[Article ID] 1003- 6326(2001)05- 0738- 05

Effects of alloying elements on nitrogen diffusion behavior around TiN/Ti interface α region in as-cast titanium alloys①

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[Abstract] To characterize the effects of alloying elements on inclusion dissolution of titanium nitride, the content profiles of elements around TiN/Ti boundary α phase regions in liquid titanium alloys have been experimentally carried out. Four kinds of commercial alloys of CpTi, Ti64, Ti17 and Ti6242 containing different α-stabilizing or β-stabilizing elements are examined through artificially embedding the TiN sponge particle into liquid alloys in VAR conditions. The content profiles of nitrogen and alloying elements around TiN/Ti boundary were measured by WDX and microprobe for as-cast samples. The content profiles of nitrogen and alloying elements around N-containing solid in αTi region of these alloys show a common features of a steep change. In particular, the content profiles of elements for Ti6242 demonstrate unique change of a more gentle change tendency and further deeper into the alloy matrix. The experiment results show that, the differences among composite effects of alloying elements in different alloys within nitrogen-induced diffusion α region result in different dissolution and diffusion behaviors to overcome the α phase region barriers.

[Key words] titanium nitride inclusion; content profiles; nitrogen; diffusion
[CLC number] TG 146.2 **[Document code]** A

1 INTRODUCTION

The dissolution and removal of hard α inclusion in liquid titanium alloys have been a concern in manufacture and research sectors. These inclusions mainly consist of titanium nitride (TiN) particles or other α stabilizer elements[1,2]. To eliminate these possible α inclusions from the ingot, the processes such as Vacuum Arc Remelting (VAR) depend on particle dissolution within the resident time of these particles in the molten ingot pool. To predict hard α inclusion survival, it is necessary to fully understand the effects of the thermal environment (e. g. fluid-flow modeling) on particle behavior for each process as well as to characterize particle-dissolution rates in the hearth or ingot environments.

There have been many modeling researches to describe the heat transfer, fluid flow and dissolution and diffusion of titanium nitride in the remelting processes of titanium alloys[3~6]. Bellot et al[3] studied the dissolution rates of TiN particle sponge and rods in the molten titanium alloys, a numerical representation of the dissolution problem was developed. It is also assumed that the dissolution of the nitrogen-stabilized inclusions occurs by nitrogen diffusion inside the inclusion and in the boundary layer around the inclusion. Reddy[4] measured a dissolution rate for TiN in Ti64 of 0.004 cm/min at 1923 K under static pool conditions. Using these experimental values, survival of nitride particles in titanium has been modeled as a function of particle density and diameter[1]. This model assumes spherical shape and calculates terminal floating or sinking rates based on a balance of drag force with buoyancy force for the moving particle.

On the other hand, there are relatively few publications related to effects of alloying elements on nitrogen diffusion and phase equilibria in the higher component Ti-rich alloys. The Ti-N binary phase diagram has being widely investigated by researchers[7~9]. Yolton et al[10] presented the results of a stepwise multiple linear regression analysis of the effect of chemistry on the β transus temperature and the C-curve nose time and temperature for α precipitation, for the metastable β class of titanium alloys. The majority of the alloys have compositions, which are characteristic of lean metastable beta. The systems Ti-Al-N[11], V-Al-N, Ti-V-N[12], N-Ti-V[13] in terms of previously assessed binary systems have been also published. The phase equilibria in the quaternary system Ti-Cu-Al-N, yielding the observation of 18 four phase spaces of the 850 ℃ isotherm has been investigated by XRD, metallography and EDX[14]. The phase diagram modeling for a variety of titanium alloys Ti-Al-V-O-(N, C) has been performed[15] but with particular reference to the oxygen. These models were combined with data for the binary subsystems of Ti-Al-V to predict the effect of O on the β transus of a Ti64 alloy. Moreover, a

① [Received date] 2000- 10- 19; [Accepted date] 2001- 03- 15

database, named Ti-DATA, for titanium-base alloys for modeling software of Thermo-Calc was established[16]. This Ti-DATA contains the following elements: Ti-Al-Cr-Fe-Mo-Nb-Si-Sn-Ta-V-Zr-C-O-N-B. The phases, which are included in this database, are Liquid, bcc (β), hcp (α), Laves_ C14, Laves_ + C15, TiFe_ B2, Ti_5Si_3, α_2-Ti_3Al, TiB, MC_ carbide, Ti_3AlC and SiC. However, there is very little information on α/ β compositions. Even though there are nearly 30 commercial Ti-base alloy systems included in Ti-DATA, no more detailed database for examining the effects of N on the phase equilibria of these titanium alloys. In the liquid phase the O and N interactions are included only for Ti due to the complexities of fully modeling these elements in liquid metals.

As one of a variety of approaches to characterize the dissolution behaviors of titanium nitride inclusion in liquid titanium alloys, the effects of alloying elements in various alloys on the content profiles of nitrogen as well as content profiles of alloying elements themselves are experimentally investigated by artificially embedded nitride titanium sponge to liquid CpTi, Ti64, Ti17 and Ti6242 alloys.

2 EXPERIMENTAL

The sponge titanium nitride particle TiN is Timet nitrided sponge (average content of N is 15% in mass fraction). CpTi, Ti64, Ti17 and Ti6242 are commercial alloys. The experiments are conducted in VAR furnace with Ar atmosphere. All the furnace parts are cooled with circulating water. The sponge TiN particle is fastened to the end of a stainless rod wrapped with tungsten wire and implanted at a sealed hole, extending to the melting pool surface in a copper crucible cooled with circulation water. The chamber is filled with flowing Ar atmosphere. The melting operation inside the furnace can be observed through filtered lenses. A motor can move up and down to control both the electrode and furnace cover. As long as the alloys melting after ignition, the sample is emerged to molten alloys for 5 min, then power is turned off and the samples are taken out once they are cooled to ambient temperature. The samples are cut into cubics for as-cast analysis. The samples after grinding, polishing and etching, were observed and analyzed by SEM and WDX (Wavelength Disperse X-ray Spectrometry) to determine the content profiles of elements around TiN/Ti matrix boundary while WDX analysis mean was used to measure the concentration of nitrogen profiles. The error for nitrogen and that for alloying elements are 0.25% and 0.15% in mass fraction respectively.

3 RESULTS AND DISCUSSION

3.1 Content profiles of elements

To compare the diffusion of nitrogen and alloying elements in various alloys, the concentration profiles of elements for as-cast (1900 ℃) alloys are plotted respectively. For any following figures, the zero point of distance scale is microprobe starting point at TiN/ α interface along the matrix alloy. The concentration profiles of nitrogen around α regions for CpTi and Ti64 alloys are shown in Fig. 1.

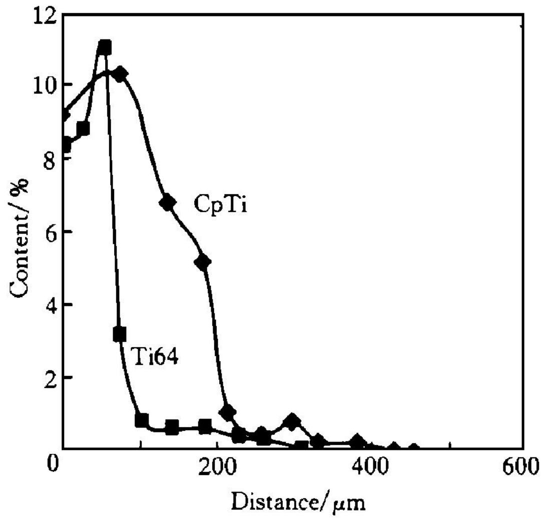

Fig. 1 Content profiles of nitrogen around α area of as-cast CpTi and as-cast Ti-64 alloy

As shown in Fig. 1, for both alloys the nitrogen contents increase and finally get to a highest value, and then steep decrease is observed along the matrix alloy. Moreover it is also obvious that the content profile of nitrogen for CpTi shows a relatively gentle decrease while that for Ti64 demonstrates a steep change. This phenomenon implies that a wide α shell region has formed around TiN/ αTi region induced by the diffusion of nitrogen into matrix titanium, which plays a role of a diffusion barrier.

In regard of the phase equilibrium associated with this process, there are a lot of assessed works regarding Ti-N binary system[6~9]. The peritectic temperature of Ti-N binary phase diagram assessed by Wriedt and Murray[8] is (2020 ±25) ℃, but the temperature determined by Ohtani and Hiller[9] is 1971 ℃. The phase change induced by nitrogen is well represented by Ti-N binary phase diagram as shown in Fig. 2. Moreover, it has been thermodynamically examined that the titanium nitride particle can not decompose at 1900 ℃ in melting pool except it floats to the superheat surface[2,3].

From viewpoints of dissolution mechanisms of titanium nitride, the defects of titanium nitride can be classified as an αTi-N solid solution. The light element nitrogen takes up the interstitial sites of hcp, α, bcc and β phases, while heavy elements such as Ti, Al, V take the substitutal sites[15]. Hence, the diffusion of nitrogen behaves in a manner of interstitial diffusion.

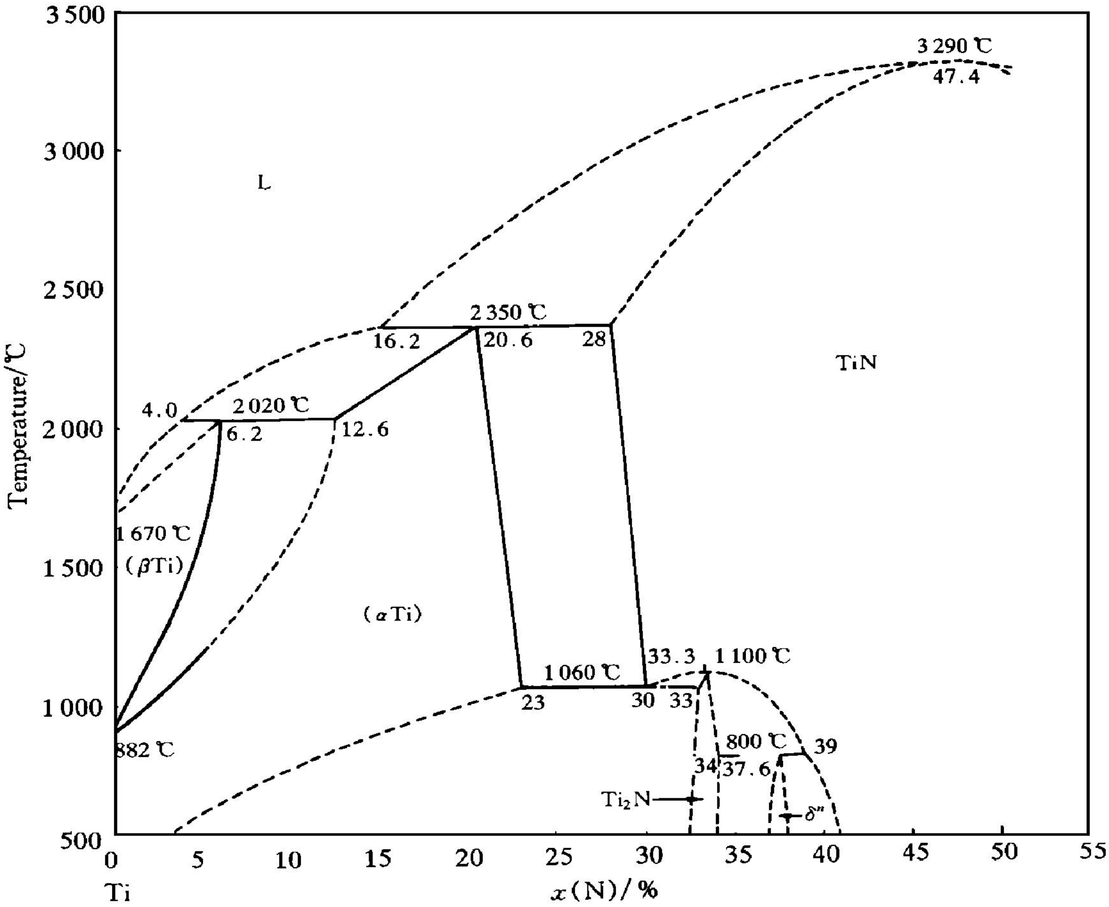

Fig. 2 Assessed Ti-N phase diagram (condensed system)[8]

During the dissolution process of titanium nitride, the alloys solidify quickly due to the narrow gap of liquidus and solidus line in Fig. 2; the dissolution of titanium nitride is determined by diffusion mechanisms in melts and solidified α phase region. At the steady state, the decrease of component activity of TiN results in the further transport of nitrogen.

As a result of diffusion of interstitial element nitrogen, an intermediate shell layer —α region around TiN/Ti boundary forms. The melting points of this region increase with the increase of nitrogen. The diffusions of elements are slowed due to the higher melting point feature. Simultaneously, liquid titanium together with alloying elements will infiltrate backward into the porous ceramic sponge compact through the intermediate phase change region. The efficient dissolution of titanium nitride sponge is more dependent on enhancing the diffusion of nitrogen within α region shell; In particular, the composite effects of alloying elements in matrix alloys determine the features of intermediate alpha layers.

In Fig. 3, the curves indicate how the alloying elements in matrix, Al and V for as-cast Ti-64 alloy diffuse into α region while nitrogen diffuses. The nitrogen profile is also plotted together for comparison. The composite effects of Al and V as α stabilizing and β stabilizing elements, retard the diffusion of nitro-

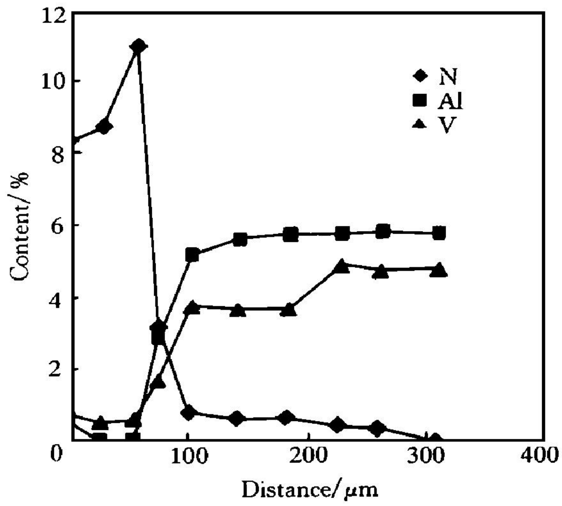

Fig. 3 Content profiles of Al, V and N of as-cast Ti-64 around α region interface

gen and themselves in α region.

For Ti17 alloy, the content profile of nitrogen is demonstrated in Fig. 4 together with those profiles of CpTi and Ti64 for comparisons. The steep change of nitrogen content for Ti17 around α region is also observed. This implies that the alloying elements impose similar effects on the behaviors of α phase regions between the boundary of nitride sponge and ti-

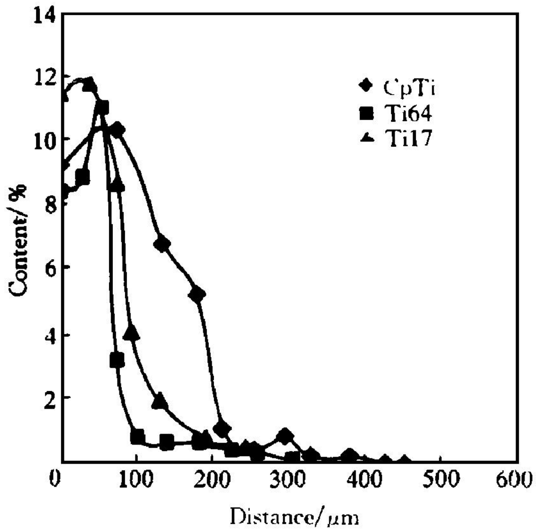

Fig. 4 Content profiles of nitrogen in Ti17 together with CpTi, Ti64 alloys

tanium matrix as Ti64 behaves. The content profiles of alloying elements in Ti17 are also plotted in Fig. 5 for comparison.

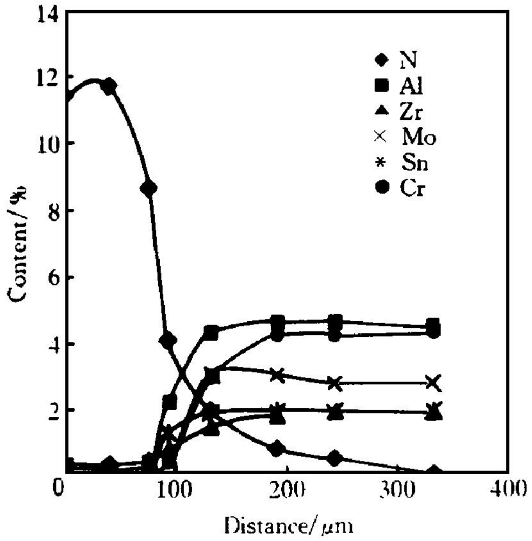

Fig. 5 Content profiles of alloying elements of as-cast Ti-17 around α region interface

In particular, in the case of Ti-6242, the content profile of nitrogen demonstrates much unique features as shown in Fig. 6. The gentle decrease of nitrogen along the matrix titanium shows different behaviors from those discussed above. This implies that, compared the cases in CpTi, Ti64 and Ti17 alloys, the further into the titanium matrix the nitrogen diffuses from the α region boundary. Hence, under the same operation conditions, the easier dissolution of titanium nitride inclusion could be expected.

As shown in Fig. 7, it is obviously noticed that the contents of alloying elements of Ti6242 are much higher than those of Ti64 and Ti17 (in Fig. 3 and Fig. 5). As described by Bewlay et al[6], for Ti6242 alloy, the matrix element infiltration to porous sponge nitride particle has been apparently observed, which reveals the beneficial promotion of diffusion by com-

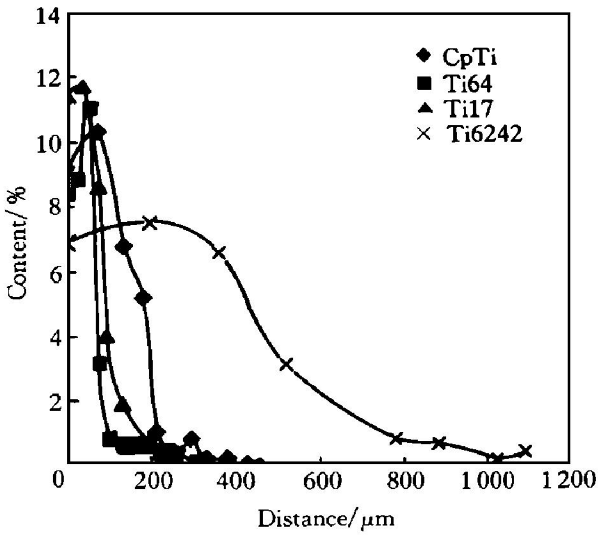

Fig. 6 Content profile of nitrogen in Ti6242 together with CpTi, Ti64 and Ti17 alloys

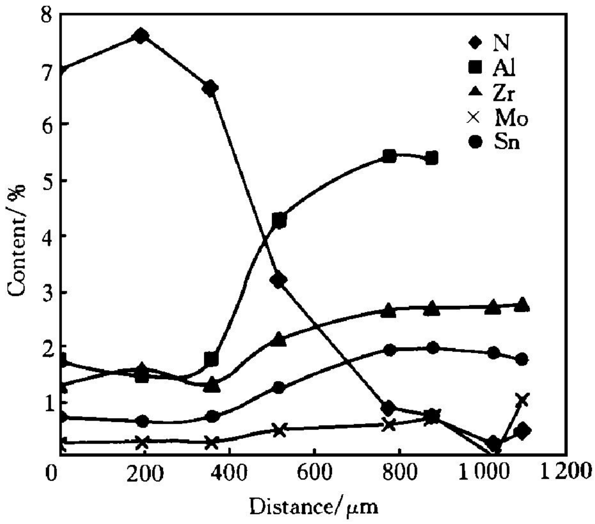

Fig. 7 Content profiles of alloying elements of as-cast Ti-6242 around α region interface

posite effects of alloying elements of Ti6242.

3.2 Numerical identification approach

To identify the effects of each element in various alloys on the phase change behaviors as well as the contribution to the diffusions of nitrogen and alloying elements themselves has been a challengeable approach. The detailed characterization of dissolution and diffusion in this problem may depend on the understanding of fluid mass transfer in liquid alloys, other than on the solid-state diffusion simulations. The latter has being well established with the aid of available or being developed computer programs like ThermoCalc and DICTRA[17]. Bellot et al[3] developed a numerical representation of the dissolution problem including the transient diffusion of nitrogen through intermediate solid phases. The second Fick Law in the form of spherical coordinates was employed and the thermodynamic equilibrium at local interface was assumed. However, it seems that much works to identify the contribution of each element to the problem need to be done.

4 CONCLUSIONS

1) The phenomenal facts of content profiles of nitrogen and alloying elements by experimentally embedding nitrided particles in various titanium alloys are presented.

2) The diffusion of nitrogen is retarded by composite effects of alloy elements, particularly due to some α stabilizing elements contained in alloys. The typical tendencies of steep decrease of nitrogen around α phase region are common for all of alloys while the alloying elements within this region also behave relatively steep increase along into the matrix titanium. The gentle change nitrogen profiles for Ti6242 imply that the removal of nitride particle inclusion will be more efficient than others in practical remelting processes.

3) Though well observed experimental facts have been obtained, due to the complexity of interaction effects of alloying elements, the precise mechanism interpretation such as the numerical characterization needs to be further approached.

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(Edited by HE Xue-feng)