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# Probability of twin boundary formation associated with the nucleation of equiaxed grains on icosahedral quasicrystal templates

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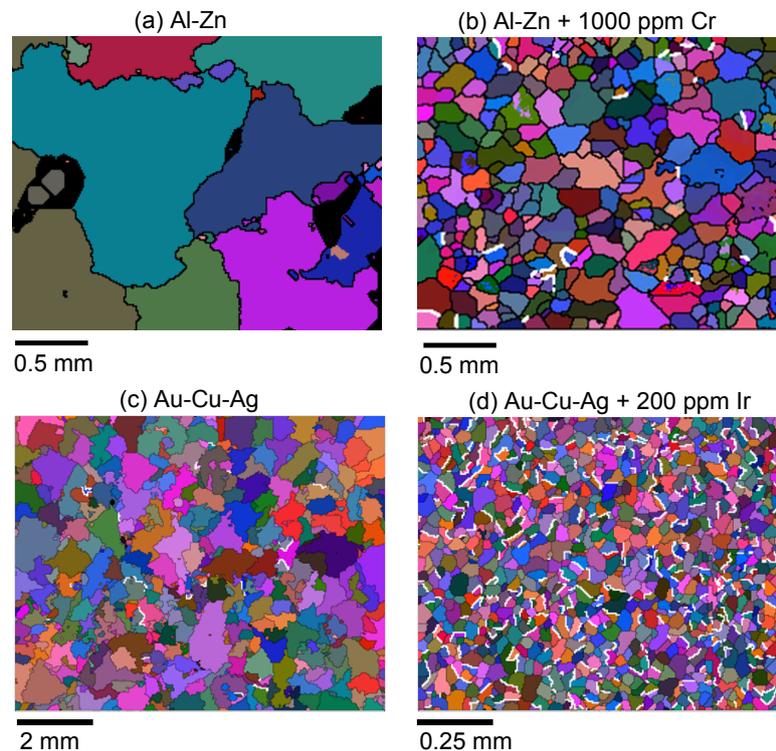
**Abstract.** Recently, we have shown that minute Cr additions (typically 0.1 wt%) to Al-Zn alloys solidified in a uniform temperature field lead to the formation of fine equiaxed fcc Al grains [1]. Furthermore, these grains exhibit an unexpectedly large number of twin, or near-twin, relationships with their nearest neighbors and some of them even show a 5-fold symmetry multi-twin relationship with a common  $\langle 110 \rangle$  direction. Similar observations have been made for yellow gold alloys (Au-12.5wt%Cu-12.5wt%Ag) inoculated with very small amounts of Ir (5-200 ppm) [2]. These results become fully consistent when one considers that the primary fcc phase forms on facets of icosahedral quasicrystals (iQC's), either by heteroepitaxy solidification or by peritectic transformation, with the following relationship:  $\langle 111 \rangle_{\text{fcc}} \parallel$  3-fold symmetry iQC axes,  $\langle 110 \rangle_{\text{fcc}} \perp$  2-fold symmetry iQC axes. The present study contributes to a better understanding of the frequency of twin boundary formation by the nucleation of fcc phase from an iQC template. A simple stereological model for the formation of equiaxed grains on such iQC templates has been derived. It is based on a 3D Voronoi tessellation of randomly distributed and oriented iQC template centers. Each iQC nucleation template site is the origin of 20 fcc grains with the heteroepitaxy relationships mentioned above on the 20 facets of the iQC. Therefore, the neighboring grains having a common iQC nucleation site contributes to the twin boundary frequency, while those coming from different iQC sites have random grain boundary orientations. The twin boundary frequency of the grains nucleated from iQC templates seen in 2D metallographic sections is compared with that measured in EBSD reconstructed grain structures.

## 1. Introduction

A new nucleation mechanism has recently been evidenced in which icosahedral quasicrystals (iQC's) are responsible for the formation of the fcc Al phase during solidification of an Al-20wt.%Zn alloy when a small amount of Cr is added [1]. The density of twin boundaries and the grain size in Al-Zn with and without Cr is shown in the EBSD reconstructed grain structures of Fig. 1. While the average grain size of Al-20wt.%Zn sample is greater than 1 mm (Fig. 1(a)), that of Al-20wt.%Zn-0.1wt.%Cr sample is only 135  $\mu\text{m}$  (Fig. 1(b)). Furthermore, a twin boundary frequency of 2.3% was present in Al-Zn-Cr alloys. These boundaries are highlighted with white segments in Fig. 1(b).

Several multiple-twinned (MT) nearest neighbor grain configurations were also identified with a symmetry relationship which could be explained only if they were assumed to form on





**Figure 1.** EBSD maps of different as-solidified alloys show the grain refinement effect of minute Cr and Ir additions to Al and Au alloys, respectively. a) Al-20wt.%Zn, b) Al-20wt.%Zn-1000 ppm Cr, c) Au-12.5wt.%Cu-12.5wt.%Ag and d) Au-12.5wt.%Cu-12.5wt.%Ag-200 ppm Ir (after References [1, 2]). Twin boundaries are outlined with white lines.

a single regular, or interlocked, icosahedron with the epitaxial relationship:  $\langle 111 \rangle_{fcc} \parallel$  3-fold symmetry iQC axes, and  $\langle 110 \rangle_{fcc} \perp$  2-fold symmetry iQC axes. These experimental findings are a fairly clear indication that fcc grains nucleate from an icosahedral template, known to be present as iQC's in the supercooled liquid or as building blocks of the crystalline structure of the approximant  $Al_{45}Cr_7$  phase [3, 4]. The phase initiated from a melt can be the one that is closest in free energy to that of the liquid, and not necessarily the most thermodynamically stable one [5]. Metastable iQC in supercooled metallic liquid is the most probable candidate to form initially due to its low interfacial energy [6, 7]. Upon further solidification and cooling, the iQC's disappear due to peritectic reaction between liquid, fcc Al and approximant phase or iQC [8], while the fcc phase grows with multiple twin or near-twin relationships between the various grains. Once the fcc phase reaches a critical radius, the solid-liquid interface destabilizes, thus leading to the formation of twinned dendrites [9, 10, 1].

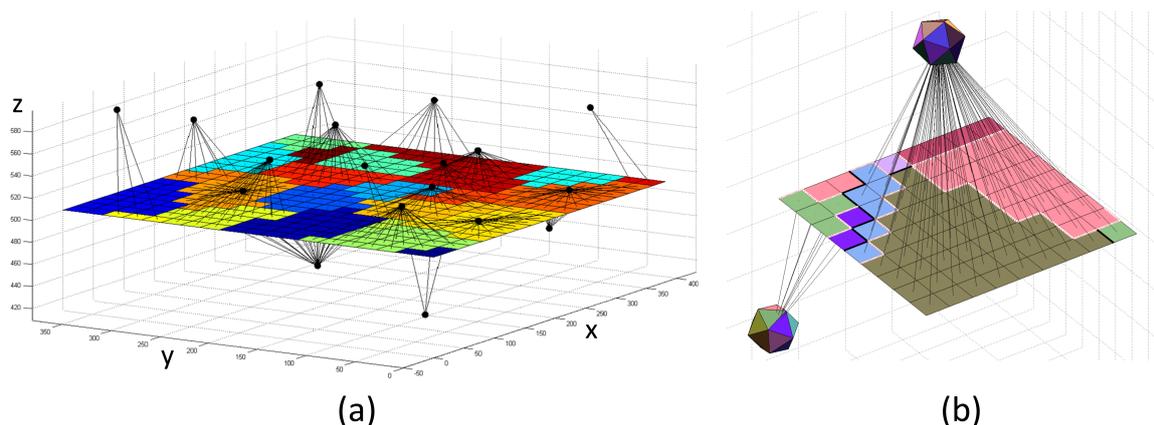
This iQC enhanced nucleation mechanism evidenced in Al-Zn-Cr alloys has been shown to operate also in yellow gold alloys (Au-12.5wt.%Cu-12.5wt.%Ag) when minute amounts of Ir ( $\leq 200$  ppm) are added to the melt [2]. Inoculation of such alloys with Ir is a grain refining technique currently used in industry and known for nearly half a century [11, 12, 13]. As can be seen in Fig. 1(c-d), it has also a drastic effect on the grain size in yellow gold alloys: it is about  $250 \mu m$  in the specimen without Ir addition, and only  $30 \mu m$  in the specimen with 200 ppm Ir (Fig. 1(d)). The grain refinement is accompanied by a very large increase of the fraction of twin boundaries, from less than 1% without Ir to 11% with 200 ppm Ir. It also promotes the formation of MT grains in a way comparable to minute Cr additions to Al-Zn alloys. Several

grains are shown to have orientation relationships compatible with the icosahedron or interlocked icosahedron geometry. All these findings lead to the same conclusion that icosahedral symmetry is responsible for this nucleation mechanism, although no iQC has been reported so far in such gold alloys.

In the present study, a model has been developed to calculate the frequency of twin boundaries formed by this iQC enhanced nucleation mechanism. It is based on the hypothesis of randomly distributed iQC's centers in 3D with a random orientation. Each iQC leads to the formation of 20 MT fcc grains with the heteroepitaxy relationship mentioned before. The twin boundary frequency of the fcc grains nucleated from these iQC templates and the grain structures are then deduced in 2D metallographic sections for both Al-Zn:Cr and Au-Cu-Ag:Ir alloys.

## 2. Model

A stereological model for the formation of equiaxed grains has been derived based on the 3D Voronoi tessellation of random iQC nucleation centers of random crystallographic orientation. Each nucleation site produces 20 fcc grains with the heteroepitaxy relationships compatible with the 20 facets of an icosahedron, and are thus multiple twinned. Therefore, the neighboring fcc MT grains having a common iQC nucleation center contribute to the twin boundary frequency, while boundaries between grains formed on different iQC's do not.



**Figure 2.** Schematic view of the model used for the nucleation of equiaxed grains from randomly distributed and oriented iQC templates: (a) Determination of orientations and grain boundaries in a 2D metallographic section; (b) Twin boundaries formed between the grains nucleated on the adjacent facets of a single iQC template. Only the iQC centers giving a contribution to the 2D section are shown in (a). While grain boundaries are shown by black lines, twin boundaries are highlighted by white lines.

In a first step, iQC nucleation centers are positioned pseudo-randomly within a given volume: the volume is subdivided into a certain number of regular cubic volume elements, within which a single iQC with a random orientation is positioned (i.e., the size of a cubic element is directly related to the mean volume occupied by the 20 MT fcc grains). Assuming that all the iQC's and fcc MT grains form at the same time and grow at the same speed in the uniform temperature field, the random boundaries correspond to the Voronoi tessellation of the iQC's centers. The grain structure is then calculated in a 2D metallographic section by a scan along its  $x$ - and  $y$ -directions with a regular grid spacing  $h$  corresponding to the pixel size of an EBSD reconstructed map. For each position  $(x_i, y_i)$ , the model first identifies the iQC center  $I$  which is the closest (see Fig. 2(a)). Then, the facet  $\nu$  of this iQC on which the direction connecting

pixel  $i$  to the center  $I$  falls is searched (see Fig. 2(b)). The crystallographic orientation attributed to this pixel  $i$  is based on the orientation of facet  $I\nu$  and using the heteroepitaxy relationship described before. Please note that a perfect icosahedral symmetry is kept during the growth of the fcc grains, i.e., each individual grain has the exact epitaxial relationship of  $\langle 111 \rangle_{\text{fcc}} \parallel$  3-fold iQC symmetry axes, and  $\langle 110 \rangle_{\text{fcc}} \perp$  2-fold iQC symmetry axes with facet  $I\nu$ . Therefore, the misorientation of 1.47 deg. from a perfect twinning relationship between two neighboring fcc MT grains is kept during growth for the sake of simplicity. This is not the case in Al-Zn:Cr and yellow gold:Ir alloys investigated by EBSD analysis, in which five grains issued from 5 iQC facets sharing a common 5-fold symmetry axis exhibit at the end 4 twins and one near-twin relationship with a 7-8 deg. misorientation.

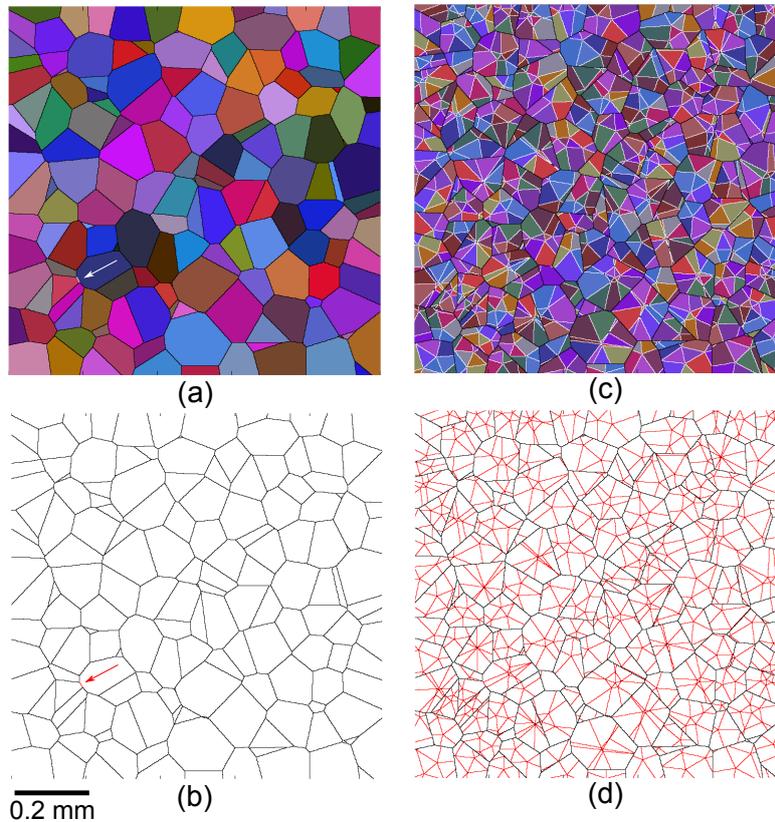
Once the whole surface has been scanned, the frequency of twin grain boundaries is determined among this 2D simulated section by checking the crystal orientations of adjacent grains for each grain boundary within a 5 deg. tolerance, as in the EBSD analysis of real grain structures (Fig. 1).

### 3. Results and Discussion

Figure 3(a) shows the simulated structure of randomly oriented grains on a 2D plane in the case of regular nucleation centers which are not iQC's. Taking a random orientation of a grain with respect to a reference grain, the probability to be in a twin relationship within the 5 deg. tolerance can be calculated as 0.3% according to Reference [14]: This is confirmed by our calculations: 3336 twin boundaries with a 5 deg. tolerance have been identified from  $10^6$  grain boundaries. There is only one grain boundary with a twin relationship in Fig. 3(a,b) for 159 grains and 430 grain boundaries. If now 20 grains nucleate on the 20 facets of icosahedral templates having the same nucleation centers in the volume, the average grain size decrease (factor of about  $20^{3/2}$ ) is accompanied by an increase in twin density due to grains nucleated on the adjacent facets of the same iQC (Fig. 3(c,d)). Each iQC template generates 1 to 15 MT fcc grains visible in a 2D section.

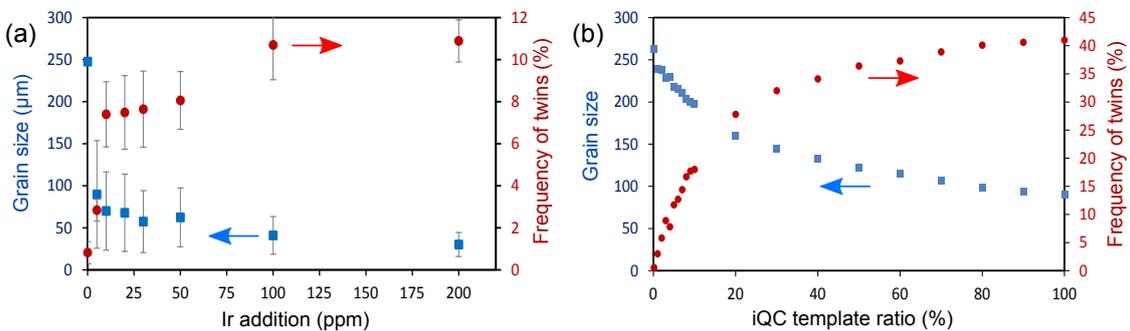
In a volume of  $25 \times 25 \times 6 \text{ mm}^3$  and on 2D section of  $25 \times 25 \text{ mm}^2$  having a pixel size of  $10 \text{ }\mu\text{m}$ , 950 regular grains have been simulated with  $915 \text{ }\mu\text{m}$  average grain diameter, 10 twin boundaries and 2722 grain boundaries (Fig. 3(a,b)). The average number of neighboring grains is 5.7, which is similar to what was observed in EBSD measurements of Al- and Au-based alloys. In the case of iQC enhanced nucleation (Fig. 3(c,d)) with the same nucleation centers, 7475 grains have been calculated with an average grain diameter of  $326 \text{ }\mu\text{m}$ . The total number of grain boundaries and the number of twin boundaries are 20634 and 8546, respectively. This means that the frequency of twin boundaries increases from 0.3% to 41% if all the grains are nucleated on iQC templates. This frequency of twin boundaries value contains also the error associated with the introduction of pixels to scan the plane which produces artificial boundaries at the meeting point of 5 MT fcc grains, as for EBSD measurements having a given step size. However, it has been checked that this error does not depend on the step size, if it is smaller than 5% of average grain diameter. The average number of grain neighbors for MT fcc grains is 5.5 and does not change significantly, although many triangular MT fcc grains formed by this mechanism as shown in Fig. 3(c,d).

In [2], the effect of different Ir amounts on the grain size and twin frequency has been investigated in yellow gold alloys and is summarized in Fig. 4(a). The error bars for the grain size correspond to the standard deviation of the distribution and the ones for twin density correspond to a 99% confidence interval for the corresponding total number of grain boundaries. With only 5 ppm addition of Ir, the grain size drops from  $250 \text{ }\mu\text{m}$  to  $90 \text{ }\mu\text{m}$ . Further addition of Ir continues to decrease the grain size, but to a lower extent. The grain size drops to about  $60\text{-}70 \text{ }\mu\text{m}$  for 10-50 ppm Ir addition and it further decreases to  $30\text{-}40 \text{ }\mu\text{m}$  with 100-200 ppm Ir addition. As mentioned above, the decrease in grain size is accompanied by an increase in twin



**Figure 3.** (a,b) Simulated grain structure of equiaxed grains in a 2D section. (c,d) Grain structure for MT fcc grains formed by the iQC nucleation mechanism with the same density of nucleation centers in the volume. While grain boundaries are shown with black lines, twin boundaries are identified with red or white lines.

frequency from less than 1% without Ir to 11% with 200 ppm Ir.



**Figure 4.** (a) Grain size and frequency of twins as a function of Ir addition in Au-Cu-Ag alloys [2]. While error bars show the standard deviation for grain size, they show the error limits for twin frequency with a confidence interval of 99%. (b) Average grain size and frequency of twin boundaries for different icosahedral template ratios by taking into account two different nucleation mechanism: (i) one grain nucleates from one site, (ii) 20 grains nucleate from one iQC template.

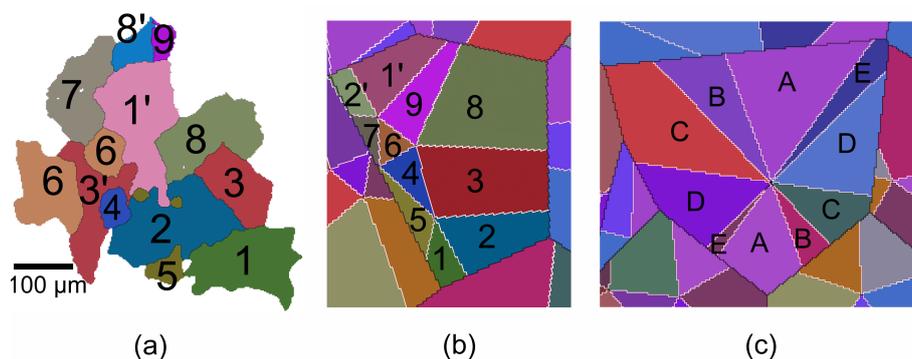
For the twin boundary densities investigated in Al and gold alloys [1, 2], there can be a competition between a classical nucleation mechanism (each grain nucleated on a single site) and the iQC enhanced nucleation mechanism. In order to analyze the effect of this competition on grain size and twin density, different calculations have been performed and the equiaxed grain structure characterized with various percentages of iQC nucleation sites for a fixed total density of nucleation sites. Fig. 4(b) shows the effect of the percentage of iQC templates on the average grain size and twin frequency. For a low iQC template ratio, up to 20%, the twin frequency increases from 0.3% to about 30%. Further increase in the iQC template ratio from 20 to 100% generates only 11% additional twin boundary frequency. Similar tendency is present for the grain size as a function of the iQC template ratio. The reason for this behavior is that, since each additional iQC template generates 20 new grains in the volume, the ratio of 20 grains over total number of grains decreases with the increase in total number of grains, which is itself proportional to the fraction of iQC template.

Figure 4(b) demonstrates that, although the iQC enhanced nucleation mechanism generates twin boundaries, the decrease in grain size for a certain twin frequency is very limited in the simulations as compared with the values measured in gold alloys (Fig. 4(a)). For a twin frequency of 11% in gold alloy with 200 ppm Ir, the grain density is multiplied by a factor of 600, which cannot be more than 20 in the simulations for a fixed number of nucleation sites. Therefore, the addition of Ir does not only promotes the formation of iQC templates, it also significantly increases the density of nucleation sites as could be expected.

Addition of minute amounts of Cr and Ir also promotes the formation of MT fcc grains in Al-Zn and yellow gold alloys, respectively. However, the number of MT grains observed in EBSD maps is very limited as compared with simulation which produces always MT grains for the iQC enhanced nucleation mechanism. This might be due to a growth mechanism which is not accounted for in the simulations. When 20 MT fcc grains form, they are all assumed to grow with a spherical symmetry. However, having a twin between two MT fcc grains creates a cusp in order to satisfy mechanical equilibrium at the triple line between the two twinned fcc grains and the liquid. Salgado et al. [15] have shown that this naturally leads to a twinned dendrite with a liquid groove in between, during directional solidification. In equiaxed growth with a uniform temperature field, one of the MT fcc grains can overgrow its neighbor by solute rejection. This mechanism would explain why we have less MT occurrences in metallographic sections and also why we have a lower fraction of twin boundaries in reality.

Figure 5(a) shows the EBSD reconstructed map of 9 grains in a 20 ppm Ir-gold alloy [2]. The six 5-fold symmetry axes of an icosahedron have been revealed by their twin or near-twin orientation relationships. Figure 5(b) shows the same occurrence of 9 grains nucleated on a single iQC template. Both measured and simulated grains are numbered from 1 to 9 in order to demonstrate that the grains having the same number in Fig. 5(a) and (b) have similar orientation relationships. 6 groups of MT fcc grains sharing a common  $\langle 110 \rangle$  direction, i.e., formed on 5 facets of an iQC around a 5-fold symmetry axis, have been identified. They reproduce the 6 5-fold symmetry axes of an iQC. These grain groups are (1/2/3/4/5), (5/4/6/7), (3/4/6/9/8), (7/2/3/8), (1/2/7/6/9) and (5/1/9/8). The detailed orientations of experimental grains can be found in Ref. [2]. Adjacent grains in the same group have MT relationship as shown in Fig. 5(b) by white lines. While grains on EBSD map have complex morphologies, simulated ones form convex polygons due to the limitations of the model.

Figure 5(c) shows another example for the simulated grain morphology. If an iQC template is very close to the cutting plane and one of the 5-fold symmetry axis is perpendicular to the plane, 10 MT fcc grains with 5 different crystal orientations (indicated as A, B, C, D and E in Fig. 5(c)) can be observed in the section. It looks as if we had a 10-fold MT relationship.



**Figure 5.** (a) EBSD reconstructed map of 9 MT fcc grains in Au-Cu-Ag alloy with 20 ppm Ir [2]. These MT grains share 6 common  $\langle 110 \rangle$  directions by groups which reproduce the 6 5-fold symmetry axes of iQC. These 6 grain groups are (1/2/3/4/5), (5/4/6/7), (3/4/6/9/8), (7/2/3/8), (1/2/7/6/9) and (5/1/9/8). Adjacent grains in the same group have MT relationships (After Ref. [2]). (b) Simulated 9 MT fcc grains nucleated on a common iQC site having the same crystal symmetry as in (a). (c) Simulation of 10 grains with 5 different crystal orientations (A, B, C, D and E) when the iQC template is close to the 2D section and one of the 5-fold symmetry axis is perpendicular to the section. Twin boundaries are highlighted by white lines.

#### 4. Conclusion

A simple stereological model for the formation of equiaxed grains by the iQC enhanced nucleation mechanism has been developed. It is based on randomly distributed and oriented iQC template centers. Each iQC template generates 20 MT fcc grains with the heteroepitaxy relationships on the 20 triangular facets of the iQC. Therefore, neighboring grains having a common nucleation site contributes to the twin boundary frequency, while those coming from different iQC sites have random grain boundary orientations. The morphology, occurrences of multiple twins and twin boundary frequency of the grains nucleated from iQC templates seen in 2D metallographic sections is compared with those obtained by EBSD reconstructed maps in yellow gold alloys. It has been found that the twin boundary frequency increases from 0.3% for a randomly oriented regular fcc grain to 41% when all the fcc grains are formed on iQC's.

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