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New Developments in Cold Spray Based on Higher Gas and Particle Temperatures

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In cold spraying, bonding is associated with shear instabilities caused by high strain rate deformation during the impact. It is well known that bonding occurs when the impact velocity of an impacting particle exceeds a critical value. This critical velocity depends not only on the type of spray material, but also on the powder quality, the particle size, and the particle impact temperature. Up to now, optimization of cold spraying mainly focused on increasing the particle velocity. The new approach presented in this contribution demonstrates capabilities to reduce critical velocities by well-tuned powder sizes and particle impact temperatures. A newly designed temperature control unit was implemented to a conventional cold spray system and various spray experiments with different powder size cuts were performed to verify results from calculations. Microstructures and mechanical strength of coatings demonstrate that the coating quality can be significantly improved by using well-tuned powder sizes and higher process gas temperatures. The presented optimization strategy, using copper as an example, can be transferred to a variety of spray materials and thus, should boost the development of the cold spray technology with respect to the coating quality.

Keywords cold spraying, cold spray system, particle impact, temperature effect, bonding, coating properties

1. Introduction

In cold spraying, particles are accelerated in a preheated high pressure gas stream passing through a de Laval type nozzle before they impact the substrate. In contrast to conventional thermal spraying, particles are only slightly heated prior to the impact. The impact velocities range from 200-1200 m/s and depend mainly on nozzle geometry, particle size and shape, type of process gas, and process gas conditions such as pressure and temperature (Ref 1-3). The impacting particles form a dense coating with low oxide content. Bonding in cold spraying is caused by the particle deformation during impact and depends on impact conditions and various powder characteristics (Ref 4, 5).

Up to now, the focal point in the process optimization in cold spray was the development of nozzle shapes providing more effective particle acceleration (Ref 1, 2). In most cases, spray powders were tuned to fine particle size distributions because only small particles reach the requested high velocities for bonding (Ref 1, 2, 6). Newer publications also show that the strategy to use as fine particles as possible to achieve maximum particle velocities is not effective to reach optimum coating qualities because size effects, which can be very important for the bonding of the impacting particles, are neglected (Ref 5). These size effects can be based on dynamic effects like a very fast thermal compensation of the localized heat, generated during the impact, as well as an increased strength due to strain-rate-hardening. Apart from these, the higher surface to volume ratio of smaller particles can also play a role for these size effects (Ref 5).

The optimization of the coating microstructure and coating properties demands a systematic variation of spray conditions, which, especially for unknown spray materials, can be time consuming and costly. A generalized description of impact phenomena, containing the effect of particle size and particle impact temperature on bonding, is used for process optimization (Ref 5). This generalized description provides some simple equations to estimate optimum impact conditions, working with general material properties, which are available for most materials (Ref 7). These calculated impact conditions are realized by a newly developed temperature control unit, integrated in conventional cold spray equipment.

The current study focuses on the influences of the optimized process parameters on properties of cold sprayed copper coatings, but the overall strategy is transferable to a wide variety of spray materials and should enhance applications of the cold spray process.

2. Theoretical Background

It is well known that the velocity of sound is a function of the gas temperature. Thus, the increase of the process gas temperature in cold spray will consequently increase the gas velocity in the nozzle. The reachable particle velocity mainly depends on the velocity of the accelerating gas stream and in second order, on its density (Ref 1). A gas temperature limitation due to nozzle plugging or to the thermal robustness of the nozzle material is the main obstacle for further process developments in cold spraying, because this limits the reachable particle impact veloc-

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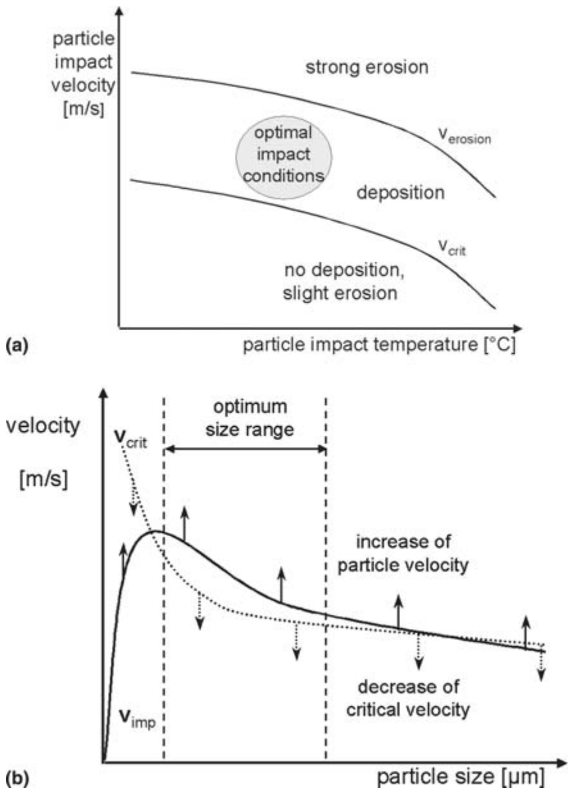

Fig. 1 (a) Critical particle impact velocity as a function of particle temperature, superimposed with the window of sprayability and an optimum window of impact conditions. (b) Process optimization by using an optimized size distribution, by decreasing critical velocity and increasing particle impact velocity

ity and in consequence, the reachable particle impact temperature. Higher particle impact temperatures will decrease the critical velocity of the spray material due to thermal softening (Ref 5). This is schematically shown in Fig. 1(a). The two lines in Fig. 1(a) indicate the critical and the erosion velocities, both being temperature dependent. Between these two lines, there is a window of successful particle deposition. Using a certain spray material, the optimum spray parameters would be those producing a particle impact velocity and temperature lying in the center of this window of deposition. Figure 1(b) shows schematically the critical velocity together with the particle impact velocity as a function of the particle size. The critical velocity is decreasing toward coarser particles and will finally run out in a plateau. The particle impact velocity shows a maximum because very small particles are accelerated to high velocities, but are decelerated in the bow shock in front of the substrate. Coarser particles are less accelerated in the gas stream and thereby have lower impact velocities. There, where the impact velocity is higher than the critical velocity, the particles will stick under ideal impact conditions (vertical impact to a plane surface). Between the two intersections of the critical velocity and the impact velocity lines, there is an optimum particle size fraction for this spray condition. To obtain the best particle bonding and coating quality possible, one should aim to use a powder size cut that fits in the center of this optimal distribution and also to increase the distance between the two lines in this region.

The particle impact velocity can be increased by nozzle design, higher gas temperatures, or higher gas pressures (Ref 1). The critical velocity can be decreased by higher particle impact temperatures and bigger particle sizes (Ref 5). The current study demonstrates that the coating quality and bonding of cold sprayed copper coatings can be significantly improved by using new optimization strategies. For this purpose, all particle velocities and particle temperatures are determined by gas dynamic calculations. The gas expansion in the nozzle is assumed to be isentropic in these calculations. The particle deceleration in front of the substrate (bow shock effect) is implemented by a simple approximation.

3. Methodology

3.1 Strategies for an Improved Cold Spray System

The major aim of this study is to realize higher particle impact temperatures for decreasing the critical velocity of the spray material by thermal softening (Ref 4). Apart from that, higher particle impact temperatures will also increase the ductility of less deformable spray materials that can be decisive for successful bonding (Ref 5). For increasing particle temperatures, the heating of powder feed lines appear as a suitable solution but can not exclude the gas stream cooling taking place in the expanding process before and after the throat of the nozzle. A different and more effective approach can be followed by the heating of both the spray particles and process gas.

Figure 2 shows the thermal history of a 5 and a 50 µm copper particle and of the gas, passing the prechamber from the point of injection through the nozzle throat to the nozzle exit. The 5 µm particle immediately reaches the process gas temperature but then rapidly cools down in the expanding gas stream of the de Laval type nozzle. Therefore, for small particles, there is obviously no opportunity to increase the impact temperature significantly by preheating. The heating rate of the 50 µm particle, being injected in the prechamber, and also the cooling rate of this particle in the expanding gas stream is much lower than for the 5 µm particle. A preheated coarser particle would have a significantly higher impact temperature than a nonpreheated one.

The current concept to preheat powder particles and to limit the cooling is to inject coarser powders in an elongated prechamber to increase the impact temperature by a longer duration of the exposure to the hot process gas. This is shown in Fig. 3 for a 50 µm copper particle. Increasing the distance from the particle injection to the nozzle throat from the typically 20-30 mm (Ref 1, 3) to 150 mm increases the particle impact temperature by 150 °C. Figure 4 shows the effect of the injection in an elongated prechamber as a function of the particle size. Only particles coarser than 15 µm show a significant rise in the impact temperature.

The commercially available CGT (Ampfing, Germany) cold spray system enables reaching a temperature of 600 °C at a pressure of 30 bars with nitrogen as the process gas. The tungsten carbide MOC-nozzle permits spraying copper powders up to this parameter setting without any nozzle plugging or erosion of the nozzle material. Such high gas temperatures impose a very high thermal and mechanical load to the flexible hot gas hose. A further increase of the gas temperature seems to be im-

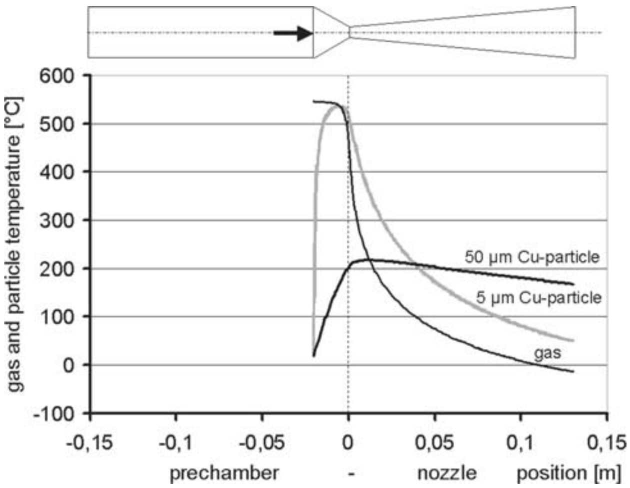

Fig. 2 Thermal history of a 5 and a 50 µm Cu-particle, passing through the prechamber and nozzle. Process parameters: nitrogen at 30 bars and 600 °C, MOC-nozzle. The heating and the cooling rate of the 50 µm particle in the gas stream is significantly lower than for the 5 µm particle.

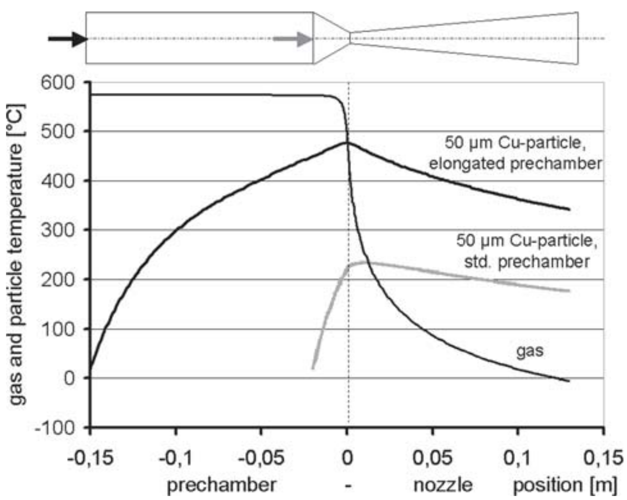

Fig. 3 Thermal history of a 50 µm Cu-particle, passing through the prechamber and nozzle. Process parameters: nitrogen at 30 bars and 600 °C, MOC-nozzle. The lower heating and cooling rates of coarser particles in the gas stream allow a significant increase of the particle impact temperature by preheating the particles using an early injection in an elongated prechamber.

possible in this configuration. Thus, a new spray gun was developed at Helmut Schmidt University, which is shown in Fig. 5. It can be integrated into an existing spray system with low expenditure. This spray gun contains a compact 17 kW electrical heater that is directly installed at the prechamber, providing gas temperatures up to 900 °C. At the inlet side, this new spray gun withstands gas temperatures up to 600 °C and thereby, can be lined up with other heaters connected by a hot gas hose. It is designed for gas pressures up to 45 bars. The particles can be injected in an isolated, elongated prechamber. The prechamber is exchangeable and available in different lengths. In consequence, even coarser particles can be heated up in the process gas before they pass the nozzle throat. Considering the particle

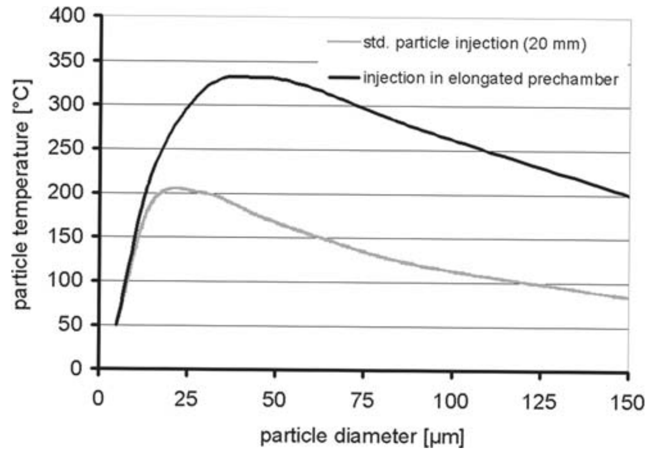

Fig. 4 Particle impact temperature as a function of the particle diameter using a standard particle injection and an early particle injection 150 mm in front of the nozzle throat. Process parameters: nitrogen at 30 bars and 600 °C

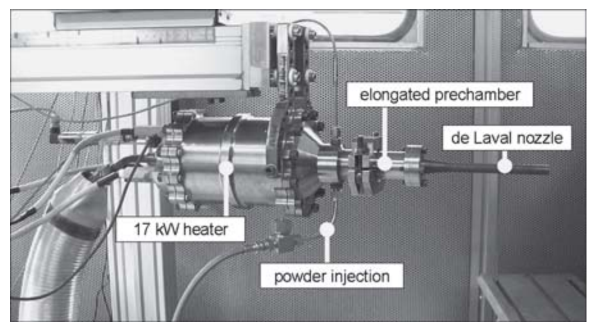

Fig. 5 Newly developed spray gun integrated into a CGT spray system, containing a compact 17 kW electrical heater, which is directly attached to the elongated prechamber. At a gas pressure of 40 bars a gas temperature of up to 900 °C can be reached.

cooling in the de Laval type nozzle, the particle impact temperature of a 50 µm Cu-particle can reach up to 600 °C at a process gas temperature of 900 °C. Using such high gas temperatures, the tungsten carbide nozzle must be cooled from outside. This is realized by an easy to assemble air cooling system.

In the current study, Cu-powder having size distributions of −25 + 5 µm and −38 + 11 µm were used. As process gas, nitrogen at a pressure of 30 bars was chosen. The process gas temperature was increased in a range from 200 to 800 °C in steps of 100 °C. The fraction of cold carrier gas was 10%. Spray experiments were performed with a standard particle injection 20 mm in front of the nozzle throat and with a particle injection in an elongated prechamber, 135 mm in front of the nozzle throat. In all experiments, a bell shaped tungsten carbide nozzle, designed by the method of characteristics (MOC-nozzle, Type 24, available at CGT), was used. During the spray experiments, the deposition efficiency (DE) was determined. The critical velocity of the mean particle diameter of the used powder fractions was determined by calculating the particle impact conditions (impact velocity and impact temperature) for a DE threshold of 50%. By using the calculated temperature dependence of the critical ve-

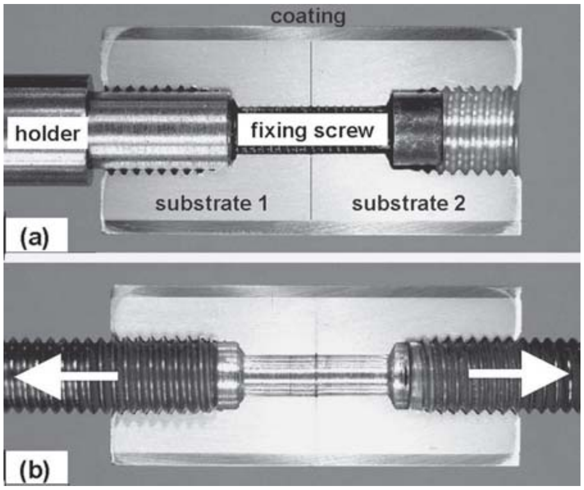

Fig. 6 Longitudinal section of a rotation-symmetrical coated TCT specimen (a) screwed on a holder and (b) screwed for testing in a tensile machine

locity (Ref 5), the experimentally determined critical velocity for the 50% DE threshold can be standardized to room temperature impact conditions.

3.2 Investigation of Microstructure and Properties

The powder morphologies of the feedstock materials were analyzed by scanning electron microscopy (SEM). Cross sections of coatings were investigated by optical microscopy (OM) in as-polished and as-etched conditions. For chemical etching a solution of 25 ml H_2O, 25 ml ammonia (25% in H_2O) and 5 ml hydrogen peroxide (3% in H_2O) was used. Spectrometric methods using a commercial analyzer (Leco TC300, Poing, Germany) were applied for the quantitative analysis of the oxygen contents of the feedstock materials and coatings. Hardness measurements were performed on polished cross sections of feedstock powders and coatings using a Vickers indenter. The electrical conductivity was measured on a 40 × 5 × 0.5 mm specimen by a 4-point measurement system. Respective samples were cut out of a coating by spark erosion.

3.3 Tubular Coating Tensile Test (TCT-test)

To evaluate differences in the bonding quality, the tensile strength of as-sprayed coatings was determined by an in-house developed tubular coating tensile test (TCT-test). Due to the comparatively low effort in the sample preparation, this method served as an additional process control, providing information on the bonding quality complementary to the DE and coating microstructure. In the TCT-test, two cylindrical substrates are fixed face to face by a screwable holder, which later is fixed to a lathe chuck (Fig. 6a). The substrates remain in this fixed position during preparation and during the coating process. Modified bond strength samples consisting of aluminum were used as substrates (EN 582 or ASTM C633) (Ref 8). The substrate surface is machined to a roughness of less than 40 μm. The prepared substrates were coated with typical cinematic parameters with respect to radial and axial advance. Typical coating thickness ranged from 500-1500 μm. The specimens were pulled after unscrewing them from the holder, using the same tensile machine equipment as for the bond strength test (Fig. 6b). Similar to conventional bond strength test, three samples are tested for each parameter setting. A finite element stress analysis of the specimens during testing shows that the geometrical design of the two coated substrates leads to a local stress concentration in the pulled coating (notch effect) and increases the Mieses stress at the gap between the substrates to a factor of 1.5 of the average Mises stress. This effect must be considered for estimating real mechanical coating strengths. Nevertheless, this test supplies valuable information about the strength of coatings and the influence of spray conditions on it.

3.4 Micro Flat Tensile Test (MFT-test)

For a more quantitative investigation of the mechanical properties of the cold sprayed coatings, the micro flat tensile test (MFT-test), which is an in-plane tensile test, was used to apply simple one dimensional stress conditions (Ref 9). A 3 mm thick coating is sprayed on an aluminium substrate. The micro flat specimens (5 mm × 28 mm, gauge length 9 mm) were cut out of this coating by spark erosion as 1 mm thick slices. The direction of load was chosen parallel to the spray tracks. For each spray condition, three samples were prepared and tested. During testing of the samples, the load was increased continuously at a rate of 2 N/s. The elongation is measured at the sample surface using an angular scanner laser extensometer. In comparison to the TCT-test, the MFT-test supplies more information but requires much more effort with respect to the sample preparation and more sophisticated equipment for the mechanical testing.

4. Results and Discussion

4.1 Strategies for an Improved Cold Spray System

For the spray experiments, the CGT system was used as basic equipment and has been complemented by the newly developed spray gun with the additional 17 kW heater and an elongated prechamber, as shown in Fig. 5.

To highlight differences in attainable microstructures and mechanical properties, this study focuses in detail on two process parameter settings. The first setting is the standard parameter for the cold spraying of copper and serves as the reference: nitrogen at 30 bars and 350 °C, MOC-nozzle, particle injection 20 mm in front of the nozzle throat, −25 + 5 μm Cu-powder. Figure 7 shows the calculated critical velocity and particle impact velocity as a function of the particle size for this parameter setting (compare schematic in Fig. 1b). For the calculation of the critical velocity, the particle impact temperature, which depends on the particle size and spraying parameters, was considered. The other setting of the spray parameters is represented by the newly developed optimum conditions for cold spraying copper, by using nitrogen as process gas at 30 bars and 800 °C and a MOC-nozzle. The particles of a −38 + 11 μm Cu-powder are injected 135 mm in front of the nozzle throat. The calculated critical velocity and particle impact velocity of this parameter set

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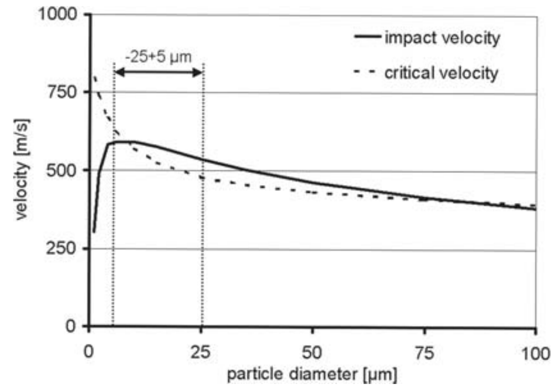

Fig. 7 Critical velocity (considering the particle impact temperature) and particle impact velocity as a function of the particle diameter for standard parameter settings for copper (nitrogen at 30 bars and 350 °C, MOC-nozzle)

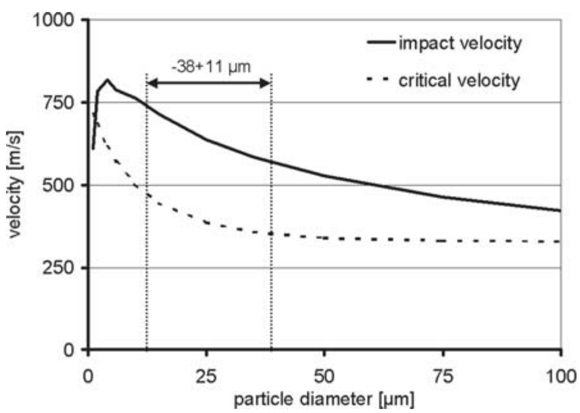

Fig. 8 Critical velocity (considering the particle impact temperature) and particle impact velocity as a function of the particle diameter for optimized parameter settings for copper (nitrogen at 30 bars and 800 °C, MOC-nozzle, elongated prechamber) and optimized particle size distribution

are shown in Fig. 8. Comparing Fig. 7 and 8 for respective size distributions, the larger distance between the critical velocity line and the impact velocity line of Fig. 8 indicates that significantly better coating qualities should be obtained under optimized process conditions (see Section 2. Theoretical Background).

4.2 Microstructures and Properties

The measured size distribution of the powders used agree well with the given specification and the particles have a regular spherical morphology. These powders particles have a hardness in a range between 50 and 60 HV0.01 and an oxygen content between 0.015-0.025%.

Figure 9 shows the etched cross sections of coatings obtained by the two main parameter settings. The etched microstructure of the coating sprayed with the standard parameters (Fig. 9a) is dense, but shows that particle–particle interfaces are more revealed by etching than those of the coating sprayed under optimized conditions (Fig. 9b). In the latter, most particle-particle

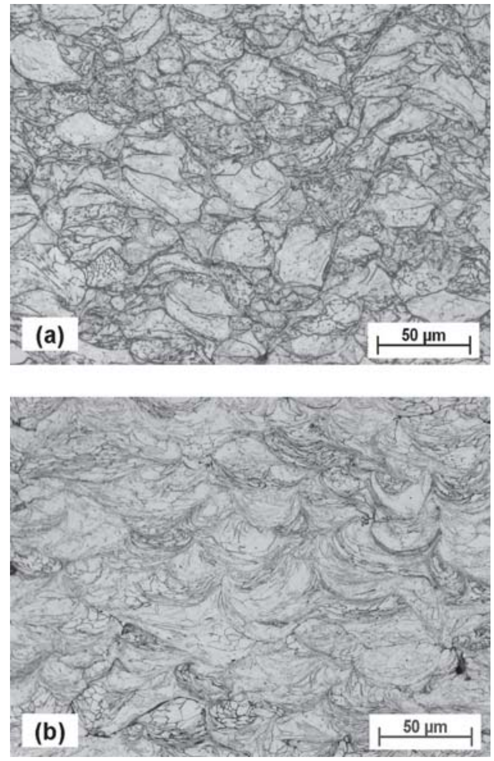

Fig. 9 Etched cross sections of cold sprayed copper coatings. (a) Standard parameter settings and (b) optimized parameter settings with optimized particle size distribution

boundaries show a similar contrast as the normal grain boundaries, indicating similar chemical stabilities and tight bonds. Even at the parameter settings working with higher gas temperatures, the oxygen content of the coatings was very low (0.025-0.04%). The electrical conductivity of the coatings in the as-sprayed condition was increased from 50% for the standard condition to 80% in the optimized condition, taking annealed bulk copper as reference (100%) (Ref 10). Under standard conditions, a coating hardness of 155 HV0.3 was obtained, whereas under optimized conditions the coating just reached 125 HV0.3. The lower hardness can be explained by the thermal treatment of the coating by the hot gas stream.

4.3 Mechanical Strength of Coatings (TCT-test and MFT-test)

So far, a range of maximum changes was described by comparing a standard and a newly defined optimum parameter. Experimental results of gradual changes between these fix points are illustrated in Fig. 10 to highlight the development of the mechanical strength (Fig. 10a) and DE (Fig. 10b) as a function of the process gas temperature. The −38 + 11 µm Cu-powder was used as the spray material and nitrogen at 30 bar as the process gas. Spray particles were injected 20 mm in front of the nozzle throat (standard particle injection). The comparison demonstrates that first the DE improves steeply with increasing process gas temperature. The mechanical strength of the coatings is only slightly increased until the DE reaches a saturation limit. In this

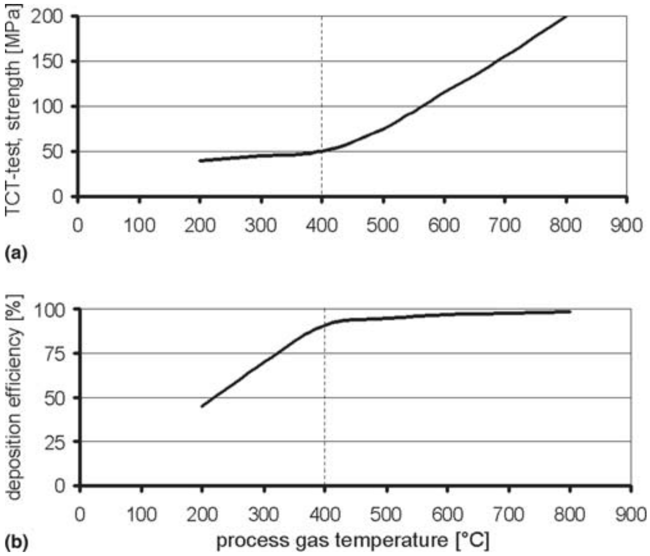

Fig. 10 (a) Coating strength, determined by TCT-tests and (b) DE as a function of the process gas temperature. Cu-powder with the optimized size distribution (−38 + 11 μm) was used. Spray conditions were nitrogen at 30 bars and standard particle injection 20 mm in front of the nozzle throat.

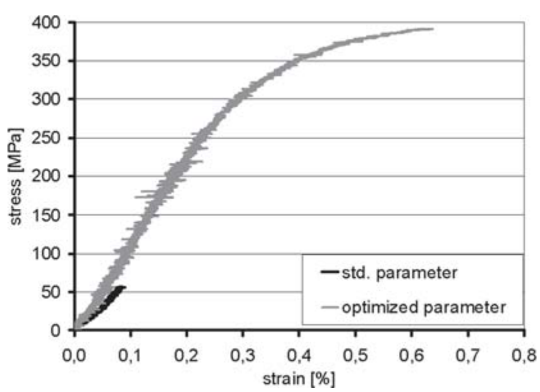

Fig. 11 Stress-strain curves of MFT-tests for a coating sprayed using standard or optimized conditions

parameter range the coating strength is dominated by the particle fractions, which just at this parameter setting start to stick. Thus, the amount of bonded areas does not increase significantly. After reaching this saturation limit for the DE, the mechanical coating strength rises steeply. In this parameter range, every increase in particle impact velocity and particle impact temperature results in a significant increase of the bonded areas. With further process optimization, the coating strength approaches a maximum, similar to the strength of highly deformed copper (about 460 MPa), as shown in Fig. 11.

Figure 11 is showing two stress-strain curves of copper coatings measured with the MFT-test. One specimen was prepared from a coating sprayed with the standard parameter settings (black line). This sample ruptured at 57 MPa after reaching an elongation of 0.08%. The Young's modulus was determined to be 71 GPa, being much smaller than the reference data for copper from the literature (125 GPa). The difference can be explained by the insufficient and inhomogeneous particle bonding and contributions by plastic deformation at the locally bonded particles before the brittle fracture in the elastic regimen. The other sample was cut from a coating sprayed under optimized conditions (gray line). This sample fractured at 391 MPa at an elongation of 0.63%, demonstrating properties close to highly deformed bulk material. In agreement, the measured Young's modulus of 117 GPa is similar to the literature value for copper.

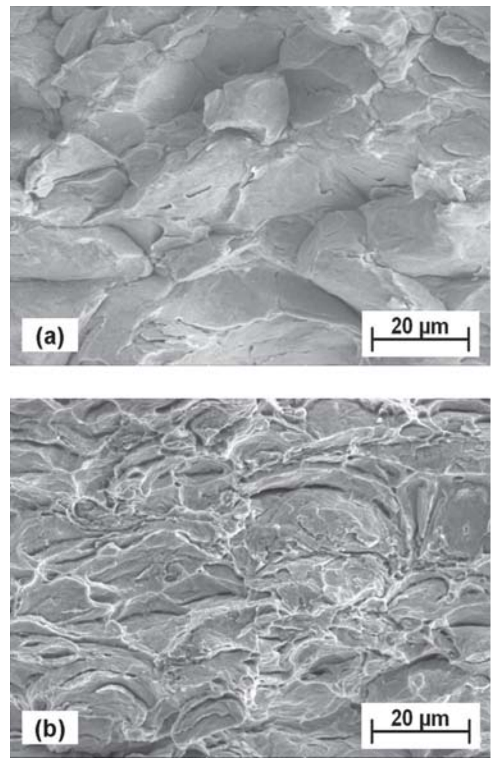

Fig. 12 Fracture morphologies of MFT-samples (a) standard spray conditions, strength 57 MPa and (b) optimized conditions, strength 391 MPa

Figure 12 shows the fracture morphology of both MFT-specimens. The sample sprayed under standard conditions shows mainly transparticle cleavage and comparatively low amounts of ductile failure, which is covering only about 10-15% of the fracture surface (Fig. 12a). The sample sprayed under optimized conditions shows ductile fracture at 90-95% of the rupture surface and to a high extent interparticle cleavage (Fig. 12b).

Figure 13 summarizes the attainable strengths for different process gas temperatures (MFT-test) and the correlation between TCT- and MFT-tests. For these experiments nitrogen at 30 bars was used as process gas and the particles were injected 135 mm in front of the nozzle throat. As demonstrated in Fig. 13(a), the mechanical tensile strengths of copper coatings increase with the process gas temperature within a regimen in which the DE already reached a saturation limit (compare Fig. 10). Figure 13(b) shows the experimental correlation of strengths obtained by the MFT- and TCT-tests. The experimentally determined correlation factor of 1.7 fairly well matches the calculated fatigue notch factor of 1.5. The difference can be at-

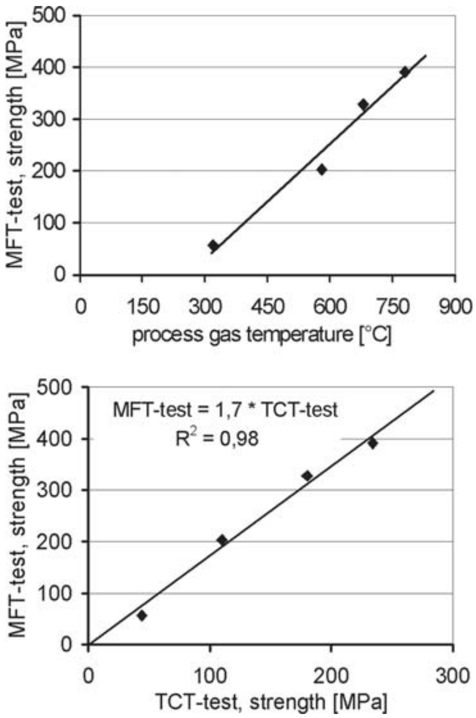

Fig. 13 (a) Mechanical strength of Cu-coatings, determined by the MFT-test as a function of the process gas temperature and (b) correlation of the copper coating strength determined by the MFT- and by the TCT-tests for the same parameter settings

tributed to the irregular surfaces between the substrate and the coating and the presence of non well bonded particle–particle interfaces, which both enhance the local stress concentration.

5. Conclusions

The current study demonstrates that the properties of cold sprayed copper coatings can significantly be improved by using higher process gas temperatures in conjunction with some modifications of the presently available cold spray systems. Size effects in impact dynamics are considered by an optimized size distribution. The particle impact temperature is maximized by an optimized particle injection and increased process gas temperatures of up to 900 °C, using a newly developed spray gun. Fluid dynamic calculations show that the particle impact velocity and the particle impact temperature are significantly increased by both the optimized particle injection and the higher process gas temperatures, which is confirmed by experimental investigations of coating properties. By the new process developments, strength as well as electrical conductivity of copper coatings are significantly increased as compared with standard conditions. Moreover, the results of this study prove that the generalized parameter window for cold spray deposition in conjunction with the optimization strategy presented here are a powerful tool for further process developments in cold spraying.

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