Thermally induced morphology changes of wire arc sprayed copper and corrosion-resistant steel (316L)

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Abstract. This contribution deals with the determination of the mechanical and thermal properties of thermally sprayed materials. To this end, a comprehensive characterization of copper (Cu 98.7) and corrosion-resistant steel (316L) is carried out by temperature-dependent tensile, three-point bending and calorific tests within a temperature range from 293 K up to 1173 K. For this purpose, thick coatings were manufactured by wire arc spraying. The resulting volume was further processed by electrical discharge machining into suitable test samples. Reference specimens from the corresponding solid materials were also tested for evaluating the morphological features of the coatings. During the calorimetric examinations, the thermally applied materials were exposed to temperatures of up to 1173 K. As a result, permanent property changes could be observed. To investigate these heat treatment effects, metallographic preparations and XRD analyses were performed. Based on the results, conclusions on the morphology of the thermally applied materials could be drawn.

1. Introduction
Modern material hybrids are used to reduce moved masses with the aim of increasing energy and resource efficiency. The thermal spraying process offers the possibility of producing metallic layer systems on thin metal, polymer and ceramic substrates. For example, thermoplastics can be coated with metals such as titanium (cold gas spraying [1]), copper and aluminum (wire arc spraying [2, 3], cold gas spraying [4]) as well as hard material layers, for example WC-Co (high velocity oxygen fuel spraying [5]). The resulting coatings are characterized by their, in comparison to the corresponding solid material, differing mechanical and thermal performance due to their porous and oxidized morphology as well as former spray particle surfaces that form inter-splat boundaries within the coating’s microstructure. For this, the determination of the characteristics of thermally processed materials is often carried out by using miniaturized samples and specially adapted test equipment [6-9].

In this contribution, two different metallic coating materials, Cu 98.7 (05T Praxair Tafa) and 316L (85T Praxair Tafa), are characterized by means of their mechanical and thermal material parameters. To achieve this, a thick coating of each material is applied to a thin steel substrate. The resulting material volume is further processed by wire electrical discharge machining (EDM) to the final specimen geometries. The specimens are characterized by tensile tests, three-point bending and laser flash analysis (LFA).
2. Materials and Methods

2.1. Wire Arc thermal spraying process

For the present study, Cu 98.7 (solid wire: Cu 98.7 (wt.%); Sn Trace; Si Trace; Mn Trace) was selected as typical intermediate layer material, suitable for buffering residual stresses as well as thermal protection of the substrate. The second selected material 316L (solid wire: Fe Balance, Cr 17, Ni 12, Mo 2.5, Mn 2, Si 1, C 0.08, P 0.04, S 0.03 (wt.%)) serves as an example for wear protection applications. The result is a single-phase, homogeneous and economically producible coating. Table 1 shows the optimized spraying parameters for both materials.

| Material | Current (A) | Voltage (V) | Pressure (MPa) | Traverse speed (m/s) | Track spacing (mm) |
|----------|-------------|-------------|----------------|---------------------|--------------------|
| Cu 98.7  | 100         | 28          | 0.33           | 0.5                 | 5                  |
| 316L     | 100         | 46          | 0.33           | 3                   | 8                  |

Table 1. Parameters for wire arc spraying (Visu-Arc 350).

Standardized test conditions are required to determine correct characteristic values. The miniaturization of the specimens is limited due to the specific features of the processed material. Hence, a correspondingly large volume of the coating must be produced for manufacturing of the specimens. The wire arc spray system Visu-Arc 350 (Oerlikon Metco) is used for the thermal spraying process. A 2 mm thick sheet of carbon steel (1.0038) is used as substrate. The automated coating application (robot KUKA KR 30) is carried out using a meandering track program on a surface of 200 mm x 100 mm. Layer thicknesses of approx. 50 μm to 100 μm are sprayed per transition. After each 5 layers, a 5 minute cooling phase is performed in air. The result is a 14 mm thick semi-finished product, consisting of 170 individual layers. The material reservoir for specimen preparation is taken from the middle part of the coating. The further machining of the specimens to their final dimensions is done by EDM.

2.2. Mechanical and thermal properties

The mechanical properties of the thermally processed materials are determined using tensile and three-point bending tests. The specimens have a cross-section of 12 mm² for the tensile tests (bone sample, measuring length 15 mm, width 4 mm, thickness 3 mm) and 20 mm² for the three-point bending tests (sample length 45 mm, width 10 mm, thickness 2 mm). The geometry allows the usage of standardized testing devices. The experiments are carried out in a climate chamber with a temperature range from 293 K to 518 K. Thus, a broad database is generated. The universal testing machine Zwick/Roell Allround-Line 20 kN is used for applying the necessary loads. The tensile tests are carried out with a crosshead speed of 1 mm/min and a pre-load of 10 N. The measurement of the elongation is achieved by using tactile sensors. Tensile strength, yield strength and Young’s modulus (tensile modulus) are determined from the resulting stress-strain curve. The three-point bending tests are used for verification of the data obtained from the tensile tests. A crosshead speed of 1 mm/min, an abutment distance of 40 mm and a pre-load of 100 N are used. As a result, the Young’s modulus (flexural modulus) is determined.

In addition to the mechanical tests, caloric material parameters are determined for characterizing the specific thermal properties of the sprayed materials. The required specimens are also produced by EDM from the semi-finished products. The thermal diffusivity is determined by laser flash analysis (LFA 427, Netzsch Gerätebau, measurement in argon atmosphere, cylindrical specimen ø 12.3 mm x 3.5 mm). Since the thermal diffusivity is temperature-dependent, this experiment is carried out in a defined temperature range from 293 K to 1173 K.

To describe the morphology of thermally sprayed materials, XRD analyses were performed as well as metallographic preparation. An X-ray diffractometer "D8 Discover" from Bruker with Co-Kα
radiation was used. The samples were measured with spot focus, a 1 mm collimator and a LynxEye-XE detector. The measuring time per sample was 8.1 h.

3. Results and discussion
The tensile and bending test results of the Cu 98.7 and 316L specimens reveal fundamentally different mechanical properties of the thermally sprayed material in contrast to its solid equivalent. The solid copper (rolled, annealed) has the expected ductility with a distinctive elastic and plastic deformation. At 293 K, a tensile strength of 247 MPa (flexural strength 411 MPa) and a maximum elongation of 40% are achieved. In contrast, the thermally sprayed material shows brittle failure with a significantly reduced maximum elongation of 0.3% and a tensile strength of 118 MPa (flexural strength 202 MPa).

At elevated temperatures, the maximum elongation increases drastically up to 0.9%. The solid material shows a significant plastic deformation under the development of a constriction, while the thermally processed material fails in brittle mode after low elastic elongation. The interfacial adhesion between the individual spraying particles is weakened by intervening oxides and pores. Hence, the particles slide along their adjacent interfaces when load is applied. Consequently, a clearly increased number of pores with enlarged volume occur in the fracture area.

Similar observations have been made for 316L. The values of flexural strength (410 MPa, brittle failure) are significantly reduced compared to the solid material (flexural strength 702 MPa, no fracture).

Figure 1 illustrates the Young’s moduli for Cu 98.7 and 316L determined by the three-point bending tests for a temperature range of 293 K to 518 K. The value decreases significantly with increasing temperature and differs widely between the tested solid and thermally processed material states. The Young’s modulus is reduced to about 50 % (Cu 98.7 thermally sprayed: 48 GPa, solid: 103 GPa, 316L thermally sprayed: 95 GPa, solid: 196 GPa at 293 K).

Figure 2 shows the results of the LFA obtained for thermally sprayed copper. Specimen 1 was first heated at intervals of 100 K from 373 K to 1173 K. The graph of the thermal diffusivity in the heating process is not linear and differs clearly from the reference material. Based on the curve illustrating the cooling process, a significant change in the morphology of the thermally sprayed copper is indicated.

Figure 1. Young’s modulus determined by bending tests, comparison between Cu 98.7 and 316L in solid as well as in thermally sprayed state.
Consequently, it can be assumed that sintering of the copper particles took place at elevated temperatures over 973 K. This effect is known for thermally sprayed coatings, and was used and especially evaluated in cold sprayed copper layers [10-12]. The lasting effect of the heat treatment is confirmed by the repetition of the test (Figure 2: specimen 1 rep.). To prevent the particles from sintering, the experiment was repeated up to a maximum temperature of 573 K for specimen 3. At lower temperature levels, the effect is much less pronounced, since heating and cooling curve are almost congruent. Thus, the determined thermal diffusivity represents the characteristic behavior of the thermally sprayed material (Cu 98.7 thermally sprayed: 40 to 50 mm²/s, solid: 117 mm²/s at 293 K).

![Figure 2. Thermal diffusivity of thermally sprayed Cu 98.7 at different heating conditions.](image)

For the thermally sprayed 316L, a similar behavior can be observed in the test. Figure 3 shows the determined curves (test conditions according to Cu 98.7). Again, after the cooling process, a significant change in the thermal diffusivity is detectable. The graph is not linear in the heating process and also changes slightly during the cooling phase. By repeating the heating process of the specimen, the permanence of the change is confirmed (Figure 3: specimen 1 rep.). Another specimen (Figure 3: specimen 3) was heated up to 573 K. At this temperature, no significant change in thermal diffusivity could be observed (316L thermally sprayed: 1 mm²/s, solid: X12CrNi18-8, 3.8 mm²/s at 293 K).

With the temperatures used in the test, no sintering can be assumed for steel-based materials. The effect may possibly indicate phase transitions. To clarify the effects of the heat treatment, a supplementary metallographic preparation and an XRD investigation are performed.

Figure 4 shows the micrographs of thermally sprayed copper for different heating conditions. In the initial state (as-sprayed, Figure 4a), single particles and lamellar oxidized intermediate phases can be observed. After heat treatment at 573 K (Figure 4b), there is no change in morphology optically detectable. However, as a result of the treatment with 1173 K (Figure 4c and d), significant changes can be identified. The number of visible particle boundaries is significantly reduced and the shape of the oxidized intermediate phases has changed to globular. Thus it can be assumed that sintering processes and phase transformations have taken place. On this basis, the strongly deviating caloric property profile of heat-treated Cu 98.7 can be explained in comparison to the as-sprayed state.
Figure 3. Thermal diffusivity of thermally sprayed 316L at different heating conditions.

Figure 4. Thermally sprayed copper, as-sprayed (a), heat treatment 573 K (b), heat treatment 1173 K (c, d).
Figure 5 shows the results of the additionally performed XRD analysis for all heat treatment conditions (as-sprayed, 573 K, 1173 K) of the thermally sprayed copper. According to the diffractograms (Figure 5), copper as well as copper oxide (copper (I) oxide) can be detected. The diffractograms of the three different states indicate the same phase composition. The change of thermal diffusivity (Cu 98.7, specimen 1, Figure 2) is therefore due to the observed sintering effect.

Figure 5. XRD analysis, diffractograms of thermally sprayed copper (Cu98.7) for different heat treatment conditions (as-sprayed, 573 K, 1173 K).

In Figure 6, the micrographs of thermally sprayed 316L for the three different heating conditions are displayed. The initial state (as-sprayed, Figure 6a) is characterized by a typical lamellar structure of deformed particles and oxidized intermediate phases. After heat treatment at 573 K (Figure 6b), the morphology has not changed similar to the copper sample. As a result of the treatment at 1173 K (Figure 6c and d), again optical changes occur. Especially in the intermediate phases, phase changes become optically visible. However, the well-defined particle boundaries remain. In accordance with the assumption for steel-based materials, sintering of the particles can thus not be concluded. A possible change in the phase composition is checked by the final XRD analysis.

Figure 7 shows the results of the performed XRD analysis for all heat treatment conditions (as-sprayed, 573 K, 1173 K) of the thermally sprayed 316L. The material consists of three main phases in the as-sprayed state, the austenitic stainless steel, ferrite and magnetite as well as additional oxidized phases. After heat treatment at 573 K, this composition remains almost unchanged. However, after heat treatment at 1173 K, most of the austenitic phase has been converted to ferrite and martensite. The amount of magnetite is also slightly reduced. The heat treatment was carried out under argon atmosphere, so no additional oxygen could be incorporated into the material. The phase transformation takes place as a consequence of diffusion processes and oxidation of the alloying elements, especially of the austenite-stabilizing nickel and manganese. The thermal diffusivity of iron (22.8 mm²/s) differs significantly from unalloyed steel (<0.4% C, 12 mm²/s to 15 mm²/s) or high-alloyed steel (X12CrNi18-8, 3.8 mm²/s). It can therefore be assumed that the increase in thermal diffusivity is due to the effects of phase transformations.

The investigations show two typical mechanisms for property changes of thermally sprayed materials. The material-specific operating temperatures are of crucial importance and must be taken into account in order to avoid unwanted effects.
Figure 6. Thermally sprayed 316L, as-sprayed (a), heat treatment 573 K (b), heat treatment 1173 K (c, d).

Figure 7. XRD analysis, diffractograms of thermally sprayed 316L for different heat treatment conditions (as-sprayed, 573 K, 1173 K).
4. Summary
Mechanical and thermal properties of wire arc sprayed Cu 98.7 and 316L have been studied. A novel approach for producing non-miniaturized specimens by EDM from thick coatings has been presented. The use of larger specimens reduces the influence of pores and oxides, which are considerably present in thermally sprayed material. Thus, error influences are reduced and the quality of the obtained data is increased. The mechanical test results revealed drastically reduced Young’s moduli (Cu 98.7: 49%, 316L: 48%, measured at 293 K) of the thermally sprayed materials in comparison to their solid equivalent.

The laser flash analysis (LFA) was performed in a temperature range of 373 K up to 1173 K for both thermal sprayed materials. The graphs of the thermal diffusivity in the heating process showed atypical behavior especially at higher temperatures above 573 K, which indicated significant and permanent changes in the morphology of the thermally sprayed materials. At lower temperatures, the behavior also deviates from the solid materials but does not show any permanent changes.

To clarify the effects of the heat treatment, a supplementary metallographic preparation and an XRD investigation were performed.

For the tested copper (Cu 98.7), the micrograph after heat treatment with 1173 K revealed a significantly reduced number of visible particle boundaries. The shape of the oxidized intermediate phases changed to globular. Thus it can be assumed that sintering processes have taken place. The XRD diffractograms of the three different states showed no change in phase composition.

For the thermally sprayed 316L, a major phase change after heat treatment with 1173 K could be shown through metallographic preparation and XRD analysis.

The investigation shows fundamental property changes of thermally sprayed materials at elevated temperatures. The material-specific operating conditions are of crucial importance to avoid unwanted effects.

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