Titanium nitride (TiN) precipitation in a maraging steel during the vacuum arc remelting (VAR) process - Inclusions characterization and modeling

V Descotes¹, J-P Bellot², V Perrin-Guérin¹, S Witzke¹ and A Jardy²
¹ Aperam Alloys Imphy, BP 1 Centre de recherches P. Chevenard, F-58160 Imphy, France
² Institut Jean Lamour – UMR CNRS 7198 – Université de Lorraine, LabEx Damas, Parc de Saurupt – CS 50840, 54011 Nancy, France

E-mail: vincent.descotes@aperam.com

Abstract. Titanium Nitride (TiN) inclusions are commonly observed in a Maraging steel containing Nitrogen and Titanium and remelted in a VAR furnace. They can be easily detected by optical microscopy. A nucleus is observed next to a large number of TiN inclusions. A TEM analysis was carried out on a biphasic nucleus composed of a calcium sulfide (CaS) and a spinel (MgAl₂O₄), surrounded by a TiN particle. An orientation relationship between these three phases was revealed, which suggests a heterogeneous germination of the TiN particle on the nucleus by epitaxial growth. Based on this observation, on thermodynamic considerations and on previous work, a model has been developed and coupled to a numerical simulation of the VAR process to study the formation and evolution of a TiN distribution in the VAR ingot. Microsegregation is modeled using the lever rule, while the kinetics of precipitation is mainly driven by the supersaturation of the liquid bath. This model highlights the influence of the melt rate on the final size of TiN particles.

1. Introduction

The inclusion cleanliness is identified as a key parameter to extend the fatigue life properties of an alloy. In a maraging steel produced by Aperam (Imphy, France), containing Fe, 18%Ni, 9%Co, 5%Mo, 0.45%Ti and some traces of Nitrogen, Titanium nitride inclusions (TiN) are identified as the most harmful defect. This inclusion is very commonly observed in optical metallography [1]. It appears as a squared, yellow-colored particle. The thermodynamics of its formation has been studied by numerous authors, among them Morita and Kunisada [2] and more recently Kim et al. [3]. These studies conclude to the high stability of this kind of inclusion, which forms during the solidification of the alloy.

The production route involves a double remelting into a vacuum induction furnace (VIM) and a vacuum arc furnace (VAR). In this last process, an electric arc is generated between the electrode and the base of the copper mold in a vacuum atmosphere. Once the remelting has begun, the arc is set between the electrode and the growing ingot. The objective of this operation is to better control the solidification of the final ingot, its inclusion population, and possibly take advantage of the vacuum to pursue the steel refining [4].

A study of the TiN precipitation during solidification was carried out by Rocabois et al. [5] and then Lehmann et al. [6], who considered heterogeneous nucleation and diffusion kinetic laws, but no engulfment. Ohta and Suito [7] experimentally characterized the effect of the germs on the TiN sizes and show the particular benefit of MgO particles to increase the numeral density of inclusions and thus reduce their size.

The aim of this paper is to study the formation of the TiN inclusions in VAR ingots. It follows a previous article published on the same subject in 2013 [8].
Industrial and experimental facts are compiled in a first part. Counts of inclusion populations were performed and are presented using log-normal laws.

A model was proposed in previous work [8] to predict the nucleation and growth of a TiN distribution during the solidification of the alloy, which causes segregation of Ti and N in the liquid. This approach is here recalled and coupled to a 2D-axisymmetric model of the VAR process (SOLAR code, [9]) in order to quantify the inclusion cleanliness in a whole ingot. The results of the simulation are compared to an experimental remelting. This tool highlights the heterogeneous inclusion size in the VAR ingots and enables one to optimize the process.

2. Thermodynamical considerations and experimental observations

2.1 Nucleation of TiN inclusions

The TiN precipitation obeys to the following chemical reaction: \( +N = TiN(s) \). It is characterized by the solubility product \( K_{TiN}(T) \) related to the activities of solutes in the steel by:

\[
K_{TiN}(T) = a_{Ti}^{eq} \cdot a_{N}^{eq}
\]  

(1)

Using the software Thermo-Calc [10] and the TCFE7 Steels/Fe-alloys database version 7 [11] to compute the composition at equilibrium, it is found that with 4500ppm of Titanium in the liquid bath, the Nitrogen maximal mass fraction before precipitation starts is 17ppm. Since a Nitrogen mass fraction as low as 10ppm is commonly reached in the electrode, the inclusions that may exist in the bath are unstable and dissolve. As suggested by Young and Mitchell [12], it is assumed that complete dissolution takes place in the VAR liquid pool before solidifying the alloy. At that time, segregation will make the solute concentrations rise above the solubility limit, therefore triggering the precipitation of nitrides.

A detailed characterization of a mixed CaS – MgAl_2O_4 - TiN inclusion with a shell-core structure has been presented in reference [13]. An orientation relationship between all phases was found, which suggests that the CaS formed over the spinel, and that the TiN formed itself by epitaxial growth on the two nuclei. This observation strengthens the hypothesis of a heterogeneous nucleation of TiN particles on germs, i.e. inclusions that are stable in the liquid steel above the liquidus temperature. This hypothesis is also evoked by Rocabois et al. [5], Kunze et al. [14] and Lehmann et al. [6].

2.2 Optical counts and treatment

An automated count of all inclusions on a polished sample is performed using an optical microscope. The surface of each inclusion is measured, and then converted into an equivalent radius.

It is noticed that a large amount of small inclusions are not detected by optical microscopy, although they truly exist (they are detected with SEM). Atkinson and Shi [15] report three methods to characterize such an inclusion population and especially choose an indicator of the maximal inclusion size: using a log-normal distribution law, using the extreme value method [16], or using a Pareto distribution law to model the tail.

The modeling of the entire inclusion population using a log-normal distribution law may be more uncertain than only characterizing the tail, as noted by Atkinson and Shi [15], but it enables us to introduce the number density of inclusions in our characterization, which provides fundamental elements to understand the cleanliness differences between samples.

The counting provides a sequence of \( n \) inclusion radii that can be sorted in ascending order \( r(i) \) (\( i \) being the index of each inclusion in the sequence). The distribution of the inclusions will be approximated by a log-normal law with two parameters \( \mu \) and \( \sigma \). The cumulative distribution function of this law is expressed by:
$$F(r; \mu, \sigma) = \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\ln r - \mu}{\sigma \sqrt{2}} \right)$$

(2)

A threshold is set at a radius of 2.5\(\mu\)m. As the total number of inclusions on a sample \(n_{tot}\) remains unknown, the model is built with three parameters \(\mu, \sigma\) and \(n_{tot}\):

$$\forall i \in [2; n], \quad i = n_{tot} (F(r(i); \mu, \sigma) - F(r(1); \mu, \sigma))$$

where \(n_{tot}\) is the theoretical total number of particles that are present on the sample, \(n\) the number of particles effectively detected, \(i\) the particle index in the radii sequence \(r(i)\) sorted in ascent order, and \(r(1)\) the smallest radius detected. An optimization on the three parameters is performed using the non-linear least squares "fit" routine of MATLAB and leads to an estimation of \(n_{tot}, \mu\) and \(\sigma\).

A total volume density of particles can be derived, one assuming a uniform spatial distribution of the particles on the sample of surface \(S_0\):

$$n_{tot}^v = \frac{3}{4} \sqrt{\pi} \left( \frac{n_{tot}}{S_0} \right)^{3/2}$$

where \(S_0\) is the area of the sample. An estimation of the upper radius bound with probability 97% is determined using the inverse log-normal cumulative function:

$$r_{97} = \exp \left( \sigma \sqrt{2} \text{ erf}^{-1} (2 \cdot 0.97 - 1) + \mu \right)$$

where \(\text{erf}^{-1}\) is the inverse error function.

Figure 1 presents the diameters \(d_{97} = 2 \cdot r_{97}\) calculated on several industrial samples. It experimentally highlights that:

- the particle diameter \(d_{97}\) increases with the Nitrogen content of the alloy;
- at a given chemical composition, the distribution of nitrides over a large number of nucleation sites decreases the size of the particles.

An effect of the local solidification conditions may explain some of the discrepancies between the samples.

![Figure 1: Diameter \(d_{97}\) of the TiN inclusions characterized on several samples, related to the Nitrogen mass fraction in the sample](image-url)
3. Precipitation model and VAR process modeling

Precipitation is thought to happen during solidification thanks to segregation. The VAR ingot growth and solidification was modeled using a 2D - finite volume code. The ingot geometry is discretized into a 2D axisymmetric mesh. The precipitation model developed in ref. [8] is summarized below.

3.1 Hypotheses of the inclusion model

Based on the experimental observations (section 2.1), it is considered that TiN inclusion form on an inert, pre-existing oxide distribution that act as nuclei. Nucleation is therefore considered to be only heterogeneous.

It is also considered that the precipitation reaction stops in the solid phase. This assumption is supported by the fast cooling rate of the ingot during the VAR process, which prevents the establishment of a significant diffusion in the solid state to pursue precipitation.

3.2 Inclusion precipitation model

A competition takes place between the segregation which brings solutes in the liquid phase and the precipitation which consumes solutes. The supersaturation is defined as:

\[ S = \frac{a_T \cdot a_N}{K_{TiN}} \]  

(6)

The TiN nucleation model is derived from the classic thermodynamics theory developed in several books as in Refs. [17,18]. It considers the Gibbs energy of the chemical reaction of precipitation and an interfacial energy term that acts against the nucleation. Therefore, nucleation can occur only if the supersaturation of the bath is at least higher than unity, the exact threshold depending on the size of the oxide. After nucleation, the growth of an inclusion is described by a first-order kinetic law involving the distance to equilibrium. As stated in [8], a transport equation in the internal coordinate space (inclusion size) for the particle distribution can be derived:

\[ \frac{\partial n_{TiN}^l}{\partial t}(r,t) = -k_c(S - 1) \frac{\partial n_{TiN}^l}{\partial r}(r,t) \]  

(7)

where \( n_{TiN}^l \) is the distribution of TiN in the liquid phase (density number of inclusions of radius \( r \) per unit volume of liquid metal and per unit length of particle radius), \( r \) is the radius of an oxide-TiN assembly (m), \( S \) the supersaturation, and \( k_c \), a kinetic factor which gathers the chemical phenomena at the interface and the Ti and N mass transport from the supersaturated bulk liquid to the TiN particle surface.

When solidification proceeds, the solidification front engulfs some TiN inclusions from the liquid into the solid. Those inclusions will no more be available in the liquid to grow further, so they become inert.

A lever rule model is brought into play to describe the solidification of the alloy, thus assuming infinite diffusion of the solutes within the two phases [19]. The liquid concentration is lowered by the solute consumption from the precipitation reaction, as described in [8].

3.3 SOLAR model and coupling

Simulating the VAR process has been successfully attempted over the past decades. The result of these efforts is collected into several calculation codes like BAR [20], MeltFlow [21] or SOLAR [9].

The SOLAR code has been developed in Nancy during several PhD [9, 22]. It takes as input the electrical current, voltage and the recorded melt rate in order to simulate the VAR process. Fluid dynamics, electromagnetic fields, thermal exchanges, solidification and solute transports are calculated in transient regime using a finite volume SIMPLE numerical scheme [9, 23].
The water cooling of the copper mold and the Helium pressure injected in the gap between the ingot side and the mold are modeled by thermal resistances [22]. The turbulence is computed by a k-ε model. The mesh is refined at the ingot top and side. The growth of the ingot is performed by periodical splitting and continuous growth of cells. It introduces advective source terms in the numerical scheme [24].

A weak coupling is introduced with the precipitation model in each cell: the variation of the solid fraction $g_s$ and associated segregation given by SOLAR determine the precipitation sequence over one time step: germination, engulfment, growth of particles, solute consumption. The coupling between the cells is achieved through the solute transport equation solved in SOLAR.

4. Experimental remelting

A full-scale ingot was remelted at Aperam in order to study the effect of remelting parameters on the inclusion cleanliness. It must be stated here that the usual industrial practice largely differs from the remelting conditions that were chosen for this ingot.

4.1 Remelting parameters and etching procedure

The melting rate is suspected to have the main impact on the solidification in VAR process, and therefore on the inclusion cleanliness. Two melt rates were tested, with steep transitions between the two steady-state regimes. A brutal cut of the electrical input was applied at the end of the remelting to freeze the last liquid pool.

A longitudinal slab was extracted from the ingot and cut into four pieces. Each part was polished and chemically etched to reveal the grain structure using FRY7 reactant (HCl + CuCl₂). A reconstruction of some liquid pools was performed assuming that the solidification front was perpendicular to the grain columns. Three samples were taken along the axis at different heights and analyzed.

4.2 Results - experimental ingot

The approximation of the TiN counts by a log-normal law lead to the values of table 1. We notice that sizes decrease when the melt rate increases.

| Height (m) | $\sigma_f$(µm) | Comments       |
|-----------|---------------|----------------|
| 0.54      | 4.2           | Low melt rate  |
| 0.85      | 3.0           | Low melt rate  |
| 1.28      | 3.7           | Higher melt rate |

It was observed on the axial section of the ingot that the depth of the liquid pools changed when the melt rate was increased. A deep pool was obtained at the end, materialized by an equiaxed solidification. This structure comes from the abrupt stop of the remelting without wafering the ingot.

5. Numerical results

Simulations of the inclusion cleanliness using the coupled model were carried out on the experimental ingot.

5.1 Temperature field

Figure 2 shows the temperature field calculated in the ingot at different steps of the remelting. The mushy zone is materialized by two thick lines. A melt pool depth of around 40cm is achieved at the end, which is what was observed on the etched plate. It can be seen that the mushy zone extent is higher near the end, when a high melt rate is achieved.
5.2 Cleanliness aspects
Cleanliness is characterized by the TiN mass fraction in the solid phase and by the radius $r_{97}$ which represents the upper bound radius of 97% of the TiN distribution in the solid phase (figure 3). The precipitation is influenced by the macrosegregation of N or Ti, which is shown on maps. The end of the solidification after shutting down the power was not simulated.
It is seen that the maximal sizes of TiN particles are reached at mid-radius and rather in the bottom part of the ingot where the melt rate was the smallest. A higher melt rate seems to diminish the inclusion sizes, especially during the transient between the two regimes. Maximal radii of about 5.5µm are achieved. A macrosegregation in Ti and N is visible in the central axis due to the convective movements in the liquid pool.

6. Conclusion
Thermodynamic calculation shows that TiN inclusions are unstable in the liquid bath. Segregation in the mushy zone during the solidification raises the Ti and N contents in the interdendritic liquid, making the precipitation reaction possible. Experimental characterization of the inclusions shows that the nucleation is heterogeneous, and that the size distribution is related to the Nitrogen content and to the density of nucleation sites.

A precipitation model was set up in a previous work to study the coupling between these two phenomena [8]. This model was coupled to the SOLAR software to simulate the VAR remelting process and the TiN precipitation in the mushy zone. The results were compared to a full-scale melt with two different remelting conditions: a small melt rate and a high melt rate. It appears that:
• the liquid pool shapes are rather well predicted by the model for this melt;
• the largest inclusion size can usually be found at mid-radius; a heterogeneity of the inclusion sizes along the radius is clearly seen on the simulations;
• the melt rate may play a certain role on TiN size, by changing the local solidification time.

7. Acknowledgments
The authors gratefully acknowledge J. Ratafika (Aperam) who carried out the VAR casting experiment, and G. Pinton and P. Guichard of CRPC Aperam Alloys Imphy who characterized the ingot.

8. References
[1] Durand-Charre M 2003 La microstructure des aciers et des fontes - Génèse et interprétation (Paris: SIRPE Éditeur)
[2] Morita Z and Kunisada K 1977 Tetsu-to-Hagané 63 1663–71
[3] Kim W Y, Jo J O, Chung T I, Kim D S and Pak J J 2007 ISIJ International 47 pp 1082–89
[4] Yu K O 2002 Modeling for Casting and Solidification Processing (New York – Basel: Marcel Dekker, Inc.)
[5] Rocabois P, Lehmann J, Gaye H and Wintz M 1999 Journal of Crystal Growth 198/199 pp 838–43
[6] Lehmann J, Rocabois P and Gaye H 2001 Journal of Non-Crystalline Solids 282 pp 61–71
[7] Ohta H and Suito H 2007 ISIJ International 47 pp 197–206.
[8] Descotes V, Bellot J P, Witzke S and Jardy A 2013 Modeling the titanium nitride (TiN) germination and growth during the solidification of a maraging steel Proc. of the 2013 Int. Symp. on Liquid Metal Processing & Casting (Austin, TX, USA, 22-25 September 2013) ed Krane M J M, Jardy A et al (Warrendale: TMS) pp 201–206
[9] Hans S 1995 Modélisation des transferts couplés de chaleur, de soluté et de quantité de mouvement lors de la refusion à l’arc sous vide (VAR) - Application aux alliages de titane, Ph.D. thesis, Institut national polytechnique de Lorraine
[10] Andersson J, Helander T, Höglund L, Shi P and Sundman B 2002 Calphad 26 pp 273–312
[11] Thermo-Calc Software, Thermo-Calc Console Mode User Guide 2013 3.1 edition (Stockholm: Foundation of Computational Thermodynamics)
[12] Young E and Mitchell A 2001 High Temperature Materials and Processes 20 pp 79–101
[13] Descotes V, Migot S, Robaut F, Perrin-Guérin V, Witzke S, Bellot J P and Jardy A 2015 Metallurgical and Materials Transactions A 46A pp 2793-5
[14] Kunze J, Spitzer K H, Oswald S and Mickel C 1997 Zeitschrift für Metallkunde 88 pp 182–90.

7
[15] Atkinson H and Shi G 2003 *Progress in Materials Science* **48** pp 457–520

[16] Murakami Y 2002 *Metal fatigue: Effects of Small Defects and Nonmetallic Inclusions* (Amsterdam: Elsevier)

[17] Dantzig J, Rappaz M 2009 *Solidification* (Lausanne: EPFL Press)

[18] Lesoult G 2010 *Thermodynamique des matériaux* (Traité des matériaux vol 5) (Lausanne: PPUR)

[19] Kurz W and Fischer D 1998 *Fundamentals of Solidification* (Pfaffikon: Trans Tech publication Ltd)

[20] Bertram L, Schunk P, Kempka S, Spadafora F and Minisandram R 1998 *Journal of Metals* **50** pp 18–21

[21] Kelkar K, Patankar S, Mitchell A, Minisandram R and Patel A 2010 *ASM Handbook* vol 22B ed Furrer D and Semiatin S (ASM International) pp 196–213

[22] Quatravaux T 2004 *Évolution de la modélisation du procédé VAR - Contribution à la description de la dispersion inclusionnaire dans le puits liquide et à la prévention de défauts de solidification*, Ph.D. thesis, Institut national polytechnique de Lorraine

[23] Patankar S 1980 *Numerical Heat Treatment and Fluid Flow* 1st ed (Washington D.C.: Hemisphere Publishing Corp)

[24] Jardy A, Quatravaux T and Ablitzer D 2004 *Multiphase Phenomena and CFD Modeling and Simulation in Materials Processes* (Charlotte, NC, USA, 14-18 March 2004) ed Nastaq L and Li B Q (Warrendale: TMS) pp 265–277.