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Effect of Mn on microstructure of as-cast Ti47Al8Nb(1~ 2) Mn alloys^①

XU Jing-wen(许敬文), LIN Jurr-pin(林均品), WANG Yan-li(王艳丽), CHEN Guo-liang(陈国良)
(State Key Laboratory for Advanced Metals and Materials, University of Science and
Technology Beijing, Beijing 100083, China)

[Abstract] The microstructures of Ti47Al8Nb x Mn (mole fraction, %) alloy with $x = 1$ or 2 were studied on as-cast, as HIPped and on heat-treated samples. The results showed that Mn element is β phase stabilizer and promotes the formation of β (B₂) phase. B₂ phase exists at the dendrite cores of the as-cast microstructures. This phase is metastable and can completely decompose into α and(or) γ during 1 200 °C, 200 MPa, 4 h HIP process. In the as-HIPped alloy with 1% (mole fraction) Mn addition, the $\alpha_2 + \gamma$ lamellae structure is interrupted and decomposed resulting in grain refined near gamma microstructure. The $\alpha_2 + \gamma$ lamellae structure near interdendritic regions decomposes almost completely into γ grains, but near dendrite cores incompletely into γ grains with a small amount of α_2 particles or needles around or in it. However, compared with the alloy with 1% (mole fraction) Mn, more α_2 phase is retained in the alloy with 2% (mole fraction) Mn. α_2 phase contains more Mn and is more stable in the alloy with 2% (mole fraction) Mn than in that with 1% (mole fraction) Mn. This makes its grain refinement more difficult. The amount of α_2 phase decreases following (1 250 °C, 7 h—1 150 °C, 15 h) for 3 cycles heat treatment.

[Key words] cast high-niobium TiAl alloy; microstructure; effect of Mn element

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1 INTRODUCTION

Two phase γ -TiAl based alloys have attracted a great deal of attention for high temperature application due to their promising properties such as high specific modulus, excellent strength, attractive stiffness, creep resistance and adequate oxidation resistance at high temperature^[1, 2]. These prominent properties are due to the ordered structure of aluminides which reduces dislocation mobility and diffusion processes. However, this is often accompanied by low ductility and low fracture toughness at ambient temperature. The practical use of this compound is limited by these defects. It has been shown that alloying and structure modification by heat-treatment improve the ductility and optimize the general properties. Addition of Mn, Cr and V is known to improve the ductility of TiAl-based $\alpha_2 + \gamma$ two-phase alloys^[3, 4]. The improvement of ductility by adding Mn to TiAl alloy is mainly contributed to that the increase of super dislocation mobility and the decrease of stacking fault energy enforce twin mobility^[4].

In this study, we report the microstructure development of the as-cast Ti47Al8Nb(1~ 2) Mn alloy through HIP process and heat-treatment and discuss the effect of Mn alloying on it.

2 EXPERIMENTAL

Two alloys used for this study had nominal com-

positions of Ti47Al8Nb1Mn and Ti47Al8Nb2Mn (both in mole fraction). They were produced from titanium sponge (99.99%), aluminum ingot (99.99%), and Mn and Nb commercial-purity alloys by non-consumable arc melting under pure argon atmosphere. The alloys were first made into buttons. The buttons were flipped three times and remelted to ensure complete mixing of the constituents. Then they were cast in a copper mould.

Hot-isostatic pressing (HIPing) was carried out with following parameters: 1 200 °C, 200 MPa for 4 h. The samples with a dimension of 10 mm \times 10 mm \times 10 mm were cut from HIPed bar by spark-erosion. These samples were encapsulated in silica tubes which were evacuated and backfilled with argon and sealed. Heat treatments were conducted on them by annealing three cycle times between 1 250 °C and 1 150 °C for 7 and 15 h respectively.

Metallographic samples were ground and electropolished with 7% H₂SO₄ and 93% methanol (volume fraction) at -20 °C and ~15 V. The microstructure features were studied by scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The SEM was operated in a back-scattered imaging mode to obtain strong atomic number contrast, ideal imaging segregated structures. Quantitative chemical information was acquired with EDS system calibrated with the appropriate standards.

Table 1 shows the result of EDS by analyzing the

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Table 1 Compositions of as-cast alloy
(mole fraction, %)

Alloy	Ti	Al	Nb	Mn
Ti47Al8Nb1Mn	43.7	47.1	8.2	1.0
Ti47Al8Nb2Mn	43.3	46.7	8.1	1.9

as-cast alloy compositions.

3 RESULTS AND DISCUSSION

3.1 As-cast microstructure

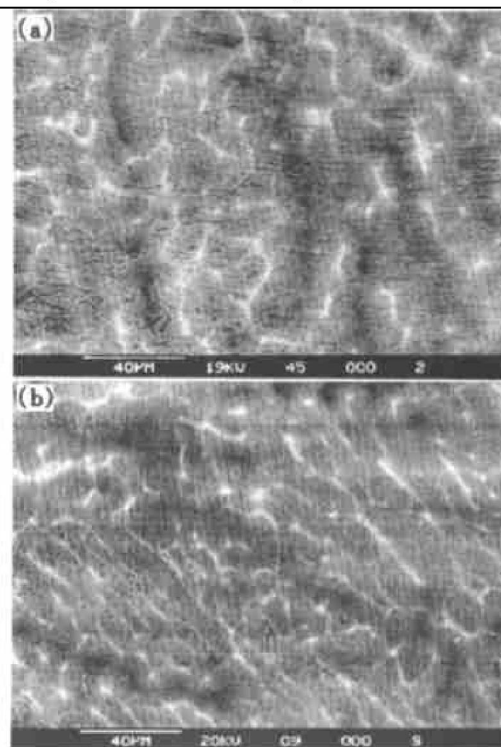
Fig. 1 shows BSE micrographs taken from the as-cast Ti47Al8Nb1Mn (a) and Ti47Al8Nb2Mn (b) alloys respectively. The microstructures of the alloys have large column grains growing in radius direction. It is seen that the as-cast microstructure clearly reveals a dendritic structure in both alloys consisting of large lamella colonies, a small amount of segregated γ grains as is seen in the base alloy Ti47Al, and bright B_2 cores within lamella colonies. The bright cores are surrounded by grayish regions of α_2 (Ti₃Al) + γ (TiAl) lamella and a dark network of the interdendritic γ regions. EDS spectra acquired from the center to the periphery of the dendrities (Table 2) shows that the bright cores containing the B_2 phase are enriched in Ti, Nb and Mn and depleted in Al. Whereas, the dark interdendritic γ regions, where the last liquid solidifies, are enriched in Al, but depleted in the other elements. And the composition of the gray α_2 + γ lamella region is among them. It is also shown that the as-cast microstructure of Ti47Al8Nb2Mn (Fig. 1(b)) contains more amount of bright B_2 phase than that of Ti47Al8Nb1Mn (Fig. 1(a)). And the amount of Mn in B_2 phase rises when the amount of Mn in the alloys increases. It is evident that Mn element makes β (B_2) phase more stable and enforces its forming.

Table 2 Compositions of different phases
in as-cast alloys (mole fraction, %)

Alloy	Phase	Ti	Al	Nb	Mn
Ti47Al8Nb1Mn	B_2	48.1	40.7	9.4	1.8
	α_2 + γ	44.8	45.8	8.3	1.1
	γ	42.9	48.3	8.0	0.8
Ti47Al8Nb2Mn	B_2	47.5	40.3	9.2	3.0
	α_2 + γ	44.7	44.8	8.4	2.1
	γ	41.5	48.7	8.1	1.7

As shown in McCullough and his co-workers' work^[5, 6], for the binary TiAl-based alloys in the range of 40% ~ 49% Al (mole fraction), which only contain α_2 and γ phases in the cast microstructures, β was found to be the primary phase in local equilibrium with the liquid. The primary β phase transforms into α directly or through $L + \beta \rightarrow \alpha$ peritectic reaction according to Al content of the alloy. Then α den-

drites transform from solid state into a lath structure consisting of layers of α_2 and γ . γ segregation was observed above 46% Al (mole fraction) and its fraction increased with Al content. Whereas, for TiAl alloys with the addition of the β -stabilizing elements, such as Fe, Ru, W, Mo, Cr, V, Nb and Ta, the β phase can be retained at room temperature; the retained B_2 phase may either be metastable or in equilibrium depending on the degree of stabilization as a function of the nature and amount of alloying elements^[7~10]. When the B_2 phase is retained, the B_2 , α_2 and γ three phases have following Burgers orientation relationship^[11]: $(0001)_{\alpha_2} \parallel \{111\}_{\gamma} \parallel \{110\}_{B_2}$, $\langle 1120 \rangle_{\alpha_2} \parallel \langle 110 \rangle_{\gamma} \parallel \langle 111 \rangle_{B_2}$.

**Fig. 1** Back-scattered SEM images
of as-cast alloy
(a) —Ti47Al8Nb1Mn alloy;
(b) —Ti47Al8Nb2Mn alloy

Solidification velocity is usually too high to approach equilibrium solidification. Solute redistribution occurs during solidification of alloys. Microsegregation can form in structure of solidified alloys because of limited solute diffusion in liquid and solid during solidification^[12, 13]. In our investigation with addition of β -stabilizing elements Nb and Mn in 47Al alloys, the dendritic segregation formed during solidification is more severe. At the beginning of solidification, the primary β phase forms, in which the content of Nb and Mn is more, and Al is less, than the average concentration in the alloys. Al is rejected from the solid-liquid interface and diffuses limitedly into liquid, so the liquid at the front of the interface of solid-liquid is enriched in Al and depleted Nb and Mn. As the temperature falls quickly, the composition of β phase does not homogenize because of the

limited diffusion of solutes in the liquid and solid. When the first peritectic reaction temperature reaches, the peritectic reaction occurs at the interface of liquid with higher Al content and β phase to form second solid α phase: $L + \beta \rightarrow \alpha$. The new α phase surrounds the primary β phase and the peritectic reaction proceeds only by the diffusion of solutes through the α phase. The limited diffusion of solutes prevents the peritectic reaction from taking place completely. The primary β at the dendrite cores and a small amount of liquid enriched Al at the interdendritic regions still exist till the second peritectic reaction temperature reaches. Then the peritectic reaction occurs: $L + \alpha \rightarrow \gamma$, and forms interdendritic γ phase. During the cooling in the solid state, the firstly solidified primary γ phase at dendritic cores is retained till ambient temperature and orders into B_2 , the interdendritic γ grains is also retained. Such dendritic segregation of non-equilibrium microstructures with B_2 phase at dendritic cores and γ phase at interdendritic area is progressively decreased by long term diffusive aging as discussed in the following text.

3.2 As-HIPed and heat-treated microstructure

HIPing is often used to remove the pore of the cast alloys^[1]. The HIPed microstructure of Ti47Al8Nb1Mn at 1 200 °C, 200 MPa, 4 h are shown in Fig. 2(a). Compared with as-cast microstructure in Fig. 1(a), it changes greatly and forms equiaxed near γ microstructure with a small amount of α_2 phase around or in it. The white B_2 cores disappears and decomposes

completely into α and(or) γ , the segregation in interdendritic region is relieved. The $\alpha_2 + \gamma$ lamella also decomposes. The composition is different (Table 2) between regions near core area and near interdendritic area so that their driving forces of $\alpha_2 + \gamma \rightarrow \gamma$ transformation are different. The $\alpha_2 + \gamma$ lamella near the γ interdendritic area, which is formed because of much Al element segregation in the interdendrite during solidification, almost completely decomposes into γ and forms equiaxed γ grains. However, for the $\alpha_2 + \gamma$ lamella near the dendrite core area, Al content is lower and Nb and Mn contents are higher so that the α_2 lamella is more stable and decomposes incompletely, α_2 particles and needles are retained there. It is shown that the dendrite segregation of the as-cast microstructure is decreased and the large as-cast column grains tend to transform into smaller equiaxed grains in the HIP process.

The as-HIPed microstructure of Ti47Al8Nb2Mn is shown in Fig. 2(b). As found in the as-HIPed Ti47Al8Nb1Mn, its B_2 phases all decompose. And $\alpha_2 + \gamma$ lamella colony also decomposes but more α_2 phases are retained. The α_2 needles are longer and have different orientations. The compositions of α_2 and γ phase of the as-HIPed microstructure are listed in Table 3. It can be seen that Mn content of α_2 phase is much higher in HIPed Ti47Al8Nb2Mn than that in Ti47Al8Nb1Mn. The increase of Mn content from 1% (mole fraction) to 2% (mole fraction) in alloys rises Mn content of α_2 phase and makes it more stable. It is difficult for α_2 lamella with higher Mn content to decompose, interrupt and dissolve.

Table 3 Compositions of different phases in as-HIPed alloys (mole fraction, %)

As-HIPed alloy	Phase	Ti	Al	Nb	Mn
Ti47Al8Nb1Mn	α_2	46.4	44.1	8.3	1.2
	γ	43.6	47.3	8.1	1.0
Ti47Al8Nb2Mn	α_2	46.5	42.9	8.2	2.4
	γ	42.0	47.9	8.3	1.8

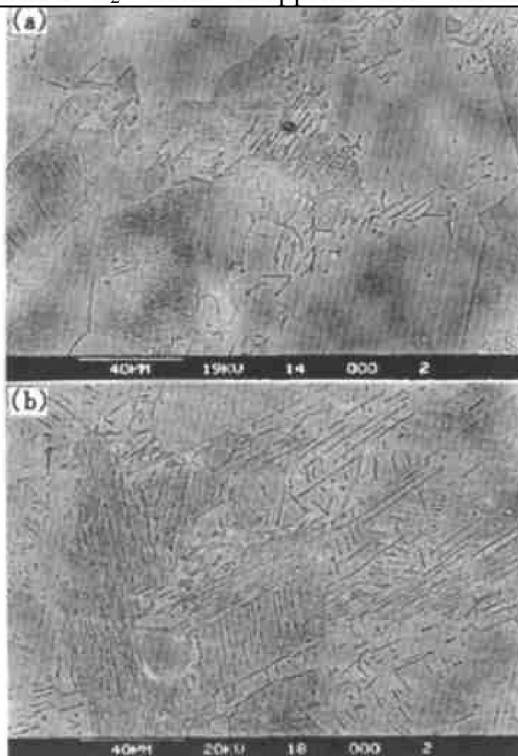


Fig. 2 Back-scattered SEM micrographs of as-HIPed alloy

(a) —Ti47Al8Nb1Mn alloy; (b) —Ti47Al8Nb2Mn alloy

The microstructures of as-HIPed alloys followed by cycle heat treatment (1 250 °C, 7 h —1 150 °C, 15 h) for three times are shown in Fig. 3. They are near γ microstructures. There is α_2 phase of block and needle shape distributing in the γ matrix or at grain boundary. And more fraction of α_2 phase exists in the heat-treated alloy with 2% Mn (mole fraction) than with 1% Mn (mole fraction). And α_2 needle is much longer and has evident orientation in the alloy with 2% Mn (mole fraction). This phenomenon also demonstrates that Mn element improves the stability of α_2 phase. When this kind of near γ microstructure is heat treated in α phase or $\alpha + \gamma$ two-phase region, α grows along the former needles, though it may participate on four close packed (111) plane along the

$\langle 110 \rangle$ directions of γ phase. The discontinuous α needles with same orientation will grow and join into longer needles, and larger grains can be formed. This is not good for grain refinement. It can be seen that the alloy with 2% Mn (mole fraction) is more difficult to refine grains because the higher content of Mn element increases the stability of α_2 phase.

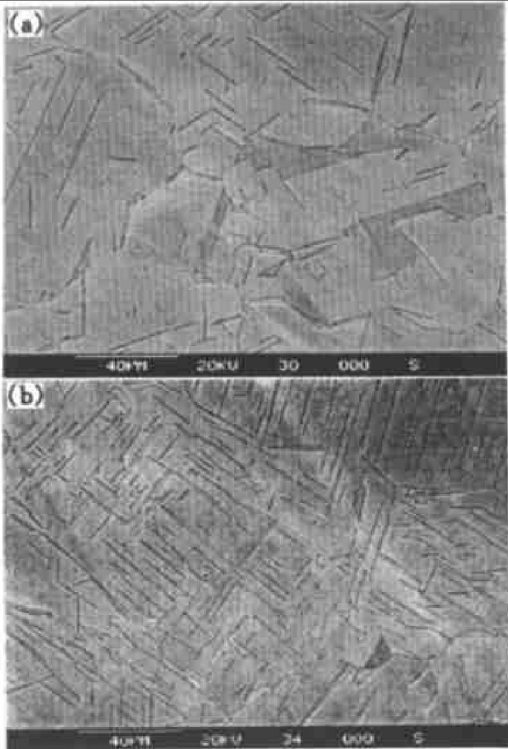


Fig. 3 Back-scattered SEM micrographs of heat-treated specimens (1 250 °C, 7 h—1 150 °C, 15 h for three cycles)
(a) —Ti47Al8Nb1Mn alloy;
(b) —Ti47Al8Nb2Mn alloy

4 CONCLUSIONS

(1) There exists B_2 phase in the dendrite cores in the as-cast microstructures of the Ti47Al8Nb(1~2) Mn alloys. B_2 phase enriches Mn, Nb and Ti. More B_2 phases form when Mn content in the as-cast alloy is increased. Mn content of B_2 phase is the highest among B_2 , α_2 and γ . And Mn content of B_2 phase rises up if Mn content of the alloy is increased. Mn is β phase stabilizing element. It promotes β (B_2) phase formation.

(2) B_2 phase is metastable. It can decompose completely after the as-cast alloys are HIPed at 1 200 °C, 200 MPa for 4 h.

(3) Mn also increases the stability of α phase. α_2 (α) phase is more stable in Ti47Al8Nb2Mn than in Ti47Al8Nb1Mn alloy. There are more α_2 phases existing in the HIPed and heat-treated Ti47Al8Nb2Mn alloy. Mn content is higher in α_2 phase.

(4) The cast column grains trend to transform into equiaxed grains and are refined by HIP process in the Ti47Al8Nb1Mn alloy. However, it is more diffi-

cult for the alloy with 2% Mn (mole fraction) to get grain refinement by the same HIP process and heat treatment.

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