Mechanisms of TiAl alloys isomorphous inoculation from cryomilled Ti-Al-Nb powders

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Abstract. Isomorphous inoculation has recently been introduced by the authors as a successful method to grain refine cast titanium aluminides [1]. Analyses of the cast grain size together with introduced particle size distributions revealed anomalously high grain refinement efficiency which was attributed to the particles breaking up during the holding stage prior to solidification [2]. In the present work, the microstructure of the inoculant powders is investigated in both the cryomilled state as well as after simulated thermal cycles to reproduce their heating and holding in the melt. Results show that milling time does not impact the grain size in the particles, only their size distributions. Heat treatments between 1500 and 1600°C for short periods of time allowed the activation energy for grain growth and evaluation of the grain size evolution in the particles during the isomorphous inoculation process to be determined. Assuming that grain boundary melting is the predominant break up mechanism, a model to estimate dissolution of the powders is presented which includes diffusion and fluid flow. Despite its relative simplicity, the predicted number of particles remaining after heating and holding, which lead to grains in the as-cast structure, are in good agreement with the measured grain size. Finally, the paper summarizes the main features and mechanism making isomorphous inoculation a promising route for grain refining as-cast alloys.

1. Introduction

Inoculation is an efficient way for grain refining as-cast structures by adding exogenous particles on which heterogeneous nucleation will be favored, or even controlled. These particles must be stable in the melt and are typically borides, carbides or nitrides. For some alloys, such particles can be detrimental to the as-cast properties, such as $\gamma$-TiAl alloys. For these alloys, the authors developed the process of isomorphous inoculation consisting in inoculating the alloy with particles having the same phase as the primary solidification phase [1, 2]. Isomorphous inoculation has been successful in reducing the grain size in cast alloys. Analyses of the cast grain size together with introduced particles size distributions revealed anomalously high grain refinement efficiency, i.e. one introduced particle would lead to more than one new grain in the final ingot. This was attributed to the particles breaking up during the holding
stage prior to solidification by preferential melting at the grain boundaries. In this contribution, the mechanism leading to these anomalous efficiencies is highlighted. First, the heat treatment undergone by the particles prepared by cryo-milling is simulated in salt baths at 1500 and 1600°C. A model for the particle dissolution is then introduced and used to predict the evolution of the particle size distribution in the melt.

2. Experimental
All the alloys were prepared by induction melting from commercially pure metals (purity>99.7%) as described previously [3]. A Ti-46Al alloy was inoculated with a Ti-Al-Nb powder cryo-milled in a Retsch CryoMill apparatus at -196°C for 3, 6, 9 or 11h. The as-milled powders were characterized by on-axis transmission Kikuchi diffraction (TKD) [4]. High purity calcium fluorine (> 99.95 %) was heated and melted at 100 K/min in alumina crucible at 1500 and 1600°C and held for 30 minutes to reach thermal equilibrium under argon atmosphere. The powders were then introduced into the molten salt for different holding times ranging from 20 to 300 s before quenching the crucible into a water bath. The microstructure of the heat-treated powders was analysed from SEM-BSE images to determine the grain size after heat treatment.

3. Modelling

3.1. Grain growth
The grain growth kinetics, neglecting the heating stage of the particles, can be modelled using the approach of Malow and Koch [5]:

\[ d^n - d_0^n = k_0 e^{\frac{Q}{RT}} \]

where \( d \) is the grain size, \( d_0 \) is the initial grain size, \( n \) is the grain growth exponent, \( k_0 \) is a constant and \( Q \) is the activation energy for grain growth.

3.2. Dissolution
To model the dissolution of the particles, the model developed by Hsu and Lin [6] was used. The model is based on diffusion fluxes and accounts for fluid flow. The main feature of the model is that the diffusion boundary layer is controlled by the intensity and length of the flow boundary layer. The reader is invited to read ref. [6] for full details.

4. Results and discussion

4.1. Evolution of the powder microstructure
Figure 1(a) and (b) shows the microstructure of the powders after 3h and 9h of cryo-milling, respectively. As can be seen the grain size is relatively similar, in the order of a few hundred nanometers, but the grains after 3h of milling are more elongated. This means that after 3h of cryo-milling, the grain size inside a particle will not evolve drastically, thus further milling will only decrease the particle size (see ref. [1, 2] for full details about particle size distributions) but not the grain size within the particle. In Figure 2 the microstructures of the heat-treated powders are shown. Depending on the efficiency of the quench in the calcium fluoride bath, some \( \alpha \)-phase can form inside the particles from which the former \( \beta \) grains can still be easily identified, while the \( \alpha \) phase present at the particle periphery is likely due to oxygen contamination. For the analysis, only the grain size at the center of the particles were considered, and lead to values of \( k_0= 10 \text{ m}^2/\text{s} \) and \( Q=320 \text{ kJ} \) assuming a parabolic growth \((n=2)\) in eq. 1, which is consistent with values found in the literature [7].
Figure 1. IPF map by on-axis TKD in SEM of Ti-Al-Nb samples prepared by FIB, after 3h (a) and 9h (b) cryomilling.

Figure 2. Grain structure in the heat-treated powders at different temperature and for different times for particles with 3h cryo-milling.

It must be mentioned that no difference between in grain size was found between the different milling times, meaning that whatever the particle size and/or the milling time, all the particles contain β grains with the same average grain size of 37 µm. The consequence is rather important, since the particles dissolve preferentially at grain boundaries [2]. This means that the cryo-milling time is affecting the particle size distribution, but after heating up to the melting temperature, all the particles will have the same grain size. The knowledge of the particle size distribution and considering the preferential dissolution at the grain boundary will allow the number of grains (rather than particles) that will act as inoculant and contribute to the grain refinement in cast TiAl alloys to be calculated. However, since the particles do not have diffusional stability in the melt, the complete dissolution of some particles must also be accounted for. The approach used here is presented and discussed in the next section.

4.2. Application to isomorphic inoculation

For each particle size class, the dissolution and the grain growth steps are treated independently. As illustrated in Figure 3, for each particle of size dp, the length dissolved during the holding in the melt is calculated. In parallel, the final grain size within a particle is calculated. For a given particle population, a particle size distribution after dissolution is obtained. Knowing the grain size within a particle and assuming a complete melting of the grain boundaries, a number of grains that will act as grain initiator in the cast alloys can be found. Figure 4 shows the grain density found in the as cast-ingots vs. the number of grains introduced (left) for the case were only the grain growth is considered (black circles) and when dissolution and grain growth are both considered (white circles). The concept of isomorphic
inoculation is that the solidifying grain does not nucleate but grows by epitaxy from the inoculant particle, such that each inoculant should produce a single grain in the as-cast materials, which correspond to the 1:1 black line in Figure 4. As can be seen from the figure, accounting for dissolution and grain growth most of the points determined from the different milling time (and thus different particle size distributions) are quite close from the 1:1 ratio. The only point which is farther corresponds to the 3-hour milling time, in which particles are the largest and contain many cracks that might add a supplementary phenomenon that would have to be accounted for.

Figure 4 also shows the efficiency factor, defined as the number of inoculant particles introduced divided by the number of grains in the as-cast alloy vs. the number of particles introduced (right). The factor being higher than one indicates that a single particle produces more than one grain in the final casting. It can be seen again that considering dissolution and break up along grain boundaries leads to a reasonably good agreement with the experimental data. It indicates that these two phenomena are sufficiently well accounted for; while it could potentially be improved by coupling dissolution and grain boundary melting.

Figure 3. Method to determine the number of grains available for solidification after heating and holding in the melt.

Figure 4. Grain density found in the as-cast ingots vs. the number of grains introduced (left) and efficiency factor vs. the number of particle introduced (right), both considering the initial particle size distribution and the distribution after dissolution and break-up of particles at the grain boundaries.
5. Conclusions
In this short contribution, the mechanism by which grain refinement is achieved through isomorphic inoculation by cryo-milled powder was demonstrated. Analysis of the microstructure evolution of the powder during the thermal cycle has shown that grain size in the particles does not change with milling time and remains around 200 nm and does not change after heating and high temperature holding remaining around 40 µm independent of the particle size. Accounting for the grains rather than the particles and using a simple model for dissolution of the particles, it has been shown that knowing the particle size distributions is necessary but not sufficient to predict the finale grain size in the ingot, as an important parameter is the grain size within the particles. The obtained results showed a good agreement with the experiments despite the simplicity of the model.

References
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