



Article Interfacial Modification of Ti₃AlC₂/Cu Composites by Multi-Arc Ion Plating Titanium

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Abstract: Cu matrix composites reinforced with Ti_3AlC_2 ceramics can be applied for electrical contact materials, such as vacuum contact material or a pantograph slide plate. However, Ti_3AlC_2 particles substantially decomposed because lattice diffusion is the main way that Al atoms diffused into the Cu matrix and were uniformly distributed. In order to suppress the decomposition of Ti_3AlC_2 ceramics and improve the properties of Ti_3AlC_2/Cu composites, the surface of Ti_3AlC_2 was modified by multi-arc ion plating Ti. The results shows that, with the volume fraction increasing of Ti_3AlC_2 , the decomposition of Ti_3AlC_2 is exacerbated and the lattice constant of Cu(Al) solid solution is bigger. In the meanwhile, the structure of Ti_3AlC_2 changes from dispersed granules to flakes, then to a continuous network. Multi-arc ion plating Ti effectively inhibits the diffusion of Al atoms into Cu matrix. The Ti coating reacts with Cu and generates Cu_xTi in the interface between the Cu and Ti coating, which inhibits the diffusion of Al atoms so as to inhibit decomposition., the inhibition of decomposition of Ti_3AlC_2 ceramics weakened solid solution strengthening and decreased the content of hard phase TiC_x . Furthermore, the good mutual diffusion between Cu_xTi layer and Cu effectively improves the interfacial bonding strength.

Keywords: copper matrix composites; interfacial modification; surface treatment; titanium

1. Introduction

Ceramics-reinforced Cu matrix composites have attracted much attention in the last decades for their excellent electric and heat conduction ability of the Cu matrix, as well as the high mechanical properties of ceramics. Compounding with different ceramics, Cu matrix composites are provided with various abilities and a wide range of applications [1–5].

Cu matrix composites reinforced with MAX ceramics can be applied for electrical contact materials, such as vacuum contact material or a pantograph slide plate. MAX are hexagonal structure ceramics consisting of transition metals (M), IIIA or IVA group elements (A) and carbides or nitrides (X) [6]. MAX phase, which is characterized by its excellent combination of chemical, physical, electrical and mechanical properties, combines the advantages and characteristics of metals and ceramics in many aspects [7–10]. Attributed to its supreme performance especially for low density and high electrical conductivity, Ti_3AlC_2 is a classic MAX phases compared with the others [11]. Comparing the physical properties of Ti₃AlC₂ with conventional Cu matrix composites' reinforcement such as WC, Al₂O₃, SiC, etc. Ti₃AlC₂ have the advantages of low density and high elastic modulus under the condition of little loss of resistivity and thermal conductivity. What is more, Ti₃AlC₂ has a unique layered structure providing with the self-lubrication [12,13]. In the ceramic/metal system, it is of great significance to enhance the interface between the ceramic-strengthening phase and the metal matrix because the material properties depend on the interface microstructure to a large extent [14]. The improvement in the properties of the composites is not only up to each reinforcement's properties itself but also up to the microstructure such as interface in particular. The structure stability of



Citation: Wang, Y.; Gao, Y.; Fan, Y. Interfacial Modification of Ti₃AlC₂/Cu Composites by Multi-Arc Ion Plating Titanium. *Coatings* 2022, *12*, 1754. https:// doi.org/10.3390/coatings12111754

Academic Editor: Günter Motz

Received: 23 October 2022 Accepted: 12 November 2022 Published: 15 November 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Ti_3AlC_2 is precarious, which is caused by the diffusion of weakly bonded Al atoms into Cu matrix during the sintering process [15,16]. The decomposition of Ti_3AlC_2 have both advantages and weakness. For one side, it has been studied that the wettability of TiCx, the decomposition product of Ti_3AlC_2 , and Cu is closely related to the value of x. When x > 0.7, the wettability angle between TiC_x and Cu is more than 90 degrees, while, when x < 0.7, that is less than 90 degrees, and the wettability between TiC_x and Cu is better [17,18]. Therefore, the interface of Ti_3AlC_2/Cu changes into the interface of TiC_x/Cu in a certain way. Hence, the decomposition of Ti_3AlC_2 has the advantage of improving the wettability and adhesion of the two phases. However, to mark the opposition to the previous advantage of the decomposition, the loss of Al atoms directly destroys the ternary layered structure of Ti₃AlC₂, which results in a decrease of not only self-lubrication but also electrical conductivity [19]. Therefore, in order to retain the properties of reinforcement itself and, moreover, to enhance the interfacial bonding, it is important to find a way to control the decomposition process and improve the wettability simultaneously. Thus, the solutions for preventing Ti₃AlC₂ from decomposing and establishing a new interfacial phase are essential. From now on, some studies on copper- or nickel- coated Ti₃AlC₂ have been published [20,21], however, the decomposition is still existed. In our previous study, different metals were attempted to be deposited on the surface of graphite for the interfacial modification of Cu matrix graphite composites, such as nickel [22], copper [23], silver [24,25], tin [26] and titanium [27]. These metals enhance the mutual diffusion of copper and carbon atoms and, accordingly, increase the interface strength. Additionally, the production costs are nearly same as the existing solutions and show better application prospects.

The purposes of this work were to explore a practical method to produce Cu reinforced with a relatively complete Ti_3AlC_2 particle, which keeps an effective ternary layered structure, by multi-arc ion plating titanium. The preparation of Ti_3AlC_2/Cu composites is mainly divided into four parts: plating, milling, compressing, and sintering. The characterization of the microstructure, decomposition mechanism and interface modification mechanism of the composites were investigated. The mechanical properties were also measured through a micro-Vickers hardness and three-point bending test. It is expected that the titanium-modified Ti_3AlC_2/Cu composites show better mechanical properties, self-lubrication and electrical conductivity with higher Ti_3AlC_2 content. In the future, these materials will be the substitutes applied in the field of self-lubrication and electrical conductivity materials in high-speed railways, automobiles, aerospace and aircraft.

2. Materials and Methods

The pressureless sintering method was used to prepare Cu matrix composites reinforced with Ti₃AlC₂ whose raw materials were Cu powder (from the Tianjiu Metal Materials Company, Changsha, China) with an average particle size of 12 μ m in diameter and Ti₃AlC₂ powder (from the Forsman technology company, Beijing, China) with an average particle size of 22 μ m in diameter. Both powders were uniformly mixed in a planetary ball mill, with an increasing Ti₃AlC₂/Cu volume ratio of 10:90, 30:70 and 50:50. An agate-ball-to-powder-weight ratio of 5:1, a rotation speed of 200 rpm and a milling time of 2 h were applied. The mixed powders were compressed into a round-shaped body under 600 MPa pressure for 180 s by bidirectional metal mold compressing. Then, the round mixture sample in the graphite mold was sintered in 850 °C for 1 h in vacuum.

In order to modify the interface of Ti_3AlC_2 and Cu phases, multi-arc ion plating titanium was applied to the starting Ti_3AlC_2 powder four times, for 30 min each time in argon atmosphere before ball milling. Then, through milling, compressing, and sintering processes, titanium-modified Ti_3AlC_2/Cu composites ($Ti@Ti_3AlC_2/Cu$ Composites) were prepared for testing.

The phases of samples were analyzed by XRD (D8 Advance, Bruker, Billerica, MA, USA) using a step-scanning diffractometer with Cu–K α radiation at a scanning step of 0.2°. To investigate the components of composites and diffusion mechanism of Al atoms, the

samples were characterized by SEM (Gemini 500, Zeiss, Oberkochen, Germany) and EDS (X-MAX 80, Zeiss, Oberkochen, Germany) for element distribution.

A microhardness test was employed with a pressing force of 10 gf and a loading speed of 0.2 mm/s for 10 s to represent the wear-resistance ability in a way. A three-point bending test was carried out with a strip shape of width 5 mm \times height 3 mm and span length of 20 mm, with a loading speed of 0.2 mm/min in order to represent the bonding strength of the interface to a certain degree.

3. Results and Discussion

3.1. The Microstructure of Ti₃AlC₂/Cu Composites

As shown in Figure 1, the XRD pattern of different volume fractions of Ti_3AlC_2/Cu composites indicate the decomposition reaction between Ti_3AlC_2 and Cu.



$$Ti_3AlC_2 + Cu \to TiC_x + Cu(Al) \tag{1}$$

Figure 1. X-ray diffraction patterns of different volume fractions of Ti₃AlC₂/Cu matrix composites.

There is no new compound emerging between Cu and Al. In theory, the chemical formula of TiC_x is TiC0.67. The displacement of the Cu diffraction peak increases significantly with the growing content of Ti₃AlC₂ ceramics when the θ angle of the solid solution of Cu(Al) decreases and the lattice distortion caused by Al atoms' diffusion [6]. The shift of Cu reflection is apparent to see when the volume ratio of Ti₃AlC₂ is only 10 vol.%, which is largely due to Al atoms' diffusion mechanism.

Figure 2 shows SEM micrographs of Ti_3AlC_2/Cu composites with different content under low magnification. Most of the Ti_3AlC_2 particles are fine particles and disperse uniformly in the copper matrix and a small amount of them aggregate in the sintering process and form massive structure, with no obvious defects on the surface when the volume fraction of Ti_3AlC_2 is 10 vol.%, as shown in Figure 2a. Most of the Ti_3AlC_2 particles are massive and disperses in the copper matrix, while some of them are continuous and massive with a countable number of defects that begin to appear on the surface when the volume fraction of Ti_3AlC_2 is 30 vol.%, as shown in Figure 2b. Ti_3AlC_2 ceramics begin to show the morphological characteristics of network distribution, and part of it is continuous network distribution. The increasing speed of both defect number and area becomes quicker simultaneously, accompanied by the growth of Ti_3AlC_2 particles' ratio when the volume fraction of Ti_3AlC_2 is 50 vol.%, as shown in Figure 2c. These defects are mainly divided into pores and spalling concentrated at Ti_3AlC_2 particles and at the interface between Ti_3AlC_2 and the Cu matrix. The melting points of Ti_3AlC_2 and Cu are at about 3000 °C and 1000 °C, when the sintering temperature is at 850 °C, which means that the sintering process is low-temperature solid-state sintering. Because of the weak deformation ability of solid Ti_3AlC_2 , it is easy to form a gap between Ti_3AlC_2 particles, which evolves into difficult-to-eliminate pores and would be aggravated by the increase in Ti_3AlC_2 content leading to increases in segregation. The spalling at the interface between Ti_3AlC_2 and the Cu matrix, which is easily caused by the external force due to the low bonding strength at the interface. In Figure 2, for Ti_3AlC_2/Cu composites with 10, 30 and 50 vol.%, correspondingly, the mass fractions are 4.09 wt.%, 14.13 wt.% and 27.74 wt.%, respectively. The network fractions are quantitatively calculated by the image software, as shown in Figure 2d, and the results of threshold concentration is 45.90 vol.%.



Figure 2. Typical morphology of Ti_3AlC_2/Cu composites with different content: (**a**) the volume fraction of Ti_3AlC_2 is 10 vol.%; (**b**) 30 vol.% Ti_3AlC_2 ; (**c**) 50 vol.% Ti_3AlC_2 , (**d**) network fractions of threshold concentration.

Figure 3a shows SEM micrographs of Ti_3AlC_2/Cu composites when the volume fraction of Ti_3AlC_2 is 10 vol.% under high magnification. A gap comes into being between Ti_3AlC_2 particles in the agglomeration process, which leads to the result that Ti_3AlC_2 particles are agglomerate rather than single. The dark black structure is the defect; the bright gray structure is the Cu matrix; the dark gray structure is Ti_3AlC_2 , and the light gray structure is Ti_3AlC_2 , and the light gray structure which means that Ti_3AlC_2 decomposed in a serious way. Figure 3b–d shows EDS mapping results of Figure 3a to figure out element distribution, both EDS point scanning (the results of spots on Figure 3a) and EDS mapping scanning with the whole area (the results in Figure 3b–d) were tested. Cu mainly distributed the matrix and diffused into Ti_3AlC_2 particles in large quantities. Ti were almost all retained in Ti_3AlC_2 , while Al atoms were not obviously aggregated, which further verifies that the large scale of the diffusion of Al atoms leads to the serious decomposition of Ti_3AlC_2 particles in XRD analysis. Figures 4 and 5 indicate the same phenomenon as above when the volume fraction of Ti_3AlC_2 is 30 vol.% and 50 vol.%.



Figure 3. Typical morphology and EDS mapping of Ti_3AlC_2/Cu composites when the volume fraction of Ti_3AlC_2 is 10 vol.%: (a) Ti_3AlC_2 particles agglomerate and (b) scanning results of the Cu element, (c) Ti element and (d) Al element.



Figure 4. Typical morphology and EDS mapping of Ti_3AlC_2/Cu composites when the volume fraction of Ti3AlC2 is 30 vol.%: (a) SEM micrograph and (b) scanning results of the Cu element, (c) the Ti element and the (d) Al element.



Figure 5. Typical morphology and EDS mapping of Ti_3AlC_2/Cu composites when the volume fraction of Ti_3AlC_2 is 50 vol.%: (a) central Ti_3AlC_2 particle almost decomposed; (b) scanning results of the Cu element, (c) the Ti element and (d) the Al element.

Table 1 shows the EDS pointing results of Figures 3–5 in order to demonstrate the phases of different microstructure. Point a is located at the dark gray structure in Ti_3AlC_2 ; point b is located at the light gray structure in Ti_3AlC_2 , and point c, d is in the Cu matrix. There are high levels of Cu, Ti and Al element in point a, which is judged to be a compound of Ti_3AlC_2 and Cu. Some of the Cu atoms diffuse along the channels left by Al atoms' diffusion and some of them diffuse into Ti_3AlC_2 crystals after reaching the channels. Compared with point a, the content of Cu atoms at point b increases, and the content of Al atoms decreases significantly by nearly 0 because Al atoms in Ti_3AlC_2 particles diffuses rapidly and have a high degree of diffusion, which leads to the result that Ti_3AlC_2 at point b has basically decomposed into TiC_x . At the same time, the content of Cu atoms diffusing into TiC_x is very high because the decomposition product TiC_x binds well with Cu. Thus, point b is judged to be composed of Cu and TiC_x compound. Point c and d indicate that Al atoms almost completely diffused into the Cu matrix. However, Cu matrix did not completely become a solid solution of Cu(Al), and so the distribution of Cu(Al) is not uniform when the volume fraction of Ti_3AlC_2 is low.

A EDS scanning line through the Cu matrix, Ti_3AlC_2 and TiC_x particles of about 11 µm was drawn when the volume fraction of Ti_3AlC_2 is 50 vol.%, and the law of element distribution and atomic diffusion could be indicated as shown in Figure 6. It can be seen that the diffusion distance of copper is long, and it distributes in the whole particle, but the content of copper in Ti_3AlC_2 is much lower than that in TiC_x , which indicates that the bonding strength between Ti_3AlC_2 and Cu is much lower than that between TiC_x and Cu, which corresponds to the results of point scanning. Meanwhile, the diffusion path and the steps of Cu atoms in the decomposition process are verified. As Ti_3AlC_2 still exists at the interface, Ti atoms did not diffuse into the Cu matrix as shown in Figure 6d. The decrease in Ti peak strength in TiC_x and the Cu compound is due to the relative decrease in the Ti atoms are $Ti_3AlC_2 > Cu(Al) > TiC_x$, because Al atoms did not remain in the decomposition process, so Al is mainly retained in Ti_3AlC_2 or diffused in Cu(Al). The content of Al in the TiC_x part mainly comes from Ti_3AlC_2 , which is not

completely decomposed. The element distribution of C is similar to Ti because there is no diffusion at the interface between Ti_3AlC_2 and Cu.

Point	Volume Fraction/%	Cu/at.%	Ti/at.%	Al/at.%	C/at.%	Phases
a	10	31.0	23.3	4.3	41.4	
	30	13.7	41.8	6.1	38.4	$Ti_3AlC_2 + Cu$
	50	10.2	60.8	6.3	22.7	
b	10	43.4	18.2	0.8	37.6	
	30	28.1	32.0	1.6	38.3	$Cu + TiC_x$
	50	15.4	41.0	1.8	41.8	
с	10	68.5	0	2.3	29.2	
	30	64.5	0	3.5	32.0	Cu(Al)
	50	74.1	0	3.6	22.3	
d	10	73.3	0	0	26.7	
	30	68.9	0	3.8	27.3	Cu
	50	72.7	0	3.9	23.4	

Table 1. EDS pointing results of Ti₃AlC₂/Cu composites.



Figure 6. EDS lining of Ti_3AlC_2/Cu composites when the volume fraction of Ti_3AlC_2 is 50 vol.%: (a) the interface between Cu matrix and Ti_3AlC_2 , (b) scanning results of all elements: (c) the Cu element, (d) the Ti element, (e) the Al element and (f) the C element.

The micro-Vickers hardness and flexural strength of Ti_3AlC_2/Cu composites with different volume fractions is shown in Figure 7. The micro-Vickers hardness increases first and then decreases with the raise of Ti_3AlC_2 content. First, the hardness of pure copper is about 0.4 GPa and that of pure Ti_3AlC_2 is about 4 GPa. Reinforced with Ti_3AlC_2 , the hardness of the composites is improved in general because Ti_3AlC_2 plays a second phase-strengthening role in the matrix of copper. Secondly, with the increase in Ti_3AlC_2 ceramics' content, the decomposition reaction and diffusion is aggravated, resulting in the increase of Al atoms in the Cu(Al) solid solution, which enhances the solid solution strengthening effect

hindering the movement of dislocations. Finally, the content of TiC_x , a hard phase with hardness up to 30 GPa, also increases along with the increase in the composites' hardness. However, when the volume fraction of Ti_3AlC_2 reaches a high level, the agglomeration of Ti₃AlC₂ results in a number of pores in Ti₃AlC₂ particles. Once the composite material is subjected to compressive stress, stress concentration easily occurs in the defects. Thus, the hardness decreases sharply, and the nonuniform structure caused uneven hardness. The flexural strength of Ti_3AlC_2/Cu composites, which decreases by about 60% compared to 30 vol.% Ti₃AlC₂/Cu composites with 10 vol.% Ti₃AlC₂/Cu composites, while that of 30 vol.% and higher Ti₃AlC₂/Cu composites decreases slowly decreases with the increase in the Ti_3AlC_2 volume fraction. On the one hand, the fracture behavior of composites changes from ductile fracture with dimples to mixed fracture of ductile and brittleness, and then to brittleness. On the other hand, when the volume fraction of Ti_3AlC_2 is 10 vol.%, Ti_3AlC_2 is basically fine particles dispersed in the matrix of Cu, which plays the role of dispersion reinforcement and maintains the flexural strength to a certain extent. With the increase in the reinforcement's content, the shape of particles gradually changes from fine to slice, then to mesh, the segregation of Ti₃AlC₂ particles increases, the volume of particles becomes larger, and the particles become larger. At the same time, lots of pores and defects of Ti_3AlC_2 are generated. When exerting stress, cracks easily occur from Ti_3AlC_2 particles and rapidly expand, which directly leads to the rapid decrease in the flexural strength of composite materials.



Figure 7. The micro-Vickers hardness and flexural strength of Ti₃AlC₂/Cu composites with different volume fractions.

The diffusion model is simplified to the mutual diffusion model of Al and Cu, two kinds of FCC structure metals for rough estimation. According to the diffusion study of single-crystal silver and polycrystalline silver, it can be seen that, when the melting point (T_m) of Al is about 770 °C and the sintering temperature is much higher than 0.75 T_m , the contribution of lattice diffusion in this grain size is much greater than that in grain boundary diffusion, and so the degree of decomposition of Ti_3AlC_2 is high. The decomposition mechanism of Ti_3AlC_2 can be divided into four stages as shown in Figure 8. Figure 8a shows that there is mechanical bonding between Ti_3AlC_2 and Cu before sintering in the first stage. Figure 8b shows that, at the beginning of sintering, because of the high vacancy of Ti_3AlC_2 , the diffusion of Al atoms takes the form of lattice diffusion, grain boundary diffusion and interfacial diffusion at sintering temperature, and TiC_x comes into being in the second stage. Figure 8c shows that, with further sintering, the diffusion of Al atoms is mainly lattice diffusion, and so a large number of TiC_x produces in the Ti_3AlC_2 grain, and the TiC_x phase aggregates many infiltrated Cu atoms due to the good mutual diffusion ability of Cu atoms and TiC_x in the third stage. Figure 8d shows that part of



 Ti_3AlC_2 is surrounded by TiC_x where Al atoms can not diffuse, and the decomposition reaction terminates, while part of Ti_3AlC_2 continues to decompose until it disappears.

Figure 8. Model of the decomposition mechanism of Ti_3AlC_2 : (a) the first stage: before sintering; (b) the second stage: at the beginning of diffusion; (c) the third stage: massive lattice diffusion; (d) the fourth stage: continuous decomposition of Ti_3AlC_2 .

3.2. The Microstructure of Ti@Ti₃AlC₂/Cu Composites

Figure 9a shows the morphology of Ti_3AlC_2 powder treated by multi-arc ion plating Ti. There is a uniform Ti coating of about 1 µm thickness at the edge of the Ti_3AlC_2 ceramic powder, as shown in Figure 9b. EDS line scanning of the interface is shown in Figure 9c. By comparing the element distribution at the interface, Ti and Al elements distribute evenly in Ti_3AlC_2 particles. The content of Al element decreases rapidly at the Ti coating, while the Ti element still maintains a high content. Comparative analysis shows the bright gray structure is the deposited active Ti coating. Ti_3AlC_2 ceramics' surface were successfully coated with Ti.





Figure 9. Characterizations of Ti_3AlC_2 powder coated with Ti: (**a**) microstructure of Ti_3AlC_2 powder coated with Ti, (**b**) the interface of powder, (**c**) EDS line scanning of the interface.

Figure 10a,b shows the morphology of Ti_3AlC_2/Cu composites coated with Ti when the volume fraction of Ti_3AlC_2 is 10 vol.% under low and high magnification. Under low magnification, most Ti_3AlC_2 particles are dispersed uniformly in Cu matrix. Under high-power morphology, Ti_3AlC_2 particles are relatively complete, without an obvious decomposition structure to observe. However, there are still small holes at the intersection of Ti_3AlC_2 particles and interface between Ti_3AlC_2 and Cu. The results of EDS mapping for Cu, Ti, Al and C elements are shown in Figure 10c–f. The content of Cu in Ti_3AlC_2 particles decreases compared with that in Ti_3AlC_2 particles without Ti plating, while the distribution of Al is still not concentrated in Ti_3AlC_2 particles.



Figure 10. Typical morphology and EDS mapping of Ti_3AlC_2/Cu composites coated with Ti when the volume fraction of Ti_3AlC_2 is 10 vol.%: (a) SEM micrograph under low magnification, (b) SEM micrograph under high magnification, (c) scanning results of the Cu element, (d) the Ti element, (e) the Al element and (f) the C element.

Figure 11a shows the interface morphology of Ti_3AlC_2/Cu matrix composites coated with Ti under high magnification. There is a small amount of decomposition structure in the particles. The results of EDS line scanning are shown in Figure 11b–f. Cu still diffuses into Ti_3AlC_2 particles, and the element curve of Ti drops from an abscissa of 11.5 to 12 µm, while that of Al and C decline at 10.5 µm with a certain slope. The tendency of Al distribution means that multi-arc ion plating Ti inhibits the diffusion of Al to a certain extent. It can be seen from Figure 10e that the diffusion degree of Al remains high. However, the content of Al on both sides of the interface is significantly different, although Al atoms still diffuse into the matrix of Cu and the diffusion path is long, which means that the inhibition is still not ideal. The difference in the decreasing point of the element indicates the existence of a Ti coating on MAX ceramics. There is no good mutual diffusion between Ti and Cu, and the curves of Cu and Ti change in the same section. The above phenomena indicate that the Cu matrix reacts with the Ti coating and produces a Cu_xTi compound to inhibit the diffusion of Al atoms. The high content of Cu in Ti_3AlC_2 particles indicates that Cu still diffuses into Ti_3AlC_2 particles to a large extent.



Figure 11. EDS lining of Ti_3AlC_2/Cu composites when the volume fraction of Ti_3AlC_2 is 10 vol.%: (a) interface between the Cu matrix and Ti_3AlC_2 , (b) scanning results of all elements, (c) Cu elements, (d) Ti elements, (e) Al elements, (f) C elements.

The micro-Vickers hardness and flexural strength of Ti_3AlC_2/Cu composites coated with Ti is shown in Figure 12. The change in the hardness and flexural strength of Ti_3AlC_2/Cu composites maintains the same trend before and after Ti plating, but the hardness of Ti_3AlC_2/Cu composites decreases after Ti plating in total. On the one hand, due to the effect of inhibiting diffusion after Ti plating, the diffusion of Al atoms decreases, and so the content of Cu(Al) decreases, which weakens the solid solution strengthening. On the other hand, the content of hard-phase TiC_x decreases with the decrease in the decomposition degree of Ti_3AlC_2 . The flexural strength of Ti_3AlC_2/Cu composites coated with Ti is improved, as shown in Figure 12. There is not only diffusion bonding between TiC_x and Cu but also diffusion bonding between Cu_xTi and Cu after Ti plating. The interface bonding strength is higher than that before Ti_3AlC_2 plating, so the flexural strength of the composites becomes higher.

The interface modification mechanism of Ti_3AlC_2 coated with Ti can be divided into four stages as shown in Figure 13. The Figure 13a shows that there's mechanical bonding between Ti_3AlC_2 and Ti coating and Cu before sintering in the first stage. The Figure 13b shows that at the beginning of sintering, the Ti coating layer near the copper matrix reacts with Cu to produce Cu_xTi compounds, which have good mutual diffusion with Cu matrix in the second stage. The Figure 13c shows that with the further sintering, Cu_xTi compounds gradually accumulate to form a certain thickness of residual layer, which hinders the diffusion of Al atoms. The Figure 13d shows that when the Cu_xTi layer at the interface reaches a certain thickness, the diffusion of Al atom will be hindered and the decomposition reaction will be terminated. The Cu_xTi layer generated not only inhibits the decomposition of Ti_3AlC_2 but also increases bonding strength with Cu matrix.



Figure 12. The mechanical properties of Ti_3AlC_2/Cu composites before and after coating: (a) Micro-Vickers hardness of different content; (b) Flexural strength of different content.



Figure 13. Model of the interface modification mechanism of Ti_3AlC_2 : (**a**) the first stage: before sintering; (**b**) the second stage: at the beginning of sintering; (**c**) The third stage: the Ti coating reacts with Cu; (**d**) the fourth stage: the Ti coating reacts completely.

4. Conclusions

With the volume fraction of Ti_3AlC_2 increasing, the decomposition of Ti_3AlC_2 is exacerbated and the lattice constant of Cu(Al) solid solution is bigger. In the meanwhile, the structure of Ti_3AlC_2 changes from dispersed granules to flakes, then to a continuous network. Furthermore, a highly defective morphology of Ti_3AlC_2 forms when the porosity becomes higher with the higher content of Ti_3AlC_2 .

Multi-arc ion plating Ti effectively inhibits the diffusion of Al atoms into the Cu matrix. The Ti coating reacts with Cu and generates Cu_xTi in the interface between the Cu and the Ti coating, which inhibits the diffusion of Al atoms so as to inhibit decomposition. The inhibition of decomposition of Ti_3AlC_2 ceramics weakened solid solution strengthening and decreased the content of hard-phase TiC_x . Furthermore, the good mutual diffusion between the Cu_xTi layer and the Cu effectively improves the interfacial bonding strength.

In the future, the titanium-modified Ti_3AlC_2/Cu composites will be the focus of studies on the enhancement of self-lubrication properties and modifying the parameters of industrial production to decrease the production costs. We hope these materials could

take the place of the graphite/Cu and C/C composites in the field of self-lubrication and electrical conductivity materials.

Author Contributions: Y.W.: conceptualization, methodology, investigation, formal analysis, writing original draft, writing—review and editing. Y.G.: conceptualization, funding acquisition. Y.F.: writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Natural Science Basic Research Program of Shaanxi (2021JQ-049), China Postdoctoral Science Foundation Funded Project (2021M692515), the Open Fund of National Joint Engineering Research Center for Abrasion Control and Molding of Metal Materials (HKDNM202103), National Key Research and Development Program of China (2021YFB3701204).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

Acknowledgments: We thank the Instrument Analysis Center of Xi'an Jiaotong University for their assistance with materials analyses.

Conflicts of Interest: The authors declare no conflict of interest.

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