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Microstructure evolution and nitrides precipitation in in-situ Ti₂AlN/TiAl composites during isothermal aging at 900 °C

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Abstract: Microstructures of Ti₂AlN/TiAl composites prepared by in-situ method were characterized in in-situ and aging treatment conditions and the nitride precipitation was investigated in Ti₂AlN/TiAl composites aged at 900 °C for 24 h after being heat treated at 1400 °C for 0.5 h. The in-situ composites consist of $\gamma+\alpha_2$ lamellar colonies, equiaxed γ grains and Ti₂AlN reinforcements. Matrix with nearly fully lamellar structure formed after solution and subsequently aging treatment. With the increase of Ti₂AlN content, the nearly fully lamellar structure becomes instable for the aged composites. According to TEM study, fine Ti₂AlN precipitates are found to distribute at the grain boundaries of lamellar colony. Needle-like Ti₃AlN precipitates arrange in line with growing axis parallel to [001] direction of the γ -TiAl matrix and another needle-like Ti₃AlN precipitates; aging treatment **Key words:** TiAl composites; Ti₂AlN; in-situ synthesis; microstructure; precipitates; aging treatment

1 Introduction

y-TiAl based alloys have attracted great attention for their high potential application at elevated temperatures due to their low density, high specific strength and oxidation resistance [1,2]. However, poor lowtemperature ductility and insufficient elevated temperature strength are the main obstacles for their practical application. Many researches have been carried out to improve the shortages, especially for elevated temperature strength, which is ultimately important for their application. Alloying with the third element and microstructural modifications through thermomechanical treatments are usually considered to improve the elevated temperature strength of TiAl alloys [3-6]. Meanwhile, fabrication of TiAl-based composites with ceramic particles is also an effective way. Some investigations have shown that the properties of TiAl alloy could be obviously improved by addition of reinforcements, such as Al₂O₃, TiB₂, Ti₅Si₃, Ti₂AlC and Ti₂AlN [7-12]. Among these, Ti₂AlC and Ti₂AlN, as a group of ternary compound, exhibit metallic and ceramic properties, such as low density, high elastic modulus, easy machinability and high-temperature oxidation resistance. They are regarded as the promising candidates for reinforcement of TiAl composites [13-15].

SHU et al [9] investigated the mechanical properties of Ti₂AlC/TiAl composites. The ultimate compression strength and the true fracture strain of the composites were improved significantly. RAMASESHAN et al [16] also found that the 0.2% proof strength of Ti₂AlC/TiAl composites was higher than that of un-reinforced TiAl alloy both at ambient and elevated temperatures. As for Ti₂AlN, KAKITSUJI et al [10] and MABUCHI et al [17] reported that the strength and the fracture toughness of Ti₂AlN/TiAl composites were superior to those of unreinforced TiAl alloy. It is especially interesting that the elevated temperature strength of the composites at temperature as high as 900 °C was obviously higher than that of the unreinforced TiAl alloy, which demonstrated enormous potential for high-temperature application. Thus, investigation on Ti₂AlN/TiAl composites shows great attraction.

As elevated-temperature structural material, creep resistance is an important consideration for its practical application. To improve the creep resistance of TiAl alloy, precipitates such as nitrides, carbides and silicides are generally used to pin the dislocations or stabilize the microstructure. In the TiAl alloy containing nitrogen, some coarse Ti₂AlN and fine Ti₃AlN precipitates were observed at colony boundaries and interlamellar

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interfaces during aging treatment, which had a significant influence on the creep resistance for TiAl alloy [18–20]. With addition of carbon and silicon in TiAl alloy, Ti₂AlC, Ti₃AlC and Ti₅(Si, Al)₃ that were formed by thermal or mechanical treatment offered a remarkable improvement in creep behavior [21,22]. With regard to the Ti₂AlN/TiAl composites, there is a certain solubility of nitrogen in the matrix which would lead to the precipitation of nitrides during aging treatment and play an important role in creep strengthening. However, few investigations have concerned about the nitride precipitation in the Ti₂AlN/TiAl composites. Thus, the aim of this work is to investigate the microstructure evolution and ternary compound nitride precipitation of Ti₂AlN/TiAl composites during aging process.

2 Experimental

The Ti₂AlN/TiAl composites investigated in this study were prepared by an in-situ method. The elemental powders of titanium (99.9% purity, mass fraction) and aluminum (99.9%, mass fraction) and TiN powder (99%, mass fraction) were used as raw materials and mixed with compositions of 10% Ti48Al (mole fraction) -10%, 20%Ti₂AlN (volume fraction). The powder mixtures were cold-pressed into cylindrical samples and then sintered at 1200 °C for 2 h in a vacuum sintering furnace. During heating process, combustion reaction was carried out. After that, the resultant samples were prepared as 30 g buttons and remelted three times in order to promote densification and homogeneity by a non-consumable vacuum arc-melting. The buttons were then heat treated at 1400 °C for 0.5 h followed by furnace cooling. Subsequently, the heat treated samples were aged at 900 °C for 24 h.

To identify the phase content, X-ray diffraction (XRD) analysis was conducted using DX-2700 diffractometer with Cu K_{α} radiation. The microstructure characteristics of the composites were investigated by Olympus-PMG3 optical microscope (OM)and JSM-6700 scanning electron microscope (SEM) in back-scattered electron (BSE) mode. The morphologies of the nitrides precipitation were examined by Tecnai G2 F30 transmission electron microscope (TEM). TEM specimens were cut from the center of aged composites, then prepared by standard mechanical polishing and twin-jet electropolishing using a solution of 6% (volume fraction) perchloric acid + 34% butanol + 60% methanol at -20 °C and 25 V.

3 Results and discussion

3.1 In-situ Ti₂AlN/TiAl composites

Figure 1 shows the X-ray diffraction patterns of

Ti₂AlN/TiAl composites. The result confirms that the in-situ composites consist of γ -TiAl, α_2 -Ti₃Al and Ti₂AlN phases. The peak intensity of Ti₂AlN increases with the increase of Ti₂AlN content in composites from 10% to 20%.



Fig. 1 XRD patterns of in-situ $Ti_2AlN/TiAl$ composites: (a) 10% Ti_2AlN ; (b) 20% Ti_2AlN

The microstructures of composites with 10% and 20% Ti₂AlN are shown in Fig. 2, which are composed of colony grains, equiaxed single phase and a certain fraction of particles homogenously distributed in the matrix constructed by both structures demonstrated above. According to the results of energy-dispersive spectra (EDS) in Fig. 2, the matrix of composites consists of $\gamma + \alpha_2$ lamellar colonies and equiaxed γ grains and the particle is identified as Ti₂AlN phase. By comparing Figs. 2 (a) and (b), it can be seen that morphology of Ti₂AlN reinforcement develops from granular type for 10% Ti₂AlN composite to rod-like type for 20% Ti₂AlN composite. The mean grain size of lamellar colonies decreases from about 62 µm to 39 µm with increase of Ti₂AlN content. The microstructure refinement can be explained by the nucleation effect of Ti₂AlN particles which may act as the nucleation sites during solidification of composites.

3.2 Phase and microstructure of aged Ti₂AlN/TiAl composites

Figure 3 shows the XRD patterns of Ti₂AlN/TiAl composites with heat treatment of (1400 °C, 0.5 h) +(900 °C, 24 h). The constituent phases are γ , α_2 and Ti₂AlN, the same as those of the in-situ composites. Nevertheless, compared with the XRD patterns in Fig. 1, the intensity of α_2 peaks decreases noticeably. The characteristic microstructures of the composites heat treated at 1400 °C for 0.5 h and 900 °C for 24 h are shown in Fig. 4, respectively. After solution treatment at 1400 °C for 0.5 h, a matrix with nearly fully lamellar structure is obtained and consists of colonies of α_2/γ



Fig. 2 Results of SEM-EDS analysis of in-situ Ti₂AlN/TiAl composites with (a) 10% and (b) 20% Ti₂AlN



Fig. 3 XRD patterns of Ti₂AlN/TiAl composites aged at (1400 °C, 0.5 h)+(900 °C, 24 h): (a) 10% Ti₂AlN; (b) 20%Ti₂AlN

lamellae and equiaxed γ , as shown in Figs. 4 (a) and (b), which is different from Ti48Al alloy. According to binary Ti–Al phase diagram, a fully lamellar structure will be produced by heat treatment at α phase field with furnace cooling. Addition of Ti₂AlN may lead to change of phase transformation of the TiAl matrix. Figures 4 (c) and (d) show the microstructure of the composites aged at 900 °C for 24 h after solution treatment. For 10% Ti₂AlN composite, the nearly fully lamellar structure is found to be maintained, while for 20% composite the nearly fully lamellar structure becomes instable, as shown in Fig. 4(d). In the lamellar colonies, α_2 laths become thinner and dissolve and γ laths coarsen. The equiaxed γ grains also coarsen. This indicates that the change is more noticeable with the increase of Ti₂AlN content. In Figs. 4(c) and (d), many fine bright particles can be found to distribute at the boundary of lamellar colonies and interfaces of lamellar. In order to investigate these precipitates, TEM analyses were carried out in the following sections.

3.3 Nitrides precipitation in aged Ti₂AlN/TiAl composites

The representative TEM image of the fine precipitates in the aged composites is shown in Fig. 5. Figure 5(a) shows some fine precipitates of $0.4-1 \mu m$ located at the boundaries of colony grains. According to the electron diffraction patterns of these precipitates, as shown in Fig. 5(b), they can be identified as Ti₂AlN phase.

In addition, some fine needle-like precipitates can be found to distribute homogenously and arrange along a particular direction in the matrix of aged composites, as shown in Fig. 6(a). By electron diffraction analysis in Fig. 6(b), it is identified that the needle-like precipitates are Ti₃AlN phase and the matrix is γ . The growing axis of the needle-like precipitates parallels [001] direction of the matrix.

There is also another needle-like precipitates with larger size in the γ matrix, as shown in Fig. 7(a). Figure 7(b) shows the dark field image of this kind of precipitates. A plenty of dislocations can be found to distribute around these precipitates. Electron diffraction confirms that this kind of precipitate is also Ti₃AlN phase.



Fig. 4 SEM images of 10% Ti₂AlN/TiAl (a), 20% Ti₂AlN/TiAl (b) composites with heat treatment of 1400 °C for 0.5 h and 10% Ti₂AlN/TiAl (c), 20% Ti₂AlN/TiAl (d) composites aged at 900 °C for 24 h after solution treatment



Fig. 5 TEM image showing Ti₂AlN precipitates at boundaries of colony grains (a) and corresponding SAED pattern (b)



Fig. 6 TEM image showing Ti_3AIN precipitate (a) and corresponding SAED pattern (b)



Fig. 7 TEM images showing Ti₃AlN precipitate distributed at dislocations (a) and dark field image of precipitates (b)

Formation of the two different types of precipitates is related to crystal structure, misfit, structure of the interphase boundary between precipitate and matrix, and stress applied during aging treatment [23,24]. Generally, when the crystal structures are basically the same and the misfit is small, the precipitate takes the form of a sphere. The shape of the precipitate will change from spherical to needle-like, finally to plate-like with the increase of misfit between the precipitate and the matrix. When crystal structures of the precipitates and the matrix are different, the structure of interphase boundary becomes determining factor for the morphology of precipitates [25]. As discussed by TIAN and NEMOTO [25], the lattice misfit between TiAl matrix and Ti₃AlN has a smaller value in the [001] direction of Ti₃AlN and the growth of Ti₃AlN precipitates displays preferential orientation in [001] direction of the matrix. Thus, the Ti₃AlN precipitates show the needle-like morphology with growing axis parallel to [001] direction of the matrix.

The precipitation of these nitrides is related to nitrogen dissolved in the matrix. It is known that nitrogen atom has certain solid solubility in γ -TiAl alloys [20]. During in-situ preparation, the nitrogen atoms may decompose from TiN and dissolve into the matrix and precipitate as a form of nitrides in the matrix during aging treatment. It is also understood that nitrogen has much greater solubility in α_2 phase (about 0.3% in mole fraction) compared with γ phase. So, precipitation of nitrides in γ matrix was favored [26], as shown in Figs. 6 and 7. It indicates that α_2 would be consumed and causes the growth of γ phase during the formation of these precipitates, leaving the precipitates behind in γ matrix. The process can be deduced as the type of $\alpha_2 \rightarrow \gamma +$ precipitates.

In the matrix of aged composites, it is interesting to note that some dislocation networks and walls can be found, as shown in Fig. 8. Due to the structure difference



Fig. 8 TEM images showing dislocation structure in aged $Ti_2AIN/TiAl$ composites: (a) Dislocation network; (b) Dislocation wall

between TiAl matrix and precipitates, the stress is produced during nitrides precipitation and thus induces the generation of dislocations.

CHRISTOPH et al [27] investigated the deformation structure of TiAl alloys with perovskite Ti_3AlC precipitates and found that perfect and twinning partial dislocations were pinned by the precipitates. The high glide resistance provided by the precipitates is

manifested by the strong bowing-out of the dislocation segment. In this work, it also can be inferred that the nitrides precipitates formed in TiAl matrix during aging treatment could act as barrier grid to inhibit the movement of dislocation in the matrix, which is beneficial to enhance the strength of the $Ti_2AIN/TiAI$ composites.

4 Conclusions

1) The microstructure of in-situ Ti₂AlN/TiAl composites consists of $\gamma + \alpha_2$ lamellar colonies and equiaxed γ grains and Ti₂AlN phase. With the increase of Ti₂AlN content, morphology of Ti₂AlN develops from granular type for 10 % Ti₂AlN composite to rod-like type for 20% Ti₂AlN composite and mean grain size of lamellar colonies decreases.

2) Nearly fully lamellar matrix consisted of colonies of α_2/γ lamellae and equiaxed γ was obtained by solution treatment at 1400 °C and subsequent aging treatment at 900 °C. The nearly fully lamellar structure becomes instable as Ti₂AlN content increases.

3) Two kinds of precipitates form in the aged Ti₂AlN/TiAl composite. Fine particle precipitates of Ti₂AlN of 0.4–1 μ m distribute at grain boundaries of lamellar colony. Needle-like precipitates of Ti₃AlN arrange in line with growing axis paralleling to [001] direction of the γ -TiAl matrix. Another needle-like Ti₃AlN precipitates with larger size distribute at dislocations in γ matrix. Formation of nitride precipitates would happen in process of $\alpha_2 \rightarrow \gamma + \text{precipitates}$.

4) Some dislocation patterns such as networks and walls were found in the matrix of aged $Ti_2AIN/TiAI$ composites, which would be beneficial to the elevated temperature strength of $Ti_2AIN/TiAI$ composites.

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原位合成 Ti₂AIN/TiAI 复合材料 900 °C 时效过程中的组织演化及氮化物沉淀相析出

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摘 要:对原位合成 Ti₂AlN/TiAl 复合材料在原位合成及时效热处理条件下的显微组织特征进行分析,并对 Ti₂AlN/TiAl 复合材料进行 1400 °C, 0.5 h 固溶及 900 °C, 24 h 时效热处理,研究其氮化物沉淀析出。结果表明, 原位合成复合材料的显微组织由 y+a₂ 片层团、等轴 y 晶粒和 Ti₂AlN 增强相组成。经固溶和时效处理后,获得近 全片层基体结构。随着 Ti₂AlN 含量的增加,基体近全片层结构变得不稳定。对时效后的复合材料进行 TEM 研究, 发现在片层团晶粒边界上分布着细小的 Ti₂AlN 沉淀相。在 y-TiAl 基体内,针状 Ti₃AlN 沉淀相以其轴向平行于基 体[001]方向排列,而另一种具有较大尺寸的 Ti₃AlN 沉淀相则在位错处沉淀析出。 关键词: TiAl 复合材料; Ti₂AlN; 原位合成;显微组织;沉淀相;时效处理

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