantly improved, reaching up to 300 MPa, higher than the coatings produced by other (thermal) spray techniques. Also, the moduli of the coatings are approaching those of the respectively polycrystalline bulks [8]. These factors allow for production of thick coatings and cold spray is capable of being implemented in additive manufacturing (freeform fabrication, [17, 18]). This allowed for manufacturing of reactive bulk deposits for intermetallic materials production.

1.4 CGDS as compaction process for in situ intermetallics production

The intermetallic materials present an interesting group with some outstanding qualities. Intermetallics usually have high strength and lower ductility – characteristics that are connected to their crystal lattice type. Applications of intermetallic materials are very diverse, starting from electronic industry (GaAs, InAs, InSb); use of intermetallic precipitates (NiAl) for strengthening of superalloys; to bulk materials used as casting alloys (TiAl, NiAl).

Iron aluminides - FeAl and Fe₃Al phases are attractive for their high temperature properties and also because the raw materials are relatively cheap. Iron aluminides have low specific weight and high resistance against oxidation and carburization. They exhibit reasonable resistance in the presence of sulphur as well. So besides the high temperature

applications, which are common to all aluminides, use in chemical industry is also applicable for iron aluminides [20, 21].

Usually these materials are manufactured using casting technologies such as precision casting under protective atmosphere or vacuum and consecutive limited machining. Powder metallurgy also represents one of the very promising and sometimes the currently only realistic manufacturing route for some intermetallics. As such, powder metallurgy inherently brings limitations to possible size of the final product or its shape variability, should the machining and the amount of inevitable scrap material be reduced as much as possible. As it was mentioned earlier here, the cold spray process allows creating bulk deposits that need not to rely on substrate considering overall shape and component strength. It is possible to deposit big amounts of material in times allowing for real technical use.

To test the possibility of using cold spray in place of compacting steps such as cold pressing, extrusion or HIP, cold spray has been used to form massive deposits with arbitrary shapes from heterogeneous bi-metallic mixtures [22, 23].

2. Experimental

Cold spray technology produces coatings with little or no phase and structure changes as compared to the original feedstock, post-spray heat treatments to restore initial phase composition are therefore unnecessary. In combination with high coatings machinability this allows for refurbishment of worn metallic components, such as e.g. damaged shafts, gears, of steels, aluminium or magnesium alloys [19]. Similar approach was used in the presented experiments, where metallic powders were deposited on relatively thin aluminium sheet, which was subsequently peeled off from the much thicker and bulkier deposit material.

Always bi-metallic powders were used for deposition. Deposits were produced by low-pressure cold spray technique using nitrogen was used as working gas with temperature $T = 400\text{ }^{\circ}\text{C}$ and pressure about 50 bar. Gas flow was about 250 slm. The samples were deposited by 8 to 20 passes. (Fig. 3) Thickness of the deposits varied between 6 and 12 mm. Cu, Fe, Al, Ti and Ni Powders were purchased from GTV and HC Starck.



Fig. 3. As deposited bulk samples (NiFe, CuFe FeAl, from left to right).
(full colour version available online)

The deposits were subjected to extensive annealing experiments in protective atmosphere of Ar. The annealing temperatures ranged from 300 to 1100 $^{\circ}\text{C}$. The samples were heated fast to the desired temperature; 2 hours were used for the isothermal annealing. After two hours, the samples were moved out from the hot zone, but still left in the protective Ar atmosphere until cooled to 100 $^{\circ}\text{C}$. Only then were the samples left to cool on air.

The samples showed microstructures altered by diffusion controlled reactions with new intermetallic phases or solid solutions precipitates. Typically, porosity was formed along with intermetallic materials. This observation was also reported by other authors on particular FeAl based materials elsewhere [24]. Microstructure was evaluated using metallography and analytical SEM (Fig. 4).

Fracture behaviour was assessed by breaking the samples at room temperature.

3. Results description

3.1 As-deposited materials

The microstructure of the as-deposited material consisted of metallic matrix and nickel, aluminium or iron individual grains which corresponded to original individual powder particles. The deposited materials showed a shift in the chemical composition favouring aluminium, titanium, copper, nickel or iron in different systems [16, 24, 25]. This phenomenon corresponds to different deposition efficiency of the different metals deposited together (Table 1). The as-deposited microstructure of the samples typically exhibited a porosity of less than 1%. On fracture surface, typically the metallic matrix, although severely deformed still exhibited ductile fracture, while the minority phase particles delaminated from matrix.

Table 1

Chemical composition of as-deposited (CGDS) materials, (wt%).

weight		weight	
Ti-Al		Ni- Fe	
Al	23	Ni	95.3
Ti	77	Fe	4.7
Ni-Al		Fe- Cu	
Al	55	Cu	90.2
Ni	45	Fe	9.8
Fe-Al			
Al	49		
Fe	51		

3.2 Deposits after annealing

Fe-Al system

Al_5Fe_2 phases were identified in the material already after annealing starting at 500 °C. Minor part of the iron particles reacted after two hours of annealing leaving

heterogeneous structure. Annealing at 600 °C created FeAl and FeAl_2 microstructure with substantial porosity. The material changed its character into open interconnected porosity structure. The outer shape of the sample was maintained, although the macroscopic dimensions of the sample increased. Some remnants of un-reacted iron could be seen in the microstructure in Figs. 5 and 6.

Ti-Al system

First intermetallic phases were identified after 300 °C annealing. Layer of $\text{Al} + \text{TiAl}_3$ and layer of $\text{TiAl} + \text{TiAl}_2$ mixtures formed at the $\text{Al} - \text{Ti}$ particles interface. Gradual formation of the TiAl_3 intermetallic phase started after 450 °C annealing. 550 °C showed distinctive intermetallic areas at Al-Ti contacts and at boundaries between originally individual titanium particles. Some newly formed porosity can be seen at 550 °C and interconnected porosity has evolved after annealing at 600 °C/2h when also local melting could be identified. Even at 600 °C areas of pure unaffected titanium could be identified, while no pure aluminium areas were found in the microstructure in Fig. 7.

Ni-Al system

The deposits exhibited first intermetallic formation of Ni_3Al phase after 450 °C. At 500 °C concentric layers of intermetallic phases Ni_2Al_3 , NiAl and NiAl_3 with gradually changing chemical proportions of nickel and aluminium formed on the nickel particles. Sample annealed at 550 °C showed distinctive areas of the Ni_2Al_3 and NiAl_3 intermetallic phases with interconnected porosity (Fig. 8). The pores are comparable in size with the original powder particles. Unreacted nickel particles remains were still visible after 550 °C.

Fe-Cu system

The system shows practically zero solubility in solid state at room temperature, therefore no intermetallic was observed.

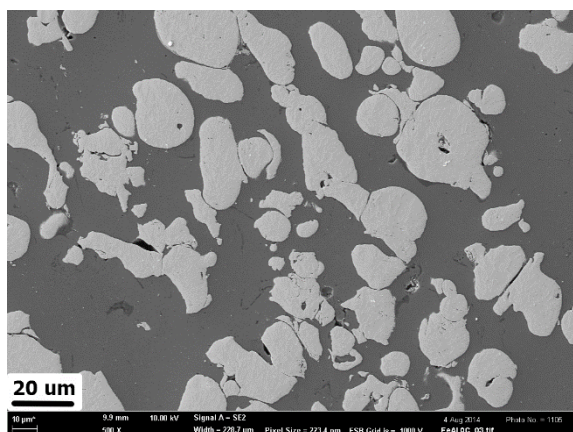


Fig. 4. Typical microstructure of well deposited material by cold spray (FeAl in BSE mode, dark aluminium, light iron).

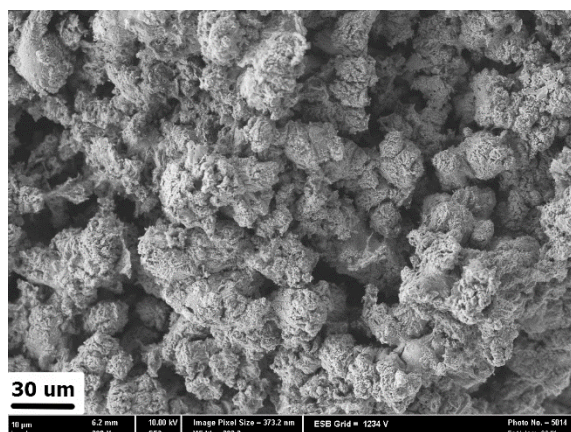


Fig. 5. Typical morphology of porous reacted deposit (FeAl 600°C, reacted intermetallic particles with open porosity in SE mode).

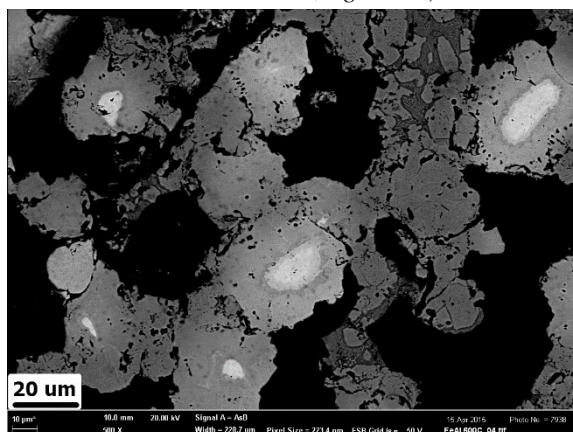


Fig. 6. Typical microstructure of mostly reacted material after annealing with massive porosity (FeAl 600°C, bright areas unreacted iron, grey areas Fe-Al intermetallic phases, black areas are pores).

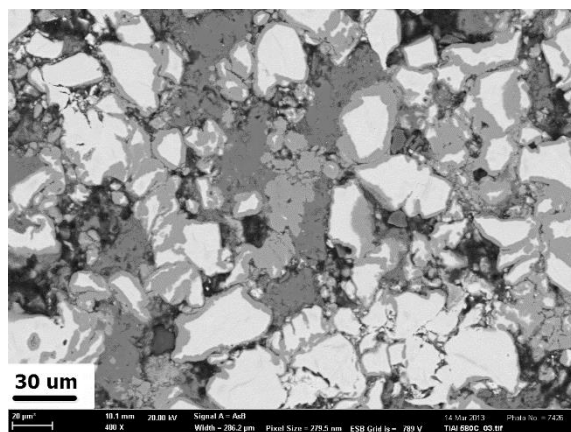


Fig. 7. Gradual evolution of intermetallic phases in TiAl deposit after annealing at 500°C. (bright unreacted titanium particles surrounded with TiAl intermetallic bands – light grey, TiAl3 dark grey areas, black pores).

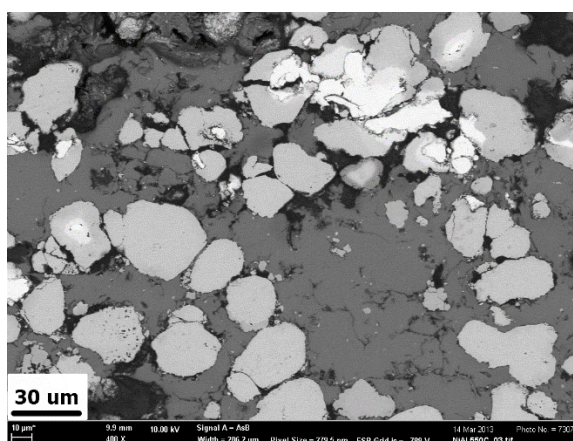


Fig. 8. Microstructure of NiAl deposit after 550°C annealing – intermetallic particles NiAl medium grey in unreacted dark grey Al matrix, some bright Ni unreacted particles still visible.

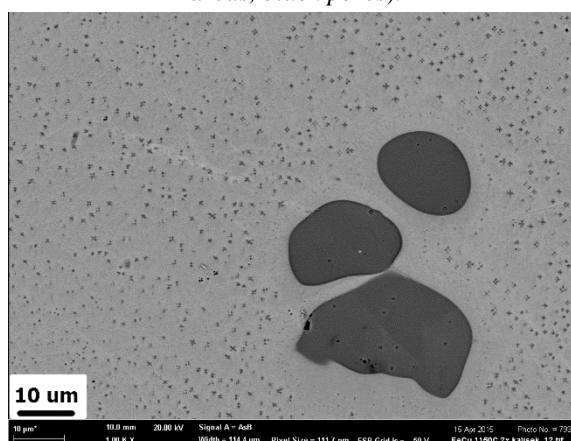


Fig. 9. Fine Fe rich precipitates in Cu phase arising from immiscibility in FeCu system, three big original Fe particles. After 1150°C annealing.

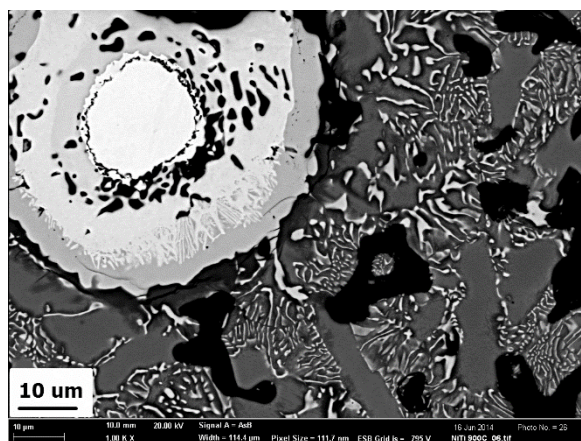


Fig. 10. Kirkendall porosity around gradually dissolving Ni particle and porosity from Ti deposited particles in NiTi sample after 900 °C annealing (brightest unreacted Ni core surrounded by NiTi and Ti₂Ni intermetallic rings and matrix of eutectoid mixture αTi-Ti₂Ni with black pores).

However evolution of precipitation microstructures with both precipitated in iron and in copper based grains was identified (Fig. 9). The iron based particles contained 3 at. % Cu and 3 at. % Fe were found in copper particles. Iron precipitates had size about 1–2 μm. Strengthening was measured in both iron and copper particles caused by precipitation of the other counterpart element form the system.

Fe-Ni system

Solid solution of about 90 at.% Fe and 10 at.% Ni was partially formed after 500 °C annealing, which was followed by extensive homogenization at higher temperatures. Due to low iron content, the iron could be dissolved in nickel matrix without any microstructural effects.

Ni-Ti system

The NiTi samples annealed at temperatures of 600 and 700 °C exhibit already minor new phases formation. At 800 °C new phases were formed rapidly around the nickel particles by mutual diffusion. Both Ti₂Ni and TiNi₃ were identified. This mixture is likely to be the result

of decomposition of NiTi under 620 °C. Also eutectoid mixture can be found occasionally, which indicates the presence of beta titanium solid solution. Homogeneous microstructure of eutectoid accompanied by Ti₂Ni intermetallic and titanium solid solution was generated after high temperature annealing of 900 °C.

4. Conclusions

Cold spray technology produces coatings with little or no phase and structure changes as compared to the original feedstock and has been found as efficient tool for preparation of surface coating and bulk (composite) materials.

Intermetallic phases formed in the studied cold spray deposits once sufficient temperature was reached. Since these reactions predominantly happen at solid state, the formation of new phases is controlled by mutual diffusion of the two reactants. This in all of the samples eventually results in formation of porosity in material. As the two constituents diffuse mutually intermetallic phase is formed and Kirkendall type (in the solid state) of porosity arises creating concentric circles around individual particles in some cases.

At higher temperatures even liquid-solid reaction of (aluminium rich) melt and the still solid second constituent particles could be identified the best in the Ni Al system. The semi- melted state during intermetallics formation leads to increased open porosity caused by flow of the melted component on the still solid scaffold from already reacted intermetallics and second unreacted component. When aiming for bulk material, which usually is the ultimate goal of similar studies, porosity is regarded as negative feature. However, when this open porosity is uniform in size and can be reproduced, the annealed deposit represents a new material quality.

As such the reacted intermetallic sponge can be used as high temperature creep resistant support for catalysts, filtering applications or for manufacturing of metal matrix composites by infiltration of the sponge by appropriate liquid metal. Also the use in biomedical applications as reconstructive bone scaffolding can be considered.

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