Cold Spray Deposition of Copper/Tungsten Composite Coatings

M Doubenskaia¹, Yu S Latfulina ² and M N Samodurova ²

¹Lyon University, ENISE, LTDS Laboratory, UMR CNRS 5513, 58 rue Jean Parot, Saint-Etienne Cedex 2, 42023 France
²Processes and Machines of Metal Forming by Pressure Department, South Ural State University, 76, Lenin prospect, Chelyabinsk, 454080, Russia

E-mail: samodurovamm@susu.ru

Abstract. This work is devoted to the study of the microstructure and the properties of the Cu-W composite coatings deposited using cold spray technology. This process allows fabrication of high-quality coatings on large surfaces of different types of materials. The technology is widely used and investigated due to technological simplicity, wide range of sprayed materials and operating temperatures. However, there are some technological problems which appear when materials with low melting temperatures are sprayed. During softening, the particles adhere to the nozzle walls and block spraying. By the way, it is possible to solve the problem adding some ceramics particles to the spraying mixture of powders. As a result, the formed coating will have better mechanical properties and the technological problem will be solved. The analysis of the general results of the microstructure studies and experiments, and comparison with other coating methods are given. Moreover, the experimental procedure of samples preparation and used equipment are given. It is shown the microstructure before and after heat treatment of the samples sprayed, microhardness measurements, thermal conductivity measurements.

1. Introduction

Tungsten copper (W-Cu) composites are widespread refractory material [1–4]. They are prospective materials for such areas of manufacturing like arcing resistance electrodes, heavy duty electronic contacts, electrical contacts and electrodes, electro-forging and welding dies, heat sinks, packaging material and thermal management devices owing to their outstanding properties [7].

For use in these areas of production [4], the materials should have the highest possible thermal conductivity and low coefficient of thermal expansion (CTE) with the possibility of its regulation, the same as for an electronic substrate such as gallium arsenide (CTE=5.8×10⁻⁶/K). Tungsten/copper composites have priority over other materials as the best candidates for heat sinking because they have high thermal conductivity (~200 W/m K) and low CTE (~6.5×10⁻⁶/K).

The production of tungsten/copper coatings by infiltration is very expensive due to the need to use high temperatures for tungsten copper impregnation [5].

The cold spraying process is more suitable in terms of production costs due to the lack of high temperatures and does not change the properties of the sprayed surface. Therefore, H.-K. Kang and S.B. Kang [5, 6] studied the cold spraying of tungsten/copper composition (Figure 1) and compared it with the plasma spraying method. As a result, copper oxidized during the plasma spraying process and deteriorated the coating properties, while copper did not get oxidized after the cold spraying process (Figure 2).
Microstructural analysis also showed the dependence of the amount of porosity on the tungsten content in the composition. The more tungsten is in a certain area of coating, the greater the number and size of pores. (Figure 3.)
The content of tungsten in the coating thickness of about 100-200 μm was the maximum (Figure 4), then showed its decline after increasing the thickness of the coating, which showed the ineffectiveness of applying coatings thicker than 200 μm.

![Figure 4. Tungsten content and porosity versus location in the deposited layer.](image)

It can be seen that cold spray technology is promising for the production of coatings on different materials. In contrast to other additive manufacturing methods, cold spraying technology does not use high temperatures and metal melting as in selective laser melting. This means that metals are not subject to thermal distortion, and for the manufacture of parts does not require the use of protective inert gas medium or vacuum seal, which allows you to create much larger structures [8–11]. In the manufacture of products using cold spraying technology, such advantages become apparent as the ability to create any shape and size of products, and capable of fusing dissimilar metals to create hybrid metal parts – materials such as titanium alloys, copper, zinc, stainless steel, aluminium, nickel, even hastelloy and inconel can be sprayed together.

2. Materials and methods

5 mixtures of different composition were taken. Compositions of mixtures are presented in Table 1.

| Copper, wt.% | Tungsten, wt.% |
|--------------|----------------|
| 95           | 5              |
| 75           | 25             |
| 50           | 50             |
| 25           | 75             |
| 10           | 90             |

Commercial cold spray equipment CGT KINETIKS 4000 with Type 40 spray nozzle was applied for coating deposition. Deposition was performed on aluminum plates under parameters listed in Table 2. Thick coatings (more than 1 mm) were applied in order to minimize an influence of substrate on the kinetics of coating formation. Coating composition was defined using image analysis. The image analysis was performed using cross-section images obtained by scanning electron microscopy.
Table 2. Spraying parameters.

| Gas type | Gas pressure, bar | Gas temperature °C | Powder feeder speed mm/s | Manipulation speed, mm/s | Track overlapping, mm | Number of layers | Spraying distance, mm |
|----------|-------------------|---------------------|--------------------------|--------------------------|-----------------------|------------------|----------------------|
| Nitrogen | 30                | 400 °C              | 8                        | 20                       | 3                     | 2-10             | 30                   |

The obtained samples were prepared for further metallographic studies by using the BRILLANT 230 and Buehler SimpliMet 1000. The sample preparation system “Buehler Phoenix 4000” was used for surface grinding and polishing as the standard procedure. The specimens were etched in order to observe the microstructure of the composite coatings. The specimens were studied by a Zeiss AxioCam ICc 3 Microscope. For more detailed studies, the scanning electron microscope (SEM) Tescan was used. SEM analyses were performed using a 15 kV beam voltage. The specimens were analyzed under magnifications in a range of ×50 to ×2000 at two modes: back-scattered electron (BSE) to observe a phase contrast and secondary electron (SE) to get high-resolution images of a sample surface, revealing details less than 1 nm in size [12].

3. Results and discussion

3.1. Deposition efficiency
Images of obtained cross-sections are presented in Figure 5. Hard particles (light) of tungsten are distributed in soft matrix of copper.

During the chemical analysis the percentage of tungsten in the coating was found (Table 3).

Table 3. The amount of tungsten in coatings after cold spray.

| Composition     | Amount of tungsten, wt.% |
|-----------------|--------------------------|
| Cu + 5% W       | 5                        |
| Cu + 25% W      | 9                        |
| Cu + 50% W      | 15                       |
| Cu + 75% W      | 30                       |
| Cu + 90% W      | 49                       |

Figure 5. SEM images of coating cross-section deposited using different blends; (a) – Cu + 5% W, (b) – Cu + 25% W, (c) – Cu + 50% W, (d) – Cu + 75% W, (e) – Cu + 90% W.

From the experimental results it can be seen that the maximum concentration of tungsten does not exceed 48–50%. After the chemical analysis, it becomes obvious that the maximum content of tungsten in the mixture will not exceed 50%. The sharp drop in the effectiveness of the coating deposition is
noticeable after an increase in the tungsten content of more than 10–15% of the total weight of the composition. This phenomenon is due to the high hardness of tungsten particles. If the hard particle meets the surface covered by previously bonded hard particle, the impact energy is not high enough for bonding and hard particle rebounds.

3.2. Microhardness results
The Vickers hardness test [13] was performed on the well-polished cross-sections of the specimens. To get an average hardness level the measurements were carried out in 5 equal lines consisted of 50 indentations with the 350-μm-distance between two of them in the direction from the top of the composite coating to the steel surface. The microhardness level of the two samples was examined by the Buehler MicroMet 5100. The load was 25 g. The indenter is a diamond in the form of a square-based pyramid.

Microhardness measurement was carried out for samples before the application of heat treatment and after the application of heat treatment. In Table 4 results of the measurement are presented. Average value of microhardness is mentioned.

| Composition | Heat treatment | Microhardness, HV |
|-------------|----------------|------------------|
| Cu + 5%W    | -              | 109              |
| Cu + 25%W   | 400°C, 1 h     | 100.75           |
| Cu + 50%W   | 400°C, 2 h     | 126.95           |
| Cu + 5%W    | 600°C, 2 h     | 85.7             |
| Cu + 25%W   | 600°C, 2 h     | 83.45            |
| Cu + 50%W   | 600°C, 2 h     | 58.75            |

It can be seen that microhardness decreases during heat treatment. The higher the heat treatment temperature, the more intense the drop in the microhardness values. The relative error of the experiment in microhardness is 15%.

Apparently, the hydrogen content in the initial copper powder, which is the reason for the increase in porosity after heat treatment of the samples, decreases the microhardness with increasing heat treatment temperature.

As the coating thickness increases, the porosity decreases due to the overlapping of the pores by subsequent metal layers, therefore the coating thickness must be such that it is generally non-porous or with a minimum number of pores. The coating must have a strong adhesion with the base metal and not peel off under mechanical action. Therefore, depending on the requirements of the coating, it is necessary to choose the most optimal coating thickness. But this drop in microhardness can be useful in further machining the surface, if necessary.

3.3. Microstructure after heat treatment
The purpose of heat treatment in this case is to improve the mechanical properties of the coating material and eliminate boundaries between copper grains for obtaining of homogeneous structure and chemical composition.

During heat treatment, copper and its alloys can interact with oxygen, hydrogen, water vapor and other compounds (CH₄, etc.). When ingots and semi-finished products are heated in a reducing environment of H₂, H₂O, CH₄, and other compounds containing hydrogen, they dissociate, the resulting
atomic hydrogen quickly diffuses into the metal, since the diffusion coefficient of hydrogen in copper is quite large. Hydrogen interacts with copper oxide in copper by the reaction \( \text{CuO} + \text{H}_2 \rightarrow 2\text{Cu} + 2\text{H}_2\text{O} \). Water vapor and other gases released are insoluble in copper and create high pressure, leading to discontinuities along the grain boundaries and voids in the grain body. The discontinuities then develop into cracks, which is especially pronounced during hot pressure treatment [15].

The evolved gas may include steam and sulphur dioxide as well as hydrogen. The composition and quantity of the gas evolved is determined mainly by the following factors:

- the alloy composition in respect of components which form very stable oxides, thereby reducing the activity of dissolved oxygen;
- the opportunity for hydrogen absorption from the environment;
- whether the metal is melted under oxidizing or reducing conditions;
- deoxidation and degassing practices;
- the degree of sulphur contamination, if any [16].

Copper and alloys based on it actively interact with oxygen and water vapor at elevated temperatures. In this regard, during the heat treatment of copper products and its alloys, protective atmospheres are often used.

In Figures 6, 7 and 8 it can be seen 3 composition without heat treatment and with heat treatment at 400° and 600°C. In all three compositions the grain boundaries became less visible after heat treatment, and porosity appeared at the grain boundaries. The air between the copper particles when exposed to high temperatures appear to be subjected to high pressure intergranular space, which led to the formation of pores. The occurrence of this phenomenon in the longer term may lead to embrittlement of the coating and the formation of defects in it, leading to the destruction of the material.

![Figure 6](image6.jpg)

**Figure 6.** Composition Cu+5%W: (a) – without heat treatment; (b) – after heat treatment at 400°C; (c) – after heat treatment at 600°C.

To avoid such a defect in especially important products it is necessary to control the content of oxygen and other gases in the original composition.

![Figure 7](image7.jpg)

**Figure 7.** Composition Cu+25%W: (a) – without heat treatment; (b) – after heat treatment at 400°C; (c) – after heat treatment at 600°C.
3.4. Thermal conductivity measurements

The effective use of materials used for the manufacture of coatings in various areas is largely determined by the accuracy of information on their thermophysical properties, and in particular, on thermal conductivity in a wide range of concentrations and temperatures.

The study of the physicochemical properties of these materials in a wide range of changes in temperature and concentration is necessary for a deeper understanding of temperature-concentration changes in their structure when solving technological problems.

The measurements were carried out by an indirect method. It includes the measurement of conductivity by measuring the specific heat, thermal diffusivity and density.

Mass heat capacity was measured by C80 Setaram calorimeter [14]. The C80 calorimeter is one of the world's most versatile calorimeters. It uses the principle of Calvet, which makes it possible to work in scanning and isothermal temperature conditions in a wide range of temperatures from room temperature to 300°C and is capable of detecting low-energy thermal phenomena. Designed in particular for measuring the heat dissipation of reactions and mixtures.

In order to compare the theoretically and experimentally obtained values of the thermal conductivity of the objects of study, a numerical model has been used.

Thermal conductivity was measured for two samples: Cu+25%W and Cu+50%W.

The first step of measurements is thermal diffusivity measurement. In Table 5 the results of the measurements for two samples at room temperature and 150°C are presented.

Table 5. Diffusivity measurements.

| Composition | Temperature of the experiment, °C | Apparent thermal diffusivity, $10^{-6}\text{m}^2/\text{s}$ | Uncertainty, $10^{-6}\text{m}^2/\text{s}$ |
|-------------|----------------------------------|-------------------------------------------------|-------------------------------------|
| Cu+25%W     | 24                               | 89.5                                            | 6.3                                 |
|             | 150                              | 85.3                                            | 6.0                                 |
| Cu+50%W     | 24                               | 85.1                                            | 6.0                                 |
|             | 150                              | 81.2                                            | 5.7                                 |

Apparent thermal diffusivity of a pure copper is $117\cdot10^{-6}\text{m}^2/\text{s}$ [18].

The next step is measurement of mass thermal capacity of the samples. In Table 6 the results of the measurements are presented.

Apparent mass thermal capacity of pure copper is 385 J/kg/K at room temperature [18].

With using of values of density from Table 7 it could be possible to calculate thermal conductivity of the samples (Table 8).

Apparent volumetric mass of pure copper is 8933 kg/m³ at room temperature [18].
Table 6. Mass thermal capacity measurements.

| Composition | Maximum temperature of the enthalpic peak, °C | Apparent mass thermal capacity, J/kg/K | Uncertainty, J/kg/K |
|-------------|-----------------------------------------------|----------------------------------------|---------------------|
| Cu+25%W     | 28.3                                          | 357                                    | 18                  |
|             | 149                                           | 375                                    | 19                  |
| Cu+50%W     | 28.3                                          | 325                                    | 16                  |
|             | 149                                           | 344                                    | 17                  |

Table 7. Density measurements.

| Composition | Measurement conditions | Apparent volumetric mass, kg/m³ |
|-------------|------------------------|---------------------------------|
|             | T, °C      | Relative humidity, %       |
| Cu+25%W     | 21.4        | 38.5                         | 9245                |
| Cu+50%W     | 21.4        | 38.5                         | 9956                |

Table 8. Thermal conductivity results.

| Composition | T, °C | Average apparent thermal conductivity, W/m·K |
|-------------|-------|---------------------------------------------|
| Cu+25%W     | 26    | 295.2                                       |
|             | 150   | 296.2                                       |
| Cu+50%W     | 26    | 275.1                                       |
|             | 150   | 278.4                                       |

Thermal conductivity of pure copper:
- \(\lambda(300K) = 401\) W/m.K;
- \(\lambda(400K) = 393\) W/m.K;
- \(\lambda(600K) = 379\) W/m.K \[18\].

Thermal conductivity can be calculated in different ways. Several mathematical models have been created for this purpose. Hasselman and Johnson presented the most recent model of them. \[17\]. This model shows that the TC of a composite with continuous matrix and dilute volume fractions of spherical reinforcement is expressed as

\[
K_c = K_m \left[ \frac{2 \left( \frac{K_p}{K_m} - \frac{V_p}{ah_c} - 1 \right)}{1 - \frac{K_p}{K_m} + \frac{K_p}{K_m} \frac{V_p}{ah_c} + \frac{K_p}{K_m} + 2 \frac{K_p}{ah_c} + 2} \right]
\]

where \(K\) is the thermal conductivity, \(V\) the volume fraction of reinforcement, and the subscripts c, m and p refer to the composite, matrix and reinforcement, respectively; \(a\) is the radius of the spherical reinforcement and \(hc\) is the thermal boundary conductance. In the absence of an interfacial thermal resistance, i.e., \(hc = \infty\), an ideal thermal conductivity can be obtained by equation and the equation becomes agreeable to the expression of Maxwell \[18\]. In this work, the thermal conductivity of two composites sprayed with Cu+25%W and Cu+50%W powder with 12 μm tungsten was estimated by equation under the condition of \(hc = \infty\). The concentration of tungsten taken for calculation was 9% and 15% respectively (the concentration of tungsten after the cold spraying process). At room temperature, the thermal conductivity of tungsten is chosen as 162.8 W/mK. The matrix of the composite sprayed is considered as copper, and its thermal conductivity is 401 W/mK (equable to the thermal conductivity of
pure copper). At 150°C copper is also considered as the matrix material in the composite sprayed with Cu+50%W powder, and has 393 W/mK thermal conductivity, and for tungsten it is 155.9 W/mK thermal conductivity. Substitution of these data into equation yields 375.55 and 368.06 W/mK for the composites from Cu+25%W powder at room temperature and at 150°C respectively and for Cu+50%W powder thermal conductivities are 356.08 and 348.98 W/mK at room temperature and at 150°C respectively.

The comparison between calculated and experimentally measured data is presented in Table 9.

Table 9. Comparison between experimental and numerical model data.

| Composition | Temperature, °C | Experimental data, W/mK | Numerical model data, W/mK |
|-------------|-----------------|--------------------------|---------------------------|
| Cu+25%W     | Room temperature | 295.2                    | 375.55                    |
|             | 150             | 296.2                    | 368.06                    |
| Cu+50%W     | Room temperature | 275.1                    | 356.08                    |
|             | 150             | 278.4                    | 348.98                    |

These values are higher than the measured values. Hence, the influence of the intense porosity and oxidation at grain boundaries on the thermal conductivity is very obvious for the composites.

4. Conclusions

From the experimental results it can be seen that the maximum concentration of tungsten does not exceed 48–50%.

The sharp drop in the effectiveness of the coating deposition is noticeable after an increase in the tungsten content of more than 10–15% of the total weight of the composition. This phenomenon is due to the high hardness of tungsten particles. If the hard particle meets the surface covered by previously bonded hard particle, the impact energy is not high enough for bonding and hard particle rebounds.

The hydrogen content in the initial copper powder, which is the reason for the increase in porosity after heat treatment of the samples, decreases the microhardness with increasing heat treatment temperature.

As the coating thickness increases, the porosity decreases due to the overlapping of the pores by subsequent metal layers, therefore the coating thickness must be such that it is generally non-porous or with a minimum number of pores. The coating must have a strong adhesion with the base metal and not peel off under mechanical action. Therefore, depending on the requirements of the coating, it is necessary to choose the most optimal coating thickness.

Copper and alloys based on it actively interact with oxygen and water vapor at elevated temperatures. In this regard, during the heat treatment of copper products and its alloys, protective atmospheres are often used.

In all compositions the grain boundaries became less visible after heat treatment, and porosity appeared at the grain boundaries. The air between the copper particles when exposed to high temperatures appear to be subjected to high pressure intergranular space, which led to the formation of pores. The occurrence of this phenomenon in the longer term may lead to embrittlement of the coating and the formation of defects in it, leading to the destruction of the material. To avoid such a defect in especially important products it is necessary to control the content of oxygen and other gases in the original composition.

The values obtained from numerical model for calculation of thermal conductivity are higher than the measured values. Hence, the influence of the intense porosity and oxidation at grain boundaries on the thermal conductivity is very obvious for the composites.
References

[1] Alkhimov A P, Klinkov S V and Kosarev V F 2010 Cold gazdynamic spraying. Theory and practice (Moscow: Fizmatlit) p 535
[2] Robitaille F, Yandouzi M, Hind S and Jodoin B 2009 Surf. Coat. Technol. 203 2954–2960
[3] Lupoi R and O’Neill W 2010 Surf. Coat. Technol. 205 2167–2173
[4] Zweben C 1992 The Journal of The Minerals, Metals & Materials Society 44–7 15–23
[5] Kang H-K and Kang S B 2003 Scripta Materialia 49 1169–1174
[6] Kang S B, Kang H-K and Euh K 2005 Materials Science Forum 475–479 945–948
[7] Dong L L, Ahangarkani M, Chen W G and Zhang Y S 2018 Int. J. of Refractory Metals and Hard Materials 75 30–42
[8] 2012 Cold spray. A guide to best practice (Arbegast Materials Processing and Joining Lab: South Dakota School of Mines and Technology, United States)
[9] Hussain T, McCartney D G, Shipway P H and Zhang D 2009 J. Therm. Spray Technol. 18(3) 364–379
[10] Huang R, Ma W and Fukanuma H 2014 Surface and Coatings Technology 258 832–841
[11] Sova A, Maestracci R, Jeandin M, Bertrand Ph and Smurov I 2016 Surface and Coatings Technology
[12] Goldstein J and Newbury D 2003 Scanning electron microscopy and X-ray microanalysis (Kluwer) p 689
[13] ISO 6507-1:2005 Metallic materials. Vickers hardness test. Part 1: Test method
[14] Calvet Calorimeter C80 From ambient to 300 °C by Setaram 2019 Online. Available: SETARAM Instrumentation: www.setaram.com
[15] Akulov A I 2003 Technology and equipment for fusion welding and thermal cutting (Moscow: Bauman Moscow State Technical University)
[16] Talbot D E J 1975 International Metallurgical Reviews 20(1) 166–184
[17] Manchang G, Suk B K and Kwangjun E 2004 Scripta Materialia 52 51–56
[18] Incropera F P, DeWitt D P, Bergman T L and Lavine A S 2011 Fundamentals of Heat and Mass Transfer (John Wiley & Sons) p 1024

Acknowledgments

The work was supported by Russian Science Foundation (project No. 20-19-00304).