

Article

Optimization of Copper Thermocompression Diffusion Bonding under Vacuum: Microstructural and Mechanical Characteristics

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Abstract: The optimization of the autogenous diffusion copper bonding via thermocompression at vacuum environment was investigated. The influence of various bonding parameters on the interdiffusion efficiency was studied in detail at the micro (SEM-EBSD) and nano (TEM) scales. Bonding at 1000 °C for 90 min under pressure (10 MPa) presented optimum structural and mechanical results. Under these conditions, interdiffusion phenomena were observed at a significant extent through the swelling transformation of existing fine grains or the formation of equiaxed copper grains with an orientation parallel to the bond interface. Transmission electron microscopy revealed the importance of the grain size of the base material on the bond quality. In the regions with fine-sized copper grains, the formation of small equiaxed recrystallized twins was observed. Their length within the bonding zone was in the order of 200 and 400 nm. On the contrary, in the regions with coarse grains the interdiffusion was poorer. The processing temperature and duration presented a significant effect on the bonding strength (BS). BS exceeded 100 MPa in case of processing conditions of $T \geq 850$ °C and $t \geq 60$ min, while the maximum BS value achieved (≈ 180 MPa) was comparable with the respective value of the base material. The microhardness of the optimum bond reached 55 HV—slightly higher in comparison to the hardness of the initial copper material. The results indicated that the proposed thermocompression process is appropriate for the production of Cu-Cu bonded structures that can be potentially used as electrical components under mechanical stress.

Keywords: copper; thermocompression; bonding; diffusion; microstructure characterization

1. Introduction

Non-fusion bonding consists of a solid-state process in which the joining between two metal surfaces is achieved via interdiffusion and grain growth across the bonding interface [1,2]. In the case of Cu-Cu autogenous bonding, several non-fusion techniques have been developed, including low and high-temperature thermocompression, forge and roll, friction, explosion, electric resistance, and ultrasonic processing [1,3–6]. Vacuum thermocompression consists of the most widely followed process due to its sufficiently controlled conditions and the formation of Cu-Cu bonds with various physicochemical specifications according to respective applications.

Low temperature thermocompression (performed between 150 and 450 °C) (LTT) and room temperature compression Cu-Cu bonding have been extensively studied due to their potential application in future three-dimensional integrated circuits. LTT processes impart high electric

conductivity and low-medium mechanical strength properties, while they assure low thermal stress avoiding damages to the bonded microelectronics [7]. Bonding (tensile) strength (BS) values of up to 70 MPa have been reported in the case of thermocompression between 200 and 400 °C [8–10], while a BS value around 10 MPa is achieved at room temperature compression [11]. Exceptionally high BS values (>200 MPa) have been referred to in the case of annealed and pre-treated copper surfaces using H₂/Ar plasma or formic acid vapor [12].

On the other hand, high-temperature Cu-Cu bonding has not been thoroughly investigated. A limited number of studies describe that the process is performed using a diffusion bonding furnace with hydraulic load equipment in the temperature range of 600–1000 °C [13,14]. Moreover, recently there has been an interest in Cu-Cu bonded structures with advanced mechanical properties that can be used for the construction of bar-wound stators in vehicles [15] or as components in particle accelerators [16,17]. High-temperature bonding technology is compatible with these applications as the existence of thermal deformation phenomena does not consist of a deterrent factor.

The current investigation aims for the optimization of a simple, high-temperature (750–1000 °C) Cu-Cu bonding process using an induction vacuum furnace. The bond quality, in terms of bonding conditions, was studied via microscopy and mechanical tests, while the optimum accomplished bond was examined using scanning electron microscopy (SEM) in conjunction with electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM).

2. Materials and Methods

2.1. Cu-Cu Thermocompression Bonding

Commercially pure (99.9% purity) Cu foils (200 µm thickness, 2 cm width) were used for the bonding tests. The foils were initially placed for 10 s in a hydrochloric acid bath (5% v/v) and subsequently were cleaned with acetone aiming to the removal of a potential thin oxide film, which could impede the interdiffusion mechanism during the bonding process. A stainless steel clamp with an appropriately designed recess was used for the tightening of 28 foils (Figures 1 and 2a). During its screwing, the clamp with the sample was compressed at 10 Mpa. Literature data and preliminary tests showed that the compression between 7 and 10 MPa is efficient for Cu-Cu bonding performance. The superficial interdiffusion between the foils and the clamp was avoided by the coating of the clamp's recess with a thin, fine powdered graphite layer. Bonding tests were performed using a customized Termolab induction graphite vacuum furnace in the temperature range between 750 and 1000 °C under 5×10^{-2} mbar pressure. The furnace's chamber consists of a vertical cylindrical graphite tube (internal dimensions: $d = 24$ cm, $h = 21$ cm) capped by bottom and top graphite elements ensuring heating uniformity (Figure 2b).

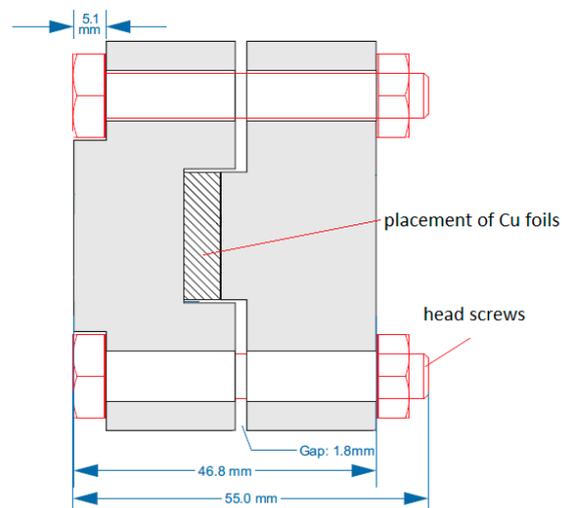


Figure 1. Technical drawing of the clamp used for the autogenous copper bonding.

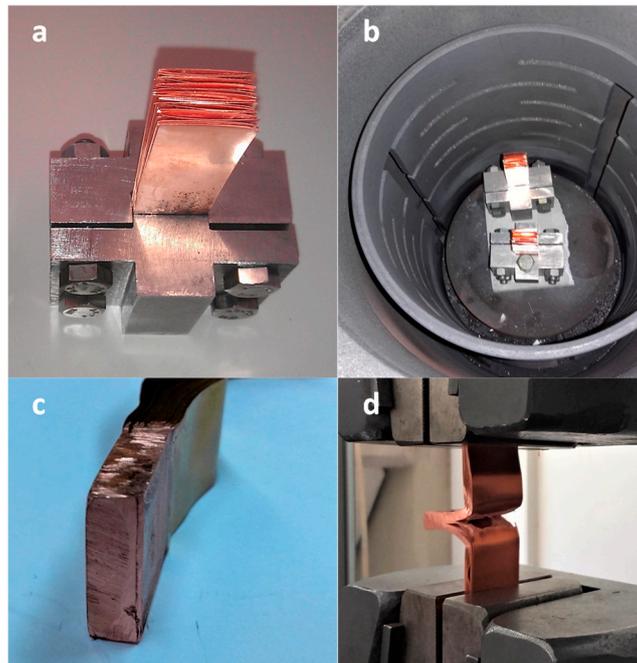


Figure 2. Processing steps of autogenous Cu bonding and mechanical characterization; (a) Cu foils in the pressing clamp, (b) placement of samples in the graphite furnace, (c) Cu foils after bonding and (d) bonding strength test.

2.2. Diffusion Bonding Characterization

The microstructure of the copper bonds was initially examined by optical metallurgical microscopy (BX41M model, Olympus, Shinjuku, Japan), while a more detailed investigation was performed using a JEOL 6380 LV Scanning Electron Microscope (JEOL, Tokyo, Japan) at 20 kV, coupled with Energy Dispersive System (SEM-EDS). Electron backscatter diffraction (EBSD) analysis was carried out, focusing on the grains generation and crystals orientation in the diffusion zone, using a Nordlys EBSD detector (Oxford Instruments, Abingdon, England). The sample under investigation was tilted 70° to the electron beam and placed at 15 mm of working distance, whereas the EBSD orientation maps were recorded from a selected region of the diffusion zone at 20 kV, with a scan step size of 300 nm. Prior to the SEM examination and the EBSD characterization, all samples were prepared by grinding and mechanical polishing. SEM samples were polished with a 6 μm and 1 μm diamond paste, and then successfully etched with a NH_4OH and H_2O_2 solution. The EBSD sample (optimum bond) was subjected to a final polishing stage using a 0.1 μm diameter colloidal silica suspension. Nanoscale investigation of the optimum bonded specimen was performed with a high resolution JEOL JEM-2100 LaB6 transmission electron microscope (HRTEM) (JEOL, Tokyo, Japan), operating at 200 kV. Ion-beam milling at 5 kV in a Gatan Precision Ion Polishing system (PIPS, Gatan Inc., Pleasanton, CA, USA) was used for the sample's thinning. Bonding strength measurements were carried out at room temperature and the stress-strain curves were obtained using a universal testing machine (Model 4482, max load: 100 kN) at a crosshead speed of 1 mm/min (Figure 2c,d). Vickers microhardness tests were conducted with a Shimadzu type M microhardness tester (Shimadzu, Kyoto, Japan), working at a magnification of 500 \times .

3. Results and Discussion

The bonding consists of a multi-factorial process mainly affected by the applied pressure on the sample, the heating temperature/duration, and the vacuum quality. According to the literature, these parameters dramatically affect the plastic deformation of the surface asperities, resulting in the increase of contact between the surfaces and control of the diffusion mechanism of the atoms across

the interface. The quality of thermocompressed Cu-Cu bonds, in respect to temperature and time processing, is examined in the current study. The parametric tests were performed under a standard loading pressure (10 MPa) and vacuum degree value (5×10^{-2} mbar).

3.1. Microstructural Investigation

In order to investigate the effect of temperature and duration on bonding, several samples were subjected to morphological examination by means of optical, scanning, and transmission electron microscopy. The section micrographs of Figure 3(a1,b1) presents, at horizontal direction, the bond line formations between 5 foils bonded at 935 °C for 45 and 90 min, respectively. As can be seen, the joint quality is improved in the case of a more prolonged processing time. Figure 3(a2,b2) shows, at higher magnification, the bond line number 1 at the same conditions. Undesirable intermediate voids are clearly visible in the case of the sample submitted to bonding for 45 min (Figure 3(a2)). On the contrary, voids are decreased, a recrystallization process is taking place, and elongated grains are grown in the interface of the sample processed for 90 min (Figure 3(b2)).

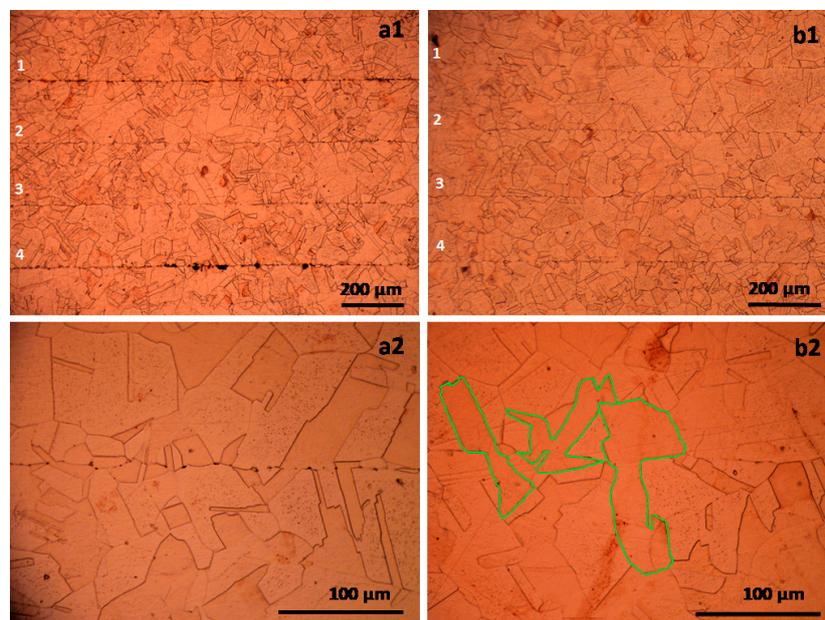


Figure 3. Metallographic micrographs of Cu-Cu bond cross sections presenting the interfaces between the copper layers. Bonding conditions: sample (a) 935 °C/45 min, sample (b) 935 °C/90 min (the numbering corresponds to the bonding lines).

The quality of bonding zones in terms of processing temperature is vividly revealed by scanning electron microscopy. After the sample's processing at 750 °C, the existence of a well-visible continuous interface between the copper layers indicates the formation of a low strength bond (Figure 4(a1,a2)). By increasing processing temperature to 935 °C, the interdiffusion process among the grains becomes more intense, and the unbonded zone is limited in specific regions (Figure 4(b1,b2)). Further temperature increments at 1000 °C lead to the creation of a uniform diffusion zone along the bond interface with minor visible unbonded regions. At this temperature, the interfacial discontinuity has been eliminated and a recrystallization has been achieved. Scanning electron microscopy indicates the absence of annealing-related recrystallization phenomena by temperature rising from 750 to 1000 °C.

In order to understand the grains evolution and their final orientation in the bonding zone, the examination of the cross-sectional thermocompressed specimens, produced under optimum bonding conditions (i.e., heating for 90 min at 1000 °C), was carried out by electron backscatter diffraction (EBSD) analysis (Figure 5).

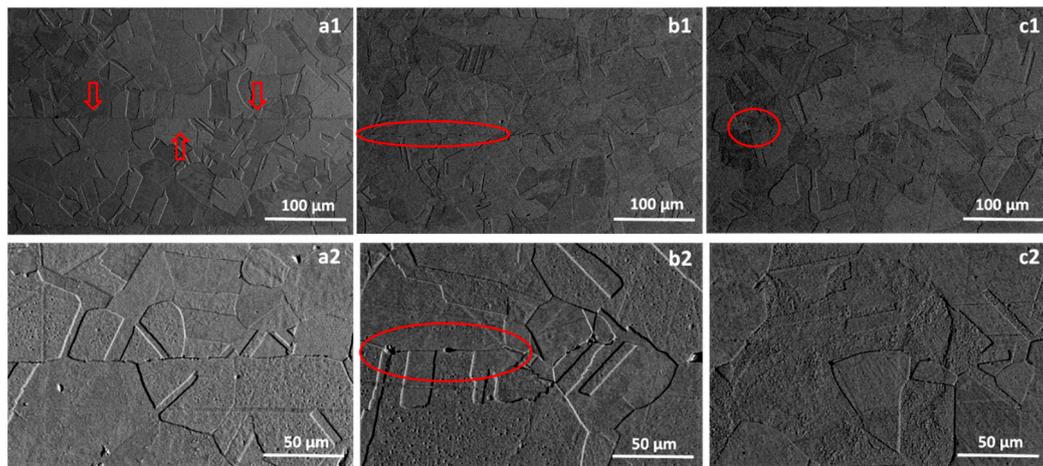


Figure 4. SEM micrographs of Cu-Cu bond cross sections presenting the interfaces between the copper layers. Bonding conditions: sample (a) 750 °C/90 min, sample (b) 935 °C/90 min and sample (c) 1000 °C/90 min.

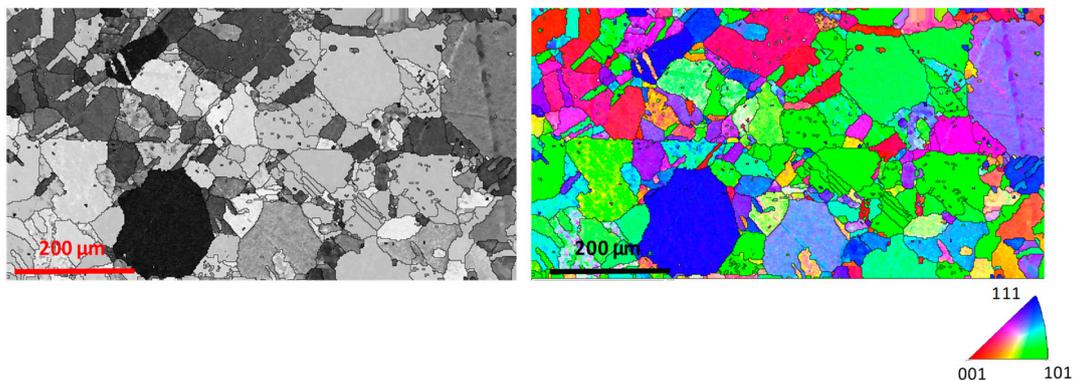


Figure 5. EBSD Band Contrast (left) and Inverse Pole Figure (IPF) (right) maps in the bonding zone. Bonding conditions of specimen: 1000 °C/90 min.

It is evident that the grains size distribution of copper base alloy has not been affected by the thermocompression process. The observed interface is strongly related to the size of the primary copper grains. The smaller Cu primary grains support either the evolution of new finer equiaxed grains (2–5 μm) of similar orientation with the initial matrix, or subserve the swelling transformation of the existing ones and their interdiffusion between the neighbor plate matrix (3–10 μm); consequently, the cohesion of the bonded plates is improved. Under the optimum thermocompression bonding conditions, frequent atomic and interface migration between contiguous copper grains has been observed, mainly due to the temperature increase under pressure, leading to the improvement of grain boundaries and the microstructure refining. On the other hand, in the case of large Cu grains, the diffusion zone in the interface is relatively limited (≈ 1 μm) and the consistency seems to be restrained. To clarify further, the copper bonding zone morphology and to investigate the interfacial microstructure formed by the diffusion bonding process, the interface of the optimum bonded specimen was additionally studied via TEM in cross-section. Interface regions with coarse (100–200 μm) and fine (<50 μm) grains were isolated for observation (Figure 6).

In the case of coarser copper grains, the thermocompression process does not significantly affect the copper diffusion mechanism, as the detected interface zone is very limited and presents a size in the range of 200 nm and 500 nm. A closer inspection revealed the existence of short vacancies, exhibiting a width of about 5–10 nm. On the contrary, in the case of the smaller neighbor copper grains, the bonding interface seems to be much higher (3–5 μm). The microstructure was composed of small equiaxed grains, with recrystallization twins in places. Some of the developed grains length within

the bonding zone was in the order of 200 and 400 nm, while dislocations were observed randomly dispersed in the copper matrix.

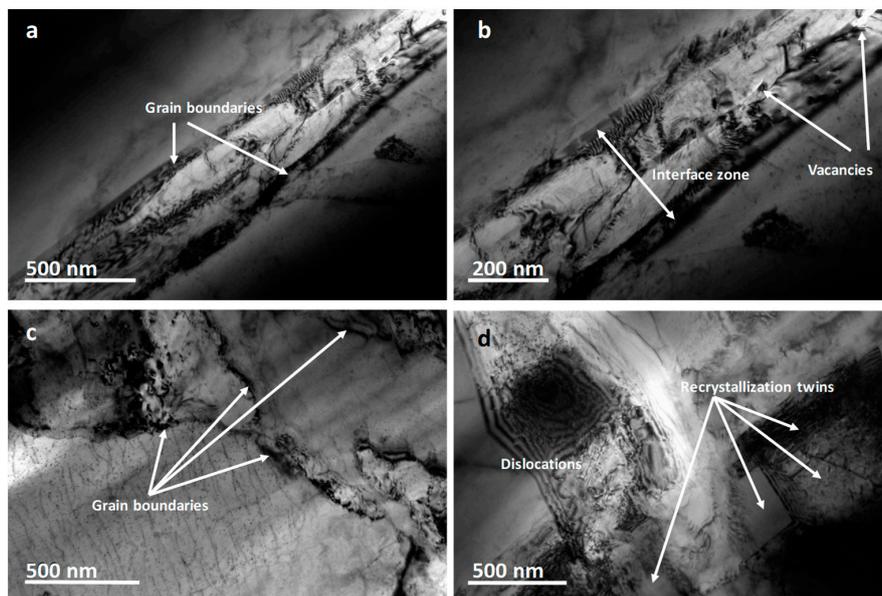


Figure 6. Transmission electron microscopy images in bonding zone applied in grains with different size: (a,b) grain size 100–200 μm , (c,d) grain size $\leq 50 \mu\text{m}$.

3.2. Mechanical Properties

Bonding strength consists of a critical parameter for the utilization of autogenous Cu bonded components in industrial applications. BS values of specimens processed under different bonding temperature and time conditions were measured. The increase of the processing temperature from 750 to 1000 °C leads to the increase of BS value from 50 to 180 MPa (Figure 7). The notable Cu-Cu diffusion improvement by the temperature rising between 935 and 1000 °C can be attributed to the increase of the kinetic energy of copper atoms as the temperature is relatively close to their melting point. Computational investigation at an atomic level is necessary in order for the copper interdiffusion to progress in relation to temperature increase to be interpreted on a theoretical basis. Relative studies have shown that displacement of the copper atoms on a substrate can take place even at gentle experimental conditions [18]. Correspondingly, an increase of the processing duration from 20 to 90 min at 935 °C raises the BS value from 27 to 120 MPa (Figure 8). The results are in accordance with the microstructural examination as it was previously described, indicating a strong correlation between the temperature/duration of the bonding and the interdiffusion efficiency. The highest BS value was achieved in the case of processing at 1000 °C for 90 min. Under these conditions, the tensile failure occurred at 180 MPa, a value which is comparable with the respective value of the base material (BM) [19]. The morphology of the bonding strength curves indicates a good ductile behavior in case of processing temperatures up to 1000 °C for ≤ 60 min. More aggressive diffusion bonding conditions resulted in the increasing of a final BS value.

Figure 9 presents the fractographs of Cu-Cu bonds fabricated at 750 and 1000 °C. According to Figure 9a,b, it can be observed that the solid-state diffusion reaction successfully proceeded in the case of bonding at 1000 °C. The grains of the Cu plates have been interspersed themselves and a “cup and cone” pattern caused by microvoid coalescence, which is characteristic of a ductile fracture mechanism. That is why the bond under investigation exhibited similar strength value with the corresponding of the base metal. In all cases the area presented extensive plastic deformation with large dimples, accompanied by void formation between the Cu plates. It should be noted that in a soft matrix (here pure Cu), the void nucleation predominately occurs by grains decohesion. Furthermore, due to heating of the whole parts, no distinct heat-affected zone has been detected. On the other hand,

in the case of bonding at 750 °C (Figure 9c,d), rounded, dendritic structures were observed, which are indicative of an incipient diffusion mainly due to deficient heat treatment.

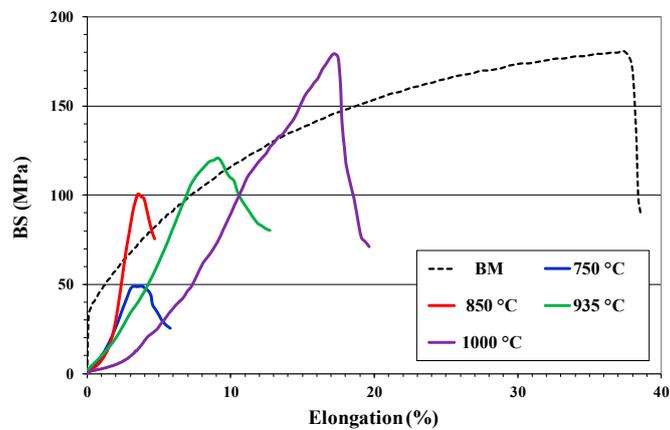


Figure 7. Bonding strength of the Cu-Cu bond in relation to the bonding temperature (processing for 90 min); BM: base material.

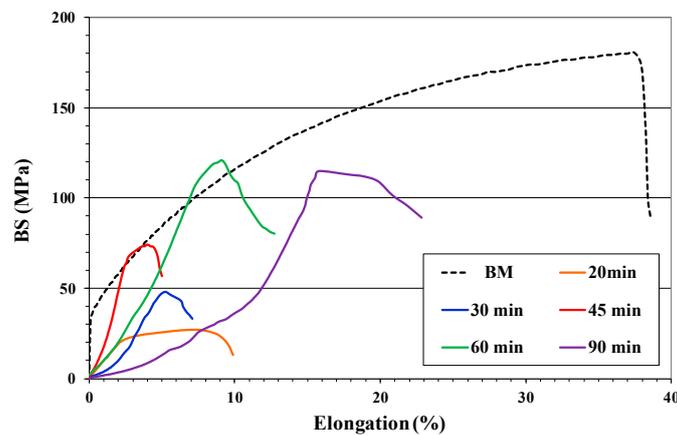


Figure 8. Bonding strength of the Cu-Cu bond in relation to the bonding duration (processing at 935 °C).

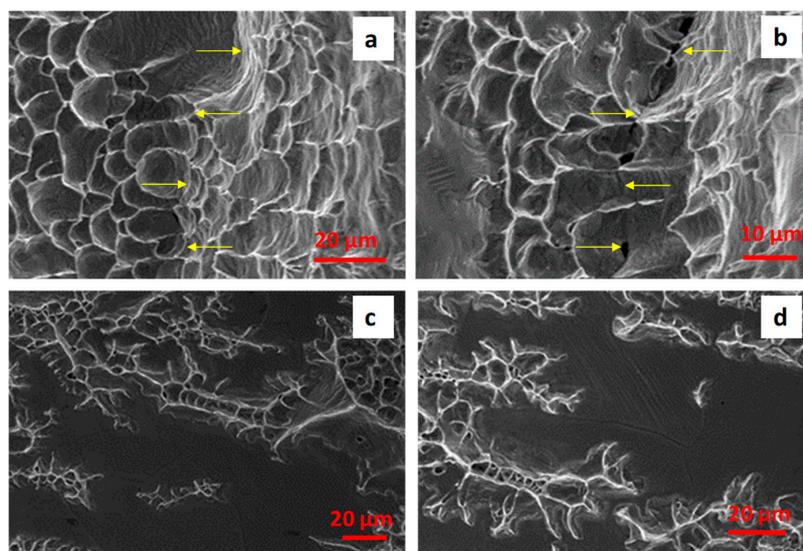


Figure 9. SEM fractographs of copper bonds; (a,b): Interface of bond fabricated at 1000 °C/90 min (the arrows show the interface orientation between the partially detached Cu plates), (c,d): fractured surfaces of Cu plates bonded at 750 °C/90 min.

The microhardness distribution across the bonding region of the samples processed for 90 min at 935 and 1000 °C (samples b and c, respectively, according to Figure 4) is presented in Figure 10. The measurements, in the case of the optimum sample (90 min at 1000 °C), reveal an increase of the hardness in the bonding interlayer, whereas the corresponding values for the base material (BM) are lower. The hardening of the interlayer can be attributed to the microstructure refinement, after the thermocompression process, and to the development of significant amount of equiaxed finer size grains, due to copper diffusion between the primary metallic plates. The results are in accordance with the EBSD micrograph, in which the presence of fine equiaxed grains distribution in the primary metallic copper plates was observed.

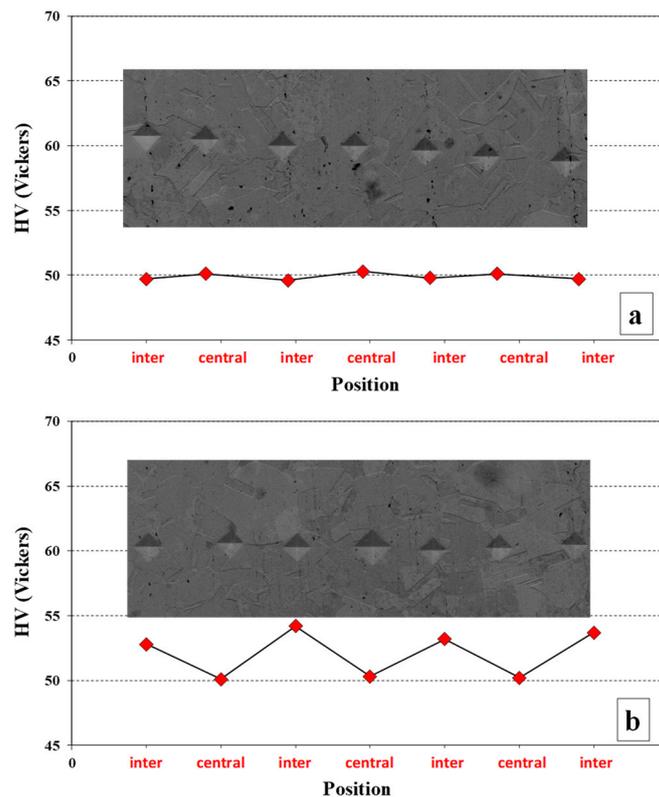


Figure 10. Transverse Hardness distribution across the bonding region; (a) processing for 90 min at 935 °C, (b) processing for 90 min at 1000 °C (inter: interlayer between the foils, central: the central point of the foil along its thickness).

4. Conclusions

The aim of the current study was the optimization of the autogenous high-temperature copper diffusion bonding process. The micro and nano structure of the bonds, as well as their mechanical properties were investigated. The main outcomes derived by the experimental procedure are as follows:

1. Cu-Cu bonds with advanced mechanical properties were successfully formatted through a thermocompression process under vacuum. Commercial copper foils with 200 μm thickness were used for the bonding tests, while a pressure of 10 MPa was applied.
2. The increase of the bonding temperature, from 750 to 1000 °C, and the duration, from 20 to 90 min, significantly improved the bonding strength of the copper bonds. The highest ultimate BS (180 MPa) approached the respective value of the base material, and was achieved at 1000 °C for 90 min. The transverse microhardness of the bond reached 55 HV, slightly higher in comparison to the respective value of the base material.
3. Electron backscatter diffraction (EBSD) investigation, of the optimum bonded specimen, reveals a satisfactory interdiffusion growth in regions with finer grains. Transmission electron microscopy

revealed the formation of small equiaxed recrystallized twin crystals in the bonding zone with a size ranging from 200 to 400 nm.

- The above mechanical and microstructural data indicated that the developed copper-bonded structure could be successfully used in devices that are submitted to intense mechanical stress (i.e., bar-wound stators in vehicles).

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