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Wetting of AgCuTi Filler Metal on Graphite Surface and Brazing with Copper

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Abstract

Given the inherent characteristics of graphite, the wetting of graphite by most brazing alloys is challenging. The study examined the impact of varied insulation times and temperatures on the wettability of active AgCuTi filler metal on the graphite surface using the seat drop method, elucidating the wetting mechanism of silver-based filler metal on the graphite surface. Successful metallization of the graphite surface was achieved under the conditions of 830 ℃ for 150 minutes. The typical microstructure of the metallized layer comprises copper-based solid solution, silver-based solid solution, CuTi, TiC, and graphite. Metallized graphite was indirectly brazed using non-active AgCu brazing material and oxygen-free copper, thereby establishing the connection between graphite and copper. Shear testing of the brazed joint revealed that fractures occurred exclusively in the matrix part of the graphite, with a maximum shear strength of 11 MPa.

Keywords

Graphite; Brazing; Copper; Microscopic Structure; Shear Properties.

1. Introduction

Graphite exhibits excellent thermal stability, high thermal conductivity, a low coefficient of thermal expansion (CTE), low density, and exceptional radiation resistance. Graphite finds applications in fields such as nuclear reactors, X-ray sources, and radiation radiators, where exceptional thermal stability and radiation resistance are imperative[1].Materials employed in nuclear reactors are subjected to harsh environments characterized by high radiation and temperature, necessitating heightened demands on the inherent performance of nuclear reactor materials[2]. Achieving a large area of high-quality brazing connection on the vertical surface of the barrel structure is essential, necessitating the urgent search for a brazing material system with excellent fluidity and reasonable cost for engineering applications[3].

Oxygen-free copper exhibits excellent surface wettability, with most commonly used brazing materials (such as Sn-Ag-Cu, Ag-Cu, etc.) effectively wetting it. However, brazing metal does not readily react with graphite during the metallurgical process, resulting in difficulty wetting the surface of graphite and compromising joint performance[4]. Conversely, significant differences in physical properties, such as the coefficient of thermal expansion, between graphite and copper result in poor joint performance when directly brazed. Furthermore, in large-scale vertical brazing and brazing joints with vertical expansion gaps, direct brazing is not suitable, and indirect brazing after graphitization assumes an irreplaceable role.

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During the indirect brazing of graphite and copper, overcoming the challenge of wetting the graphite surface and investigating its wetting characteristics are paramount. Wetting of the graphite surface is influenced by various factors. Segregation occurs at the contact interface with graphite when liquid alloys contain active elements prone to reacting with the graphite matrix. The graphite matrix is susceptible to the reaction of active elements, resulting in the formation of a continuous layer of carbides, facilitating subsequent wetting on the surface of the carbides. Studies[5] have found that the spreading rate and interfacial reaction of graphite surface brazing materials are correlated with the activity of introduced elements (Ti or Cr) in liquid SAC. SAC-Cr melt exhibits faster spreading and more intense interfacial reactions with graphite compared to Ti, attributed to the higher activity of Cr. Yang et al. [6] employed an improved stemless droplet method, utilizing a mixture of 0.5, 1.0, and 2.0 at.% in a flowing Ar atmosphere at 1373 K. Wetting of Cr on the graphite surface primarily depends on the generation of Cr-C compounds, which reduce the free energy of the graphite surface.

Song et al. [7]successfully obtained a dense and continuous metallized layer on the graphite surface using Sn0.3Ag0.7Cu-9% Ti tin-based active brazing material under conditions of 950 ℃ for 30 minutes. Subsequently, they achieved brazing of graphite and copper at a low temperature of 250 ℃ using tin-based inactive brazing material. A higher diffusion of Al, Ag, Ti, and Cu from the filler metal layer to graphite was observed compared to the metallization stage[8]. In summary, there have been some studies on the indirect brazing between metallized graphite and metal. However, there are currently few reports on the metallization and brazing process conditions applicable to graphite surfaces under high-temperature and long-term conditions.

This study explores the process of metallizing the graphite surface using AgCuTi active filler metal under vacuum conditions, analyzes the spreading and wetting behavior of AgCuTi filler metal on the graphite surface under various heating temperatures and holding times, and elucidates the wetting mechanism. Additionally, the microstructure and shear fracture characteristics of the indirectly brazed joint were characterized using silver copper eutectic brazing material with good fluidity to indirectly join the metallized graphite and oxygen-free copper.

2. Experimental Method

High-strength graphite (grade T952) and conventional oxygen-free copper (model TU1) were utilized in the experiment. Graphite blocks measuring 40mm×40mm×2mm were obtained through wire cutting, followed by sequential surface polishing using sandpaper with grit sizes of 80#, 400#, and 800#. Prior to the wettability and metallization experiments, the graphite was ultrasonically cleaned in alcohol for 15 minutes. The wettability test utilized commercial silver-based active filler metal Ag70Cu25.5Ti4.5 (wt. %) paste, with a weight of 20g applied at the center of the graphite. The filler metal was heated to its melting temperature in a vacuum furnace and reacted with graphite, as depicted in Fig. 1(a). Metallization of graphite was achieved by manual application of brazing material onto the graphite surface, conducted under vacuum conditions, as illustrated in Fig. 1(b). The wetting and metallization tests were conducted under a vacuum of 1×10^{-3}Pa, heated at a rate of 10 ℃/min to various temperatures for different durations. Following insulation, the samples were cooled to room temperature at a rate of 10/min.

Process the metalized graphite and oxygen-free copper into blocks with dimensions of 8 × 8 × 5 mm and 20 × 10 × 2 mm, respectively, for brazing. Before brazing, polish the welding surfaces with sandpaper and oxygen-free copper to clean them thoroughly, followed by ultrasonic cleaning of the two base materials in acetone, and then air drying them for later use. Utilize AgCu eutectic foil with a thickness of 0.1 mm as the brazing material, as illustrated in Fig. 2.

Following brazing, specimens of the metallized layer and brazed joints, cut along the vertical direction of the brazing interface, are utilized to obtain metallographic samples after embedding. Subsequently, sanding was performed using 400#, 800#, 1200#, and 2000# sandpaper, followed by a 10-minute polishing treatment with 0.05 μm alumina polishing solution particles. Brazed joint morphology under various process parameters was observed using an optical microscope, while the

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microstructure and phase composition of the metallized layer and brazed joints were characterized using electron microscopy (Zeiss Merlin Compact) equipped with an energy-dispersive spectrometer (EDS). Shear resistance of brazed joints at room temperature was tested using a universal material testing machine, employing a shear rate of 1mm/min. Welded parts were assembled using fixtures, with 2 samples selected for each experimental process parameter for testing. The calculated average shear strength was considered the final shear strength value under each parameter.

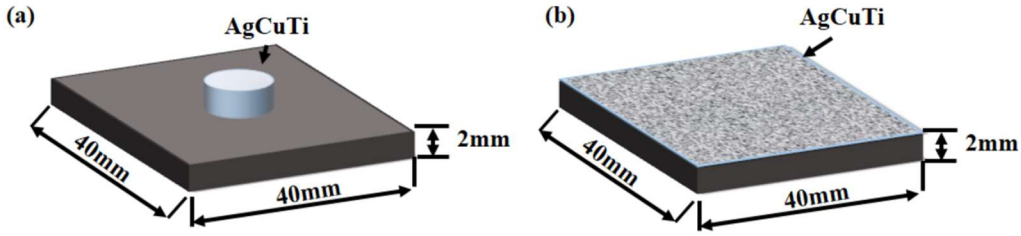

Fig. 1 Schematic diagram of wetting and metallization of graphite(a) Wetting of graphite, (b) Metallization of graphite

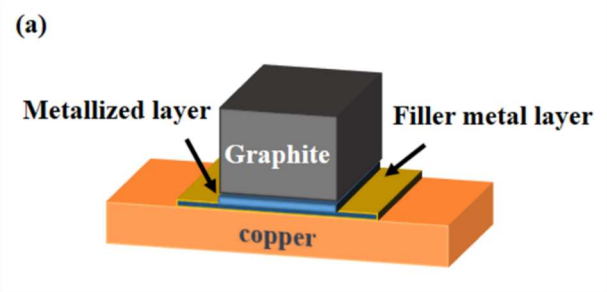

Fig. 2 Schematic diagram of brazing assembly

3. Experimental Results and Discussion

3.1 Effect of Temperature on the Spreading of Silver-based Filler Metal on Graphite Surface

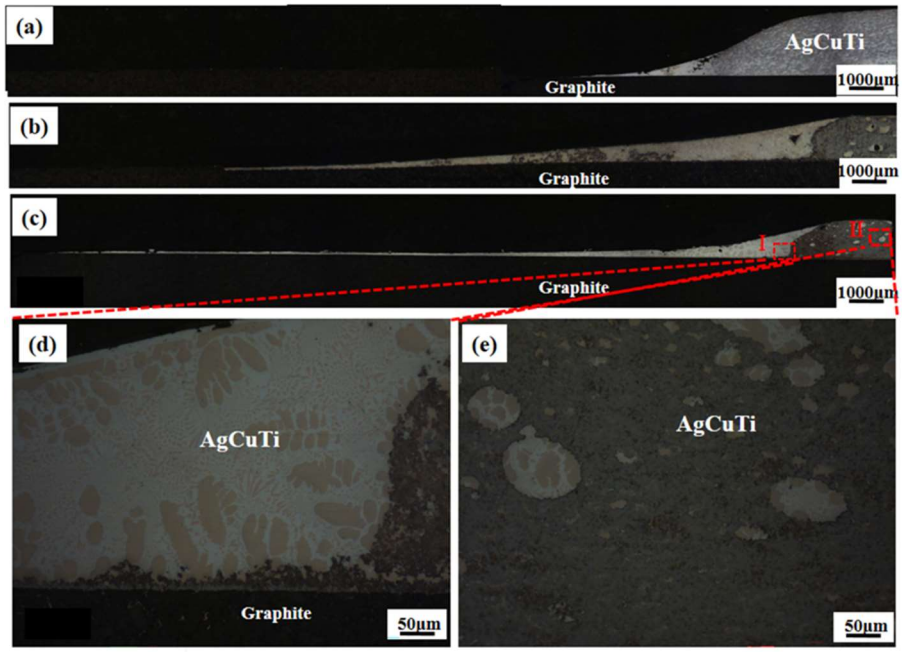

Fig. 3 Morphology of wetting droplet/graphite interface(a) 830 ℃/150min, (b) 850 ℃/150min, (c) 880 ℃/150min, (d) Enlarged image of Zone I, (e) Enlarged image of Zone II

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For the analysis of the microstructure of the wetting droplets on the graphite surface, it can be found that there are differences in the wetting angle and phase morphology at different temperatures and holding times. Therefore, special attention should be paid to the differences in the wetting angle of the three phase line and the interface reaction products. In order to analyze the wetting mechanism of AgCuTi filler metal on porous graphite, the interface microstructure of droplets/graphite was observed, as shown in Fig. 3.

The backscattered electron image of the sample interface is shown in the Fig.4, and it is obvious that the continuous permeation layer formed by the brazing material penetrates into the porous graphite matrix.

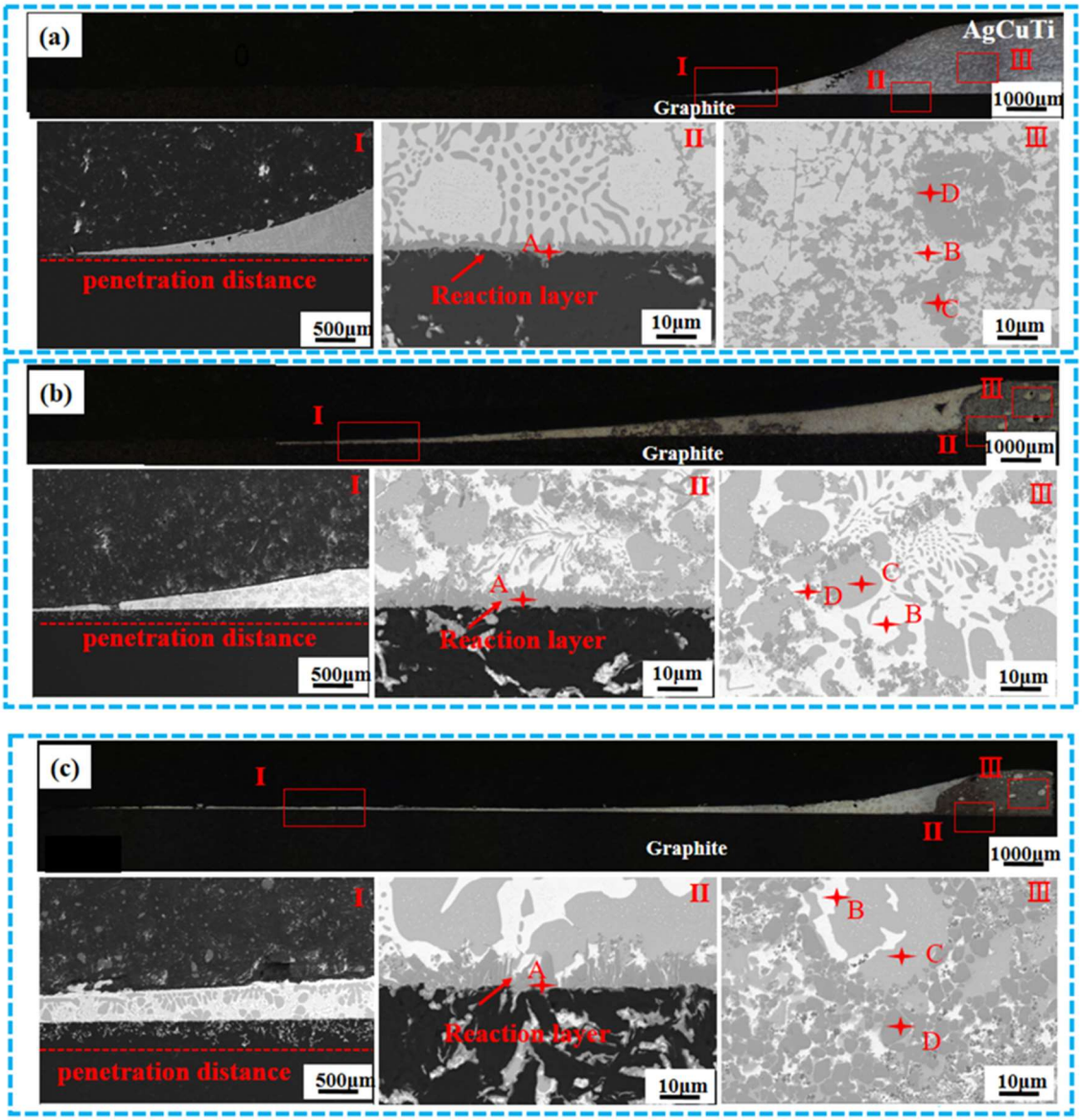

Fig. 4 Microscopic structure of droplet cross-section under various process parameters (a) 830 ℃/150min, (b) 850 ℃/150min, (c) 880 ℃/150min

As shown in Fig. 4, under the same insulation time (150 minutes), there are two regions (Region I and Region III) in the wetted samples at each temperature, and the edge curvatures of the two regions are significantly different. The details of the wetting front of the third line (Zone I), the center permeation layer of the droplet (Zone II), and the typical microstructure inside the droplet (Zone III) are also shown in the Fig.4. As shown in the high magnification image of Zone I, the edges of all

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permeable layers in graphite are further away than those of the brazed alloy. This indicates that silver-based droplets have good wetting properties on graphite at various temperatures, and the higher the heating temperature, the wider the expansion of the permeation layer.

Additionally, in region I of the four wetted samples, it is evident that the depth of penetration of the liquid filler alloy into the graphite block increases with temperature, and the depth of the penetration layer correlates with the wettability of AgCuTi filler metal on graphite [9, 10]. Under different temperature conditions, a dark gray reaction layer with a certain thickness (marked as A) forms at the interface between the infiltration layer and the filling alloy. The formation of the reaction layer is attributed to the aggregation of Ti at the interface of the silver-based brazing material and its reaction with graphite. The microstructure of Zone I exhibits a typical Ag-Cu eutectic structure. The size of the Cu-based solid solution in Zone I of these three samples increases with temperature. Zone III in the wetted samples at different temperatures comprises a bright white Ag-based solid solution and a gray phase with small particle compounds (marked as D) (labeled as C). The morphology and size of the granular compound phases vary significantly at different temperatures, with significantly more compound phases observed at 850 ℃ and 880 ℃ compared to 830 ℃.According to the ternary Ag-Cu-Ti phase diagram[11], Ag does not participate in the reaction; thus, Ti and Cu are the primary components of intermetallic compounds.

EDS point scanning was performed on the droplets and various phases at the interface, and the results are listed in Table 1. It can be seen that phase A corresponds to TiC, phase B to the Cu-based solid solution, phase C to the Ag-based solid solution, and phase D to the CuTi intermetallic compound. Additionally, in the wetted samples, a small amount of CuTi particles are present on the Cu-based solid solution, and the Ag-Cu eutectic structure constitutes the main component of the microstructure in zone II.

Table 1. EDS point analysis of marked points in Fig.5 (at.%)

position	C	Ag	Cu	Ti	Possible phases
A	32.15	59.32	24.79	42.96	TiC
B	-	91.78	5.31	-	Silver-based solid solution
C	-	3.56	95.08	1.36	Copper-based solid solution
D	-	0.48	44.34	55.18	CuTi

The formation of granular CuTi intermetallic compounds within the wetting droplets increases the viscosity of the liquid alloy, hindering the wetting of the middle part of the brazed alloy on the ceramic surface. CuTi intermetallic compound particles are formed after the brazing material melts, consuming most of the Ti in the filling alloy. Under the same insulation time, the thickness of the interface reaction layer (TiC) continuously increases, possibly due to the enrichment of more Ti at the interface at higher temperatures and the reaction occurring at C. The remaining Ag-Cu eutectic flows out from the center of the droplet with high viscosity, ultimately forming a smaller wetting angle at the edge of the wetting droplet.

3.2 Interface Structure of Graphite Surface Metallization and Brazing

As the temperature increases and the insulation time prolongs within a certain range, the wetting angle of the brazing material on the graphite surface continuously decreases, resulting in better wettability. Additionally, the brazing material exhibits better flowability at higher temperatures, resulting in a smoother metallized layer over an extended period at elevated temperatures. Fig. 5 depicts the microstructure of the interface between the metallized layer and graphite at various temperatures, aiming to investigate the influence of different process parameters on the microstructure of the graphite metallized layer.

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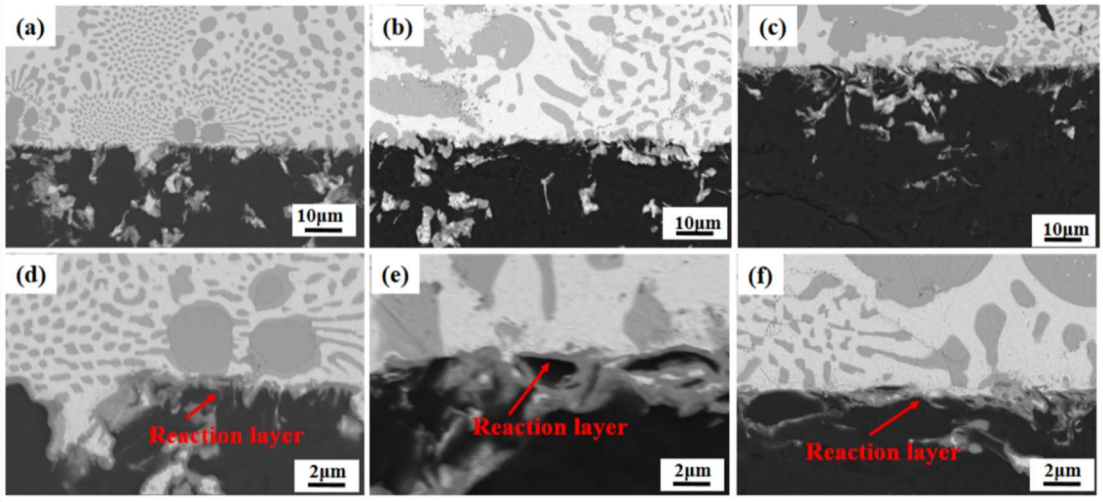

Fig. 5 Effect of different temperatures on the microstructure of the metallized layer(a) (d) 830℃/150min, (b) (e) 850℃/150min, (c) (f) 880℃/150min

Fig. 5 illustrates that the brazing material effectively metallizes graphite at various temperatures, primarily forming a silver copper eutectic in the metallized layer. Moreover, the metallized layer shows no significant alteration with temperature escalation, and the interface reaction layer does not excessively thicken with increasing temperature. Firstly, due to the restricted Ti content in the brazing material, TiC formation ceases upon Ti depletion. Secondly, the initially formed continuous TiC layer impedes the diffusion of C from graphite to the brazing material, thereby impeding further thickening of the TiC layer[12]. Considering the penetration layer thickness results in Zone I of Fig. 4 and aiming to ensure an adequate thickness of the metallization reaction layer, it is recommended to opt for a lower metallization temperature and a longer insulation time whenever feasible. Consequently, maintaining the temperature at 830 ℃ for 150 minutes represents the optimal metallization parameter, followed by indirect brazing utilizing AgCu eutectic brazing material at 880 ℃ for 60 minutes. Fig. 6 presents the microstructure and fracture morphology of the brazed joint, which demonstrates excellent bonding without any defects or cracks. The welded joint achieved an average shear strength of 11 MPa, with fracture occurring within the graphite matrix, signifying a dependable connection between the metallized layer and the graphite matrix.

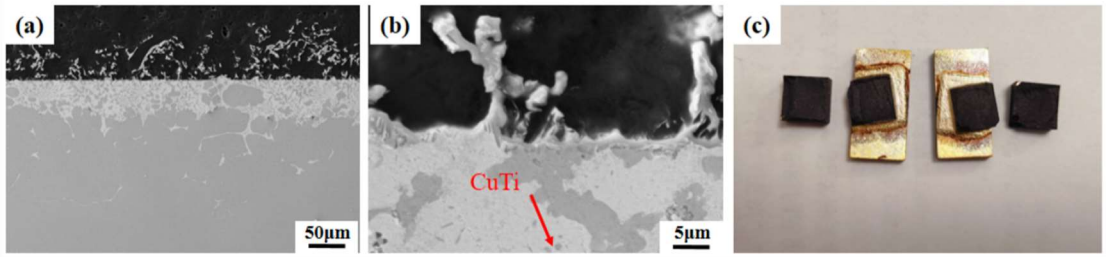

Fig. 6 Interface microstructure and fracture morphology of metallized graphite/copper indirect brazing joint at 880 ℃/60min(a) Microstructure of brazed joints, (b) Graphite/brazing material interface, (c) Fracture morphology of brazed joints

3.3 Wetting Mechanism of Silver-based Brazing Materials on Graphite

The wetting process of AgCuTi active brazing material on graphite matrix is illustrated in Fig. 7, and the wetting mechanism can be elucidated as follows:

(I) Once the temperature reaches the melting point of AgCuTi filler metal paste, the molten silver-based metal liquid filler metal penetrates into the pores of porous graphite. (II) Subsequently, through the reaction between Ti and C in graphite, a thin TiC reaction layer forms on the graphite surface,

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with its thickness steadily increasing with prolonged insulation time and elevated heating temperature. (III) Consequently, the diffusion of the infiltration layer within the graphite further accelerates the wetting of the brazing material on the graphite surface. (IV) Ultimately, the formation of CuTi intermetallic compounds in the liquid filler metal during the heating process impedes further expansion of wetting behavior. As a result, liquid Ag Cu eutectic flows out from the liquid filler metal, and CuTi particles form and diffuse onto the surface of the graphite matrix. With increasing temperature, a greater quantity of Ag Cu eutectic flows out from the brazing material, thereby enhancing the wetting effect of the silver-based brazing material on graphite.

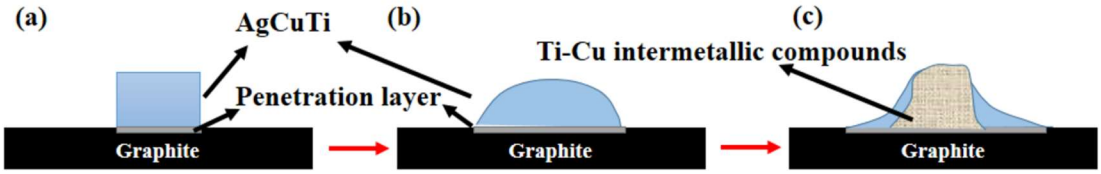

Fig. 7 Schematic diagram of wetting process

4. Conclusion

The study conducted the reaction metallization of graphite using silver-based active brazing materials and analyzed the microstructure and properties of the metallized graphite-copper joints brazed with silver-based and tin-based brazing materials. The conclusions are as follows:

(1) The wetting and spreading of silver-based brazing material on the surface of graphite continuously improve with increasing time. The formation of CuTi intermetallic compounds in the liquid brazing material during the heating process impedes further expansion of wetting behavior. With rising temperature, more silver-copper eutectic flows out of the brazing material.

(2) Silver-based brazing materials can achieve metallization of graphite at various temperatures, and the thickness of the TiC reaction layer remains consistent. The penetration layer increases with rising temperature. The typical microstructure of the metallized layer/graphite includes copper-based solid solution, silver-based solid solution, CuTi, TiC, and graphite.

(3) Metallized graphite utilizes AgCu eutectic inactive brazing material for brazing with oxygen-free copper. Fractures occur within the graphite matrix, with a maximum shear strength of 11.5 MPa.

Acknowledgments

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