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Nano-Structured Cu/W Brazing Fillers for Advanced Joining Applications

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Abstract: Nano-multilayered brazing fillers offer a high potential for joining heat sensitive materials at reduced temperatures. In the current work Cu/W based nano-multilayered coatings, fabricated via physical vapor deposition (PVD) are studied. Joints were successfully produced via deformation dilatometry at temperature of 750 ºC and a mechanism for the bonding process is suggested. The promising results indicate an attractive pathway for using the versatile ability of PVD to precisely control the microstructure on the nm-scale and enabling tunable joint properties.

Key words: Microstructure, joining, brazing, nano-structures, Cu/W nano-multilayers, thin films.

1. Introduction

Modern brazing technology increasingly faces the problem of joining heat sensitive materials without altering their often highly optimized microstructure (and the thus related material properties) by the bonding process [1, 2]. To meet these requirements, the joining process should be carried out at ever reduced temperatures and/or times. In conventional brazing the melting point of the brazing filler determines the lowest suitable joining temperature. The traditional approach to reduce the process temperature is based on the survey of low melting point alloys such as deep eutectic systems. Joining using nano-multilayer (NML) based brazing fillers has been shown to be a promising route for low-temperature joining applications [1, 3, 4]. The basic concept of this approach is to exploit nano-scale effects such as (i) the size dependency of the melting point and (ii) the high density of internal interfaces (e.g. grain boundaries, inter phase boundaries) of nano-structured materials to tailor both of the thermodynamics (temperature) [5-7] and the kinetics (time) [4, 8] of the joining process. The NML brazing fillers are composed of alternating nanolayers (individual thickness ≤ 10 nm) of a metal (or alloy) and a chemically-inert barrier (e.g. oxides, nitrides or refractory metals). So far, mainly metal/ceramic systems have been investigated such as Cu/AlN [3], Ag/AlN [9] and Ag-Cu/AlN [10, 11]. However, the choice of a refractory metal, such as W, Mo or Ta, as inert barrier has not yet been considered in much detail. The Cu-W system fulfills most criteria for the design of a NML brazing fillers: i.e. the constituents are immiscible, and according to the binary phase diagram, no solid state phase transformations occur up to the Cu melting point [12]. In addition, due to their interesting thermal and mechanical properties, Cu/W thin films and Cu/W multilayered coatings have attracted great attention both from a scientific and technological perspective [13-15].

In the current work, the feasibility of a Cu/W based NML coating, as produced by conventional magnetron sputtering for joining applications, is evaluated. Deformation dilatometry is used to perform joining experiments under controlled processing conditions,

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i.e. fixing force, temperature profile and atmosphere. Specimens in the as deposited state and after joining are analyzed using X-ray diffraction (XRD) and high resolution scanning electron microscopy (HR-SEM).

2. Experimental

The following two thin films were investigated: (i) pure Cu, with a thickness of 1 µm and (ii) Cu/W NML, where first a 25 nm-thick W buffer layer was deposited on the substrate followed by 100 repetitions of alternating Cu and W layers with an individual thickness of 5 nm, denoted as $W_{25nm} + (Cu_{5nm}/W_{5nm}) \times 100$. The coatings were deposited on polished (down to 1 µm diamond size) molybdenum blocks (99.97 purity, Plansee, Austria), having a size of 25 × 25 × 5 mm^3, by using magnetron sputtering in a high vacuum chamber (base pressure < 10^{-8} mbar) from two confocally arranged, unbalanced magnetrons equipped with 2" targets of pure W (99.95%) and pure Cu (99.99%). For the joining experiments cubes having a size of 5 × 5 × 5 mm^3 were cut from the bigger coated blocks via spark erosion.

Fig. 1 gives a detailed overview on the joining experiments performed by means of a DIL805 A/D/T deformation dilatometer (Baehr, Germany) provided by the IvP from the ETH Zurich. Joining was performed under vacuum (< 10^{-4} mbar) at 750 ºC for a dwell time of 100 min and an applied fixing force of 1,250 N, which correlates to 50 MPa considering the cube surface area of 25 mm^2.

HR-SEM analysis was performed using a Hitachi S-4800 (Hitachi High-Technologies Corporation, Japan) instrument equipped with a Bruker XFlash 6|60 energy dispersive X-ray (EDX, Bruker, Germany) detector. Cross-sectional cuts were prepared by using a Hitachi IM4000 Ar^+ ion milling system applying an acceleration voltage of 6 kV, a discharge voltage of 1.5 kV and a swing angle of ± 30º. Prior performing the cross-sectional cuts of the samples in the as deposited state an Au coating was deposited on-top of the specimens in order to protect the surface from possible contaminations/alterations.

XRD measurements (Discover D8, Bruker, Germany) in the 2θ range of 20º-90º were conducted using $CuK\alpha_{1,2}$ radiation operated at 40 kV and 40 mA.

3. Results and Discussion

Fig. 2 displays HR-SEM images of cross-sectional cuts and XRD-patterns of the coatings (with equal total thickness) in the deposited state. No indications of cracks, voids or delamination are apparent. For the Cu coating (Fig. 2a) a homogenous film with a polycrystalline grain structure can be observed. In the case of the Cu/W NML (Fig. 2b) the 25 nm-thick W

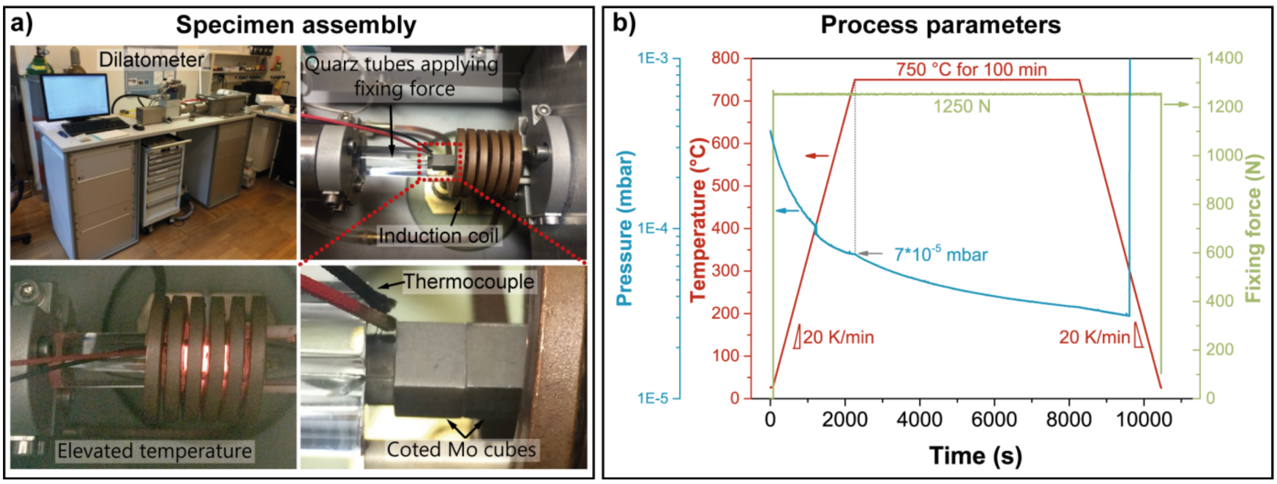

Fig. 1 Details on the joining process: (a) deformation dilatometer and assembly of the samples. The temperature was measured by means of a chromel-alumel thermocouple spot-welded to cylindrical Mo-part located on the left hand side of the cubes and (b) process parameters, i.e. chamber pressure, temperature and applied fixing force.

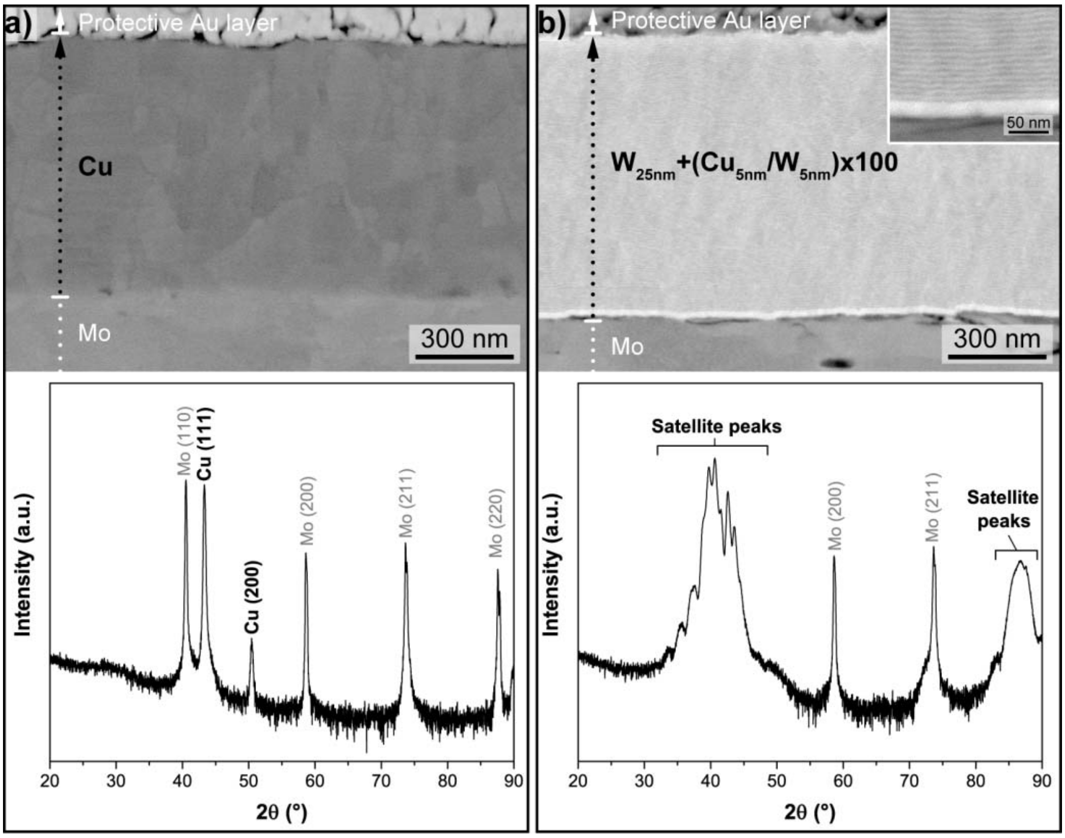

Fig. 2 Cross-sections and XRD-patterns of the of the coatings in the as-deposited state of (a) Cu coating and (b) W_{25nm} + (Cu_{5nm}/W_{5nm}) × 100.

buffer layer and the periodicity of the alternating Cu/W nanolayers is resolved (inset Fig. 2b). In the XRD spectra of the Cu coating (Fig 2a) fcc diffraction lines, indicating a polycrystalline thin film as well as bcc reflections related to the Mo substrate are visible. For the Cu/W NML (Fig. 2b), besides the Mo-substrate diffraction lines, well-defined satellite peaks of Cu (111) and W (110) are revealed in the 2θ range from 30º to 48º, which are characteristic for oriented alternating nanolayered systems (e.g. [16]).

Fig. 3 displays cross-sectional HR-SEM images of both specimens after joining at 750 ºC using the deformation dilatometer. For the Cu coated sample (Fig. 3a), a sound joint is revealed with coarsened Cu grains which partly extend over the entire joining zone. Diffusion bonding of PVD-based Cu thin films has been demonstrated for temperature 350-400 ºC [17]. Analogously, for the joining using the Cu coating, a bonding mechanism based on the interdiffusion of Cu atoms as well as grain growth can be assumed. For W_{25nm} + (Cu_{5nm}/W_{5nm}) × 100 (Fig. 3b) small pores (white arrows) and interestingly accumulations of Cu (black arrows) are observable at the bond interface, i.e. between the initial surfaces (W outermost layer) of the coating. Thus indicating that during heating Cumust have penetrated through the W layers to the top. Furthermore, the initial nanolayered structure has degraded towards a spheroidized nanocomposite (cf. insert of Figs. 2b and 3b). The microstructural evolution upon heating of the same Cu/W NML system (deposited on sapphire) has been studied in detail [18] and the corresponding stress evolution was comprehensively investigated [19]. As shown by these studies, in the as deposited state very high compressive stresses (related mainly to growth stresses initiate by the PVD process) were observed in the confined Cu (≈ -1.5 GPa) and W layers (≈ -3.5 GPa) [19]. Annealing up to 500 ºC fully releases

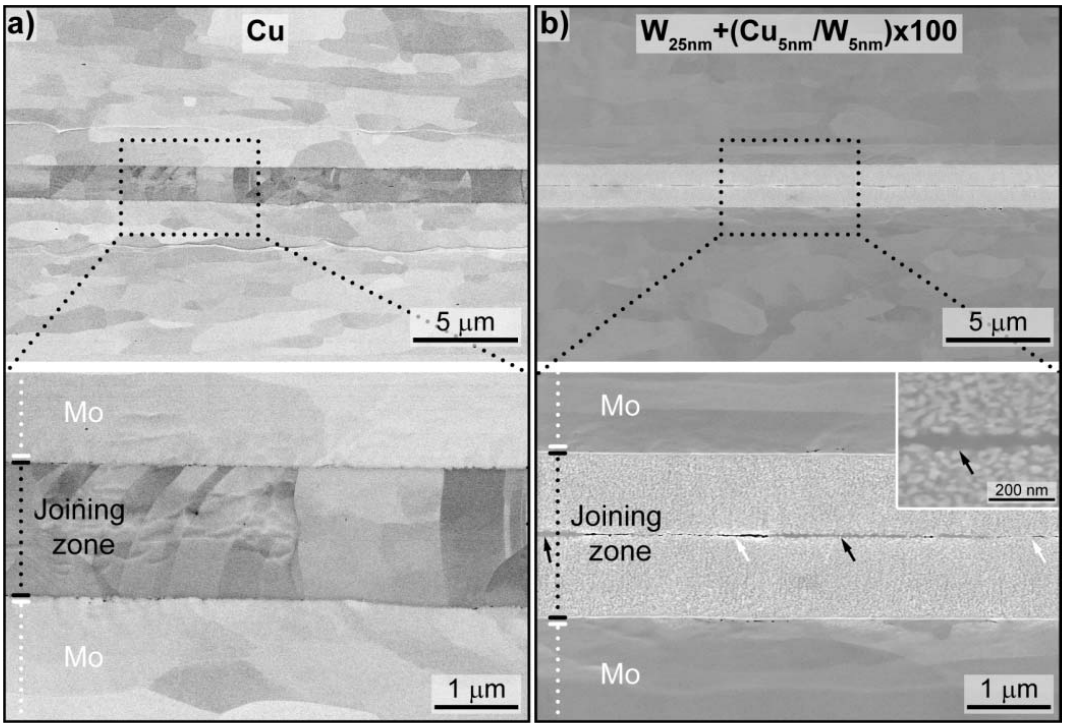

Fig. 3 HR-SEM images of cross-section after joining (a) Cu coating, (b) W_{25nm} + (Cu_{5nm}/W_{5nm}) × 100.

the stresses of the Cu nanolayers [19], which also coincides with the temperature at which a high number of Cu protrusions appear on the surface [18]. At T > 700 ºC, degradation of the NML structure occurs [18, 19]. Consequently, it is suggested for W_{25nm} + (Cu_{5nm}/W_{5nm}) × 100 that upon heating (> 500 ºC) Cu penetrates through the W layers to the bond interface. Cu-Cu bonding is established similar to the diffusion bonding process seen for the pure Cu sample. Subsequently degradation of the NML structure (> 700 ºC) by thermal grooving occurs (more details in Ref. [18]). Here it is emphasized that such Cu/W nano-composite structures can be very attractive for applications, where a combination of good thermal- and electrical conductivity with high mechanical properties is required. For example, Cu-rich Cu/W pseudo alloys, where W acts as hardening phase, show superior mechanical properties (e.g. high strength, better creep resistance) compared to pure Cu while still offering a very high electrical and thermal conductivity. Functional grades Cu/W composites can also be used to accommodate differences in thermal expansion coefficients. In this regard, combining the versatile properties of Cu/W composites with the possibility of magnetron sputering to precisely control the microstructure on a nm-scale, tunable joint properties can be envisaged. Motivated by these very promising results further investigations will be performed to study the influence of the joining process parameters, as well as to evaluate the mechanical performance of the joints.

4. Conclusions

Cu/W based nano-multilayered brazing fillers were successfully employed to fabricate joints at temperature of 750 ºC. A joining zone comprising of a spheroidized Cu/W nanocomposite and accumulation of Cu at the bond interface results. According to recent studies, it is suggested that upon heating Cu penetrates the W barrier layers (> 500 ºC) and migrates to the bond interface. Cu-Cu bonds similar as in a diffusion bonding process are established. Furthermore the initial NML structure degrades to a spheroidized nanocomposite (> 700 ºC). The results indicate an attractive and versatile approach for tailorable joint properties.

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