Materials Science & Engineering A 637 (2015) 40–47

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Effect of cold work, second phase precipitation and heat treatments on the mechanical properties of copper–silver alloys manufactured by cold spray

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ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form
3 April 2015
Accepted 3 April 2015
Available online 18 April 2015

Keywords:
Cold spray
Cu–Ag alloys
Second phase precipitation
Work hardening
Heat treatment
Yield strength

ABSTRACT

In this work, the mechanical properties of copper–silver cold sprayed deposits were studied versus composition (Ag content), deposition parameters and heat treatment temperature and duration. Low oxygen content (< 150 ppm), low porosity level (< 0.1%) and low residual stress level (< 1 MPa) were reached for deposits leading to an ultimate tensile strength higher than 600 MPa with about 10% elongation at rupture. In addition, results show that the high mechanical properties, obtained through second phase precipitation and cold work effect, can also be finely tailored by an adequate composition choice (i.e. Ag content), and further heat treatments.

1. Introduction

Cu–Ag alloys present the advantage of a high electrical conductivity but their mechanical properties remain limited while a large number of applications require both high electrical (or thermal) conductivity and high strength. Therefore the aim of this work was to try and improve the latter without hindering the former.

As observed on the copper–silver phase diagram (Fig. 1) [1], Cu–Ag is an eutectic system with very limited solubility at low temperature. Precipitation hardening can thus be performed easily. Discontinuous precipitation leads to Ag-rich phase precipitation which acts as reinforcing phase for the Ag depleted copper matrix. Second phase precipitation details (kinetics and mechanism) may be found for example in the work of Hamana et al. for a Cu–7Ag (wt%) alloy [2].

Hardening of copper alloys can also be achieved by cold working. Deformation of the matrix can be performed by several techniques such as forging [3], Equal Channel Angular Pressing (ECAP) [4] and also cold rolling, drawing or even spraying.

Sakai et al. [5] have thus developed a thermomechanical processing route (cold-rolling with intermediate heat treatments) to fabricate Cu–Ag (24 wt%) sheets with high strength (1025 MPa) and high conductivity (75% IACS) at room temperature. More recently, Freudenberger et al. [6] obtained an UTS of about 1.1 GPa with 0.7% elongation after several drawing passes for a Cu–7Ag (wt%) alloy (10% deformation for each pass).

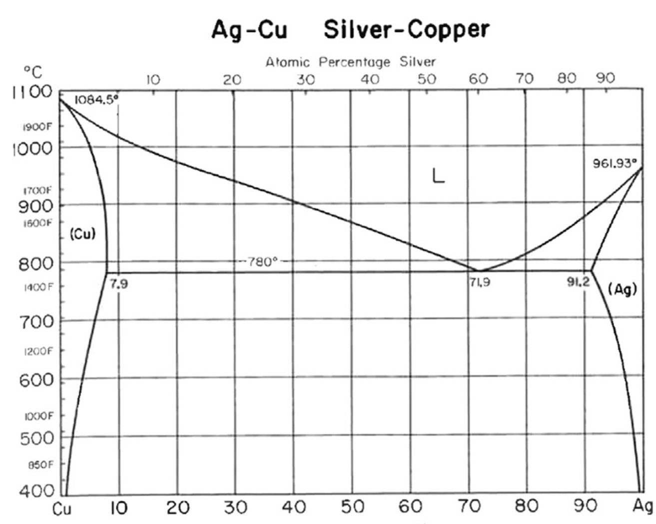

Fig. 1. : Silver–copper phase diagram [1].

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http://dx.doi.org/10.1016/j.msea.2015.04.008
0921-5093/

However, those manufacturing routes often suffer from the sensitivity of copper to oxygen contamination which hinders the performances. Moreover, the combination of hardening mechanisms (solid solution, precipitation, grain boundary pining and dislocations stacking) is difficult to perform for large items.

Considering these difficulties, the cold spray process was considered to determine its potential to produce large electromechanical parts made of Cu–Ag alloys with improved properties versus the state of the art. Thanks to the low processing temperature and the high deformation rate brought to the powder particles, low oxygen content, low residual stress, low porosity level and strong cold work effect may be obtained for the deposits [7].

Thus, from the beginning of the 21st century, cold spray deposition of oxygen sensitive materials like copper and copper alloys has been widely studied [8–10]. Meanwhile, spraying is usually performed using nitrogen as propellant gas and therefore, with classical spraying systems, particles' velocity is situated in the lower range of the "deposition window", i.e. deposition rate is low. One way of solving this problem is increasing the gas temperature [11,12]; however, working at high temperature (i) increases the risk of gun clogging, especially in the case of materials with low melting point, (ii) reduces the cold work effect potentially resulting from the plastic deformation of the powder particles impacting the substrate, and (iii) enhances oxygen pick up by the material [13].

Another way to increase the deposition rate, a little bit more difficult, is to increase the particles velocity which also comes with the benefits of enhancing the cold work effect, reducing oxygen pick up and also reducing the residual stress level.

In this work, in order to increase the speed of the particles and thus being able to reduce the temperature, helium was used as the spraying gas instead of nitrogen [14,15]. Using a classical CGT K2000 cold spray torch, three copper–silver (Cu–0.1Ag, Cu–5.7Ag and Cu–23.7Ag (wt%)) alloys were sprayed. Then, the effect of heat treatments, considering both temperature and duration, was also studied.

2. Experimental details

The feedstock materials were copper and silver granules with a purity of 99.99% and 99.95% respectively. The Cu–Ag powder was obtained by high pressure inert gas atomization (argon) in the laboratory (Nanoval process). The particles' 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).

Cu–Ag deposits were produced using a CGT K-2000 cold spray torch equipped with a MOC 24 accelerating nozzle. This nozzle has a 2.2 mm diameter circular throat and a 5.2 mm diameter exit aperture. The distance between the throat and the exit is 107.5 mm. The powder particles are fed axially from the back of the gun and injected into the centerline, 10 mm before the throat region of the cylindrical De Laval nozzle.

To avoid oxygen contamination, the gun was installed in a vacuum tight chamber. Prior to the deposition process, this chamber was evacuated and then filled with helium. Due to the limited He resources on earth, straight cold spray deposition with helium may not be a sustainable and cost effective way. Therefore, in order to drastically limit the amount of helium necessary to operate the deposition system, a closed loop circulating device, which mainly consists in cooling, filtering and compressing the gas, was implemented.

A schematic of the cold spray deposition system with the recycling helium loop is presented in Fig. 2. This system developed in the laboratory operates at a chamber pressure close to 950 mbar. The oxygen level in the deposition chamber, as measured with an electrolytic oxygen analyzer (Mecanalyse, France), was always lower than 1000 ppm. With this system, the helium consumption can be reduced to about 0.5 m^3 for 1 h of operation.

To further enhance the gas expansion and thus the deposition efficiency, an electrical heater was also used to preheat the main gas at about 600 °C but the carrier gas was not preheated. The gas temperature and pressure in the gun pre-chamber, where the gas is introduced, were monitored using a thermocouple and a pressure gauge mounted on the spray gun. During the deposition process, the gun temperature was stabilized at about 550 °C. Particles velocity was not measured but calculated with the Kinetic Spray Software of KSS GmbH (version 1.0.2).

Deposits were sprayed on AISI 4130 steel cylindrical mandrels (49.7 mm in diameter × 150 mm long). Before deposition, the steel mandrels were degreased and grit-blasted. After deposition, the steel mandrels were removed by machining and Cu–Ag sprayed cylinders were thus obtained for several Ag contents. During spraying, the substrate temperature (about 200 °C in the region close to the deposited particles) was monitored by a thermal camera (FLIR Systems SC3000, Sweden).

The main deposition parameters are reported in Table 1. As presented in a previous paper [16], a fairly high deposition rate (> 140 g/min) was achieved without significant degradation of deposits properties, thus allowing spraying large shapes (within the limits of the size of the spray chamber of course).

To characterize the tensile properties, NOL ring samples [17] were machined from the sprayed tubes. After removing the steel mandrel, the sprayed Cu–Ag cylinders, between 3 and 4 mm thick, were first machined from the bulk. Then, the cylinders were cut to obtain rings of about 10 mm height and 50 mm in diameter which were subsequently milled on both sides (10 mm width and 2.5 mm depth) to obtain the NOL ring tensile specimens.

Some tensile test specimens were tested in the as-sprayed condition while others were heat treated at several temperatures. Heat treatments were carried out in an electric furnace under

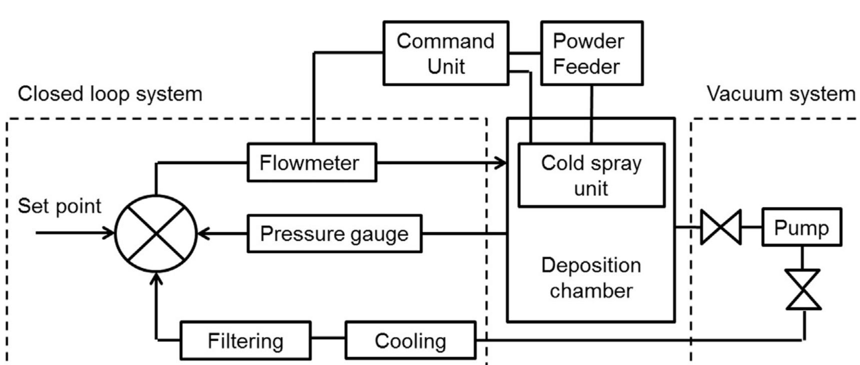

Fig. 2. Schematic of the experimental device.