

Communication

Electric Current-Assisted Joining of Copper Plates Using Silver Formed by In-Situ Decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$

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Abstract: Pulsed electric current can be used for the fast sintering of powders as well as joining of macroobjects. In this work, we brazed copper plates using a silver layer that was formed in situ by the decomposition of a silver oxalate $\text{Ag}_2\text{C}_2\text{O}_4$ powder placed between the plates. Joining was conducted in the chamber of a Spark Plasma Sintering (SPS) facility with and without a graphite die. In the die-assisted tooling configuration, indirect heating of the assembly from the graphite die carrying electric current occurred until the brazing layer transformed into metallic silver. The passage of electric current through a $\text{Cu}/\text{Ag}_2\text{C}_2\text{O}_4/\text{Cu}$ stack placed between the electrodes without a die was possible because of the formation of Cu/Cu contacts in the areas free from the $\text{Ag}_2\text{C}_2\text{O}_4$ particles. Joints that were formed in the die-assisted experiments showed a slightly higher shear strength (45 MPa) in comparison with joints formed without a die (41 MPa). The shear strength of the reference sample (obtained without a die), a stack of copper plates joined without any brazing layer, was only 31 MPa, which indicates a key role of the silver in producing strong bonding between the plates. This study shows that both die-assisted tooling configurations and those without a die can be used for the SPS brazing of materials by the oxalate-derived silver interlayer.

Keywords: silver oxalate; decomposition; electric current; Spark Plasma Sintering; joining; copper

1. Introduction

The Spark Plasma Sintering (SPS) method has attracted enormous interest from the materials science community thanks to its capabilities to consolidate different powder materials rapidly and efficiently [1]. SPS uses uniaxial pressure and pulsed direct current, which are normally applied to a die/punch assembly carrying a powder in the die cavity. In traditional tooling set-ups, die is a mandatory component, as the raw material is in the powder state [2].

Novel applications of the SPS method include surface engineering and materials joining, as recent studies have demonstrated [3]. For joining purposes, silver is a highly attractive material [4]. The process of joining by silver is essentially brazing, as silver (including nano-sized silver) has a higher melting temperature as compared with lead-based alloys used in the soldering processes. Metallic silver-based pastes are commonly used [5]. A lower melting temperature of nano-sized silver than that

of bulk silver [6] allows for a reduction in the brazing temperature when working with nanocrystalline silver-based brazing materials. During brazing, melting of the brazing material does not have to be reached, as its softening can be sufficient for the bond to form. Particles of metallic silver can be produced in situ by decomposing Ag-containing compounds during the joining process. The in situ silver has advantages over the ex situ (previously obtained) silver owing to increased sintering activity of the former [7].

Extensive data have been accumulated on the possibilities of controlling the decomposition process of $\text{Ag}_2\text{C}_2\text{O}_4$, as reviewed by Boldyrev [8]. The present work was conceived based on these data and our experience in the sintering of metallic materials by SPS, including porous materials and materials with layered structures [1]. As a general consideration, electric current offers a means to rapidly heat pieces to be joined and provides conditions for fast chemical transformations (if any) and a reduction of the total duration of the joining process [9]. Although SPS consolidation of nanocrystalline silver powders has been attempted by other authors [10], the only report on the formation of silver during SPS treatment of $\text{Ag}_2\text{C}_2\text{O}_4$ is our previous work [11]. In the present study, we demonstrate that a nanocrystalline silver brazing layer can be formed via a reactive process during the SPS treatment. We have evaluated silver oxalate $\text{Ag}_2\text{C}_2\text{O}_4$ as a silver-generating precursor in the brazing process of copper plates in a SPS set-up, using both a die-assisted configuration of the tooling and a configuration without a die. In the latter, the copper plates were stacked together with an $\text{Ag}_2\text{C}_2\text{O}_4$ powder between them and the electric current was forced through the assembly.

2. Materials and Methods

Joining of copper plates was conducted using a Labox 1575 SPS apparatus (SINTER LAND Inc., Nagaoka, Japan), which has a maximum voltage of 8 V. The pulse sequence was as follows: the pulsed current was applied for 40 ms, after which the current was off for 7 ms. The tooling configurations adopted for the experiments are shown in Figure 1a–c. Graphite punches with a diameter of 30 mm and a graphite die with an inner diameter of 30 mm were used. Joining of the copper plates was conducted under a uniaxial pressure of 13 MPa; the pressure was normal to the surfaces of the copper plates to be joined by the in situ generated silver. Copper plates with dimensions of 15 mm × 15 mm × 3 mm were used. The joints were formed over 15 mm × 10 mm areas. The copper plates were polished using #2500 SiC abrasive paper. The choice of the stack geometry was dictated by the sample geometry required for the shear strength testing of the joints. All joining experiments were conducted under conditions of dynamic vacuum (continuous pumping of the chamber); the residual pressure in the SPS chamber at the start of the experiments (before switching on the current) was 10 MPa. The heating rate in the die-assisted experiments and experiments without a die was 30 and 50 °C min⁻¹, respectively. The temperature in all experiments was measured by a K-type thermocouple inserted in a hole in the graphite die at its mid-plane (Figure 1a) or in a hole in the upper punch (Figure 1b–c). The maximum (measured) temperature during joining of the copper plates was 300 °C, the holding time at this temperature was 5 min. In the joined state, the silver layers had a thickness of about 20 µm. Comparative experiments were conducted, in which joining without a silver layer was realized.

AgNO_3 (reagent grade, “AO Lenreaktiv”, Saint Petersburg, Russia) and $\text{K}_2\text{C}_2\text{O}_4$ (reagent grade, “OOO Komponent-Reaktiv”, Moscow, Russia) were used as the reagents. Silver oxalate $\text{Ag}_2\text{C}_2\text{O}_4$ was synthesized by adding 50 mL of 1 M AgNO_3 solution to 50 mL of 0.5 M solution of $\text{K}_2\text{C}_2\text{O}_4$ upon intense mixing. The residue was separated by filtering and then washed and dried. The morphology of the synthesized $\text{Ag}_2\text{C}_2\text{O}_4$ particles is shown in Figure 2a. The powder consisted of crystals 0.5–2 µm in size. It was further mixed with a resin flux and placed between the polished copper plates. The assemblies were dried at room temperature before joining in the SPS chamber. The thickness of the dried $\text{Ag}_2\text{C}_2\text{O}_4$ layer between copper plates was 200 µm.

A model experiment was also conducted (using copper foil instead of copper plates) to obtain samples whose geometrical features made it easier to observe the structure of the Cu/Ag interface.

Pieces of the foil were joined by a porous silver layer using the SPS treatment at a (measured) temperature of 200 °C using the same $\text{Ag}_2\text{C}_2\text{O}_4$ powder. After the SPS treatment, the foil pieces were separated from each other by tearing and the observations of the Cu/Ag interface as well as the fracture surface of the porous silver layer were made. The model experiment was conducted using the die-assisted configuration.

The structure of the brazing silver layers was studied by Scanning Electron Microscopy (SEM) using a Hitachi-3400S Microscope (Hitachi, Tokyo, Japan). The shear strength of the joints was measured using the assembly shown in Figure 2b. Mechanical testing was conducted on a Zwick/Roell Z100 machine (Zwick/Roell, Ulm, Germany).

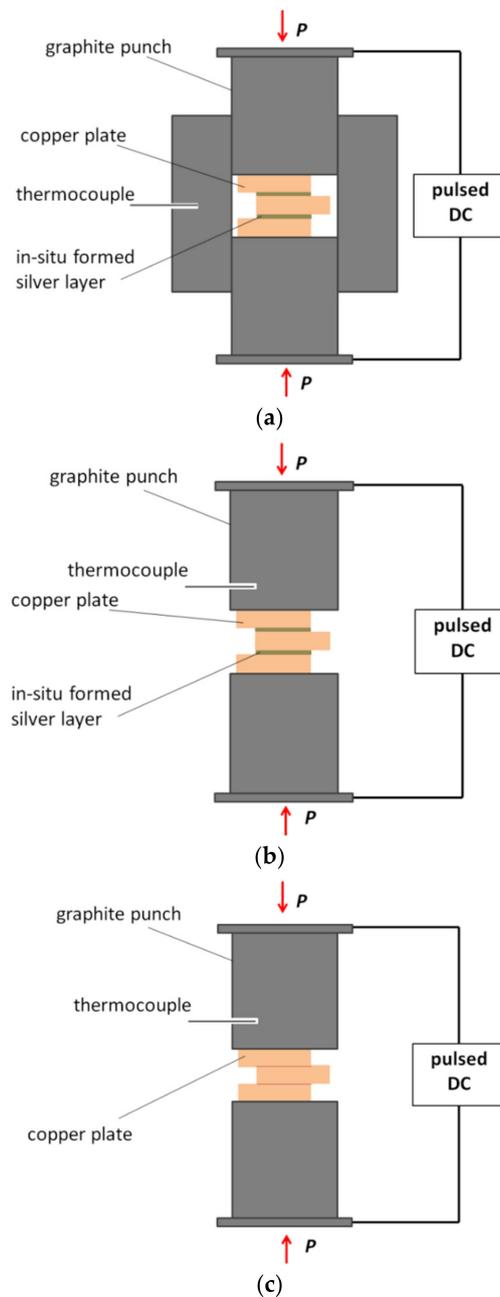


Figure 1. Schematics of the tooling configurations used for the Spark Plasma Sintering (SPS) joining experiments: (a) die-assisted configuration, with an in situ formed silver brazing layer; (b) configuration without a die, with an in situ formed silver brazing layer; (c) configuration without a die, joining without a brazing layer.

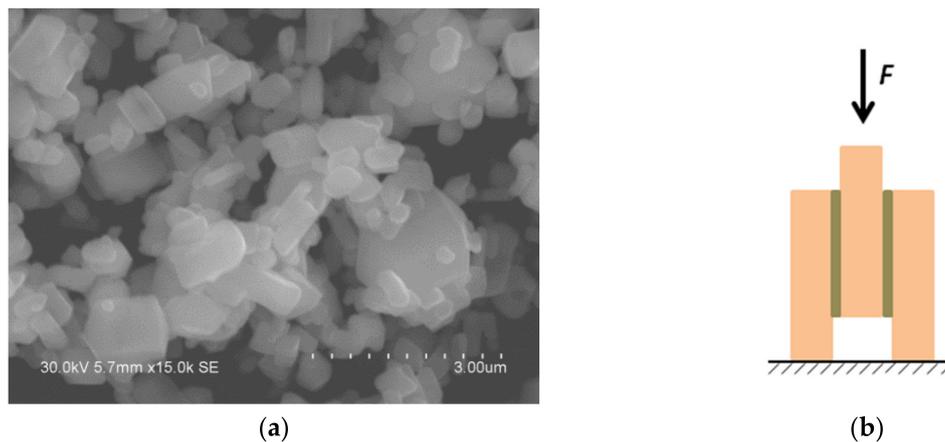
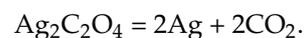


Figure 2. (a) Morphology of the synthesized $\text{Ag}_2\text{C}_2\text{O}_4$ particles (Scanning Electron Microscopy (SEM) image); (b) schematic of the assembly used for shear strength measurements (stacks joined with and without a brazing layer were tested using the same sample geometry).

3. Results and Discussion

In the die-assisted experiments, the passage of electric current through the punches and the die wall offered a means to indirectly heat the stack of copper plates. The passage of electric current through the “Cu plate/ $\text{Ag}_2\text{C}_2\text{O}_4$ /Cu plate” assembly placed directly between the electrodes without a die was enabled by the presence of Cu/Cu contacts in the areas free from the $\text{Ag}_2\text{C}_2\text{O}_4$ particles. Surface roughness of the plates remaining after polishing contributed to the formation of the Cu/Cu contacts.

Decomposition of silver oxalate occurred via the following reaction:



Nanoparticles of metallic silver sintered together and formed a brazing layer that joined the copper plates.

The fracture surface of the joints formed via brazing by the in situ formed silver is shown in Figure 3a–f. An interesting and significant result is that the structure of the silver layers formed in the stack joined inside the die (Figure 3a,b) was more uniform compared with that of the layers formed in the stack joined without a die (Figure 3d,e). As can be inferred from the corresponding images, joints formed without a die showed larger voids than those formed in the die-assisted configuration. The formation of larger voids is possibly related to the direct passage of electric current through the plate assembly and the formation of Cu–Cu contacts at the early stages of heating. These contacts, as spots of high current density and increased local temperatures, serve as locations for the early decomposition of silver oxalate.

As can be seen from the higher-magnification images of the fracture surface of the joints, the brazing layers were formed by silver crystallites 200–500 nm in size, as seen in Figure 3c,f. The obtained silver structures were finer than those reported by Kiryukhina et al. [7], which can be attributed to the use of faster heating and cooling offered by the SPS method. Note that this size is the resultant size of the crystallites observed in the brazing layers. At the beginning of the formation of the Cu/Ag interface, the silver particles were much smaller and could be expected to possess a reduced melting temperature [6]. The silver crystallites tended to grow as the formation of the metallic brazing layer continued during the SPS treatment. Notably, the size of the crystallites did not change significantly when the die-assisted configuration was changed to one that was die-free.

When the electric current can bypass the assembly and pass through the graphite die at the early stages of the process, the assembly is heated indirectly. As the temperature increases, a point is reached when the material starts conducting electricity through the metallic paths. In this case, decomposition

of the remaining oxalate is expected to proceed in an explosive manner [8]. Previously, a direct effect of electric field on decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ was observed at different values of field strengths, from $80 \text{ V}\cdot\text{cm}^{-1}$ [8] to $10 \text{ kV}\cdot\text{cm}^{-1}$ [12]. Decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ under an electric field occurs faster than in the absence of a field.

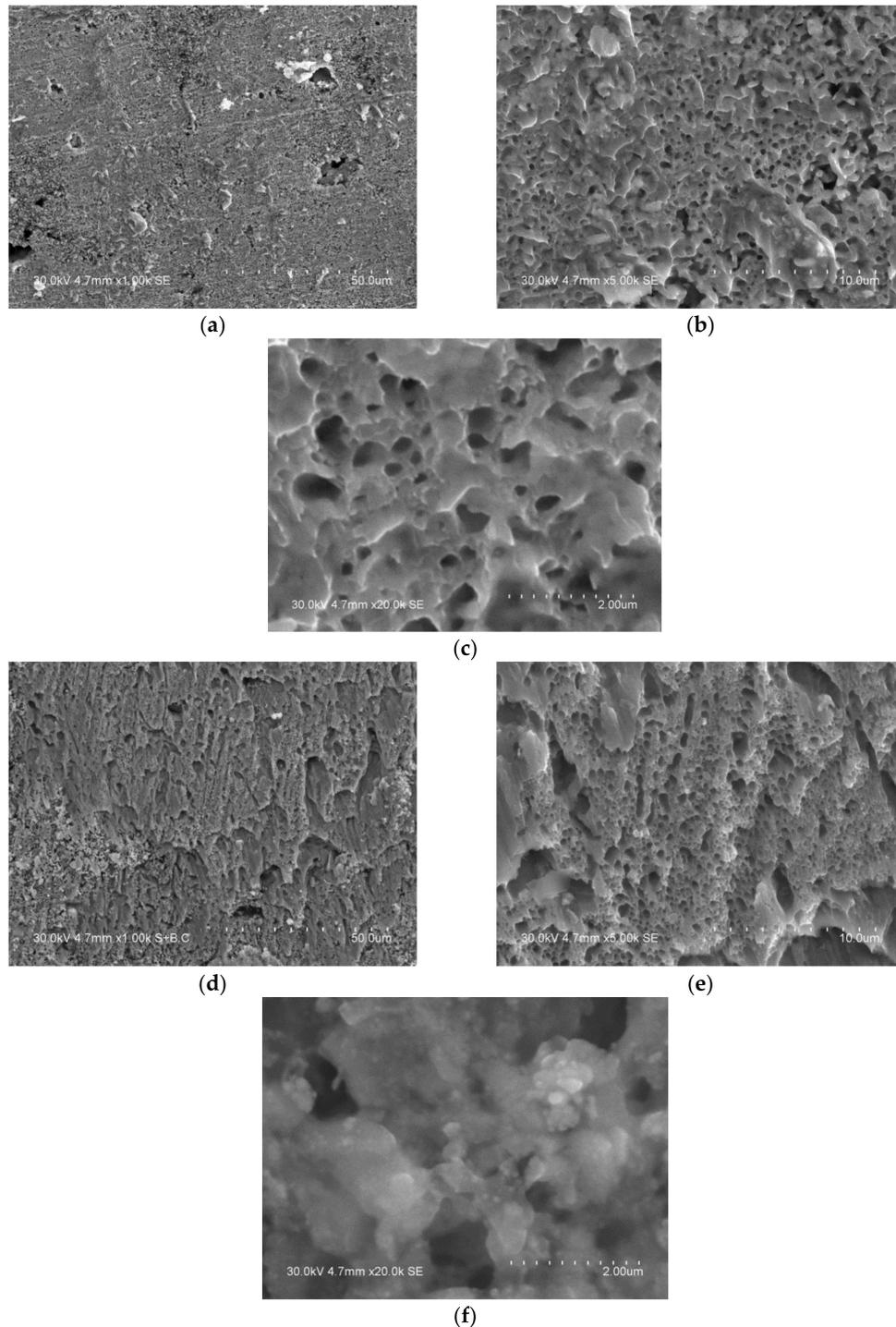


Figure 3. Fracture surface of the in situ formed silver brazing layers: (a–c) die-assisted configuration, (d–f) joining without a die (SEM images). The micrographs were taken with different magnifications to show (a,d) general view, (b,e) porous structure, (c,f) silver crystallites.

In our experiments, the voltage applied to the whole assembly was about 3 V. If we neglect the presence of graphite disks and copper plates, we can estimate the macroscopic field strength along the powder layer of $\text{Ag}_2\text{C}_2\text{O}_4$ in the joining experiments as $3 \text{ V}/200 \mu\text{m} = 150 \text{ V}\cdot\text{cm}^{-1}$. Furthermore, the field has been shown to amplify at the inter-particle contacts of dielectric materials [13]. Therefore, a direct effect of applied electric field on decomposition of silver oxalate can be expected during SPS. Although, in the present study, we did not aim at elucidating the field effect per se, we believe that the application of an electric field during the brazing process is overall advantageous, as it facilitates fast decomposition of silver oxalate leading to the formation of fine particles of silver. For the purposes of high-quality brazing, the size of silver crystallites needs to be retained as small as possible to benefit from the lowering of the melting temperature as well as impart high mechanical strength to the brazing layer.

In electric current-assisted sintering/joining, the temperatures at the inter-particle contacts or within the contact spots between macroobjects, through which an electric current is passing, are rather difficult to measure. However, indirect (microstructure-based) evidence can be instrumental in estimating the temperatures in question. As we did not observe any extended areas of dense (re-solidified) material within the joint after the SPS treatment, we can assume that there was no melting of silver or copper on a macroscopic scale. There should be some alloying between the metals at the interface for strong bonding to occur. As can be seen in Figure 4, which demonstrates the results of the model experiment, during the SPS processing, even at a (measured) temperature of $200 \text{ }^\circ\text{C}$, a well-developed interface formed between the copper foil and the in situ formed porous nanocrystalline silver layer. Further studies will be needed for understanding the alloy formation features at the Cu/Ag interface.

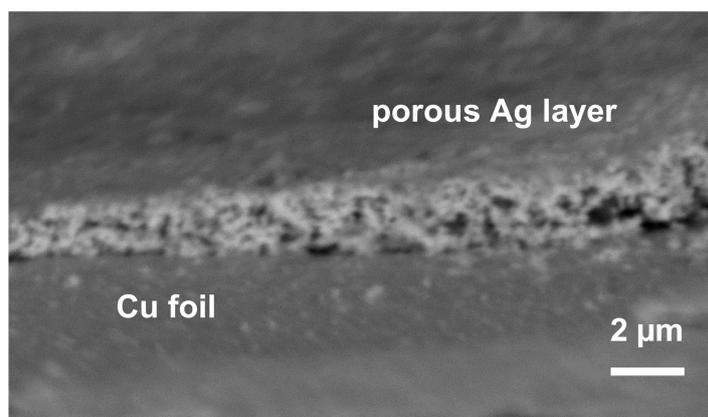


Figure 4. The interface between the copper foil and the porous silver layer formed in situ in a model SPS experiment (SEM image). For conditions of the experiment, refer to the text.

The residual pressure in the SPS chamber was monitored during the SPS joining. An increase in the residual pressure in the SPS chamber was an indication of fast decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$. An increase in the residual pressure was observed at a (measured) temperature of $167 \text{ }^\circ\text{C}$ in the die-assisted experiments [11]. The pressure returned to the initial level when the temperature reached $200 \text{ }^\circ\text{C}$. In the experiments without a die, a pronounced CO_2 evolution-related peak on the residual pressure-temperature curve was absent. A possible explanation for this difference is a more gradual decomposition of silver oxalate during the temperature ramp-up stage, which was caused by the formation of hot spots within the layer from the beginning of the brazing process. In the sample processed in the die-free configuration, starting from the early heating stages, decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ could occur locally, i.e., near the overheated Cu/Cu contact spots. Accordingly, decomposition of oxalate could be continuous upon the application of electric current. As portions of

silver oxalate experienced decomposition as heating progressed, the amounts of the evolved CO₂ were small and undetectable under conditions of dynamic vacuum of the SPS chamber.

The measured values of shear strength of the joints are presented in Table 1. The shear strength of the Cu/Ag/Cu joints obtained in the experiments with and without a die is within the range of shear strength values achieved in joints formed with the use of silver nanoparticle pastes and silver nanopowders [14]. Joints formed in the die-assisted experiments showed a slightly higher shear strength compared with joints formed by forcing electric current directly through the stack. The shear strength of a reference sample, a stack of copper plates joined without any silver addition, was lower than that of the stack containing silver brazing layers. A weaker bonding between the plates in the absence of silver points to its key role in the formation of high-quality bonding between the copper plates.

Using Transmission Electron Microscopy, Akada et al. [15] showed that nanoparticles of silver can form layers that have metallurgical bonding to copper. In a study by Akada et al. [15], bonding was realized by conventional heating of copper cylinders, which were stacked together with a silver nanoparticle paste between them. The purpose of the present study is to highlight a possibility of using silver oxalate rather than metallic silver to form a brazing layer in electric current-assisted joining. As can be seen from the results of the present work, die-assisted configurations and those without a die are suitable for joining of copper with the help of silver oxalate, using the SPS method. Notably, with die-assisted tooling configurations, non-conductive materials can also be joined. In this case, decomposition of Ag₂C₂O₄, as a precursor of the brazing material, will be induced by heating from the graphite die. Configurations without a die will work only for the SPS joining of conductive materials. A great advantage of the die-free set-ups is their flexibility in terms of sample geometry. Decomposition of compounds in the SPS chamber can produce nano-sized products owing to rapid heating conditions. In such cases, the SPS tooling becomes a reactor for the in situ fabrication of nanoparticles, which can further be used for the purposes of interface and surface engineering.

Table 1. Shear strength of Cu/Ag/Cu joints formed by passing electric current through a “Cu plate/Ag₂C₂O₄/Cu plate” assembly in the configurations with and without a die and a Cu/Cu joint. Refer to the text for details of the joining conditions.

Joint	Tooling Configuration	Shear Strength, MPa
Cu/Ag/Cu	die-assisted	45
Cu/Ag/Cu	without a die	41
Cu/Cu	without a die	31

4. Conclusions

In this work, the use of silver oxalate Ag₂C₂O₄ as a brazing material-generating precursor in an electric current-assisted joining process has been investigated for the first time. Fast joining of copper plates using pulsed electric current supplied by a SPS facility was realized in a die-assisted configuration and in a configuration without a die. The powder of Ag₂C₂O₄ decomposed during the SPS processing, producing nano-sized metallic silver, which formed a porous layer with a well-developed interface with copper. The obtained silver layer had a finer structure in comparison with silver brazing layers that were formed by the conventional heating-induced decomposition of Ag₂C₂O₄ reported in the literature. The structure of the brazing layer developed under the influence of the passing electric current; joints formed without a die showed larger voids than those formed in the die-assisted configuration, which was attributed to the direct passage of electric current through the plate assembly in the former. Joints formed in the die-assisted experiments showed a slightly higher shear strength compared with joints formed without a die. The key role of silver in the formation of strong joints was confirmed by finding that the strength of the joints formed without silver brazing layers was lower than that of joints formed by silver brazing.

This work has demonstrated that, for practical purposes, die-assisted SPS tooling configurations as well as configurations without a die can be used for brazing of copper with the help of $\text{Ag}_2\text{C}_2\text{O}_4$. A possibility of passing electric current through die-free assemblies offers a greater flexibility in terms of the geometry of the objects to be joined. In a broader perspective, a combination of the silver precursor approach and the SPS processing appears to be promising for the fabrication of silver-based joints. In future studies, the changeable SPS parameters, such as pressure, heating rate, and electric current, will allow for a flexible design of the structural and mechanical characteristics of the in situ formed silver joints.

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