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# On the mechanical and electrical properties of copper-silver and copper-silver-zirconium alloys deposits manufactured by cold spray

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ABSTRACT

In this work, several copper alloy deposits were manufactured by cold spray with helium as accelerating and carrier gas. Electrical conductivity was measured to establish the potential of cold spray as a manufacturing process for high strength ($>500$ MPa) and high conductivity ($>90\%$ IACS) copper alloys. The deposits which are characterized by a low oxygen content ($<200$ ppm) and a low porosity level ($<0.1\%$) present yield strength values up to about 700 MPa and electrical conductivity values up to 58.2 MS/m (100.3% IACS). Results show that, even if a compromise has to be made between the properties according to the objectives of the application, this additive manufacturing route appears suitable for the production of large copper alloys parts with high mechanical properties and high electrical and thermal conductivity. The role of alloy composition and post heat treatments on the strength and conductivity of the deposits was especially considered in this work. Cold spray deposits properties were finally compared with those obtained with other manufacturing routes.



## 1. Introduction

Availability of high strength copper base alloys with high electrical or thermal conductivity is a key point for the industrial development of a large number of applications. Cooling of electronic products, lead frames, connectors [1], wiring for a bullet train, sheet and wire conductors [2], combustion chambers [3], first wall and diverter of tokomaks, rocket and space shuttle engines [4], high magnetic field magnets [2,5,6] can be cited among others.

Pure copper presents high electrical (58 MS/m) and thermal ($\lambda=380\ \mathrm{W\,m^{-1}\,K^{-1}}$) conductivity but rather poor mechanical properties (tensile strength limited to 225 MPa [7]). Several alloying elements like Ag, Cr, Fe, Nb, Zr, Be, … allow reinforcing the mechanical properties of the material thanks to precipitation hardening. Thus, copper alloys composition has been widely studied in the past to improve the strength of copper alloys by precipitation hardening, phase boundary hardening and solid solution hardening. However, the nature, the percentage and the distribution of those elements often limit the conductivity.

Generally, the amount of additional elements has to remain below 5 wt% to maintain a good conductivity. Silver which also presents as a pure metal a high conductivity (about 106% IACS) is often used as a precipitation hardener to enhance the mechanical properties of copper as its solubility in this metal is very low. In this case, discontinuous precipitation (i.e. selective grain boundary precipitation) occurs that can be clearly distinguished in the micrographs [8]. It is generally considered that discontinuous precipitation is mainly linked to the difference between the atomic radii of elements in the considered alloys [9,10]. In the case of Cu-Ag alloys, already widely studied in the past [8,11], precipitation mechanisms were mainly attributed to structural transformation and related to the Fournelle and Clark's mechanism [12].

Other elements like zirconium can also be added to promote a homogeneous precipitation of the Ag rich phases which results in higher mechanical properties [13]. Indeed, zirconium acts as a grain refiner [6] and inhibits the discontinuous precipitation thus enhancing the continuous precipitation mode [5].

Another well-known way to enhance the hardening of copper alloys is to introduce a large number of dislocations into the grains. Several processes such as forging [14], Equal Channel Angular Pressing (ECAP) [7,15] and also cold rolling, drawing [6] or even spraying [16–18] have already been used to obtain the cold working hardening effect of the matrix.

In summary, the requirements to produce parts with high mechanical properties and high conductivity can be listed as follow:

- Precise management of the precipitation mechanisms to ensure high thermal and electrical conductivities,

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- Strong cold work effect to enhance the mechanical properties,
- Moderate temperature during manufacturing operations to avoid oxygen contamination,
- High productivity to fit with industrial requirements,
- Ability to work at industrial scale and to produce large items.

Considering these requirements, an additive manufacturing process working below the melting point of the material such as Cold Spray appears as a good candidate to reach these goals. Cold Spray [19] is a technique consisting in spraying small particles (10–100 μm) at temperature well below the melting point of the material thanks to a high velocity gas jet obtained via the discharge of a compressed gas inside a De Laval nozzle. Indeed, ductile materials like copper and copper alloys are particularly suitable for deposition by cold spray as the critical velocity (corresponding to the minimal velocity of the particles requested to obtain adhesion on a substrate or previously deposited layers) is relatively low (between 350 and 650 m/s) versus that requested by other materials [17,20–23]. Deposition efficiency is also a factor depending on the particles velocity but may reach very high values, close to 100%, when the velocity is situated in the upper half of the deposition window. In addition, a cold work effect (i.e. dislocations pile-up) also results from the high plastic deformation of the powder particle impacting the substrate. Indeed, each particle sprayed at high velocity is severally deformed and then cold work hardened by the following impinging particles. Previous works concerning copper have demonstrated that the dislocations stacking effect associated with a fine microstructure (average grain sizes of few hundreds nm) allows obtaining fairly high mechanical properties [24]. It is well-known that the yield strength increases as the mean grain size decreases, following the classical Hall-Petch relation. The rate increase of the yield strength relative to the grain boundary strengthening can be evaluated by dividing the Hall-Petch constant of the considered alloy by the square root of the mean grain size [25].

Generally cold spray is performed with air or nitrogen, but gases with lower atomic weight like helium can be used favorably to enhance the velocity of the gas stream and thus the particle velocity [26]. Meanwhile, as a small penalty, with helium the drag force exerted on the particles will be lower. Therefore, the distance required for the particles to reach a given fraction of the velocity of the driving gas (which is the limiting velocity) will be greater for helium [21]. Another problem may arise from the cost of the gas but recycling allows solving that problem.

Some researchers also considered the increase of the gas temperature [17] in order to enhance the deposition rate (gas speed increases due to the thermal expansion). In addition, working at higher temperature leads to thermal softening of particles that causes a decrease in critical velocity for many materials [27]. Higher particles temperature at impact can be reached by several means: preheating the powder particles, increasing the gas temperature or increasing the distance between the particle injection and the nozzle throat using an elongated chamber [17].

Meanwhile, increasing particles temperature induces a high risk of oxygen contamination. With the use of helium gas, the system can be operated at lower temperature with high particles velocity and thus oxidation occurring during the quenching of the particles from high temperature to ambient [28] can be lowered. A great advantage of this low temperature is also to reduce the residual stresses usually encountered for deposits obtained with conventional thermal spray processes working at temperature higher than the melting point of the deposited material (1083.4 °C for copper and 961.9 °C for silver), given the high thermal gradients. In the same line, Schmidt et al. reported a lower hardness value (125 HV0.3) for copper deposited at 900 °C when compared to deposits performed at 800 °C (137 HV0.3) due to the thermal treatment of the deposit by the hot gas stream as well as by the higher particle impact temperature [29].

In this work, a Cold Spray system developed in the laboratory allowed to work at relatively low temperature (below 600 °C) with high particles velocities ( > 700 m/s) thanks to the use of helium gas. Deposition was performed in a chamber equipped with recycling loop to avoid costly helium losses and also possible oxygen contamination. Copper alloys were deposited and characterized before and after heat treatment regarding their mechanical properties and their conductivity. The influence of alloys composition and heat treatments was especially considered to seek for high mechanical properties without degrading conductivity. Finally, the potential of the cold spray process to produce large parts consistent with industrial needs was evaluated.

## 2. Experimental details

### 2.1. Feedstock powder

In this work, we studied the influence of the Ag and Zr alloying content. The initial feedstock materials were copper, silver and zirconium granules with a purity of 99.99%, 99.95% and 99.2% respectively.

The alloys powders were obtained in the laboratory by high pressure argon atomization (Nanoval process). The raw atomized powder was sorted between +10 μm and −63 μm using first a Walther&Cie Type 150 classifier machine operated with argon and then a sieving mesh. The particle's size distribution was measured by laser light scattering (Malvern Mastersizer particle size analyzer). The exact composition and the oxygen content of the deposits were then determined by Atomic Emission Spectrometry (ICP-AES) and with an oxygen analyzer (LECO TC436).

### 2.2. Cold spray parameters

The cold spray deposition process allows the manufacture of large parts with complex shapes thanks to the use of a removable mandrel. Given the use of a spray chamber, the size of the part is of course limited by the size of the chamber but nevertheless it can reach in our system a size comprised in an envelope of about $1 \times 1 \times 1\ m^3$.

In this work, Cu alloys deposits were produced using a CGT K-2000 Cold Spray gun equipped with a MOC 24 accelerating nozzle. The cold spray system is equipped with a closed loop circulating device which drastically limits the amount of helium necessary to operate the gun (about $0.5\ m^3$ for 1 h of operation). This device as well as deposition conditions were reported in previous papers [18,30].

An electrical heater is used to preheat the main gas at about 600 °C to further enhance the gas expansion and thus the deposition efficiency. The distance from the particles injector exit to the nozzle throat is about 15 mm ensuring a low temperature of the deposited particles [17]. The temperature of the gun (about 550 °C) and in the region close to the deposited particles on the removable mandrel (about 200 °C) stays well below the melting point of copper. Temperatures were monitored by a thermocouple and by a thermal camera (FLIR Systems SC3000). This low temperature was chosen firstly to avoid the softening of the deposited particles which would lead to a limited cold work effect and thus to insufficient mechanical properties and secondly to avoid oxygen pick-up by the deposited alloy because, even if the oxygen level in the deposition chamber is low (lower than 1000 ppm), a higher temperature could enhance the reactivity with residual oxygen. Thus, high purity copper alloys with oxygen contents lower than 200 ppm were obtained during this work with deposition