

Heat treatment process for improving ductility of Ti-25V-15Cr-2Al-0.2C alloy^①

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Abstract: The effect of heat treatment and thermal exposure on the microstructure and mechanical properties of non-burning β titanium alloy Ti-25V-15Cr-2Al-0.2C (mass fraction, %) was investigated. It is found that the amount of α precipitation in samples after solution treatment followed by air cooling increases with increasing solution temperature. After solution treatment, the alloy was subjected to two different heat treatments to stabilize the material. The results show that the single ageing treatment (700 °C, 4 h, AC) leads to a large amount of α precipitation, while the triplex treatment (850 °C, 2 h, FC+ 700 °C, 6 h, FC+ 540 °C, 6 h, AC) significantly suppresses the formation of α precipitates. It is more important that after long-term exposure at 540 °C (the expected application temperature) samples heat-treated by the triplex treatment have markedly higher ductility than those given the single aging treatment. The intermetallic compound TiCr₂ is observed in samples after long-term exposure, which further degrades the ductility of the alloy.

Key words: non-burning; titanium alloy; heat treatment; mechanical properties; TiCr₂

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1 INTRODUCTION

Beta titanium alloys have been extensively studied for about 50 years since Ti-13V-11Cr-3Al alloy was first developed in 1952^[1]. These alloys are attractive in terms of their high strength and excellent cold formability. However, the application of these alloys was limited in the past, possibly due to their higher prices and processing difficulties. In the early 1990s, a new β titanium alloy, called alloy C (Ti-35V-15Cr), was developed in the USA, which successfully combines good mechanical properties and burning resistance^[2-4]. This alloy is claimed to be a fully stabilized β titanium alloy because of the highest molybdenum equivalency (47%) of all commercial β titanium alloys. However, after long-term exposure at high temperatures, even alloy C is not truly stabilized against α precipitation^[4]. In order to increase the cost-competitiveness while not to significantly reduce the ductility of the alloy, a small amount of Al addition has been introduced into Ti-V-Cr system alloys^[5-8]. For example, the alloy of nominal composition Ti-25V-15Cr-2Al-0.2C is a typical non-burning alloy with lower cost, which was developed by the IRC and Rolls-Royce in UK^[9,10]. In this alloy, carbon addition is used to improve the ductility of the alloy. The reason is that α precipitation can be suppressed to a certain extent through titanium carbide

gettering interstitial oxygen, thus the β matrix becomes ductile^[8]. However, after long-term exposure α precipitation still precipitates at the expected application temperatures (although much less than in alloys without carbon addition), which can markedly reduce the ductility of the alloy^[8]. The purpose of the present work is to study the effect of heat treatment and thermal exposure on the microstructure and mechanical properties of Ti-25V-15Cr-2Al-0.2C alloy. In this study, a particular heat treatment process is introduced, which can remarkably improve the microstructural stability and ductility of the alloy after long-term exposure at 540 °C (the expected application temperature).

2 EXPERIMENTAL

Titanium sponge and other elemental metal composing the Ti-25V-15Cr-2Al-0.2C alloy were first compacted into cylindrical electrodes and then double-melted and cast into a 15 kg ingot by a vacuum arc remelting (VAR) furnace. The chemical composition of the alloy is listed in Table 1.

The ingot was forged and finally hot-rolled into bars of 18.5 mm in diameter. The β -transus temperature of the alloy was determined to be around 790-820 °C in previous work^[11]. To investigate the effect of solution temperature on the microstructure of the

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alloy, as-rolled samples were solution-treated at 850 °C for 1 h, 950 and 1 050 °C for 30 min followed by air cooling (AC), respectively. The samples solution-treated at 1 050 °C were subjected to two different heat treatment processes: a single aging treatment (700 °C, 4 h, AC) and a triplex treatment composed of a low temperature solution treatment (850 °C, 2 h, FC, FC denotes furnace cooling) and a duplex aging treatment (700 °C, 6 h, FC + 540 °C, 6 h, AC). The average cooling rates were 6 °C/min from 850 °C to 700 °C and 2 °C/min from 700 °C to 540 °C, respectively. The thermal stability of the alloy was evaluated according to the changing ductility (elongation and area reduction) after exposure at 540 °C for 100 h. All heat treatment conditions performed are listed in Table 2.

Table 1 Chemical composition of alloy (mass fraction, %)

Ti	V	Cr	Al
Balance	25.6	14.7	2.03
C	O	N	H
0.20	0.088	0.008	< 0.002

Table 2 Heat treatment conditions

Heat treatment	Description
Condition 1	1050 °C, 0.5 h, AC+ 700 °C, 4 h, AC
Condition 2	1050 °C, 0.5 h, AC+ 850 °C, 2 h, FC+ 700 °C, 6 h, FC+ 540 °C, 6 h, AC
Condition 3	Condition 1+ 540 °C, 100 h, AC
Condition 4	Condition 2+ 540 °C, 100 h, AC

AC—Air cooling; FC—Furnace cooling

All samples for optical microscopy (OM) and scanning electron microscopy (SEM) were polished and etched using the etchant (5% HF+ 10% HNO₃+ 85% H₂O (volume fraction)). Thin foils for transmission electron microscopy (TEM) were prepared by a twin jet polishing using a solution composed of 6% perchloric acid, 34% *n*-butanol and 60% methanol at -40 V and -30 °C. TEM examination was carried out on a JEOL-200CX transmission electron microscope, operated at 200 kV.

Tensile tests were performed on smooth cylindrical specimens with 5 mm diameter by 25 mm gauge length, using an Instron testing machine at room temperature with a strain rate of 10⁻³ s⁻¹. Fractographic examination was carried out on a JSM-5600LV scanning electron microscope equipped with a LINK I-SIS300 EDX analytical system, operated at 20 kV.

3 RESULTS AND DISCUSSION

3.1 Microstructure of as-rolled samples

Fig. 1 shows the microstructures of as-rolled samples in both cross and longitudinal sections. The structure remains partially recrystallizing and some equiaxed β grains and titanium carbide particles (2~10 μm) are clearly seen. As shown in Fig. 1(b), carbides are aligned along the rolling direction. The carbides are distributed within grains and on grain boundaries as globular particles or short rods. Obviously, the direct effect of fine carbide particles is to refine the as-rolled microstructures of the alloy due to increasing the nucleation and pinning the grain boundaries. In addition, a very small number of fine precipitates (less than 1 μm) can also be observed, which are identified to be α phase by TEM diffraction^[11].

Fig. 2 shows the morphologies of carbide and α precipitates.

3.2 Effect of solution temperature on microstructure of Ti-25V-15Cr-2Al-0.2C alloy

Fig. 3 shows the microstructures of the samples solution-treated at 850, 950 and 1 050 °C, respectively. The microstructures of samples solution-treated at 850 and 950 °C only partially recrystallized (Fig. 3(a)), whereas a fully recrystallized microstructure is obtained in the samples solution-treated at 1 050 °C while the grain growth is significant. In addition, it can also be observed from the micrographs that the amount of α precipitation increases with increasing solution temperature, which is produced during the air cooling after solution treatment. α precipitates seem to be distributed homogeneously within the grains except that there are precipitation-free zones (PFZ) near the grain boundaries, as shown in Fig. 3(a). The occurrence of PFZ indicates that quenched-in vacancies play an important role in α precipitation sites.

3.3 Effect of aging treatment and exposure on microstructure of Ti-25V-15Cr-2Al-0.2C alloy

Solution treatment at 1 050 °C for 30 min was first performed to obtain a fully recrystallized structure. Subsequently, two different heat treatments (cf. condition 1 and 2) were carried out to stabilize the material.

SEM secondary electron images in Figs. 4(a) and (b) show the microstructures of the samples after treated under condition 1 and condition 2, respectively. It is clear that the single aging treatment at 700 °C results in higher level of α precipitation within the grains and on the grain boundaries (Fig. 4(a)), while the triplex treatment significantly suppresses the formation of α phase, especially within

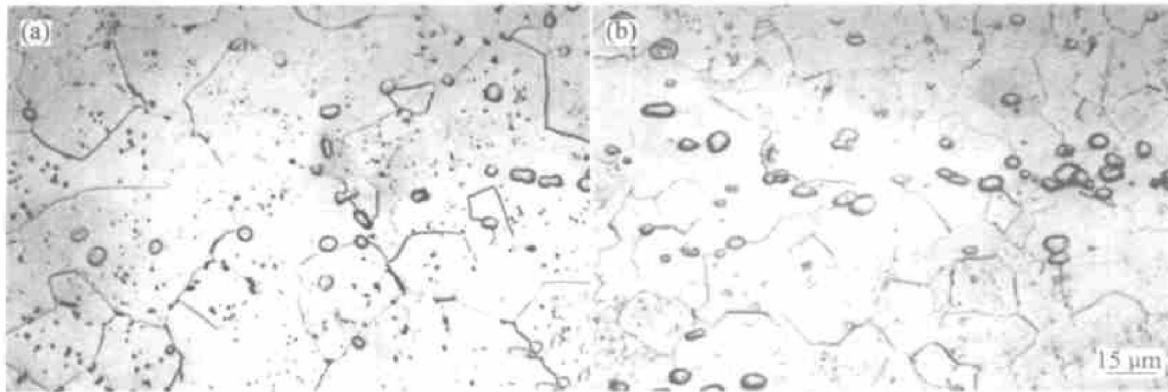


Fig. 1 Optical microstructures of as-rolled Ti-25V-15Cr-2Al-0.2C alloy
(a) —Transverse section; (b) —Longitudinal section

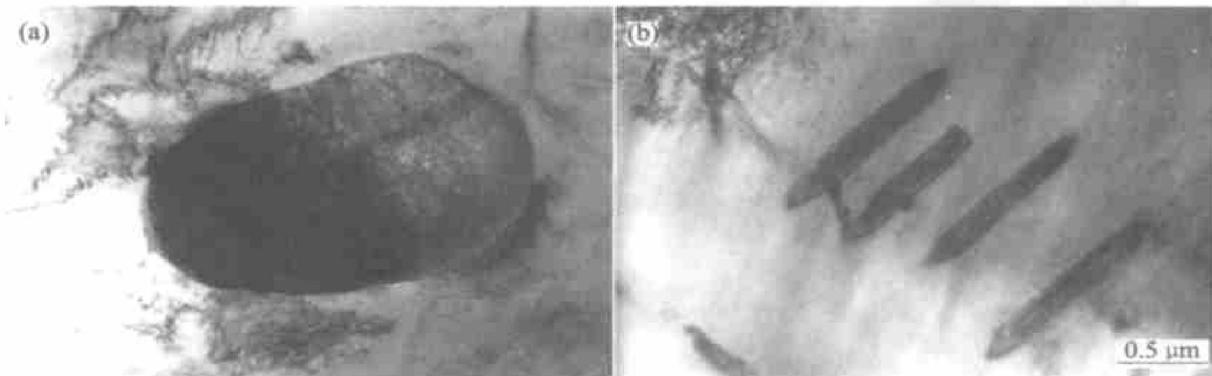


Fig. 2 TEM micrographs of carbide and α precipitation of Ti-25V-15Cr-2Al-0.2C alloy
(a) —Carbide; (b) — α precipitates



Fig. 3 Optical microstructures of as-solutioned Ti-25V-15Cr-2Al-0.2C alloy
(a) —850 °C, 1 h, AC; (b) —950 °C, 0.5 h, AC; (c) —1050 °C, 0.5 h, AC

the grains (Fig. 4(b)).

Figs. 4(c) and (d) show the microstructures of the samples exposed at 540 °C for 100 h following condition 1 and 2 treatment (cf. condition 3 and 4). It can be seen from Fig. 4(c) that in condition 3 samples larger α precipitated on β grain boundaries so that a heavy and continuous grain boundary α (GB α) film is formed. However, as shown in Fig. 4(d), although the amount of GB α precipitation increases to some extent in condition 4's samples compared with that in condition 2's samples (Fig. 4(b)), no extensive GB α precipitation occurs. Furthermore, the level of α precipitates is still lower within β grains in condition 4's samples.

The significant differences in the above microstructures can be understood on the basis of the forming conditions of α precipitates. It is well known that oxygen in solid solution has a strong effect on the occurrence of α precipitation in titanium alloys. Therefore, trying to lower the level of oxygen in the β matrix is an effective method to suppress α precipitation. In addition, vacancy defects in the β matrix should also be controlled to decrease the nucleation sites of α phase (cf. paragraph 3.2). According to the two aspects, the solution treatment at 850 °C of the triplex treatment (cf. condition 2) possibly plays a key role in suppressing α precipitates. On one hand, solution treatment at 850 °C for 2 h

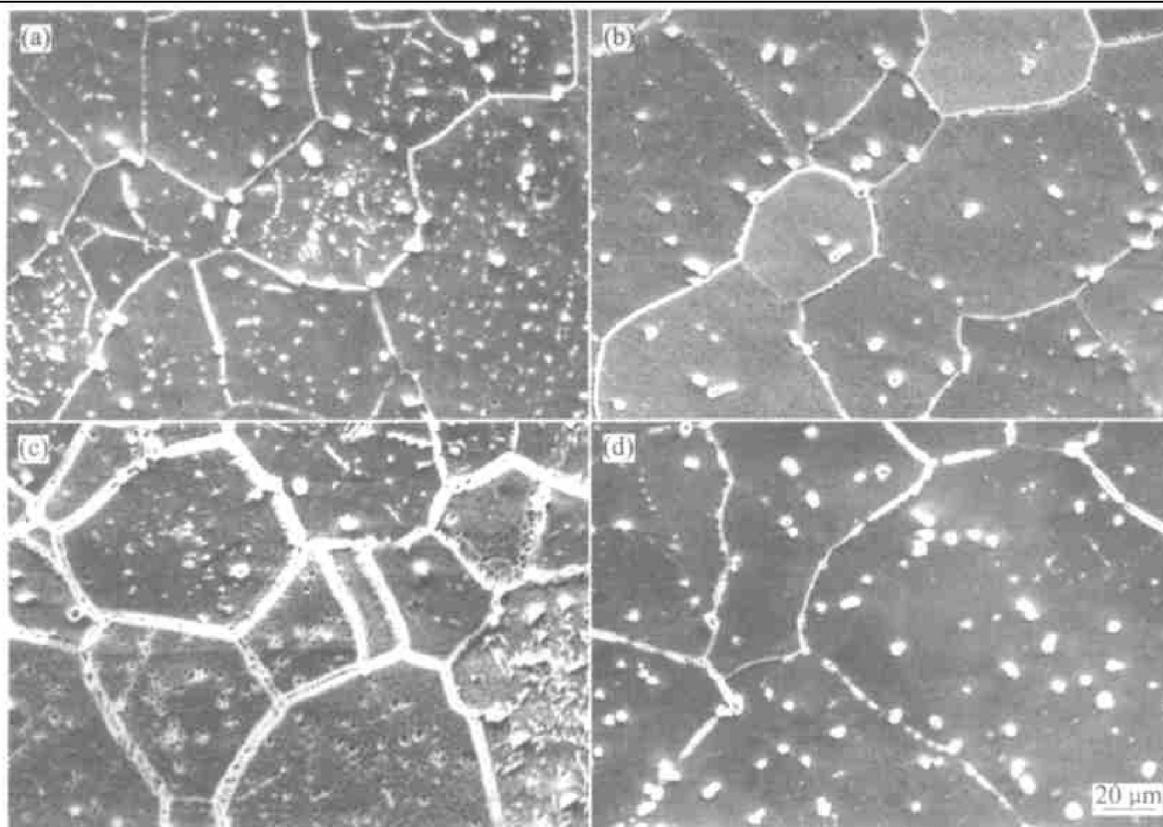


Fig. 4 SEM microstructures of Ti-25V-15Cr-2Al-0.2C alloy treated under different conditions (a) —Condition 1; (b) —Condition 2; (c) —Condition 3; (d) —Condition 4

makes it possible that a large number of interstitial oxygen atoms sufficiently diffuse towards carbides, thereby reducing the oxygen content in the matrix. To confirm this fact, further experiments on the content of oxygen in carbides need to be carried out in future. On the other hand, as described by Li et al^[9], a number of vacancies seem to be removed during the solution treatment at 850 °C.

The suppression of α precipitation is also attributed to the duplex aging treatment (700 °C, 6 h and 540 °C, 6 h), which possibly further reduces interstitial oxygen atoms and vacancy defects in the β matrix. In an attempt to suppress the formation of new vacancy defects, slower cooling rates (furnace cooling) are employed in the triplex treatment.

As a result of those possible reasons mentioned above, the tendency of α precipitation is greatly reduced in condition 2 and 4's samples, thus significantly improving the microstructural stability of the alloy.

In our work, careful TEM observation shows that after long-term exposure, a kind of new secondary phase occurs in the matrix of the alloy, which is identified to be an intermetallic compound TiCr_2 by electron diffraction. Fig. 5 shows the morphology of TiCr_2 precipitation with a corresponding electron diffraction pattern. It is also found that TiCr_2 particles tend to precipitate on β grain boundaries, thus having a detrimental effect on the ductility of the alloy. The fact that TiCr_2 precipitates are merely ob-

served in thermal exposure microstructure suggests that the formation of this intermetallic compound is a very sluggish diffusion process.

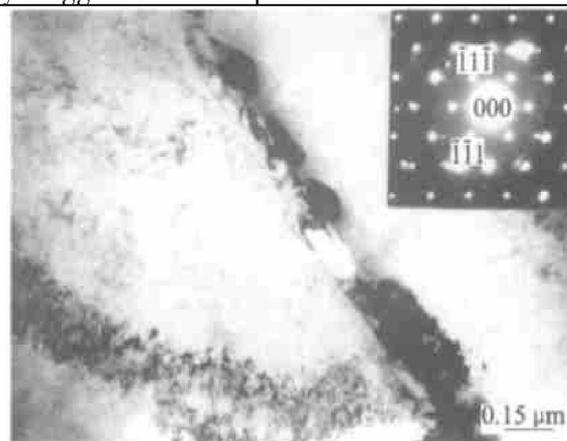


Fig. 5 TEM micrograph of TiCr_2 precipitates (The inset is SAD pattern taken from [011] pole of TiCr_2)

3.4 Tensile properties and fracture modes

The results of room temperature tensile properties of the samples after treated under different conditions are shown in Table 3. It can be seen that condition 1's samples exhibit higher strength and slightly lower ductility when compared with condition 2's samples. After exposure at 540 °C for 100 h, the ductility of condition 1's samples reduces drastically and the elongation decreases from initial value of 17% to 8% and the RA decreases from 36% to 8% (see

condition 1 and 3 in Table 3). However, it is noteworthy that condition 4's samples still retain excellent ductility, especially the elongation is almost the same as that of condition 2's samples.

Table 3 Comparison of room temperature tensile properties of samples of Ti-25V-15Cr-2Al-0.2C alloy treated under different conditions

Heat treatment	σ_b /MPa	$\sigma_{0.2}$ /MPa	δ /%	ψ /%
Condition 1	1 025	998	17	36
Condition 2	1 005	990	19	44
Condition 3	994	984	8	8
Condition 4	985	965	18	30

SEM fractographs in Fig. 6 show the fracture surfaces of room temperature tensile samples after different heat treatments. It can be clearly seen that condition 1's samples fail by a mixture of intergranular and transgranular manners (Fig. 6(a)), while condition 2's samples mainly fail by a ductile manner except that a small number of secondary cracks occur along the grain boundaries (Fig. 6(b)). As shown in Figs 6(c) and (d), the difference in the fracture character between condition 3 and 4 is noticeable.

Condition 3's samples fail by a typical brittle intergranular manner with void formation and growth occurring along β grain boundaries (Fig. 6(c)). However, in condition 4's samples higher level of intergranular and transgranular dimples can be seen (Fig. 6(d)), indicating the grain boundaries are not as weak as those in condition 3 samples.

Apparently, the degree of intergranular fracture enhances with the increase of GB α precipitates.

The changes in tensile properties and fracture modes are closely related to the amount of α precipitation in the alloy. Although α precipitation has a strengthening effect on the matrix due to the fact that α/β interfaces can act as effective obstacles to dislocation motion^[12], it will lead to the reduction in the ductility of alloy, especially the presence of excessive GB α . As discussed earlier, the triplex treatment can significantly suppress the formation of α precipitation both within grains and on grain boundaries, thereby enhancing the ductility of the alloy. By contrast, the single aging treatment give rise to larger α precipitates, thus resulting in the lower ductility.

Continuous GB α films mainly lead to the very low ductility of condition 4's samples. Moreover, after long-term exposure the occurrence of brittle

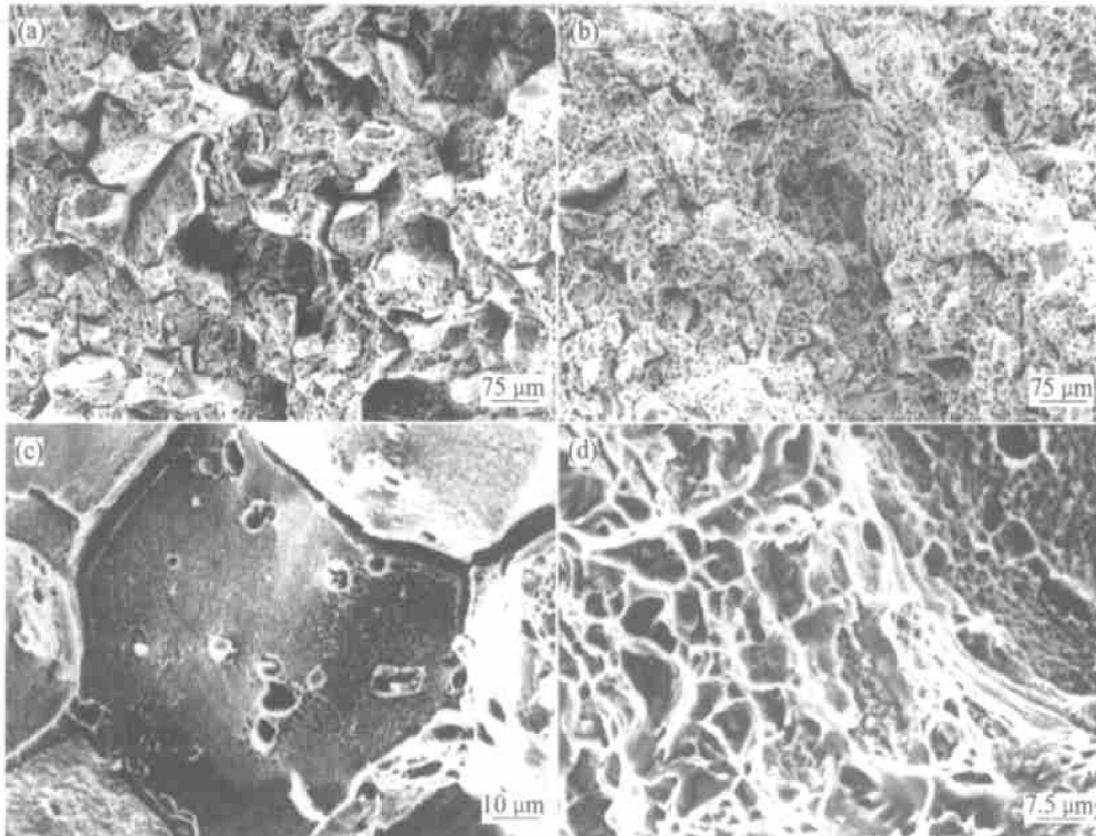


Fig. 6 SEM fractographs at room temperature tensile surfaces of Ti-25V-15Cr-2Al-0.2C alloy treated under different conditions (a) —Condition 1; (b) —Condition 2; (c) —Condition 3; (d) —Condition 4

intermetallic compound $TiCr_2$ also further exacerbates the ductility of the alloy, which is frequently produced on grain boundaries.

4 CONCLUSIONS

1) The amount of α precipitation in the samples after solution treatment followed by air cooling increases with increasing solution temperature.

2) After solution treated at 1 050 °C, the single aging treatment at 700 °C results in higher level of α precipitates, while the triplex treatment (850 °C, 2 h, FC+ 700 °C, 6 h, FC+ 540 °C, 6 h, AC) significantly suppresses the formation of α phase both within grains and on grain boundaries.

3) After long-term exposure at 540 °C, a continuous GB α film is formed in the samples heat-treated by the single aging, thus reducing drastically the ductility of the alloy. However, It is interesting to note that the samples heat-treated by the triplex treatment only give rise to a limited amount of GB α precipitation, thereby significantly improving the thermal stability of the alloy.

4) Intermetallic compound $TiCr_2$ is observed in the samples after long-term exposure, which further exacerbates the ductility of the alloy.

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REFERENCES

- [1] Bania P J. Beta titanium alloys and their role in the titanium industry [A]. Eylon D, et al. Beta Titanium Alloys in the 1990s [C]. Warrendale, PA: TMS, 1993.
- [2] Giary K. High-strength titanium resistant ignition [J]. Adv Mater Proc, 1993, 9: 7-10.
- [3] Seagle S R. The state of the USA titanium industry in 1995 [J]. Mater Sci Eng A, 1996, A213: 1-7.
- [4] Hansen J O, Novotnak D, Welter M F, et al. Properties and processing of a high strength beta titanium alloy [A]. Blenkinsop P A, Evens W J. Proceedings of the 8th World Conference on Titanium [C]. London: The Institute of Materials, 1996. 675-682.
- [5] Li Y G, Blenkinsop P A, Loretto M H, et al. Effect of aluminium on ordering of highly stabilized β -Ti-V-Cr alloys [J]. Mater Sci Tech, 1998, 14(8): 732-737.
- [6] Li Y G, Blenkinsop P A, Loretto M H, et al. Effect of aluminum on deformation structure of highly stabilized β -Ti-V-Cr alloys [J]. Mater Sci Tech, 1999, 15(2): 151-155.
- [7] Li Y G, Blenkinsop P A, Loretto M H, et al. Structure and stability of precipitates in 500 °C exposed Ti-25V-15Cr-xAl alloys [J]. Acta Mater, 1999, 46(16): 5777-5794.
- [8] Li Y G, Blenkinsop P A, Loretto M H, et al. Effect of carbon and oxygen on microstructure and mechanical properties of Ti-25V-15Cr-2Al alloy [J]. Acta Mater, 1999, 47(10): 2889-2905.
- [9] Li Y G, Loretto M H, Rugg D, et al. Effect of heat treatment and exposure on microstructure and mechanical properties of Ti-25V-15Cr-2Al-0.2C alloy [J]. Acta Mater, 2001, 49(11): 3011-3017.
- [10] LEI Liming, HUANG Xu, SUN Fusheng et al. Study of microstructure, tensile properties and deformation mechanisms of Ti-25V-15Cr-2Al-0.2C alloy [J]. The Chinese Journal of Nonferrous Metals, 2003, 13(4): 939-943. (in Chinese)
- [11] LEI Liming. Study of Microstructure and Mechanical Properties of Stabilized β Non-burning Titanium Alloys with Lower Cost [D]. Beijing: Beijing Institute of Aeronautical Materials, 2001.
- [12] Terlinde G T, Duerig T W, Williams J C. Microstructure, tensile deformation and fracture in aged Ti-10V-2Fe-3Al [J]. Metall Mater Trans A, 1983, 14A: 2101-2115.

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