

Article

Microstructure Characterization and Properties of Graphene Oxide-Reinforced TiAl Matrix Composites

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Abstract: TiAl matrix composites reinforced with graphene oxide (GO) were prepared by powder metallurgy technology. The graphene oxide plates were added into TiAl powder by ultrasonic dispersion and milling, and then, shaped by Hot Isostatic Pressing (HIPing). Microstructures of the composites were characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) as well as Raman spectrum were conducted on the composite powder. The thermal and mechanical properties were tested on the TiAl matrix composites. The results show that the compression strength and heat conductivity of the composites can be improved distinctly at both room temperature and high temperature. The heat conductivity coefficient can reach to above 23 W/m K, and the compressive strength can reach to 1700 MPa at room temperature. GO was homogeneously dispersed into TiAl matrix in the form of random film with the diameter less than 10 μm . The minimum thickness of the GO film is about 5 nm. However, The GO does not well represent thermodynamically stable reinforcement at high temperatures, GO existed not only in the form of graphene but also a certain amount of Ti_3AlC , and its size is about 2 μm rather than nanoscale, which can decrease the ductile reinforcement of GO in the TiAl matrix.

Keywords: microstructure; property; composites; graphene oxide; TiAl



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1. Introduction

TiAl alloys are considered to be promising candidates for currently used Ni-based alloys in aerospace and automobile industries because of their outstanding advantages, such as low density, high strength, and excellent oxidation resistance [1–3]. Ti-48Al-2Cr-2Nb alloy has been used for the low-pressure turbine blades of GENx engine for Boeing 787. It is necessary to further enhance the balanced mechanical properties, especially the high-temperature performance. Intermetallic matrix composites may be a way to have a good combination of the properties of intermetallic matrix and reinforcement [4,5].

Graphene is a two-dimensional material, which consists of a single layer of sp²-hybridized carbon atoms with a thickness of 0.34 nm. It has some excellent physical properties, such as very high strength (~130 GPa), high Young's modulus (~1.0 TPa), high thermal conductivity (~5000 W m⁻¹ K⁻¹), and high electronic mobility (~15,000 cm² V⁻¹ s⁻¹) at room temperature [6,7]. Due to the unique 2D structure and outstanding properties, some researchers have performed studies on graphene-reinforced metal matrix; however, investigations show that the higher potential mechanical and thermal properties of graphene in the graphene/metal system is restricted by some problems, the most important being the homogeneous dispersion of graphene, because the large specific surface area of graphene leads to the high agglomeration tendency in the metal matrix. The graphene agglomera-

tions will act as crack-initiation sites during tensile loading, and consequently deteriorate the composite strength [8–11].

Graphene oxide (GO) consisting of oxygen-containing active group have properties similar to those of graphene, but they appear hydrophilic and have better dispersion, compatibility, surfactivity, and wettability [12–14]. So, to overcome the above dispersion problem, in this study, GO was added into TiAl powders by ultrasonic dispersion and milling, and the surface of TiAl powders were sealed with surfactant, which can produce hydroxide radical, and then the active group of carboxide of GO combined with hydroxide radical, forming into H_2O . The mixed powders were shaped by Hot Isostatic Pressing (HIPing) and microstructures of the GO-modified TiAl composites will be characterized and the properties will be tested. The strengthening effect and mechanism of GO-reinforced TiAl composites were discussed. The GO-embedded TiAl matrix principle is shown in Figure 1.

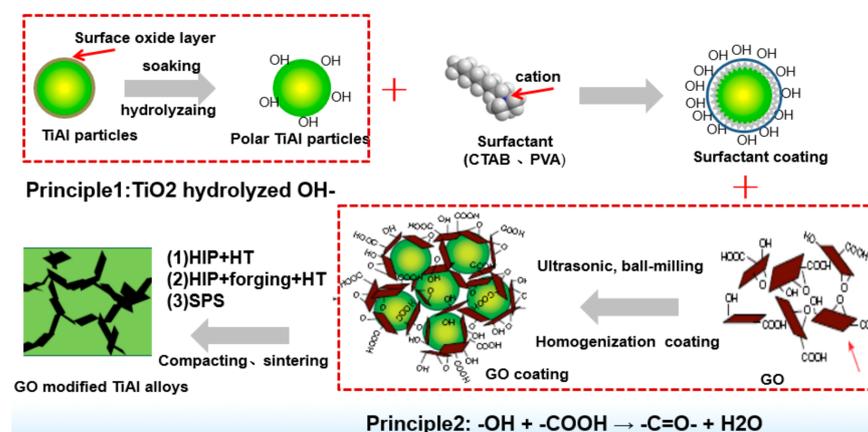


Figure 1. GO-embedded TiAl matrix principle.

2. Materials and Methods

2.1. Preparation of GO-Coated TiAl Powders

Spherical pre-alloy titanium aluminum ($Ti_{48}Al_2Cr_2Nb$) powder with average particle size of 83 μm , graphene oxide (GO), and surfactant, including $C_{19}H_{42}NBr$ (CTAB) and $[C_2H_4O]_n$ (PVA), were used as the original materials. The graphene addition content in this work is 0.4 wt%. The GO-coated TiAl powders were prepared through three steps. First, surfactant was hydrolyzed in the ultrasonic at the temperature of 60 °C, and then the surfactant was mixed with TiAl powder to form the solution in order to modify TiAl powder. Second, the GO was also dispersed by ultrasonic at the temperature of 30 °C for 1 h, then the GO suspension and the TiAl solution were placed together. In order to make the GO distribute homogeneously into the matrix, the mixture was low-energy ball-milled by a ceramic (ZrO_2) pot in a high-purity (>99.99%) argon atmosphere to avoid oxidation. The low-energy ball milling was performed at a rotating speed of 100 rpm for 48 h. Finally, the milling balls (304 stainless-steel) were filtered out and then the surfactant was dried at 500 °C in a vacuum. Three types of TiAl powders, which included original, CTAB-modified, and PVA-modified ones, were subsequently characterized by scanning electron microscopy (SEM) (FEL, New York, NY, USA) and X-ray photoelectron spectroscopy (XPS, Thermo Fay, Los Angeles, CA, USA), as well as Raman spectrum.

2.2. Fabrication and Characterization of GO/TiAl Composites

The GO/TiAl composites were prepared by powder metallurgy. The mixed powder was pressed by HIPing at 1280 °C/170 MPa for 2 h and experienced heat treatment at 900 °C for 4 h respectively, under the protection of argon and vacuum. Microstructures of the composites were characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Hitachi, Tokyo, Japan). X-ray photoelectron

spectroscopy (XPS) as well as Raman spectrum were conducted on the composites. Transmission electron microscopy (TEM) specimens were prepared by an ion milling method. Foil samples with 3 mm diameter and ~ 180 μm thickness were first cut from the as-heated treatment samples. They were ground mechanically to ~ 100 μm in thickness and then thinned with ion milling. TEM tests were performed for phase identification by using a TEM instrument (Tecnai G2 F20; FEI, USA), in which it operated at 200 kV. The GO/TiAl composites were ultrasonicated in alcohol for 40 min and then were attached to a copper ring with ultrathin carbon film for TEM tests. An X-ray photoelectron spectrometer (XPS) was also applied to detect the chemical structure and constituents. An X-ray photoelectron spectrometer (Thermal escalab 250xi; Thermal Electron, Waltham, MA, USA) was operated, in which its best scan spatial resolution is better than 3 μm and the big beam spot is 0.05 eV. Raman analysis was performed in a Raman spectrometer (Renishaw invia, London, UK), where the wavelength of incident laser is 633 nm. The graphene of layers, defects, crystal structure, and phonon band were characterized by the number of frequency, intensity, peak, and half peak width of the Raman spectrum.

2.3. Properties Tests

The thermal and mechanical properties were tested on the TiAl matrix composites and the original TiAl. The compression specimens with a gauge length of 10 mm and diameter of 5 mm were used. The compression tests were respectively conducted at room temperature and five hundred degrees. The heat conductivity and thermal coefficients were tested on the laser thermal conductivity meter (LFA457, Netzsch, Helb, Germany) according to the standards of GB/T22588-2008. The samples size was 12.5 mm in diameter and 2.5 mm in length. The square density specimens with edge length of 10 mm were tested on a precision electronic balance (Startoriorious BSA233S, Hangzhou, China) according to GB/T 1423-1996 by Archimedes principle. For each test condition, the property values depend on the average value of three specimens.

3. Results and Discussion

3.1. Characterization of GO-Coated TiAl Powders

There are three kinds of GO-coated TiAl powders, which are original, CTAB-modified, and PVA-modified ones. SEM images of different GO-coated TiAl powder morphologies are shown in Figure 2. As shown in Figure 2, GO was locally accumulated on the original TiAl powder, while a few GO flakes were distributed on the CTAB-modified one and a lot of GO nanoflakes were observed on the PVA-modified one. The thickness of GO decreases orderly in original, CTAB-modified, and PVA-modified specimens, so the best covered effect of GO is PVA-modified TiAl powders.

In order to make GO disperse more uniformly in TiAl matrix, the GO-coated TiAl powder by the PVA-modified specimen was milled. It is shown that GO appears as a very thin film on the powder surface after milling. The spectra of XPS analysis of GO-coated PVA-modified TiAl powder is illustrated in Figure 3. According to the literature [12], the peak position of GO is mainly as follows:

C=C peak: 284.6 ± 0.1 eV

C-C peak: 285.5 ± 0.1 eV

C-O peak: 286.9 ± 0.1 eV

C=O peak: 288.2 ± 0.1 eV

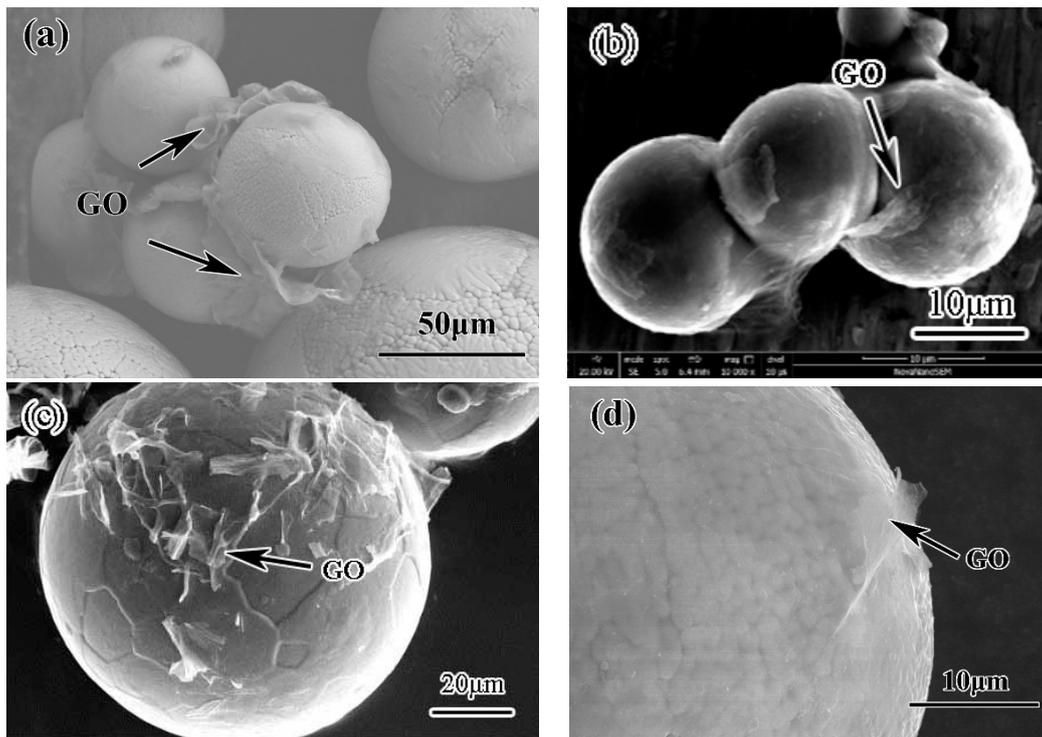


Figure 2. Scanning electron microscopy (SEM) images of the graphene oxide (GO)-coated TiAl powders: (a) original, (b) CTAB-modified, (c) PVA-modified, and (d) milled by PVA-modified.

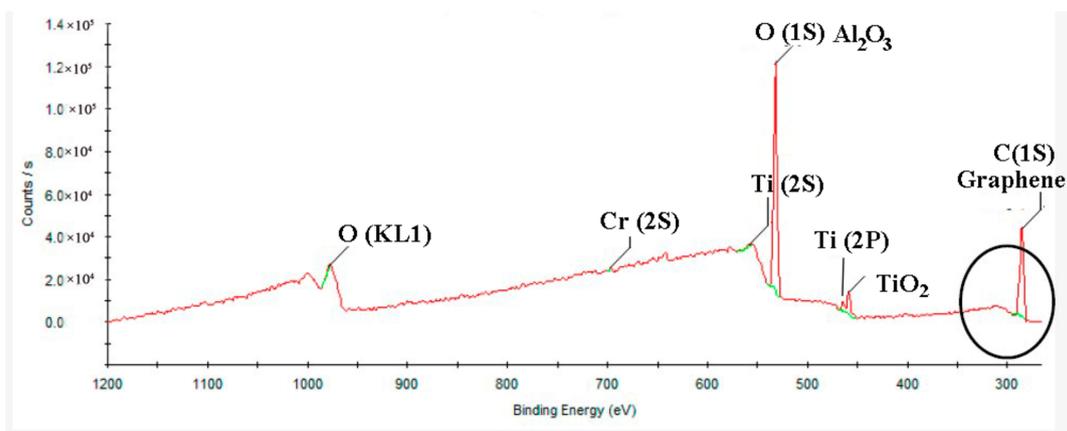


Figure 3. X-ray photoelectron spectroscopy (XPS) diagram of the GO-coated TiAl powders milled by the PVA-modified specimen.

The composite powders mainly contain Ti, C, O, and Cr elements, the Ti and Cr peaks are weak, but the C and O peak signals are stronger. The C/O element exists in C–C, C=O, and O–C=O bonds in TiAl powder surface, as shown in Figure 3. It can be confirmed that the surface of TiAl powder was coated by GO. In order to further analyze the layers of GO, Raman spectrum was used to perform on the powder samples. As shown in Figure 4, a G peak appears near 1598 cm^{-1} , which suggests that there are more than three layers of GO. A D peak appears near 1350 cm^{-1} , which indicates there are defects in the GO. From the above, it is proposed that the ultrasonic and milling can realize the GO flakes uniformly dispersed in the TiAl powders and still keep the C–C, C=O, and O–C=O bonds after undergoing a series of treatments.

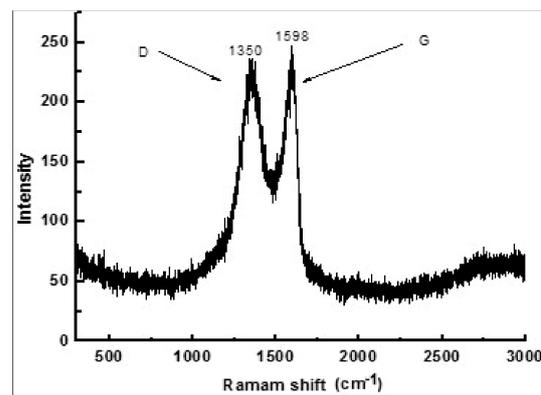


Figure 4. Raman spectrum of the GO-coated TiAl powders milled by the PVA-modified specimen.

3.2. Microstructure of GO/TiAl Composites

SEM images of the GO/TiAl composites after HIPing are presented in Figure 5. As shown in Figure 5a, there are dark grey phases and bright white phases in the matrix, and the dark grey exist in the form of a thin film. The dark grey phase dispersed homogeneously in the matrix, and parts of the bright white phase distributed near the dark grey phase. The morphology of grey phase was further observed. As shown in Figure 5b, the thin film size is less than 10 μm , and the grey phase appears in irregular shapes. It is preliminarily presumed that the dark grey phase in the form of thin film is GO.

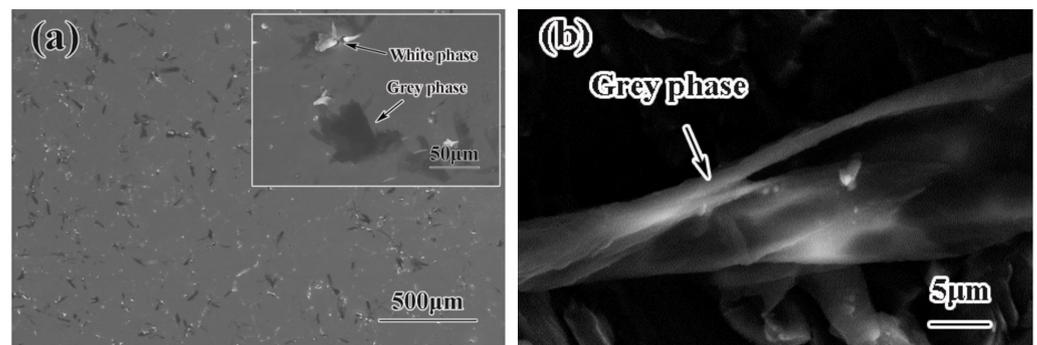


Figure 5. SEM images of GO/TiAl composites. (a) at low magnification. (b) at high magnification.

In order to further verify the dark grey phase in the form of thin film, the film region was processed into a TEM sample. During the process of sample preparation, thinning and double electrolytic can keep the integrity of the phase. TEM diffraction and high resolution were used. As shown in Figure 6, the dark grey phase spread out in the spatial distribution and its local areas are displayed as folded and curled. The thinnest place width of graphene oxide in the composite is about 5 nm.

Figure 7a,b shows SEM images of the white precipitate phase in the GO/TiAl composites at different magnifications. As shown in Figure 7a, the white phase precipitated along the original TiAl powder grain boundary in the mesh distribution feature. The red arrows in Figure 7b show that one part of the white phase presents in long strips and the others parts exhibit in spherical particles. These white phases can preliminarily be presumed to be carbides.

TEM diffraction images of the white precipitate phase in the GO/TiAl composites are shown in Figure 8a. The transformation process of the white phase was assessed by TEM diffraction. According to the diffraction spot calibration, it is confirmed that the white precipitated phase is Ti_3AlC phase, and the matrix is $\gamma\text{-TiAl}$ phase, and they are shown in Figure 8b,c. It is suggested that some parts of GO have reacted with the matrix boundary during HIPing, resulting in the formation of some carbide particles in the

GO/TiAl composites. Therefore, it is proposed that some of the GO exists in the thin film that can react into Ti_3AlC phase.

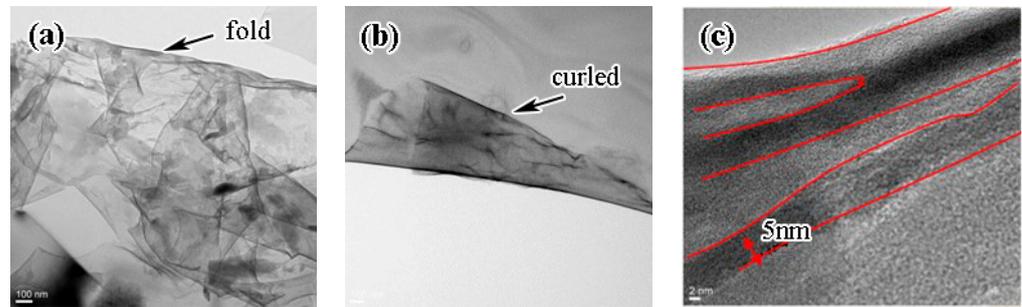


Figure 6. Transmission electron microscopy (TEM) images of the dark grey phase in the GO/TiAl composites. (a) shape of fold (b) shape of curled (c) the width of GO.

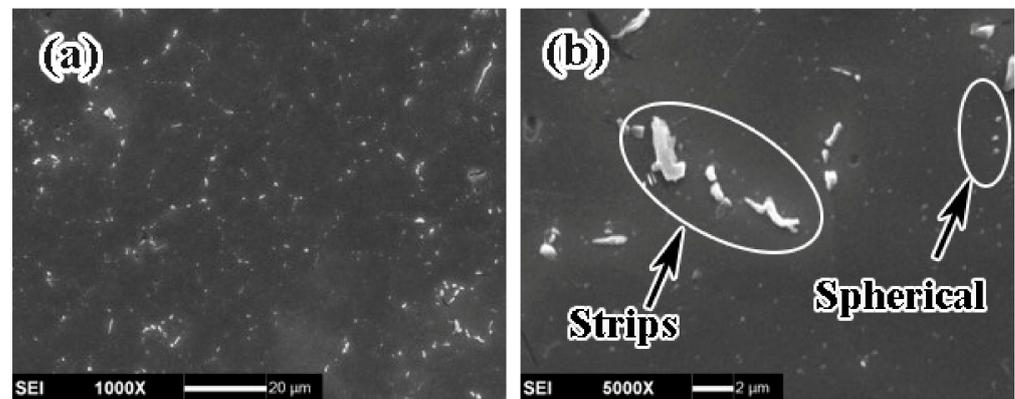


Figure 7. SEM images of the white precipitate phase in the GO/TiAl composites. (a) 1000 multiple. (b) 5000 multiple of sample.

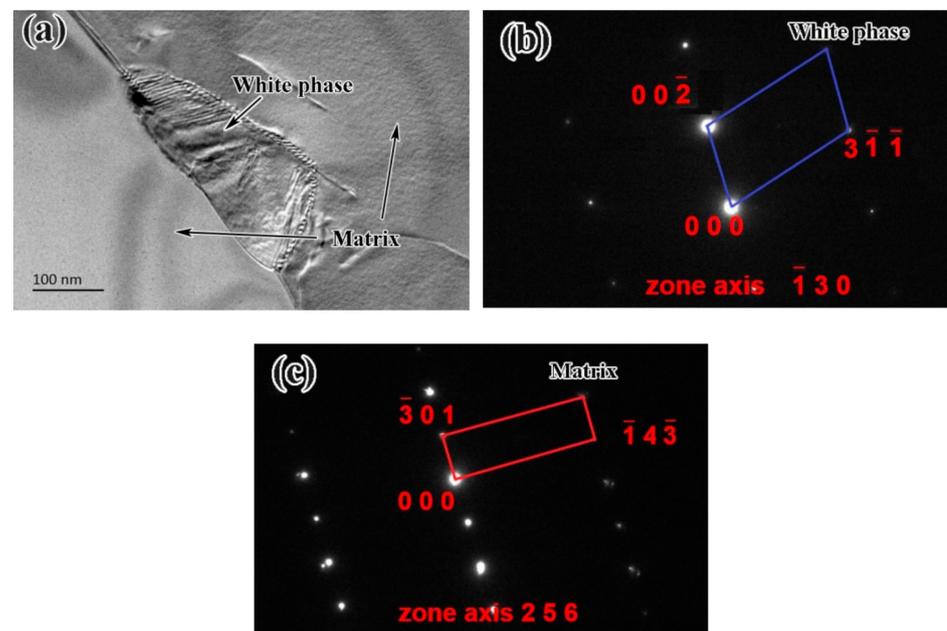


Figure 8. TEM images of the white precipitate phase in the GO/TiAl composites. (a) high resolution of white phase. (b) diffraction spot calibration of white phase. (c) and Matrix.

3.3. Properties of GO/TiAl Composites

The addition of GO has some positive effects on the mechanical properties of the TiAl matrix. In our previous research work, we found that the tensile performance of GO/TiAl composite has a brittle fracture before yielding, which cannot illustrate the effect of graphene oxide on the intrinsic ductility of TiAl alloy, so this is the major reason why we investigated the compressive properties of GO/TiAl composites in the paper. The compression properties of the GO/TiAl composites and original TiAl materials are shown in Figure 9. The materials were tested at room temperature and 550, 750, and 850 °C, respectively. As shown in Figure 9a,b, the compressive strength, R_{mc} , and compressive yield strength, $R_{pc0.2}$, of the GO/TiAl composites are all larger than that of the original TiAl at both RT and other temperatures due to the GO modification. At room temperature, the true strain and compressive strength, R_{mc} , of the GO/TiAl composites can separately reach 0.49 and 1700 MPa. The compressive yield strength of the GO/TiAl is approximately 200 MPa higher than that of the original TiAl with no GO at room temperature. When the temperature increases to 850 °C, the true strain of the GO/TiAl composite is 0.69, and the compressive yield strength of the GO/TiAl composite is also approximately 100 MPa higher than the TiAl with no GO. However, the compressive deformation curves reported in this paper show that the composite GO/TiAl is brittle at temperatures ranging from RT to 850 °C (Figure 9) compared to carbide-reinforced TiAl-based matrix composites [15]. The room temperature compression deformation of carbide-reinforced TiAl-based matrix composites of the GO/TiAl composite shows only about 0.5%.

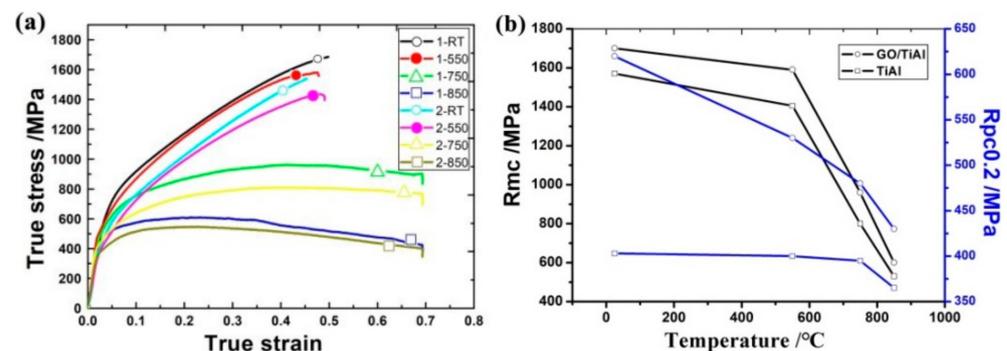


Figure 9. Compression properties of the TiAl and GO/TiAl: (a) true stress–true strain curve, in which No.1 is GO/TiAl and No.2 is TiAl, and (b) dependences of R_{mc} and $R_{pc0.2}$ on temperature.

The reason may be that GO existed in the form of graphene and Ti_3AlC in this study, so the reinforcement introduced to TiAl alloys to improve their high-temperature mechanical properties was analyzed from two aspects. On the one hand, the GO as a reinforced phase can cause dislocation pile-up and sliding stop to propagate and extend, which made the materials withstand greater loads, and then increased the compressive yield strength. On the other hand, the GO does not better represent thermodynamically stable reinforcement at high temperatures. The results show that a large amount of carbide particles are formed along the grain boundaries. It means that the GO particles are unstable, and they are decomposed to carbon and oxygen during HIPing and annealing. Carbon reacts with Ti and Al and forms Ti_3AlC particles, and its size is about 2 μm rather than nanoscale, which can decrease the GO-reinforced effects.

GO modification can also contribute to the physical properties of the TiAl matrix. Table 1 summarizes the heat conductivity coefficient, thermal diffusion coefficient, and density at different temperatures. As shown in Table 1, the heat conductivity coefficient and thermal diffusion coefficient of the composites can be simultaneously improved distinctly at both room temperature (RT) and high temperature. Only the density is increased slightly because of a little content of GO addition.

Table 1. Physical properties of the TiAl and GO/TiAl.

Materials	Temperature (°C)	Heat Conductivity Coefficient (W/m K)	Thermal Diffusion Coefficient (m ² /s)	Density (g/cm ³)
GO/TiAl	Room Temp.	15.65	6.35	3.982
	500 °C	23.79	8.07	-
TiAl	Room Temp.	14.62	5.86	3.976
	500 °C	22.62	7.97	-

4. Discussion

Graphene-reinforced metal matrix composites are difficult to realize when mixing in nanoscale, which impacts on the interface reaction and enhanced phase structure, eventually leading to the advantage of compound materials—not obviously—thus realizing that graphene sheet distributed uniformly in the metal matrix is still the key factor influencing the performance of composites. The electrochemical deposition method can achieve graphene evenly distributed in nanoscale, and keep the graphene's two-dimensional structure, but it is difficult to obtain dense large size materials. Graphene will react with the titanium substrate at high temperature to form titanium carbide phase, so the methods of thermal spraying also limited sample size and the interface reaction control. The reinforced phase and matrix were mixed in the molten state, which can enhance the reinforced phase evenly distributed in the matrix but cannot control the reaction. Solid mixture can avoid it by adjusting the processing temperature but has poor uniformity [6].

In this work, graphene can be dispersed uniformly in the TiAl-based materials with the experimental data, as shown in Figure 2d. The principles are as follows: GO was added into TiAl powders by ultrasonic dispersion and milling and the surface of TiAl powders were covered with surfactant, which can produce hydroxide radical, and then the active group of carboxide of GO combined with hydroxide radical, forming into H₂O. However, it is necessary to prove whether there is a limit of the GO dispersion in the TiAl matrix with different content, and the observation and mechanical tests of GO/TiAl composite with different GO volume fractions will be investigated in the next works.

The reinforcement introduced to TiAl alloys to improve their high-temperature mechanical properties was analyzed from two aspects. On the one hand, the GO as a reinforced phase can cause dislocation pile-up and sliding stop to propagate and extend, which made the materials able to withstand greater loads, and then to increase the compressive yield strength. On the other hand, the GO does not represent better thermodynamically stable reinforcement at high temperatures. The results show that a large amount of carbide particles are formed along the grain boundaries. It means that the GO particles are unstable, and they are decomposed to carbon and oxygen during HIPing and annealing. Carbon reacts with Ti and Al and forms Ti₃AlC particles, and its size is about 2 μm rather than nanoscale, which can decrease the GO-reinforced effects.

Improvement of the thermodynamic stability of GO is needed to realize the full potential of the GO/TiAl composites developed in this work. The reaction between graphene and TiAl matrix can limit the reinforced effect. Therefore, trying to protect the surface of GO and decrease the processing temperature is the key issue to deal with in the next study of manufactured materials.

5. Conclusions

- The forms of GO/TiAl powders' bonding are C–C, C–O, and O–C=O. The defects are observed in GO, and there are more than 3 layers of GO produced in the composites.
- GO can be homogeneously dispersed into TiAl matrix in the form of random film with the diameter less than 10 μm. The minimum thickness of the GO film is about 5 nm.
- The compression strength and heat conductivity of the composites can be improved distinctly at both room temperature and high temperature. In the GO/TiAl composites, the heat conductivity coefficient can reach to above 23 W/m K, and the compressive strength can reach to 1700 MPa at room temperature.

- The GO does not well represent thermodynamically stable reinforcement at high temperatures, a certain amount of Ti_3AlC is formed along the grain boundaries, and its size is about 2 μm rather than nanoscale, which can decrease the ductile reinforcement of GO in the TiAl matrix.

Author Contributions: Z.S. designed research and made chart and analyzed data and wrote manuscript; L.Z. searched literature; X.M. collected data; X.D. revised manuscript; H.N. provided financial and equipment support for experiment. All authors have read and agreed to the published version of the manuscript.

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References

1. Kim, Y.-W. Ordered intermetallic alloy, parts: Gamma titanium aluminides. *JOM* **1994**, *46*, 30–39. [[CrossRef](#)]
2. Kim, Y.-W. *Gamma Titanium Aluminides*; TMS: Warrendale, PA, USA, 1995; p. 637.
3. Thomas, M.; Raviart, J.L.; Popoff, F. Cast and PM Processing development in gamma titanium aluminides. *Intermetallics* **2005**, *13*, 944–951. [[CrossRef](#)]
4. Rao, K.P.; Vyas, A. Comparison of titanium silicide and carbide reinforced in situ synthesized TiAl composites and their mechanical properties. *Intermetallics* **2011**, *19*, 1236–1242. [[CrossRef](#)]
5. Lapin, L.; Štamborská, M.; Kamyshnykova, K.; Pelachová, T.; Klimová, A.; Bajana, O. Room temperature mechanical behavior of cast in-situ TiAl matrix composite reinforced with carbide particles. *Intermetallics* **2019**, *105*, 113–123. [[CrossRef](#)]
6. Sun, F.; Wang, K.; Yang, H.; Shi, Y.; Yang, J.; Lou, M. Investigation of graphene reinforced titanium matrix composites preparation process and properties. *Titan. Ind. Prog.* **2019**, *36*, 8–12.
7. Cao, Z.; Wang, X.; Li, J. Reinforcement with graphene nanoflakes in titanium matrix composites. *J. Alloys Compd.* **2017**, *6*, 498–502. [[CrossRef](#)]
8. Zhang, L.P. Properties analysis and preparation with grapheme magnesium matrix composite in sports equipment. *Hot Work. Technol.* **2015**, *44*, 140–142.
9. Luo, J.; Jiang, S.; Zhang, H. A novel non_enzymatic glu-cose sensor based on Cu nanoparticle modified graphene sheets electrode. *Anal. Chim. Acta* **2011**, *709*, 47.
10. Bastwros, M.; Kim, G.Y.; Zhu, C.; Zhang, K.; Wang, S.; Tang, X.; Wang, X. Effect of ball milling on graphene reinforced Al6061 composite fabricated by semi-solid sintering. *Composites* **2014**, *60*, 111–118. [[CrossRef](#)]
11. Guo, J.; Yuan, X. *Study on Preparation of CNTs/TiAl Alloy. Composites by Hot Pressed Sintering*; Anhui University of Technology: Maanshan, China, 2016; pp. 4–16.
12. Rafieerad, A.R.; Bushroa, A.R. Graphene Oxide Modifide Anodic Ternary Nanobioceramics on Ti6Al7Nb Alloy for orthopedic and dental application. *Procedia Eng.* **2017**, *4*, 409–417. [[CrossRef](#)]
13. Song, X.L.; Wang, H.B.; Wu, X.L. Research and development of dispersion technique for nanoparticles. *Chem. Ind. Eng. Prog.* **2005**, *24*, 47–52.
14. Yang, L.; Wang, L.; Ren, S.; Che, W. Research on mechanical of graphene reinforced TiAl self-lubricating composite materials. *J. Mech. Strength* **2019**, *41*, 1085–1089.
15. Li, M. *Effect of Boron of Carbon on the High. Temperature Feformation Microstructure of TiAl Alloy*; Harbin Institute of Techonology: Harbin, China, 2019.