Rare Metal Materials and Engineering
Volume 49, Issue 7, July 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(7): 2275-2280.

ARTICLE

Effects of Al_2O_3/ZrO_2 Layers on Carbon Steel Capsule During Consolidation of TiAl Based Alloy Powders by HIP

Lang Zebao[1,2], Zhang Yongzhong[2], Wang Liang[1], Zhang Xuhu[1]

[1] *Division of Special Metals & Processing, Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, China;*
[2] *Composite Center of General Institute of Nonferrous Metals, Beijing 100088, China*

Abstract: In order to ensure reliability of the carbon steel capsule, Al_2O_3-ZrO_2 (A-Z) layers were added to the inside wall of the 20# carbon steel capsule via thermal spraying. In the HIP experiment, the capsule with A-Z layers was used to consolidate Ti-46Al-2Cr-2Nb-(W, B) pre-alloyed powders at 1523 K and 130 MPa for 2.5 h, and then treated via HIP at 1603 K and 130 MPa for 0.5 h. To compare, the 20# carbon steel without A-Z layers was formed via processing of Ti-46Al-2Cr-2Nb-(W, B) pre-alloyed powders at 1523 K and 130 MPa for 3 h. The as-formed HIPed capsules were observed by SEM and EDS to evaluate the effects of A-Z layers. The test results reveal that the formation of brittle intermetallics is prevented upon addition of A-Z layers. During HIP, iron atoms of 20# carbon steel capsule cannot meet titanium and aluminum atoms in the TiAl based alloy powders by diffusion, hence the reliability of 20# carbon steel capsules is achieved. In addition, the compactly processed capsule of TiAl based alloy with A-Z layers is fully consolidated and it exhibits a fine, nearly full lamellar microstructure. The tensile strength and elongation of the compact at room temperature surpass 590 MPa and 2.0%, respectively.

Key words: interface reaction; Al_2O_3-ZrO_2 layers (A-Z); TiAl based alloy powders; hot isostatic pressing; microstructure; tensile properties

TiAl based alloy has been in research hotspot owing to its great mechanical strength and excellent oxidation resistant properties at high temperature[1-3]. However, TiAl based alloy has strong brittleness at room temperature, which makes it difficult to machine and form. A fully condensed compact form of TiAl based alloy can be obtained from HIP pre-alloyed powders. With proper parameters of HIP, the compact form can exhibit fine and even microstructures and be used as raw material for secondary processing or directly formed into components of the final size [4-8].

The common materials for capsule for densification of TiAl based alloy powder include pure titanium and carbon steels. Pure titanium capsule has high temperature resistance and would coexist safely with TiAl based alloy powders below 1673 K. However, the cost of pure titanium is high and the welding requires complex protection. Carbon steel is cheap, and can be removed via chemical machining and other methods after HIP. Therefore, it is suitable for forming components with complex shapes. However, carbon steel has low temperature resistance and reacts with TiAl based alloy powders at about 1533 K, which can destroy gas tightness of the capsule[9]. In the casting process of TiAl based alloy, coatings of ZrO_2, Al_2O_3, and other ceramics are often used to prevent diffusion between the titanium alloy and casting molds [10, 11]. Liu had used Al_2O_3 to make core molds for forming powder metallurgy (PM) TiAl based alloy components[12]. However, compared with metal molds, ceramic molds with large wall thickness have relatively more shielding effect towards external pressure from HIP, which may lead to uneven shrinkage of the components during HIP. In this work, 20# carbon steel capsules were used to condense TiAl based alloy powders at 1523 K and evaluate the reaction with TiAl based alloy powders. In further experiments, A-Z layers were added to inside-wall

Received date: July 25, 2019
Corresponding author: Lang Zebao, Candidate for Ph. D., Senior Engineer, Division of Special Metals and Processing, Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, P. R. China, Tel: 0086-10-68380666, E-mail: lzb0413@sina.com

of the capsule, and TiAl based alloy powders loaded in treated capsules were processed at 1603 K in order to study the effect of A-Z layers between 20# carbon steel capsule and TiAl based alloy.

1 Experiment

The chemical composition of materials used in the experiments are shown in Table 1. At the beginning of the experiment, TiAl based alloy powder was prepared via a rotating electrode method. The transforming temperature of α phase for the alloy was tested by differential scanning calorimetry (DSC) and estimated to be about 1583 K. TiAl based alloy powder was first packed into 20# carbon steel capsule and degassed at 773~873 K. After holding for 2 h, the capsule was sealed and processed in QIH-32 HIP machine at 1523 K and 130 MPa for 3 h.

In the contrast experiments, A-Z layers were added to inside-wall of 20# carbon steel capsule via thermal spraying. Therefore, TiAl based alloy powders were filled in the treated capsule, and degassed at 773~873 K. After holding for 2 h, the capsule was sealed and condensed with two steps of HIP. The process of treatment was as follows. First, the treatment was performed at 1523 K and 130 MPa for 2.5 h and then at 1603 K and 130 MPa for 0.5 h. There was no cooling between the two steps of HIP treatment.

Compacts obtained in the above experiment were observed and evaluated by scanning electron microscopy and other equipments to investigate the effect of A-Z layers.

2 Results and Discussion

2.1 Characteristics of TiAl based alloy powders

TiAl based alloy powders were observed under a scanning electron microscope and the results are shown in Fig.1. As shown in Fig.1a, the shape of TiAl based alloy powder is mostly spherical and only a little amount of powder has an ellipsoidal shape. Fig.1b has revealed the microstructure of the powders. There are equiaxed grains on the surface and dendritic grains in the interior of the powder. The reason for formation of the observed microstructure lies in the high cooling speed during the powder manufacturing. The gap between the equiaxed grains has not yet been filled by molten metal and the cooling process is completed; hence, there are small gaps at their boundaries.

2.2 Microstructure of TiAl based alloy compact gained at single step HIP at 1523 K

The reaction between the 20# carbon steel capsule and TiAl based alloy in the compact was observed and results are shown in Fig.2. As shown, the width of diffusion zone between TiAl based alloy and 20# carbon steel capsule was about 100 μm. There were several micro-cracks and micro-voids in the diffusion zone. Wu showed that the diffusion zone at the edge of TiAl based alloy is primarily composed of brittle intermetallics such as Ti_xFe_y and Fe_xAl_y[9]. The higher temperature and longer holding time of HIP can result in a wider diffusion zone in the TiAl based alloy compact. Wu[9] also found that when the HIP temperature reached 1533 K, the width of the diffusion zone increased to about 2 mm. These micro-cracks and micro-voids can reduce the compactness of TiAl based alloy compact. If the HIP temperature

Table 1 Chemical composition of materials used in the experiments (wt%)

Material	Fe	C	Si	Mn	Cr	Ni	Cu	P	S	Ti	Al	Nb	W	B
20# carbon steel	Base	0.22	0.28	0.36	0.20	0.18	0.10	0.03	0.03	-	-	-	-	-
TiAl based alloy	-	-	-	-	2.80	-	-	-	-	Base	32.42	4.46	0.45	0.14

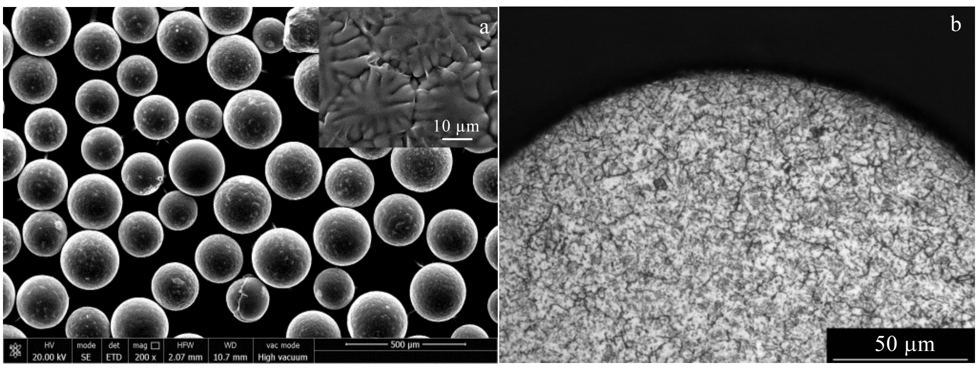

Fig.1 SEM images of TiAl based alloy powder: (a) shape of the powder and (b) microstructure of the powder

is high enough and the holding time is long enough, the compactness of TiAl based alloy may decrease to 90%.

In addition, after HIP treatment at 1523 K for 3 h, many micro-voids also appeared in 20# carbon steel capsule (see Fig.3). If the temperature and holding time of HIP treatment reaches certain values, micro-voids in 20# carbon steel would form a through channel from outside to TiAl based alloy powders, which would provide an insufficient pressure to the powder and lead to deficiency in compactness of the TiAl based alloy.

To determine the composition of the diffusion zone, the atomic distribution of titanium, aluminum, and iron was observed under electron probe in the direction from TiAl based alloy to 20# carbon steel. The results are shown in Fig.4 and reveal that the compositions of titanium and aluminum atoms reduce from the direction of TiAl based alloy compact towards the 20# carbon steel capsule. In the diffusion zone, the composition of these atoms decrease linearly. At the edge of diffusion zone and 20# carbon steel capsule, the composition of titanium and aluminum atoms decrease drastically. However, in the same direction, the iron composition increases gradually. In the diffusion zone, the iron composition increases sharply. But in the diffusion zone near 20# carbon steel, the iron composition decreases. The iron composition reaches the highest in the 20# carbon steel capsule. Therefore, atoms of titanium and aluminum meet iron atoms in the diffusion zone. According to the binary phase diagrams of Ti-Fe and Al-Fe, brittle intermetallics of Ti_xFe_y and Fe_xAl_y should be formed in the diffusion zone.

2.3 Microstructures of A-Z layers before HIP

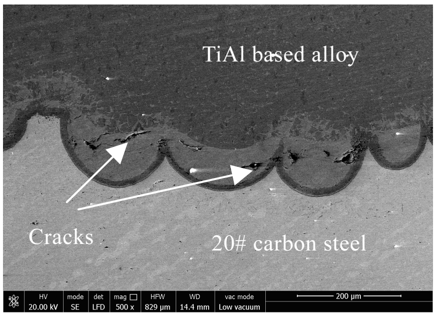

Fig.2 SEM image of the diffusion region between 20# carbon steel capsule and P/M TiAl based alloy compacts after HIP at 1523 K

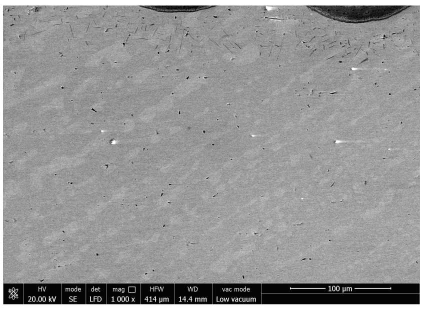

Fig.3 SEM image of HIPed 20# carbon steel capsule processed at 1523 K and 130 MPa for 3 h

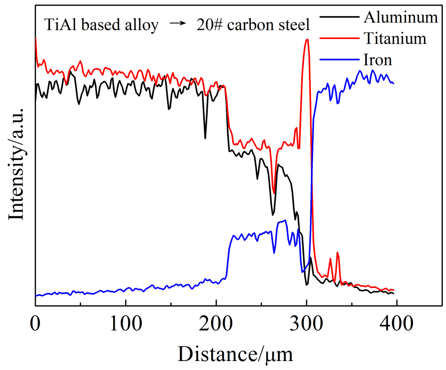

Fig.4 Element distribution of titanium, aluminum, and iron in the diffusion region formed due to HIP at 1523 K for 3 h

In the contrast experiments, before HIP treatment, A-Z layers were added to the inside-wall of 20# carbon steel capsule via thermal spraying. Microstructures of A-Z layers were observed by scanning electron microscopy and the results are shown in Fig.5. Fig.5a shows that there are several cracks on the surface of A-Z layers. However, the width of these cracks is smaller than that of the TiAl based alloy powders. Fig.5b shows the section of A-Z layers and reveal that the first layer added on 20# carbon steel capsule is ZrO_2 layer of width of about 170 μm, and then, about 40 μm thick Al_2O_3 layer is added on the surface of the ZrO_2 layer. The order of spraying is primarily due to the similar thermal expansivity of Al_2O_3 and TiAl based alloy. Multiple defects such as cracks and voids are also found in the section of A-Z layers, but the size of these defects is extremely small and no through-channel is found. TiAl based alloy powders can not pass through the A-Z layers.

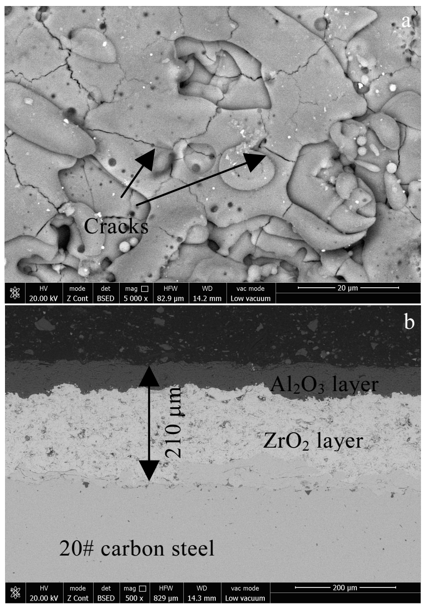

Fig.5 SEM images of A-Z layers thermal sprayed on the 20# carbon steel capsule before HIP: (a) surface of A-Z layers and (b) section of A-Z layers

2.4 Microstructure of TiAl based alloy compact obtained with two steps of HIP at 1523 and 1603 K

Samples were taken from the compact obtained at two steps of HIP and observed under scanning electron microscopy. The results are shown in Fig.6. There are no cracks or micro-voids in the TiAl based alloy and 20# carbon steel capsule. After two steps of HIP, width of A-Z layers was reduced to 117 μm and some cracks were found at the edge of ZrO_2 layer. However, boundaries of 20# carbon steel, A-Z layer, and TiAl based alloy were clear and no diffusion zone were formed.

The atomic distribution of titanium, aluminum, zirconium, and iron was observed under electron probe in the direction from TiAl based alloy to 20# carbon steel. The results are shown in Fig.7. As shown, the distribution of those atoms is different. In the direction from TiAl based alloy to 20# carbon steel, the aluminum composition increased sharply. In the zone of ZrO_2 layer, the aluminum composition fluctuated and reduced to a small range in the zone of 20# carbon steel. In the case of titanium, composition of the atoms decreases to an extremely small range in zone of Al_2O_3 layer. Also, we can conclude that there was no reaction between the Al_2O_3 layer and TiAl based alloy during the two steps of HIP. In the case of zirconium and iron atoms, zirconium can only be found in the zone of ZrO_2 layer and iron could only be found in the 20# carbon steel zone. Therefore, during two steps of HIP at 1523 and 1603 K, atoms of titanium, aluminum, zirconium, and iron cannot move through A-Z layers by diffusion, and brittle intermetallics such as Ti_xFe_y and Fe_xAl_y could not be formed. These observations correspondingly ensure the reliability of the capsule during HIP treatment.

2.5 Microstructure and tensile properties of P/M TiAl based alloy obtained from single step and two steps of HIP

Microstructure of P/M TiAl based alloy obtained from experiments was observed and results are shown in Fig.8. Fig.8a shows the microstructure of P/M TiAl based alloy obtained from single step of HIP at 1523 K. The alloy was composed of white α_2 phase and grey ($\alpha_2+\gamma$) lamellar grains. Fig.8b exhibits a nearly full lamellar microstructure of P/M

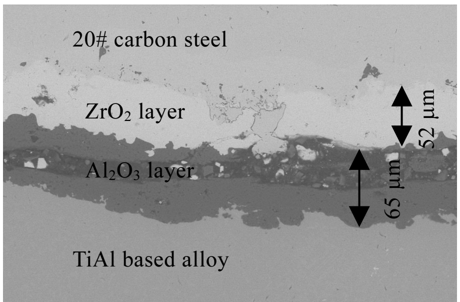

Fig.6 SEM images of the compact obtained at two steps of HIP at 1523 and 1603 K

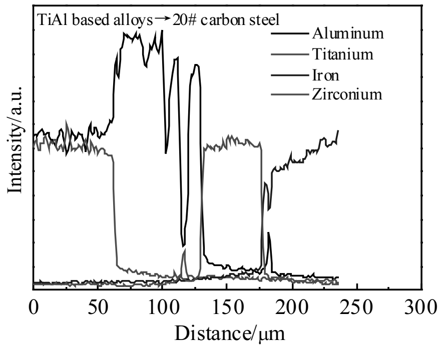

Fig.7 EDS element distributions of titanium, aluminum, zirconium, and iron in the compact gained in two steps of HIP at 1523 and 1603 K

TiAl based alloy obtained after two steps of HIP at 1523 and 1603 K. The alloy gained after two steps of HIP consists of two kinds of grains. The lamellar grains take up most of the area of the alloy and only an extremely small amount of α_2 grains can be found in the boundary of lamellar grains. The grain size of the alloy is about 39 μm.

In the traditional theory of heat treatment for TiAl based alloy, a full lamellar microstructure can be gained via heating to a temperature above α phase transformation temperature for 0.5 h and furnace-cooling to room temperature[13]. However, a nearly full lamellar microstructure was obtained after two steps of HIP at 1523 and 1603 K, and a few α_2 grains remain

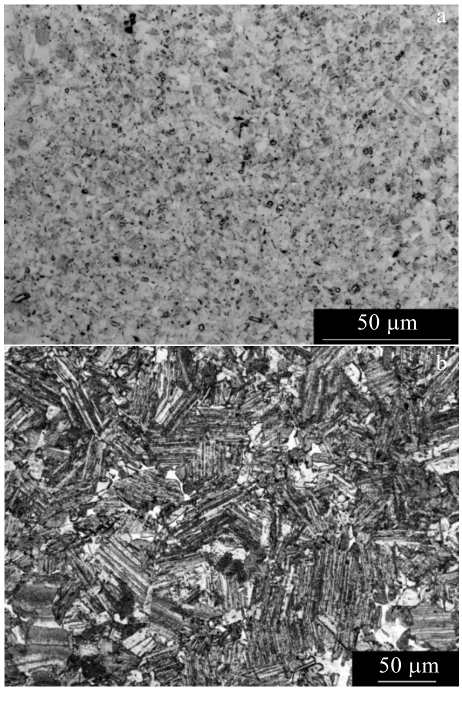

Fig.8 OM images of P/M TiAl based alloy gained by HIP: (a) single step of HIP at 1523 K and (b) two steps of HIP at 1523 and 1603 K

after HIP treatment. The study of Huang and Cao reveal that the external pressure has a significant effect on the phase transformation temperatures of the alloy and the relationship can be described as follows [14, 15]:

$$\frac{\mathrm{d}T_e}{\mathrm{d}P}=\frac{\Delta V T_e}{\Delta H} \tag{1}$$

where T_e is the equilibrium temperature, $\triangle V$ is the molar volume variation, $\triangle H$ is the enthalpy of the transformation, P is the external pressure. To estimate the effect of HIP pressure on the transformation temperature of $\gamma\rightarrow\alpha$ for TiAl based alloy, α/γ unit cell information was analyzed via XRD and results are presented in Table 2. Variation of volume in the transformation of $\gamma\rightarrow\alpha$ is about 2.1×10^{-4} nm^3. The transformation energy of $\gamma\rightarrow\alpha$ is about 15121 J/mol, and then the effect of external pressure on the transforming temperature is:

$$\frac{\mathrm{d}T_e}{\mathrm{d}P}=0.22\ \mathrm{K/MPa} \tag{2}$$

Therefore, if Ti-46Al-2Cr-2Nb-0.2W-0.4B (at%) is treated with 130 MPa, the transforming temperature of $\gamma\rightarrow\alpha$ would increase by 28.6 K. In other words, under the external pressure of 130 MPa, the transforming temperature of α phase would increase to 1611.6 K. Hence, TiAl based alloy treated with two steps of HIP at 1523 and 1603 K exhibits a nearly full lamellar microstructure.

The tensile properties of P/M Ti-46Al-2Cr-2Nb-0.2W-0.4B obtained after single and two steps of HIP were tested at room temperature and the results are shown as Table 3. As shown in Table 3, the tensile strength of P/M Ti-46Al-2Cr-2Nb-0.2W-0.4B fluctuated greatly after single step of HIP at 1523 K, and no data such as yield strength were obtained. This is because owing to a huge difference between the HIP temperature and transforming temperature of phase, less lamellar grains were formed at low HIP temperatures, leading to a poor plasticity of P/M TiAl based alloy. However, TiAl based alloy obtained after two steps of HIP at 1523 and 1603 K shows good comprehensive properties. The tensile strength is 592~617 MPa while the elongation is 2.0%~2.5%. This is because HIP temperature is close to transforming temperature of phase, and the microstructure of the alloy is a nearly full lamellar one, which result in a high tensile strength and a good elongation at room temperature.

Table 2 Dimensions of unit cells and corresponding atomic volumes of Ti-46Al-2Cr-2Nb-0.2W-0.4B (at%)

Parameter	α	γ
c/nm	0.4636	0.4085
a/nm	0.2885	0.4020
Atomic volume/nm^3	1.671×10^{-2}	1.650×10^{-2}

Table 3 Tensile properties of Ti-46Al-2Cr-2Nb-0.2W-0.4B at room temperature

Process	Tensile strength/ MPa	Yield strength/ MPa	Elongation/ %	Shrinkage/ %
Single step of HIP at 1523 K	561	-	-	-
	606	-	-	-
	437	-	-	-
Two steps of HIP at 1523 and 1603 K	617	449	2.5	4.0
	592	450	2.0	1.0
	603	491	2.0	2.0

Note: Test bar cracked before plastic deformation and no data about yield strength, elongation, and shrinkage can be obtained

3 Conclusions

1) Using 20# carbon steel capsule, a completely condensed compact of TiAl based alloy can be obtained after a single step of HIP at 1523 K. However, brittle intermetallics such as Ti_xFe_y and Fe_xAl_y are formed in the diffusion zone between the TiAl based alloy and carbon steel capsule, and several micro-cracks and micro-voids could be found at the edge of the TiAl based alloy. In addition, micro-voids are also formed in the 20# carbon steel capsule.

2) Addition of A-Z layers to inside-wall of 20# carbon steel capsule can effectively prevent the atomic diffusion of titanium, aluminum, zirconium, and iron. Therefore, brittle intermetallics such as Ti_xFe_y and Fe_xAl_y are not found in the compacts. The reliability of 20# carbon steel capsule can be ensured even when the HIP temperature is raised to 1603 K.

3) Due to the significant effect of HIP pressure on increasing the phase transformation temperature, when the pressure of HIP is 130 MPa, the α phase transformation temperature of Ti-46Al-2Cr-2Nb-0.2W-0.4B(at%) increases to 1611.6 K. Then, the TiAl based alloy obtained after two steps of HIP at 1523 and 1603 K exhibits a fine, nearly full lamellar microstructure.

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Al_2O_3/ZrO_2 涂层在热等静压致密化 TiAl 基合金粉末过程中对碳钢包套的影响

郎泽保[1,2]，张永忠[2]，王 亮[1]，张绪虎[1]
(1. 航天材料及工艺研究所 特种金属及工艺事业部，北京 100076)
(2. 北京有色金属研究总院 复合材料中心，北京 100088)

摘 要：为了确保碳钢包套在热等静压致密化 TiAl 基合金粉末过程中的可靠性，本研究利用热喷涂的方法在 20#钢包套内壁添加了 Al_2O_3/ZrO_2（A-Z）涂层，然后在热等静压试验中，带有 A-Z 涂层的 20#钢包套用于热等静压致密化 Ti-46Al-2Cr-2Nb-(W, B)预合金粉末，其工艺为：1523 K/2.5 h，130 MPa+1603 K/0.5 h/130 MPa。为了对比，利用没有 A-Z 涂层的 20#钢包套在 1523 K/3 h/130 MPa 的工艺参数开展了热等静压致密化试验。利用扫描电镜、电子探针等设施对获得的压坯进行了观测和分析。结果表明：A-Z 涂层的加入可以防止脆性金属间化合物的形成。在热等静压过程中，20#钢包套中的 Fe 原子无法通过扩散的方式与 TiAl 基合金中的钛原子和铝原子相遇。因此，20#钢包套在热等静压过程中的可靠性得到了保证。此外，通过利用添加 A-Z 涂层的钢包套获得了完全致密的 TiAl 基合金压坯，压坯呈现出了近全片层类型的微观组织，其室温下的抗拉强度和延伸率也分别突破了 590 MPa 和 2.0%。
关键词：界面反应；Al_2O_3/ZrO_2(A-Z)涂层；TiAl基合金粉末；热等静压；微观组织；拉伸性能

作者简介：郎泽保，男，1975 年生，博士生，高级工程师，航天材料及工艺研究所特种金属及工艺事业部，北京 100076，电话：010-68380666，E-mail: lzb0413@sina.com