



# Article Fabrication of a TiC-Ti Matrix Composite Coating Using Ultrasonic Vibration-Assisted Laser Directed Energy Deposition: The Effects of Ultrasonic Vibration and TiC Content

Yunze Li<sup>1</sup>, Dongzhe Zhang<sup>1</sup>, Hui Wang<sup>2</sup> and Weilong Cong<sup>1,\*</sup>

- <sup>1</sup> Department of Industrial, Manufacturing, and Systems Engineering, Texas Tech University, Lubbock, TX 79409, USA; yunze.li@ttu.edu (Y.L.); dongzhe.zhang@ttu.edu (D.Z.)
- <sup>2</sup> Department of Industrial & Systems Engineering, Texas A&M University, College Station, TX 77843, USA; huiwang@tamu.edu
- \* Correspondence: weilong.cong@ttu.edu; Tel.: +1-806-834-6178

check for updates

Citation: Li, Y.; Zhang, D.; Wang, H.; Cong, W. Fabrication of a TiC-Ti Matrix Composite Coating Using Ultrasonic Vibration-Assisted Laser Directed Energy Deposition: The Effects of Ultrasonic Vibration and TiC Content. *Metals* **2021**, *11*, 693. https://doi.org/10.3390/met11050693

Academic Editors: Andreas Chrysanthou and Ayrat Nazarov

Received: 28 March 2021 Accepted: 20 April 2021 Published: 23 April 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 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/). Abstract: Titanium and its alloys exhibit superior properties of high corrosion resistance, an excellent strength to weight ratio and outstanding stiffness among other things. However, their relatively low hardness and wear resistance limit their service life in high-performance applications of structure parts, gears and bearings, for example. The fabrication of a ceramic reinforced titanium matrix composite (TMC) coating could be one of the solutions to enhance the microhardness and wear resistance. Titanium carbide (TiC) is a preferable candidate due to the advantages of self-lubrication, low cost and a similar density and thermal expansion coefficient with titanium. The fabrication of TiC-TMC coatings onto titanium using a laser directed energy deposition (LDED) process has been conducted. The problems of TiC aggregation, low bonding quality and the generation of fabrication defects still exist. Considering ultrasonic vibration could generate acoustic steaming and transient cavitation actions in melted materials, which could homogenize the distribution of reinforcement materials and promote the dissolution of TiC into liquid titanium. In this study, for the first time, we investigate the ultrasonic vibration-assisted LDED of TiC-TMC coatings. The effects of ultrasonic vibration and reinforcement content on the phase compositions, reinforcement aggregation, bonding quality, fabrication defects and mechanical properties (including microhardness and wear resistance) of LDED deposited TiC-TMC coatings have been investigated. With the assistance of ultrasonic vibration, the aggregation of TiC was reduced, the porosity was decreased, the defects in the bonding interface were reduced and the mechanical properties including microhardness and wear resistance were increased. However, the excessive TiC content could significantly increase the TiC aggregation and manufacturing defects, resulting in the reduction of the mechanical properties.

Keywords: ultrasonic vibration; laser directed energy deposition; coating; TiC-TMC

# 1. Introduction

Titanium and its alloys have been widely used in many industries (including the automotive industry, aerospace industry and medical industry) due to their superior properties of strong corrosion resistance, a high strength to weight ratio and outstanding stiffness among other things [1,2]. However, their relatively low surface mechanical properties (hardness and wear resistance) limit the service life in high-performance applications of structure parts, gears, bearings and jet engine compressors, for example. [3,4]. Ceramic reinforced titanium matrix composites (TMCs) were coated onto titanium to improve the mechanical properties [5,6]. Compared with other ceramic reinforcements (such as Al<sub>2</sub>O<sub>3</sub>, SiC, TiN and TiB [7–10]), TiC exhibits the unique property of self-lubrication with enhanced the wear resistance, a relativity low material cost and a similar thermal expansion coefficient with titanium [11]. TiC-TMC coatings have been successfully fabricated by laser additive manufacturing processes [12–15]. The mechanism of the dissolution of TiC into titanium and the phase transformations during the fabrication have been investigated. The results show that the precipitated TiC with a refined microstructure could significantly improve the surface microhardness and wear resistance.

Laser directed energy deposition (LDED) has been widely used in the fabrications of TMC coatings onto a metallic workpiece. In LDED, the melted material can be solidified at a high cooling rate  $(10^3-10^6 \text{ K/s})$  [16], which contributes to the development of coating layers with a relatively fine-grained microstructure [17,18]. LDED also has the capability of the functionally gradient coatings fabrication, which can reduce the discontinuity of properties between base materials and reinforced layers [19]. TiC-TMC, as a kind of preferable coating material, has been deposited onto titanium and its alloys by an LDED process [12,13,20–24]. The results showed that the LDED fabricated TiC-TMC coatings could significantly improve the surface properties of microhardness and wear resistance. By optimizing the laser density, the microhardness and wear resistance could be further increased [21,22]. In addition, by utilizing the functionally gradient coating layers, the bonding quality, density and surface properties were improved [12,24].

However, there are still a few problems that exist in the LDED fabricated TiC-TMC coatings such as the reinforcement aggregation and the generation of fabrication defects. Due to the high cooling rate of LDED, TiC powders were always partially melted and dissolved into liquid titanium during the fabrication [22]. These solid TiC particles resulted in the problem of the inhomogeneous distribution of unmelted reinforcement particles. In addition, the existence of solid TiC particles in the molten pool caused the lack of fusion, which was the major reason of the generation of fabrication defects. Both problems could reduce the microhardness and wear resistance of TiC-TMC coatings fabricated by the LDED process [13]. Utilizing ultrasonic vibration-assisted LDED to fabricated TiC-TMC coatings could be a possible solution to solve the existing problems. Ultrasonic vibration had been widely utilized in the LDED process to fabricate alloys and metal matrix composites. Cong et al. pointed out that the assistance of ultrasonic vibration could reduce the grain size and porosity, increase the size of the molten pool and improve the Rockwell hardness [25]. Wang et al. found the assistance of ultrasonic vibration could refine the Laves phase in LDED fabricated Inconel 718 parts, which improved the microhardness and wear resistance [26]. Li et al. investigated the effects of ultrasonic vibration on LDED fabricated Ni/WC/La<sub>2</sub>O<sub>3</sub> coatings [27]. The assistance of ultrasonic vibration could disrupt the dendrites, refine the grain size and improve the hardness and wear resistance. The reinforcement size and mechanical properties of TiB reinforced Ti matrix composites were improved by the assistance of ultrasonic vibration, as stated by Ning et al. [28]. Ultrasonic vibration induced two direct actions on liquid materials including acoustic streaming and transient cavitation. The acoustic streaming was a steady flow in the fluid materials driven by the absorption of acoustic oscillations. Such actions could mix and stir the liquid materials in the molten pool, which could homogenize the distribution of reinforcement [25,26]. The transient cavitation was the dynamic process of growth and collapse of microbubbles in liquid materials, which promoted the dissolution of solid particles [29]. In addition, ultrasonic vibration could provide extra energy to the molten pool and promote the melting of powder materials [25].

In this study, the TiC-TMC coatings were successfully coated onto titanium by the ultrasonic vibration-assisted LDED process. The effects of ultrasonic vibration and TiC content on the phase compositions, reinforcement aggregation, bonding quality, fabrication defects, microhardness and wear resistance of TiC-TMC coatings were investigated.

#### 2. Materials and Methods

#### 2.1. Powder Materials and Treatment

The powder materials used in this study were TiC powder (99.7% purity) and Ti powder (99.9% purity) (Atlantic Equipment Engineers Inc., Upper Saddle River, NJ, USA). A pure Ti plate with a thickness of 6.65 mm was used to coat the substrate.

According to the results of the preliminary experiments, three feedstock material powders (Ti, Ti + 5 wt.% TiC and Ti + 10 wt.% TiC) were adopted to study the effects of TiC content. As shown in Figure 1, before the LDED process TiC powder and Ti powder were mixed by a ball milling machine (ND2L, Torrey Hills Technologies LLC., San Diego, CA, USA). The weight ratio of the milling balls to powders was 1:1. The milling time was 4 h with a consistent rotation speed of 200 rpm. The TiC powders were partially embedded on the surface of the Ti powders after the ball milling process.



**Figure 1.** Powder pretreatment: (**a**) Ti powder; (**b**) TiC powder; (**c**) planetary ball milling process; (**d**) prepared TiC-Ti powder.

#### 2.2. Experimental Setup

Experiments were conducted on an LDED system (LENS 450, Optomec Inc., Albuquerque, NM, USA). Figure 2 shows the experimental setup of the ultrasonic vibrationassisted LDED system. To avoid the oxidation of Ti at a high temperature, the chamber system was purged by argon gas until the oxygen level was lower than 50 ppm. Inside the chamber, a ceramic vibrator with a frequency of 29 kHz was fixed under the Ti substrate to provide ultrasonic vibration. A laser system equipped with a 400 W fiber laser source (YLM-1070, IPG Photonics, Oxford, MA, USA) was used to generate the laser beam. The movement of the substrate and the cladding head were controlled by the control system to build the designed 3D structures. During the fabrication, the laser beam was transmitted to the surface of the substrate to generate a molten pool, which caught and melted the material powders. When the laser beam moved away, the molten pool was solidified to fabricate the first layer. After the fabrication of the first layer, the cladding head moved up the distance of the layer thickness. The second layer was fabricated on top of the first layer. The designed coatings were deposited layer by layer. The laser coating parameters in this study are listed in Table 1.



Figure 2. Experimental setup.

Table 1. Laser coating parameters.

Input Fabrication Variables	Value
Laser power (W)	375
Beam diameter of laser (µm)	400
Wavelength of laser (µm)	1.07
Deposit head scanning speed (mm/min)	11
Hatch distance (µm)	380
Layer thickness (µm)	432
Powder feeding rate (g/min)	2.5
Number of layers	3
Oxygen level (ppm)	<50
Argon gas flow rate (L/min)	6
Scanning orientation (°)	45, alternate 90 per layer

## 2.3. Measurement Procedures

After fabrication, the deposited coating layers were ground and polished (perpendicular to the deposition direction) by a grinder/polisher machine (MetaServ 250, Buehler, Lake Bluff, IL, USA). The whole cross-sectional surfaces and bonding quality were observed by an optical microscope (OM) (DSX-510, OLYMPUS, Tokyo, Japan). ImageJ software (1.8.0\_172, LOCI, University of Wisconsin, Madison, WI, USA) was used to analyze the observed images under the mode of black and white [30]. The morphologies of the powders and the microstructure of the fabricated coatings were observed by scanning electron microscopy (SEM) (Phenom Pharos, Nanoscience, Phoenix, AZ, USA), which was equipped with a backscatter electron detector (BSD) system and an energy dispersive X-ray spectroscopy (EDS) system. The element compositions and phases were analyzed by an EDS and X-ray diffraction (XRD) machine (Ultima III, Rigaku Corp., Woodlands, TX, USA), respectively. In the XRD, the samples were scanned from 20 to 80 degrees (2 $\theta$ ) with a scanning step of 0.02 degrees (2 $\theta$ ), a wavelength of 0.154 nm, a voltage of 40 kV and a current of 44 mA. The weight percentages of each phase were calculated by MDI/JADE software (Version 2020, Materials Data, Livermore, CA, USA).

The microhardness of the deposited coating layers was tested by a Vickers microhardness tester (Phase II, Upper Saddle River, Bergen, NJ, USA) with a 10 N normal load and a 10 s dwell time. For each combination of inputs, two samples fabricated by the LDED process were tested. For each sample, the microhardness values were measured on ten random positions of the cross-sectional surface. The wear rate was tested and measured by dry sliding tests with a 1 mm radium silicon carbide (SiC) ball at room temperature using a mechanical testing system (PB1000, Nanovea, Irvine, CA, USA). During the dry sliding

$$V = L \times \left[ (\pi R^2) / 180 \times \arcsin(W/2R) - W/2 \times (R^2 - (W/2)^2)^{0.5} \right]$$
(1)

where *L* was the sliding distance, mm; *R* was the radius of the sliding ball, mm and *W* was the scratching width, mm. The wear rate  $W_r$  was calculated by Equation (2).

$$W_r = V/(F(vT)) \tag{2}$$

where *F* was the normal load used in the dry sliding test, N; *v* was the sliding speed, mm/s and *T* was the time of the dry sliding test, s.

## 3. Results and Discussion

## 3.1. Phase Compositions

The XRD results on the phase compositions are shown in Figure 3. The peaks were fitted and identified according to the information in the powder diffraction file (PDF) cards. Both TiC(O) and non-stoichiometric  $Ti_xC_y(P)$  had a cubic lattice structure [9,21]. The lattice parameter *a* could be calculated by Bragg's law, as shown in Equation (3) [31]:

$$1/(d_{hkl})^2 = (h^2 + k^2 + l^2)/a^2$$
(3)

where  $d_{hkl}$  was the lattice spacing, which could be calculated by the location of the peak (Degree 2-theta) and h, k and l were the Miller indices of the Bragg plane, which could be found in PDF cards. The lattice parameter of TiC(O) was 4.337 Å. As a comparison, the lattice parameter of Ti<sub>x</sub>C<sub>y</sub>(P) was 4.272 Å, which was lower than that of TiC(O).



**Figure 3.** The effects of ultrasonic vibration and TiC content on the phase compositions of TiC-TMC coatings: (**a**) 5% TiC; (**b**) 10% TiC.

The TiC(O) was the phase of original feedstock TiC powders in which the atomic ratio of Ti and C was 1:1. The  $Ti_x C_y(P)$  phase was non-stoichiometric TiC, which was precipitated from the TiC-Ti solutions during the fabrication [9,32]. Its atomic ratio of Ti and C could be changed from 1:0.55 to 1:1. The phase compositions of the feedstock powders and the LDED fabricated TiC-TMC coatings with 5% TiC and 10% TiC are shown in Tables 2 and 3, respectively. As shown in Figure 3a, at the low level of TiC content with the assistance of ultrasonic vibration, the area of TiC(O) peaks was significantly decreased. The detailed phase compositions results showed that the content of the TiC(O) phase in the TiC-TMC coatings decreased from 2.94 wt.% to 0.72 wt.%. In addition, the content of the  $Ti_x C_{\nu}(P)$  phase increased from 4.36 wt.% to 6.98 wt.%. The reason for the phase composition changes was that ultrasonic vibration could promote the dissolution and precipitation process during the fabrication. On one hand, the acoustic streaming could mix and stir the liquid materials inside the molten pool, which could enhance the movement of both solvent and solute [22,33]. In addition, the transient cavitation induced by ultrasonic vibration could increase the diffusion rate between the TiC(O) particles and the liquid titanium [34]. Due to these two actions, more solid TiC(O) particles could be directly dissolved in liquid Ti. On the other hand, the additional energy was induced to the molten pool by ultrasonic vibration, which increased the temperature of the liquid materials [15]. More TiC(O) particles could be melted at a high temperature and then dissolved into the liquid titanium. During the solidification, the solubility of the TiC in the titanium was reduced. There were more  $Ti_x C_{\nu}(P)$  phases precipitated from the TiC-Ti solution.

Table 2. Phase compositions of the feedstock powder and the TiC-TMC coatings with 5% TiC.

Conditions	TiC(O) (wt.%)	$Ti_x C_y(P)$ (wt.%)	Ti (wt.%)
Feedstock powder	5.24	0	balance
TiC-TMC coatings without UV	2.94	4.36	balance
TiC-TMC coatings with UV	0.72	6.98	balance

Table 3. Phase compositions of the feedstock powder and the TiC-TMC coatings with 10% TiC.

Conditions	TiC(O) (wt.%)	$Ti_x C_y(P)$ (wt.%)	Ti (wt.%)
Feedstock powder	10.71	0	balance
TiC-TMC coatings without UV	6.89	5.87	balance
TiC-TMC coatings with UV	5.12	8.48	balance

The XRD results of the feedstock powders and the fabricated TiC-TMC coatings with a high level of TiC content are shown in Figure 3b. It could be observed that the peaks pf of TiC(O) and Ti<sub>x</sub>C<sub>y</sub>(P) had slight changes. The detailed phase compositions are shown in Table 3. Similar to the conditions with a lower TiC content, with the assistance of ultrasonic vibration, the content of TiC(O) decreased and the content of Ti<sub>x</sub>C<sub>y</sub>(P) increased. However, the TiC(O) content in the TiC-TMC coatings was slightly reduced in comparison with that in the coatings with a lower TiC content. It meant that the effects of ultrasonic vibration on the phase transformation (from the TiC(O) phase to the Ti<sub>x</sub>C<sub>y</sub>(P) phase) were suppressed. The higher content of TiC had two major effects. First, feedstock powders need more energy to melt due to the high melting point of TiC. At a relatively high TiC content of 10 wt.%, the TiC(O) particles were harder to melt and then be dissolved into liquid Ti, which prevented the precipitation of Ti<sub>x</sub>C<sub>y</sub>(P) particles. Second, the increase of solid TiC(O) particles reduced the fluidity of the molten pool. The actions of ultrasonic vibration on the liquid materials were suppressed, which further prevented the dissolution and precipitation process.

## 3.2. Microstructure

Figure 4 shows the element compositions analyzed by EDS on the cross-section of the TiC-TMC coatings fabricated by the LDED process. There were three different kinds of

regions (black, grey and light). In these three different regions, the element compositions were analyzed (as shown in Figure 4b–d). It could be seen that the irregular-shaped black regions had an atomic ratio of titanium to carbon of 1:1 (the same as the atomic ratio of titanium to carbon in the TiC(O) phase). Associated with the XRD analysis, it could be considered that the black regions were the TiC(O) phase. The grey regions had 36 at.% of the C element, which could be considered as  $Ti_x C_y(P)$ . The major reason was that the composition range of  $Ti_x C_y(P)$  was extraordinarily wide according to the Ti-C phase diagram and its C element content was lower than that in the TiC(O) (50 at.%) [12]. Figure 4a shows that the size of the individual spherical-shaped grey regions was smaller than the size of the feedstock TiC powders, indicating the grey regions should be generated during the solidification. Similar phenomena have also been reported in other investigations on the fabrication of TiC-TMC parts [13,33]. Beside the independently distributed grey regions, there were also grey regions surrounded by the boundary of black regions. Due to the high cooling rate in the LDED process, the TiC particles with larger sizes could not be fully dissolved into the liquid titanium. The dissolution of TiC(O) into titanium took place at the boundary of the solid TiC(O) particles, which formed the TiC-Ti solution around the undissolved TiC(O) cores. During the solidification, the solubility of TiC in the TiC-Ti solution decreased, resulting in the interfacial reaction product of  $Ti_x C_{\nu}(P)$ . A similar phenomenon was also reported in the investigations of sintered TiC-TMC materials [35–37]. The light regions had 95.5 at.% of the Ti element, which indicated that these regions were the titanium matrix.



**Figure 4.** The EDS results of a laser DED fabricated TiC-TMC coating: (**a**) the microstructure morphology of the TiC-TMC coatings; (**b**–**d**) the element composistions of different regions.

The effects of ultrasonic vibration and TiC content on the microstructure are shown in Figure 5. Figure 5b,c,f,g show the cross-sectional OM images of the coatings fabricated by LDED. It could be observed that the reinforcements aggregated with the laser direction. Figure 5a,d,e,h show the enlarged view of SEM images of the aggregated regions of the reinforcements. It could be seen that the grey particles with a smaller size were relatively

evenly distributed in the Ti matrix. As a comparison, the black particles mainly caused the aggregation. As discussed in Section 3.2, the small-sized grey particles were in the  $Ti_xC_y(P)$  phase and the large-sized black particles were in the TiC(O) phase. According to the SEM images, it could be confirmed that the reinforcement aggregation was mainly caused by the TiC(O) particles. It can be seen in Figure 5e–h that with the assistance of ultrasonic vibration, there were less TiC(O) particles aggregated. As discussed in Section 3.1, with the assistance of ultrasonic vibration, the amount and size of the TiC(O) particles in the TiC-TMC coatings could be significantly decreased. The reduction of unmelted and undissolved particles could increase the fluidity of the liquid materials in the molten pool. Similar phenomena were also reported in the laser melting of TiC-Al composites [38]. These solid TiC(O) particles recirculated in the molten pool faster, which improved the distribution of the undissolved TiC(O). Both the reduction of the TiC(O) particles and the better distribution of TiC(O) could significantly release the reinforcement aggregation.



Figure 5. The microstructure of a laser DED fabricated TiC-TMC coating: (a,d,e,h) the SEM images; (b,c,f,g) the OM images.

As shown in Figure 5c,g, with the increase of TiC content, more TiC(O) particles aggregated in the LDED fabricated coatings. As discussed in Section 3.1, the TiC-TMC coatings with a higher content of TiC had more TiC(O) particles. The larger amount of solid TiC(O) particles could reduce the fluidity of the molten pool, which suppressed the movement of solid TiC(O) particles [39]. In addition, the specific heat capacity and laser absorptivity of TiC and Ti were different. The increase of the TiC content could enlarge the difference of the temperature and solidification rates inside the molten pool [40]. In the regions with a low temperature, liquid materials solidified faster. It could also suppress the movement of solid TiC(O) particles and resulted in the variation of the distribution of TiC(O) particles.

#### 3.3. Bonding Quality

The molten pool of TiC-TMC coatings generated in the laser DED process with and without ultrasonic vibration are shown in Figure 6a. With the assistance of ultrasonic vibration, the width and depth of the molten pool became larger. The major reason was that the actions of acoustic streaming could stir the liquid material in the molten pool. For the Gaussian laser used in this study, the energy at the center of the laser beam was much higher than that at the boundary, leading to uneven heat density in the molten pool [41,42]. The actions of mixing and stirring promoted the dispersion of the high-temperature liquid from the center to the boundary of the molten pool. The temperature at

the boundary then increased, which promoted the melting of the substrate materials [43]. In addition, ultrasonic vibration provided extra energy to the molten pool and increased the temperature of the liquid materials. A greater number of substrate materials could be melted at a higher temperature.



**Figure 6.** The effects of ultrasonic vibration on bonding quality: (**a**) the molten pool of the TiC-TMC coatings; (**b**) the bonding interface of the TiC-TMC coatings.

Figure 6b shows the bonding interface of the TiC-TMC coatings. The defects in the bonding regions were mainly caused by the insufficient overlap between adjacent layers, which could be significantly reduced by the assistance of ultrasonic vibration. The major reason was that ultrasonic vibration increased the depth of the molten pool on the substrate. The metallic bonding between the substrate materials and coating layers could be significantly improved. In addition, as discussed in Section 3.3, the fluidity of the liquid materials in the molten pool was improved by ultrasonic vibration. The higher fluidity increased the powder absorbability of the molten pool, which was also helpful for generating sufficient overlaps. A similar result was reported in the fabrication of zirconia-alumina ceramics using an LDED process [44].

## 3.4. Fabrication Defects

The fabrication defects of the LDED fabricated TiC-TMC coatings on a cross-sectional surface are shown in Figure 7. It could be seen that most fabrication defects were in irregular shapes. In the LDED process, the irregular-shaped fabrication defects on the cross-sectional surface were usually caused by lack of fusion, as demonstrated by Zhang et al. [45]. As the molten pool was enlarged by the assistance of ultrasonic vibration, the lack of fusion at the boundary of the molten pool was reduced. In addition, more powder could be caught by the molten pool during the fabrication, promoting the formation of sufficient overlaps.



**Figure 7.** The effects of ultrasonic vibration on the fabrication defects: (**a**) the molten pool of the TiC-TMC coatings; (**b**) the bonding interface of the TiC-TMC coatings.

With the increased TiC content, the amount of irregular fabrication defects increased due to the lack of fusion. In this study, the laser input energy was constant. The TiC needed to absorb more energy to be melted than titanium. The TiC-TMC coatings with a higher TiC content had more unmelted TiC(O) particles in the molten pool during the fabrication, which aggravated the lack of fusion. Moreover, the large number of solid TiC(O) particles reduced the fluidity of the liquid materials in the molten pool resulting in the aggregation of unmelted TiC(O) particles. In these unmelted TiC(O)-rich regions, a lack of fusion was more likely to happen, as reported in the LDED fabricated  $Ti_6Al_4V$  with trace boron and the selected laser melting of a TiB<sub>2</sub> coating on  $Ti_6Al_4V$  [46,47].

#### 3.5. Mechanical Properties

## 3.5.1. Microhardness

Figure 8 shows the effects of ultrasonic vibration and TiC content on microhardness. With the assistance of ultrasonic vibration, the microhardness value increased. As discussed in Section 3.1, more refined  $Ti_xC_y(P)$  particles were precipitated in the titanium matrix with the assistance of ultrasonic vibration. These refined reinforcements could evenly bear the load and increase the resistance of plastic deformation during the microhardness tests. A similar result was demonstrated by Shen et al. through numerical methods [48]. Moreover, as discussed in Section 3.4, with the assistance of ultrasonic vibration, the fabrication defects decreased significantly. The higher density increased the ability to support the load, which could also increase the microhardness. Compared with commercial pure

titanium coating layers, TiC-TMC coatings had a larger microhardness. The major reason was that TiC could support the load and reduce the deformation. However, the excessive TiC content led to the reduction of microhardness. As discussed before, the major reason was that the increase of fabrication defects reduced the microhardness.





## 3.5.2. Wear Resistance

The sliding width of the material removal trail and wear rate are shown in Figure 9. Both the sliding width and wear rate had a negative relationship with the wear resistance. With the assistance of ultrasonic vibration, the wear resistance increased. The significant reduction of the fabrication defects provided a smoother interface and reduced the friction coefficient of the coating layers [49]. Under the same test condition, the friction force was reduced, resulting in a smaller material removal volume and higher wear resistance. In addition, the reinforcement aggregation was reduced by ultrasonic vibration. It contributed to the formation of the uniform anti-wear protective layer during the dry sliding tests to further increase the wear resistance.



Figure 9. The effects of ultrasonic vibration and TiC content on microhardness.

Compared with CP-Ti, TiC-TMC coatings showed a higher wear resistance. In addition, the friction force was measured during the dry sliding tests. The average friction coefficients of each combination of input were calculated and are listed in Table 4. The major reason was that the hardness of TiC was extremely high, which increased the hardness of the TiC-TMC coatings. The adhesive wear mode was changed to abrasive wear, which could significantly increase the wear resistance [50,51]. In addition, during the dry sliding tests, the SiC ball would leave a rough worn surface on the samples. The spherical TiC particles might have the function of self-lubrication [52,53]. With the increase of the TiC content to a high level (10 wt.%), the wear resistance was reduced. The major reason was that the greater number of fabrication defects increased the friction coefficient.

Table 4. The average friction coefficient of the CP-Ti and TiC-TMC coatings.

Conditions	Friction Coefficient
CP-Ti without UV	0.322
CP-Ti with UV	0.324
5 wt.% TiC-TMC coatings without UV	0.201
5 wt.% TiC-TMC coatings with UV	0.129
10 wt.% TiC-TMC coatings without UV	0.296
10 wt.% TiC-TMC coatings with UV	0.268

#### 4. Conclusions

In this study, TiC-TMC coatings with different TiC contents were fabricated by an ultrasonic vibration-assisted LDED process. The effects of ultrasonic vibration and TiC content on the phase composition, TiC aggregation, bonding quality, fabrication defects and mechanical properties were investigated.

With the assistance of ultrasonic vibration, the liquid materials were mixed and stirred by the actions of acoustic streaming and transient cavitation in liquid material solidification, which promoted the dissolution of TiC(O) and the precipitation of refined  $Ti_xC_y(P)$ . In the TiC-TMC coatings fabricated by LDED without ultrasonic vibration, TiC(O) particles preferred to aggregate in a titanium matrix. In contrast, the process with ultrasonic vibration could significantly reduce the TiC(O) aggregation by decreasing the amount of TiC(O) and improving the distribution. In addition, extra heat energy was generated by the ultrasonic vibration assistant, which could increase the bonding quality and reduce the fabrication defects. The improved TiC(O) aggregation and fabrication defects were effective in enhancing the microhardness and wear resistance of the ultrasonic vibration-assisted LDED fabricated TiC-TMC coatings.

With the increase of TiC content, the phase transformation from the TiC(O) phase to the  $Ti_xC_y(P)$  phase was suppressed. The major reason was that the higher TiC content suppressed the further dissolution of TiC(O) in liquid titanium. At a high content of TiC, there were more undissolved TiC(O) particles existing in the TiC-TMC coatings after the fabrication, which aggravated the reinforcement aggregation. In addition, the higher TiC content exacerbated the generation of a lack of fusion defects as the TiC powders needed more energy to be melted than Ti. The generation of both the TiC(O) aggregation and fabrication defects decreased the mechanical properties of microhardness and wear resistance of the TiC-TMC coatings with a higher TiC content.

**Author Contributions:** Data curation, Y.L. and D.Z.; Formal analysis, Y.L.; Investigation, Y.L.; Methodology, Y.L.; Resources, Y.L.; writing—original draft, Y.L.; Writing—review & editing, Y.L., D.Z., H.W. and W.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

# References

- Peters, M.; Kumpfert, J.; Ward, C.H.; Leyens, C. Titanium Alloys for Aerospace Applications. *Adv. Eng. Mater.* 2003, *5*, 419–427. [CrossRef]
- Hartman, A.D.; Gerdemann, S.J.; Hansen, J.S. Producing lower-cost titanium for automotive applications. JOM 1998, 50, 16–19. [CrossRef]
- 3. Attar, H.; Bönisch, M.; Calin, M.; Zhang, L.C.; Scudino, S.; Eckert, J. Selective laser melting of in situ titanium-titanium boride composites: Processing, microstructure and mechanical properties. *Acta Mater.* **2014**, *76*, 13–22. [CrossRef]
- 4. Guo, C.; Zhou, J.; Chen, J.; Zhao, J.; Yu, Y.; Zhou, H. Improvement of the oxidation and wear resistance of pure Ti by laser cladding at elevated temperature. *Surf. Coat. Technol.* 2010, 205, 2142–2151. [CrossRef]
- 5. Dhanda, M.; Haldar, B.; Saha, P. Development and characterization of hard and wear resistant MMC coating on Ti-6Al-4V substrate by laser cladding. *Procedia Mater. Sci.* 2014, *6*, 1226–1232. [CrossRef]
- Cui, Z.; Yang, H.; Wang, W.; Wu, H.; Xu, B. Laser cladding Al-Si/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composite coatings on AZ31B magnesium alloy. J. Wuhan Univ. Technol. Mater. Sci. Ed. 2012, 27, 1042–1047. [CrossRef]
- 7. Song, S.X.; Ai, X.; Zhao, J.; Huang, C.Z. Al<sub>2</sub>O<sub>3</sub>/Ti(C<sub>0.3</sub>N<sub>0.7</sub>) cutting tool material. *Mater. Sci. Eng. A* 2003, 356, 43–47. [CrossRef]
- Selamat, M.; Watson, L.; Baker, T. XRD and XPS studies on surface MMC layer of SiC reinforced Ti-6Al-4V alloy. J. Mater. Process. Technol. 2003, 142, 725–737. [CrossRef]
- 9. Yoon, C.S.; Kang, S.; Kim, D.Y. Dissolution and reprecipitation behavior of TiC-TiN-Ni cermets during liquid-phase sintering. *Korean J. Ceram.* **1997**, *3*, 124–128.
- 10. Fan, Z.; Miodownik, A.; Chandrasekaran, L.; Ward-Close, M. The Young's moduli of in situ Ti/TiB composites obtained by rapid solidification processing. *J. Mater. Sci.* **1994**, *29*, 1127–1134. [CrossRef]
- 11. Yuan, P.; Gu, D. Molten pool behaviour and its physical mechanism during selective laser melting of TiC/AlSi10Mg nanocomposites: Simulation and experiments. J. Phys. D Appl. Phys. 2015, 48, 035303. [CrossRef]
- 12. Liu, W.; Dupont, J.N. Fabrication of functionally graded TiC/Ti composites by laser engineered net shaping. *Scr. Mater.* **2003**, *48*, 1337–1342. [CrossRef]
- 13. Rambo, C.R.; Travitzky, N.; Zimmermann, K.; Greil, P. Synthesis of TiC/Ti–Cu composites by pressureless reactive infiltration of TiCu alloy into carbon preforms fabricated by 3D-printing. *Mater. Lett.* **2005**, *59*, 1028–1031. [CrossRef]
- 14. Man, H.C.; Zhang, S.; Cheng, F.; Yue, T. Microstructure and formation mechanism of in situ synthesized TiC/Ti surface MMC on Ti-6Al-4V by laser cladding. *Scr. Mater.* **2001**, *44*, 2801. [CrossRef]
- 15. Gu, D.; Meng, G.; Li, C.; Meiners, W.; Poprawe, R. Selective laser melting of TiC/Ti bulk nanocomposites: Influence of nanoscale reinforcement. *Scr. Mater.* **2012**, *67*, 185–188. [CrossRef]
- 16. Joseph, J. Direct laser fabrication of compositionally complex materials: Challenges and prospects. *Addit. Manuf. Appl. Met. Compos.* **2020**, 147–163. [CrossRef]
- 17. Hu, Y.; Cong, W. A review on laser deposition-additive manufacturing of ceramics and ceramic reinforced metal matrix composites. *Ceram. Int.* **2018**, *44*, 20599–20612. [CrossRef]
- 18. Farshidianfar, M.H.; Khajepour, A.; Gerlich, A.P. Effect of real-time cooling rate on microstructure in laser additive manufacturing. *J. Mater. Process. Technol.* **2016**, 231, 468–478. [CrossRef]
- 19. Pei, Y.; Zuo, T. Gradient microstructure in laser clad TiC-reinforced Ni-alloy composite coating. *Mater. Sci. Eng. A* **1998**, 241, 259–263. [CrossRef]
- Yang, S.; Liu, W.; Zhong, M.; Wang, Z. TiC reinforced composite coating produced by powder feeding laser cladding. *Mater. Lett.* 2004, 58, 2958–2962. [CrossRef]
- 21. Kathuria, Y. Nd-YAG laser cladding of Cr<sub>3</sub>C<sub>2</sub> and TiC cermets. Surf. Coat. Technol. 2001, 140, 195–199. [CrossRef]
- 22. Wu, W. Dissolution precipitation mechanism of TiC/Ti composite layer produced by laser cladding. *Mater. Sci. Technol.* **2010**, *26*, 367–370. [CrossRef]
- 23. Ding, H.; Liu, X.; Yu, L.; Zhao, G. The influence of forming processes on the distribution and morphologies of TiC in Al-Ti-C master alloys. *Scr. Mater.* 2007, *57*, 575–578. [CrossRef]
- 24. Wu, X. In situ formation by laser cladding of a TiC composite coating with a gradient distribution. *Surf. Coat. Technol.* **1999**, *115*, 111–115. [CrossRef]
- 25. Cong, W.; Ning, F. A fundamental investigation on ultrasonic vibration-assisted laser engineered net shaping of stainless steel. *Int. J. Mach. Tools Manuf.* 2017, 121, 61–69. [CrossRef]
- 26. Wang, H.; Hu, Y.; Ning, F.; Cong, W. Ultrasonic vibration-assisted laser engineered net shaping of Inconel 718 parts: Effects of ultrasonic frequency on microstructural and mechanical properties. *J. Mater. Process. Technol.* **2020**, 276, 468–478. [CrossRef]
- 27. Li, M.; Zhang, Q.; Han, B.; Song, L.; Cui, G.; Yang, J.; Li, J. Microstructure and property of Ni/WC/La2O3 coatings by ultrasonic vibration-assisted laser cladding treatment. *Opt. Lasers Eng.* **2020**, *125*, 105848. [CrossRef]
- 28. Ning, F.; Hu, Y.; Cong, W. Microstructure and mechanical property of TiB reinforced Ti matrix composites fabricated by ultrasonic vibration-assisted laser engineered net shaping. *Rapid Prototyp. J.* **2019**, *25*, 581–591. [CrossRef]
- 29. Noltingk, B.E.; Neppiras, E.A. Cavitation produced by ultrasonics. *Proc. Phys. Soc. Sect. B* **1950**, *63*, 674. [CrossRef]
- 30. Schneider, C.A.; Rasband, W.S.; Eliceiri, K.W. NIH Image to ImageJ: 25 years of image analysis. *Nat. Methods* **2012**, *9*, 671–675. [CrossRef]

- 31. Kacher, J.; Landon, C.; Adams, B.L.; Fullwood, D. Bragg's Law diffraction simulations for electron backscatter diffraction analysis. *Ultramicroscopy* **2009**, *109*, 1148–1156. [CrossRef]
- 32. Ya, B.; Zhou, B.; Yang, H.; Huang, B.; Jia, F.; Zhang, X. Microstructure and mechanical properties of in situ casting TiC/Ti6Al4V composites through adding multi-walled carbon nanotubes. *J. Alloys Compd.* **2015**, *637*, 456–460. [CrossRef]
- Zhang, X.; Song, F.; Wei, Z.; Yang, W.; Dai, Z. Microstructural and mechanical characterization of in-situ TiC/Ti titanium matrix composites fabricated by graphene/Ti sintering reaction. *Mater. Sci. Eng. A* 2017, 705, 153–159. [CrossRef]
- 34. Komarov, S.V.; Kuwabara, M.; Abramov, O.V. High power ultrasonics in pyrometallurgy: Current status and recent development. *ISIJ Int.* 2005, 45, 1765–1782. [CrossRef]
- Chrysanthou, A.; Chen, Y.; Vijayan, A.; O'sullivan, J. Combustion synthesis and subsequent sintering of titanium-matrix composites. J. Mater. Sci. 2003, 38, 2073–2077. [CrossRef]
- 36. Ranganath, S.; Subrahmanyam, J. On the in situ formation of tic and ti2c reinforcements in combustion-assisted synthesis of titanium matrix composites. *Met. Mater. Trans. A* **1996**, 27, 237–240. [CrossRef]
- Wanjara, P.; Drew, R.; Root, J.; Yue, S. Evidence for stable stoichiometric Ti2C at the interface in TiC particulate reinforced Ti alloy composites. *Acta Mater.* 2000, 48, 1443–1450. [CrossRef]
- Yuan, P.; Gu, D.; Dai, D. Particulate migration behavior and its mechanism during selective laser melting of TiC reinforced Al matrix nanocomposites. *Mater. Des.* 2015, 82, 46–55. [CrossRef]
- Li, Y.; Hu, Y.; Cong, W.; Zhi, L.; Guo, Z. Additive manufacturing of alumina using laser engineered net shaping: Effects of deposition variables. *Ceram. Int.* 2017, 43, 7768–7775. [CrossRef]
- Nazari, K.A.; Rashid, R.R.; Palanisamy, S.; Xia, K.; Dargusch, M.S. A novel Ti-Fe composite coating deposited using laser cladding of low cost recycled nano-crystalline titanium powder. *Mater. Lett.* 2018, 229, 301–304. [CrossRef]
- 41. Wang, L.; Felicelli, S.; Gooroochurn, Y.; Wang, P.; Horstemeyer, M. Optimization of the LENS<sup>®</sup> process for steady molten pool size. *Mater. Sci. Eng. A* **2008**, 474, 148–156. [CrossRef]
- 42. Khosrofian, J.M.; Garetz, B. Measurement of a Gaussian laser beam diameter through the direct inversion of knife-edge data. *Appl. Opt.* **1983**, *22*, 3406–3410. [CrossRef]
- 43. Lang, R.J. Ultrasonic atomization of liquids. J. Acoust. Soc. Am. 1962, 34, 6-8. [CrossRef]
- 44. Fan, Z.; Zhao, Y.; Tan, Q.; Mo, N.; Zhang, M.-X.; Lu, M.; Huang, H. Nanostructured Al<sub>2</sub>O<sub>3</sub>-YAG-ZrO<sub>2</sub> ternary eutectic components prepared by laser engineered net shaping. *Acta Mater.* **2019**, *170*, 24–37. [CrossRef]
- 45. Zhang, B.; Li, Y.; Bai, Q. Defect formation mechanisms in selective laser melting: A review. *Chin. J. Mech. Eng.* **2017**, *30*, 515–527. [CrossRef]
- 46. Rashid, R.R.; Palanisamy, S.; Attar, H.; Bermingham, M.; Dargusch, M.S. Metallurgical features of direct laser-deposited Ti6Al4V with trace boron. *J. Manuf. Process.* **2018**, *35*, 651–656. [CrossRef]
- 47. Wang, R.; Gu, D.; Chen, C.; Dai, D.; Ma, C.; Zhang, H. Formation mechanisms of TiB<sub>2</sub> tracks on Ti6Al4V alloy during selective laser melting of ceramic-metal multi-material. *Powder Technol.* **2020**, *367*, 597–607. [CrossRef]
- 48. Shen, Y.-L.; Williams, J.; Piotrowski, G.; Chawla, N.; Guo, Y. Correlation between tensile and indentation behavior of particlereinforced metal matrix composites: An experimental and numerical study. *Acta Mater.* **2001**, *49*, 3219–3229. [CrossRef]
- 49. Liu, P.; Zhang, Y. A theoretical analysis of frictional and defect characteristics of graphene probed by a capped single-walled carbon nanotube. *Carbon* **2011**, *49*, 3687–3697. [CrossRef]
- Yang, J.; Gu, W.; Pan, L.; Song, K.; Chen, X.; Qiu, T. Friction and wear properties of in situ (TiB<sub>2</sub>+ TiC)/Ti<sub>3</sub>SiC<sub>2</sub> composites. *Wear* 2011, 271, 2940–2946. [CrossRef]
- 51. Li, J.; Yu, Z.; Wang, H. Wear behaviors of an (TiB+ TiC)/Ti composite coating fabricated on Ti6Al4V by laser cladding. *Thin Solid Films* **2011**, *519*, 4804–4808. [CrossRef]
- 52. Deng, J.; Liu, L.; Yang, X.; Liu, J.; Sun, J.; Zhao, J. Self-lubrication of Al<sub>2</sub>O<sub>3</sub>/TiC/CaF<sub>2</sub> ceramic composites in sliding wear tests and in machining processes. *Mater. Des.* 2007, *28*, 757–764. [CrossRef]
- 53. Feng, Y.; Zhang, J.; Wang, L.; Zhang, W.; Tian, Y.; Kong, X. Fabrication techniques and cutting performance of micro-textured self-lubricating ceramic cutting tools by in-situ forming of Al<sub>2</sub>O<sub>3</sub>-TiC. *Int. J. Refract. Met. Hard Mater.* **2017**, *68*, 121–129. [CrossRef]