Structure Transformation in Titanium Alloys during Nitrogen–rich Inclusion Dissolution in a Chamber ESR Process

A.D.Ryabtsev and V.V. Pashynsky,
Donetsk National Technical University, Donetsk, Ukraine

W.T. Carter and M.G. Benz
General Electric Global Research Center, USA

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Abstract

The current work is devoted to an investigation of the mechanism of accelerated dissolution of nitrogen-rich inclusions (NRI) from titanium alloys during Chamber ESR (ChESR) processing. Structural transformations in the inclusion and surrounding metal are investigated.

Dissolution of nitrogen-rich inclusions develops as a result of direct contact between the inclusion and molten active slag. Secondary saturation of molten metal on the electrode tip by nitrogen takes place as a result of nitrogen diffusion from the slag to the metal. The dissolution of inclusions that were made from titanium sponge saturated with nitrogen was accompanied by transformations inside the inclusion. TiN_x powder inclusions showed no transformation, and the process of dissolution occurred only on the boundary.

In addition to thermodynamic limitations, the rate of NRI destruction in the slag depends on kinetic parameters such as the circulation velocity of the slag. Circulation may be provided by axial oscillation of the electrode. Increasing the slag velocity accelerates the mass-transfer processes between the NRI and the slag.

Solidification of metal with dissolved nitrogen in the ingot leads to the formation of a uniform solid solution without harmful inclusions. Process parameters that provide the destruction of NRI at a rate 0.7 – 1.1 mm/s were developed.

Introduction

The removal of nitrogen-rich inclusions (TiN_x particles in particular) from titanium ingots and parts is a very important problem for manufacturers of titanium alloy products. The current work is devoted to an investigation of the mechanism of accelerated dissolution on the basis of structural transformations in the inclusion and the surrounding metal during a Chamber ESR (ChESR) process. As was established earlier [1-6], the use of such technology permits an increase in the rate of TiN_x inclusion dissolution by 10-100 times over conventional melting practice, and provides reliable elimination of harmful inclusions. However, the details of structural transformations that occur were not thoroughly investigated. An understanding of the mechanisms of inclusion removal my lead to more effective refining of titanium alloys.

As can be seen from the equilibrium phase diagram of Fig. 1, at temperatures above the melting point of titanium, the following phases with increased nitrogen concentration may exist: titanium nitride, TiN_x, with a minimal peritectic concentration of nitrogen 28 at-% at 2350 ^{0}C; α-Ti, with 12.7 at-%. At the peritectic temperature, 2020 ^{0}C, the solubility of nitrogen in β-Ti is 6 at-%. Thus, the character of transformation strongly depends on the temperature range during remelting. (The influence of temperature will be discussed later.)

It is known [7] that nitrogen-rich inclusions (NRI) have complex structure. At high nitrogen concentration the central part of inclusion is titanium nitride TiN_x, with structure and properties that are very different from the titanium alloy matrix. In particular, its Young's modulus is more than 5 times higher than pure titanium, which permits detection of inclusions by non-destructive methods such as ultrasonic inspection. TiN_x has a higher density than pure titanium, allowing the removal of inclusions with various metallurgical techniques.

Particles of TiN_x are surrounded by α-Ti and, sometimes, layers of β-Ti. In many cases the entire volume of the inclusion may be α-Ti. The hardness of such particles may be three times higher than the hardness of Ti. Therefore they play a role as stress concentrators and may nucleate fatigue cracks and accelerate fracture of critical titanium parts. The lattice parameter for α-Ti is 0.432 ηm, compared to 0.423 ηm for pure titanium. In addition, the densities are quite similar, leading to problems in detection via non-destructive methods. Reliable removal of these hard α-Ti inclusions is therefore a very important goal for refining processes. On the other hand, very hard and brittle particles of TiN_x are potentially more dangerous because the nucleation of microcracks may be

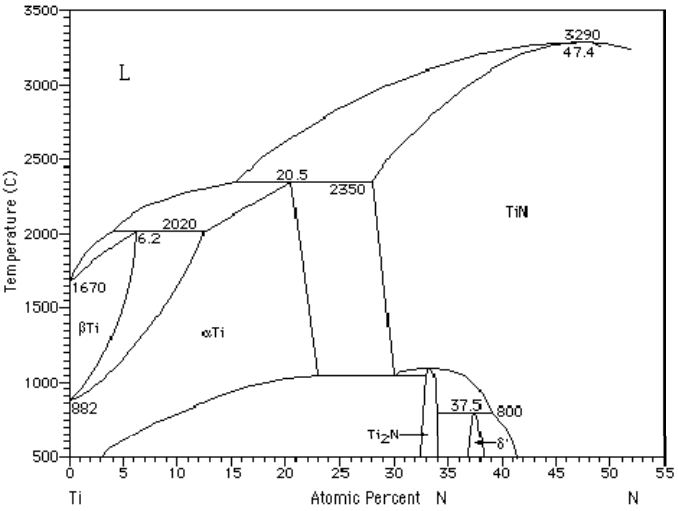


Figure 1: Equilibrium diagram for Ti – N system.

initiated on the boundary between NRI and the metallic matrix.

Therefore, emerging technologies for titanium refining must provide reliable and complete removal of both types of NRI.

Experimental

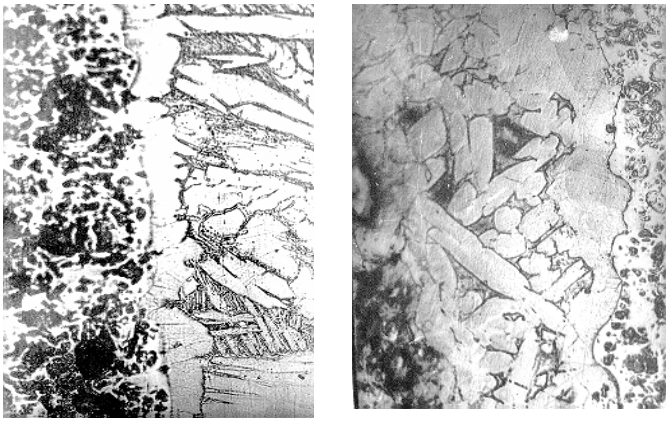
Consumable electrodes from Ti and titanium alloy Ti-6-4 75-mm in diameter and 850-mm long were used for the current work. These electrodes were artificially seeded with synthetic inclusions from nitrided titanium sponge (30 at-% nitrogen) and pressed TiN powder (49 at-% nitrogen). Details of the preparation and treatment of the electrodes is described in [6]. After ChESR melting the resulting ingots were ultrasonically inspected using a Krautkramer-Branson USN 52 tester at frequencies of 2.5 and 5 MHz. Samples for metallographic investigation were cut from locations where ultrasonic reflections were detected. Melting of electrodes with continuous inclusions was interrupted so that part of the inclusion was unmelted – the partially-melted electrode were also investigated. The sample structure was studied after polishing and etching with a water solution of hydrofluoric acid and after hot etching at magnifications x50-x500 using an optical "Neophot-21" microscope. Microhardness measurements were made using a PMT-3 microhardness tester. Photos were made using a digital camera with 3.3 Mpx resolution.

Analysis of structure transformations during diffusion dissolution of NRI

Dissolution of NRI becomes possible with the formation of liquid phases in the system. The melting point for pure Ti in accordance with equilibrium diagram (Fig. 1) is 1670 ^{o}C. Typical nitrogen content in commercial titanium alloys is 0.1 wt-%. Therefore nitrogen starts to diffuse from the inclusion to the molten metal and the concentration of nitrogen in the outer layer of the inclusion decreases. The TiN_x phase transforms to α-Ti and β- Ti. Melting of β-Ti becomes possible when the nitrogen concentration decreases below 6 at-%. But when the process temperature is higher than 2020 ^{o}C, direct dissolution of α-Ti (after decreasing the nitrogen concentration below 12.7-20.5 at-%, depending on temperature) becomes possible. Direct dissolution of TiN_x in molten metal may take place at temperatures higher than 2350 ^{o}C and nitrogen concentrations below 28-49 at-%.

If the process of TiN_x particle dissolution is not complete, the structure transformation during cooling will develop as in metal matrix, as in residual of inclusion with nonuniform distribution of nitrogen. At room temperature Ti has the structure of α-Ti, and Ti-6-4 will have a dual phase α+β structure. The outer layer around the inclusion, saturated by nitrogen, must have the α-structure. Titanium nitride Ti_2N may precipitate from supersaturated solid α-solution. Therefore, the transition zone around the inclusion residual has a complex structure.

The structure of the diffusion (transition) zone around the residual of a single NRI from nitrided sponge is shown on Fig. 2.



a b

Figure 2: Structure of diffusion (transition) zone around the residual of a single NRI made from nitrided sponge, x250: a – inclusion/matrix boundary; b – zone with decreased nitrogen concentration inside inclusion.

As can be seen in the picture, the size of the diffusion zone is small, but inside the inclusion considerable structural transformation takes place. According to the phase diagram, in all experimentally evaluated process temperatures, nitrogen concentration in nitrided Ti sponge (30 at-%) is very close to minimal possible limit of TiN_x stability (28–29 at-%). Therefore a relatively small decrease in concentration as a result of diffusion to molten metal promotes the development of structural transformations, with the formation of α-solid solution dendrites inside the particle. It was established experimentally that dissolution of large NRI from nitrided

sponge (up to 10 mm in diameter) is possible during ChESR [1,2].

In the case of dissolution of NRI from pressed TiN powder, the diffusion zone will have a different structure.

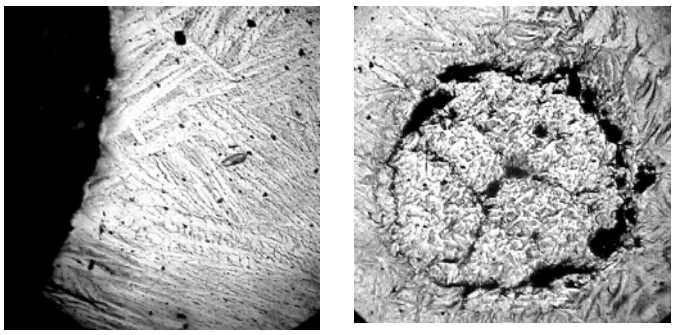


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Figure 3: Structure of the diffusion zone around TiN inclusion, x100: a) inclusion/matrix boundar; b) formation of pores on the interphase boundary.

As can be seen in the Fig. 3, the diffusion interaction develops very slowly. Due to the difference in physical-mechanical properties, the formation of pores may take place on the boundary of phases. Results show that dissolution of TiN_x inclusions is possible only for particles of very small size. The rate of TiN dissolution in a molten metal pool is very slow, 10^{-2} *mm/s* – 10^{-4} *mm/s*. Therefore, effective destruction of NRI in a ChESR process as a result of diffusion dissolution into liquid metal is unlikely.

One possible way to speed the diffusion processes during ChESR may be to increase the velocity of slag circulation. Many techniques exist for slag circulation; we have chosen the relatively simple and practical method of oscillating the consumable electrode. An oscillation control signal is added to the upper electrode drive control. This method permits an increase in mass transfer not only due to rotation of slag in horizontal plane, but also due to the generation of vertical oscillations in the slag pool. Oscillations from 0.3 to 1.5 Hz were used with an amplitude from 1 to 15 mm. Oscillation was started after the beginning of melting and after formation of a molten metal pool. Small changes of melting current appear to correspond to the oscillation frequency. Increasing oscillation frequency above 0.7 Hz causes a dramatic increase in current and the heating moves from a resistive to an arcing regime. The characteristics of the electric current and appearance of the lateral surface of the ingot (Fig. 4) are evidence of arc melting.

Ultrasonic inspection of processed ingots obtained from electrodes with a single inclusion of TiNx showed reflections from undestroyed residuals of NRI. These residuals were subsequently extracted by machining the ingot. This is related to the fact that oscillation of the electrode increases not only the rate of NRI dissolution, but the rate of electrode melting as well, causing NRI's that have not enough time for dissolution to simply fall out. Residuals of NRI of smaller size and gas pores were found during ultrasonic inspection of ingots produced from electrodes with single titanium sponge NRI.

Figure 4: View of lateral surface of ingot after ESR with oscillations.

Formation of porosity is evidence of the fact that dissolution of NRI's continues after falling into the molten metal pool. The process continues until the inclusion is overcome by the solidification front. The smaller size of NRI residual is, in this case, due to lower nitrogen content in sponge NRI, as was mentioned earlier.

Ultrasonic inspection and machining of the ingot that was produced from an electrode with a single continuous NRI nitrided titanium sponge did not reveal any inclusion residuals. The prominent part of the inclusion on the electrode surface after interruption of the melting process is evidence of the fact that the rate of melting of the electrode metal was considerably higher than the velocity of axial NRI dissolution. Thus, oscillation permits an increase in the velocity of slag circulation, which causes an increase in NRI removal rate and electrode melting rate. For electrodes with a single NRI of TiN_x, as from nitrided sponge, this causes some NIR to fall out because they do not enough time for dissolution. In addition, oscillation has a destabilization effect on electrical operation and deterioration of ingot surface quality.

Analysis of structure transformation during destruction of NRI in chamber ESR processing of titanium electrodes under calcium containing fluxes

Remelting of electrodes with continuous NRI under optimal melting parameters resulted in practically complete dissolution of the NRI [5,6]. Fig. 5 is a view of a longitudinal section of

an electrode residual with an axial inclusion of TiN_x 1 mm in diameter. (The remelting processes was purposely interrupted before the inclusion was destroyed.) The NRI residual does not extend past the surface of the electrode and the melted droplet surrounds it. The rate of inclusion dissolution corresponds to general rate of electrode melting.

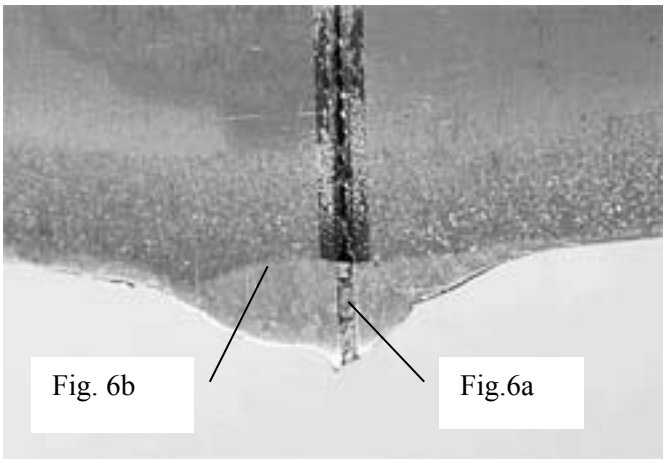

Figure 5: Section of electrode residual with continuous inclusion from TiN_x 1 mm in diameter.

Micrographs of diffusion zones indicated in Fig. 5 are shown in Fig. 6. Dendritic structure was formed far from inclusion as seen in Fig. 6b. Formation of dendrites is evidence of nonuniform chemical composition of the molten metal droplet. But at the same time, diffusion interaction of the inclusion material with surrounding liquid metal develops very weakly (Fig. 6a).

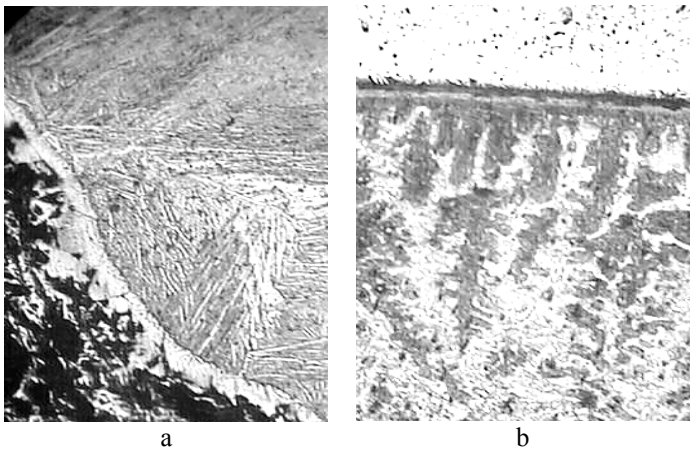

Figure. 6: Structure of transition diffusion zones in crystallized droplet of metal around the inclusion,. x100: a – inclusion/metal of droplet boundary;b – electrode/metal of droplet boundary.

Vickers hardness distribution measurement in the section of electrode residual (Fig. 7) is evidence of nitrogen concentration increasing in the metal of droplet.

As follows from the structure analysis, the inclusion cannot be the source of nitrogen for saturation of molten droplet metal. An important fact is that the highest hardness, and consequently the highest nitrogen concentration, is found in parts of the droplet that are close to the surface of the droplet. This can be explained from the assumption that the main process that dissolved the inclusion is the interaction of it with molten slag pool. The saturation of molten metal by nitrogen is the result of secondary nitiriding of liquid metal due to interaction with nitrogen-containing liquid slag.

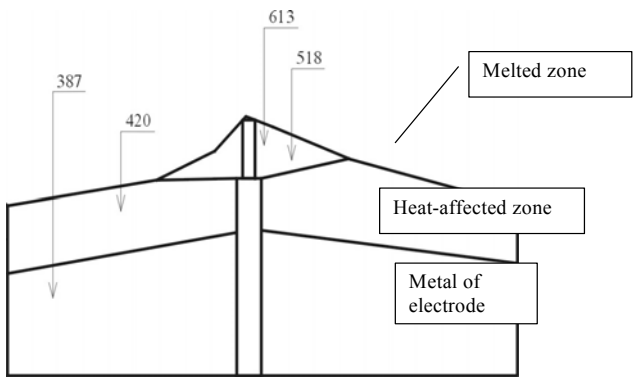

Figure 7: The distribution of the Vickers hardness on section of a sample, HV.

In prior work [5,6,8] it was shown that during ChESR under calcium containing fluxes, destruction of NRI proceeds as a result of its interaction with slag under conditions that form a gradient of partial pressures in the working space of the chamber furnace. Nitrogen that was transferred to the slag pool may redistribute in 2 directions:

- from the slag to the gas phase (the working space of the furnace with low partial pressure of nitrogen)
- from the slag to the molten metal and, after that, to the metal of the ingot.

Transfer of nitrogen to the gas phase is the favorable process that promotes removal of nitrogen from the metal and a decrease in the risk of formation of harmful nitrogen rich inclusions. Transfer of nitrogen into the metal of the ingot develops in such a way that a uniform distribution of it in the volume of liquid metal is obtained. It decreases the concentration of nitrogen in solid solution and eliminates the harmful influence of it on the mechanical properties of the metal.

Investigation through etching of the metal of the ingot in sections that correspond to the location of dissolution of the

inclusion shows that nitrogen is distributed uniformly into the liquid pool [6].

Investigation of the hardness distribution in the zone with dissolved nitrogen in the ingot shows that it increases uniformly in all sections to 20-35 HB. Metallographic and ultrasonic inspection does not reveal any traces of such inclusion formation in the entire volume of the metal of the ingot.

It is necessary to note that the electrodes that were used for these experiments have a much higher concentration of nitrogen-rich inclusions than typical for real industrial conditions. Therefore the increase of nitrogen concentration after dissolution of NRI for commercial ingots will be even lower than observed in experiments.

To obtain reliable removal of inclusions, it is necessary to provide favorable conditions for prolonged contact of the inclusions with active slag. Solidification of metal with dissolved nitrogen in the ingot leads to the formation of a uniform solid solution without harmful inclusions. Due to extremely low equilibrium partial pressure of nitrogen in all components of the system, a driving force for transfer of nitrogen from the slag to the atmosphere in the chamber is created, providing removal of dissolved nitrogen from the metal. Process parameters that provide the destruction of NRI at a rate 0.7 – 1.1 mm/s were developed.

Conclusions

1. During ChESR of electrodes with inclusions from TiN_x, effective dissolution is possible only at temperatures higher than 2350 ^oC, after diffusion decreases the nitrogen concentration on the electrode surface to below 28 at-%. Therefore the destruction of NRI due to diffusion processes is minimal. During remelting of electrodes with inclusions from nitrided titanium sponge, nitrogen concentration in the inclusion (30 at-%) is close to the minimum possible (28-29 at-%). Therefore, a relatively small decrease in concentration resulting from diffusion leads to the development of structural transformations in the inclusion with the formation of α- solid solution dendrites. If the temperature is higher than the peritectic transformation (2020^{o}C), inclusions from nitrided titanium sponge may quickly dissolve as a result of peritectic melting of α-solid solution.

2. Intensification of the diffusion processes due to oscillation of the electrode leads to an increase in NRI dissolution rate and an increase in electrode melting rate. But this may cause NRI to fall from the electrode into the ingot because the do not have enough time for dissolution. It also causes a destabilization of electrical parameters and a decrease in ingot surface quality.

3. Primary removal of NRI in ChESR processing develops as the result of interaction of the inclusion with calcium containing slag under conditions of a partial pressure gradient formed in the working space of the furnace. Nitrogen is partially removed from the inclusion to the gas atmosphere of the furnace working space, and it is partially transferred to the metal of the ingot. Formation of a uniform solid solution without precipitation of harmful nitrogen rich inclusion in ingot takes place in this case.

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