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Macro-microscopic morphology and phase analysis of TiAl-based alloys sheet fabricated by EB-PVD method

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Abstract: TiAl-based alloys sheet with thickness of 0.3-0.4 mm as well as dimension of 150 mm×100 mm was fabricated successfully by using electron beam-physical vapor deposition(EB-PVD) method. The microscopic morphology and phase composition of specimens in various states were analyzed by atomic force microscope(AFM), scanning electron microscope(SEM) and X-ray diffractometer(XRD), respectively. The results indicate that the as-deposited TiAl-based alloys sheet has good surface quality and is composed of γ , α_2 and τ phase. There is natural delamination inside the sheet, of which the microstructure is columnar crystal, and the component shows a gradient change along the normal direction of substrate. After the vacuum hot pressing treatment and subsequent homogenization treatment, the columnar crystal transforms into the coarse fully lamellar microstructure, the delamination phenomenon and τ phase disappear, α_2 phase decreases obviously, and the composition tends to uniformization.

Key words: TiAl-based alloy; electron beam-physical vapor deposition; sheet; morphology; phase analysis

1 Introduction

Titanium aluminides are considered as the most promising lightmass high-temperature structural materials, because of their high specific strength, specific stiffness and good oxidation resistance at elevated temperature. They can partially replace the Ti-based alloys and Ni-based superalloys for high temperature applications in aerospace and automotive industries[1–4]. Especially, the TiAl-based alloys sheet can be used as thermal protection system panel, exhaust nozzle, low-pressure turbine blades, etc; for these, 40% mass reductions are possible[5–7].

ZHANG et al[8] and MIAO et al[9] fabricated TiAl-based alloys sheets of 2.6–2.7 mm in thickness via the hot pack-rolling process. Plansee company[10] developed a patent (Advanced Sheet Rolling Process, ASRP), through which the sheet of 1 mm in thickness was produced, which are commercially available. For the sake of simplifying working process, JIANG et al[11] produced TiAl-based alloys sheet by element powder cold roll forming and reactive synthesis, but the high porosity of sheet is unabsorbable. As a new technology of sheet preparation, the electron beam-physical vapor deposition(EB-PVD) method can be used to prepare the brittle materials sheet and laminated composites[12–13] hardly limited by the dimension and thickness. EB-PVD method has several advantages such as higher deposition speed and thermal efficiency, purer and near-net shaped product[14]. The extreme dimension of sheet fabricated by EB-PVD method is 1 000 mm, and the sheet thickness is between 0.1 mm and 5 mm, which can satisfy the preparation requirements of different materials and different application environments for sheet.

The TiAl-based alloys sheet with thickness of 0.3-0.4 mm as well as dimension of $150 \text{ mm} \times 100 \text{ mm}$ has been fabricated successfully by using EB-PVD method. At present, there is no correlative research reporting on this field in the world. In this study, the macro-microscopic morphology was analyzed and the phase compositions of TiAl-based alloys sheet before and

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after vacuum homogenization treatment were studied.

2 Experimental

The ingots of TiAl-based alloys used in this study were received by cast two times in ALD-LPT6 type water-cooling vacuum induction melting furnace. The nominal composition of the ingots is Ti-47Al (mole fraction, %). The experimental device is UE-204 type EB-PVD equipment with horizontal feed mode, as shown in Fig.1. The low carbon steel is used as a substrate, of which the radiation heating principle is shown in Fig.2. The substrate temperature was restricted firmly by choosing the mean value of three thermocouples that were directly contacted with the substrate surface at different positions. To take off the coatings from the substrate conveniently, a ceramic stripper layer with about 20 µm should be deposited on the substrate before formal evaporation. The deposition conditions are given in Table 1. After evaporation, the substrate was removed to the load chamber, and then taken out from furnace and cooled to 423 K. At room temperature, four TiAl-based alloys sheets with dimension of 150 mm×100 mm were gained by mechanical stripping from the substrate surface.



Fig.1 Principle scheme of EB-PVD method



Fig.2 Scheme of radiation heating on substrate

Fable 1	Major	technical	parameters	of ex	periment
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Technical parameter	Value
Degree of vacuum/mPa	6.5-10.5
Substrate rotational speed/ $(r \cdot min^{-1})$	25
Substrate temperature/K	873±15
Ingot feeding velocity/(mm·min ⁻¹)	0.8
Deposition rate/($\mu m \cdot min^{-1}$)	3.7

In order to improve the density of materials, the specimens were hot pressed at 1 523 K under a pressure of 20 MPa for 1 h, and then cooled to room temperature in the ZRY45A type multi-function vacuum heat treatment furnace. Based on the consideration of obtaining fully lamellar microstructure because of their preferable combination properties at elevated temperature, the subsequent homogenization treatment was processed at 1 323 K for 24 h and 48 h, respectively, and then heated to 1 623 K for 10 min in a high vacuum. The microscopic morphology of specimens was observed by a Dimension 3100 type atomic force microscope (AFM) and an S-4700 type scanning electron microscope(SEM). The energy dispersive spectrometry (EDS) equipped with the SEM and an X-ray diffractometer(XRD, Philips X'Pert) with Cu K_a radiation at 40 kV, 30 mA and step length of 0.05° were used to characterize the phases of TiAl-based alloys sheet with and without homogenization treatment.

3 Results and discussion

3.1 Macrographs

Fig.3 shows the macrograph of TiAl-based alloys sheet fabricated by EB-PVD method. It can be seen that there is no flaw, crack and pit except a few small bulges on the surface of the sheet, which has integrated outline and good surface quality. This means that it is feasible to prepare the TiAl-based alloys sheet by using EB-PVD method.



Fig.3 Macrograph of TiAl-based alloys sheet fabricated by EB-PVD method

According to the follow-up observation, there are sputtering phenomena of microparticles on evaporating, which is the direct reason of the surface bulges. So far as we know, the sputtering volume is directly proportional to the magnitude of the electron beam current, and is inversely proportional to the density of the original ingots. But not all sputtering phenomena can cause depositional surface bulges, and this is related to the distance between ingots and substrate. Under the same sputtering volume and frequency, the smaller the distance between ingots and substrate, the higher the deposition rate, and the more serious the depositional surface bulges. Therefore, when the distance between ingots and substrate is immutable, choosing the original ingots with higher density as targets and using the smaller electron beam current are necessary for the best depositional surface quality.

3.2 Micrographs

Fig.4 shows the AFM morphology on the free surface of as-deposited TiAl-based alloys sheet. It can be seen that the grain size on the free surface of the sheet is less than 2 µm, and the surface roughness is small. The micrographs on cross-section of specimens in various states were surveyed with secondary electron and backscattered electron, as shown in Fig.5. From Fig.5(a) we can see that the original TiAl-based alloys ingots possess representative lamellar microstructure. However, there is natural delamination alternating overlaid by Ti-rich area and Al-rich area inside the as-deposited TiAl-based alloys sheet, of which the microstructure is columnar crystal (Fig.5(b)). The formation of columnar crystal is related with the substrate temperature and deposition speed[14], and the delamination phenomenon is caused by the phase evolution derived from the composition fluctuation. As shown in Fig.5(c), after vacuum hot pressing treatment at 1 523 K for 1 h, the relative density of specimens is increased obviously, and the columnar crystal transforms into the equiaxed crystal because of the recrystallization and subsequent growth of organizations. After homogenization treatment for 24 h, the delamination phenomenon is still existing, but the Ti-rich areas become smaller and the Al-rich areas become larger (Fig.5(d)). Furthermore, as we know from the Ti-Al phase diagram, there is no phase change below 1 623 K for the Al-rich areas with Al contents over 50% (mole fraction); so the fully lamellar microstructure just exists in the Ti-rich areas because of phase change. From Fig.5(e) we can see that for the unpressed specimens, relatively intense atomic diffusion process leads to the continuous cavity defects at peak value of Al-rich areas as well as lots of microcavities near peak value of Ti-rich areas after homogenization treatment for 24 h. Furthermore, higher porosity makes the atomic diffusion

easier; consequently Ti-rich areas of as-annealed specimens without hot pressing treatment seem to be bittier than those with hot pressing treatment. As shown in Fig.5(f), after homogenization treatment for 48 h, the as-pressed specimens present the coarse fully lamellar microstructure, and their delamination phenomenon disappears.



Fig.4 AFM morphology on free surface of as-deposited TiAl-based alloys sheet

3.3 Phase analysis

EDS within the selected area was used to analyze the composition of the specimen in Fig.5(b). The results show that in the as-deposited TiAl-based alloys sheet, the composition of Ti-rich areas is within the α_2 - γ coexisting phase fields in which the α_2 phase is primary; the composition of Al-rich areas is within the γ - τ coexisting phase fields; the average assay of the whole selected area has lower Al content than that of the original ingots and is about Ti-44.9Al (mole fraction, %). For the deviation of average assay of TiAl specimens around the evaporation, these are mainly dependent on the saturated vapor pressure of elements and the temperature of substrate surface, partially due to the limited analytic precision of EDS. Since having no gaseous TiAl, they must be decomposed into Ti vapor and Al vapor and then condense on the substrate surface when evaporation. Ref.[15] indicated that the higher the saturated vapor pressure of element, the faster the deposition rate, that is, the element can be deposited on the substrate surface more easily. At the same temperature, Al element has higher saturated vapor pressure than Ti element, and this can help to get the as-deposited sheet with high Al content. But at the same time, the temperature of substrate surface is adjacent to the melting point of Al, which maybe adverse to the adhesive deposition of Al and cause to the as-deposited sheet with lower Al content. The substrate temperature can determine the sticking coefficient of vapor atoms on the substrate surface and affect their deposition rate[15]. Furthermore, when the

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Fig.5 Micrographs on cross-section of specimens in various states: (a) As-cast; (b) As-deposited; (c) As-pressed with 1 523 K for 1 h, 20 MPa, FC; (d) As-pressed and annealed with 1 323 K for 24 h+1 623 K for 10 min, FC; (e) As-annealed with 1 323 K for 24 h+1 623 K for 10 min, FC; (f) As-pressed and annealed with 1 323 K for 48 h+1 623 K for 10 min, FC

temperature of substrate surface is about 923 K in our certain test, the EDS analytic results for the as-deposited specimens show that the average assay of the whole selected area has the lowest Al content and is only about Ti-41Al (mole fraction, %). Although the saturated vapor pressure of metallic elements is their inherent attribute and is variational just with the temperature, the conclusion as follows can be gained according to "saturated vapor pressure p_s of some elements in the temperature range of 1 000-4 000 K" (Fig.3.4 in Ref. [15]): the higher the surface temperature of molten pool of the original ingots, i.e. the higher the deposition rate, the smaller the difference of saturated vapor pressure between Ti and Al elements, which makes the average assay of coatings more accessible with that of the original ingots. Therefore, the TiAl-based alloys sheet with ideal composition can be gained by adjusting the

composition of original ingots, the temperature of substrate surface and the deposition rate.

Fig.6 shows the linear distribution of elements on cross-section of TiAl-based alloys sheet before and after vacuum homogenization treatment. From Fig.6(a), we can see that the Ti and Al contents inside the as-deposited sheet show a regular and periodical gradient variation along the normal direction of substrate, and the dark areas that exist alternately along with the pale area are Al-rich area and Ti-rich area, respectively. We believe that larger compositional variation should be attributed to the difference of saturated vapor pressure between Ti and Al elements. Since this difference can be reduced with increasing the temperature of molten pool; so the higher the deposition rate, the smaller the difference between saturated vapor pressure and compositional variation. According to the calculation of the activity coefficients



Fig.6 Linear distribution of elements on cross-section of specimens: (a) As-deposited; (b) As-pressed and annealed for 24 h; (c) As-pressed and annealed for 48 h

in Ti-Al binary system[16], the results indicate that the activity coefficients of Ti in α_2 phase and Al in τ phase are far higher than those of Ti and Al in γ phase at elevated temperature. And these can be verified in Fig.5(e): because the atomic diffusions at peak value of Al-rich and Ti-rich area are intense relatively, these locational microcavities accumulated by large numbers of vacancies are visible. Consequently, the diffusion reaction of α_2 and τ phases is generated inevitably during the homogenization treatment, which makes the α_2 and τ phase decrease, γ phase increase and the composition tend to uniformization continuously (Figs.6(b) and (c)). The results of XRD analysis are accordant with the above description and show that the as-deposited TiAlbased alloys sheet is composed of γ , α_2 and τ phases; after the homogenization treatment for 48 h, the τ phase disappears and the α_2 phase decreases greatly (see Fig.7).



Fig.7 XRD patterns of specimens: (a) As-deposited; (b) Aspressed and annealed for 24 h; (c) As-pressed and annealed for 48 h

4 Conclusions

1) The TiAl-based alloys sheet with thickness of 0.3-0.4 mm as well as dimension of $150 \text{ mm} \times 100 \text{ mm}$ was fabricated by using EB-PVD method. The sheet has integrated outline and good surface quality, and there is no flaw, crack and pit except a few small bulges on the surface of the sheet.

2) There is a natural delamination inside the as-deposited TiAl-based alloys sheet, of which the microstructure is columnar crystal. After vacuum hot pressing treatment at 1 523 K for 1 h with pressure of 20 MPa as well as the subsequent homogenization treatment at 1 323 K for 48 h and then heated to 1 623 K for 10 min, the relative density of sheet is increased obviously, the columnar crystal transforms into the coarse fully lamellar microstructure, and their delamination phenomenon disappears.

3) The as-deposited TiAl sheet is composed of γ , α_2 and τ phases, and the component shows a gradient change along the normal direction of substrate caused by the different saturated vapor pressures and deposition rates of Ti and Al elements. Furthermore, the average assay of the as-deposited sheet has lower Al content than that of the original ingots. After vacuum hot pressing and the subsequent homogenization treatment, the τ phase disappears, the α_2 phase decreases greatly and the composition tends to uniformization because of the diffusion derived from the high activity coefficients of Ti and Al at elevated temperatures.

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