

EBSD Microstructure Mapping of Zr_{47.5}Cu_{45.5}Al₅Co₂ Bulk Metallic Glass Matrix Composite to Ascertain the Effect of Inoculation in Promoting Crystallinity

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Abstract. Bulk metallic glass matrix composites have emerged as competent structural material of future bearing potential structural applications. However, the optimum percentage of crystallinity required to produce enough toughness that it can serve as structural component is still a matter of debate. In this study, an effort is made to address this problem by inoculation. A controlled amount of carefully selected inoculant is introduced in Zr_{47.5}Cu_{45.5}Al₅Co₂ bulk metallic glass matrix composite during melting and solidification. Its effect in promoting crystallinity is checked by detailed electron back scatter diffraction (EBSD) mapping. Proper pattern capture, background correction, binning, Hough space transformation, step size selection, indexing and matching with well-defined crystal structure files have shown to reflect upon map quality. This shows and bears direct relation with effect of inoculation. Results from two independent laboratories are reported. Inoculation treatment is shown to be advantageous.

1. Introduction

Bulk metallic glasses [1-5] and their composites [6-11] have recently re-emerged as new material bearing superior properties of strength [9, 12-16], hardness [17-21] and elastic strain limit [11, 22, 23]. However, they manifest brittleness [19] due to their parent glassy structure, possess inferior ability to absorb energy (poor toughness) [19, 24, 25], and fail catastrophically under the action of applied loads [13, 20, 24, 26]. This behaviour makes them dubious and limits their application. Various applications have been proposed which make use of their superior properties [11, 22, 27-35] but still they are limited by their scalability. Efforts have been made to address this problem from various perspective. For example, by external (*ex-situ*) [36-38] introduction of crystalline particles in melt or internal (*in-situ*) [39-45] nucleation and growth of same during processing (solidification [22, 33, 46], devitrification [47-50], powder metallurgy [51], foaming [52] or solid-state processing). However, quest for ultimate answer is still far from exhaustion. *In-situ* introduction of crystalline phases during solidification have proved out to be best solution to tackle this problem [53-55] since its inception by Prof. Johnson's group at Caltech in 2000 [56]. Various groups in the world have produced a multitude of composites using similar philosophy [7, 9-11, 22, 23, 40, 57-68]. Overtime, various studies have also been reported which shed light on different aspects of their manufacturing [23, 69, 70] and microstructural development [8, 71-73]. These include observations under transmission electron microscopy [74], synchrotron light [75-78] and *in-situ* studies [14, 74, 79, 80] but none have been made on the detailed use of more recent and advanced electron back scattered diffraction [81-88]. Few efforts have been made in this regard [32, 44, 65, 89-93], but none exist on its application on inoculated composites [22]. This is a new and unique technique which has been reported as complimentary to transmission electron microscopy [86, 94]. It has unique ability to identify [81] and map crystallinity in materials [83, 84, 87, 95]. It can not only generate diffraction patterns (kikuchi lines) [96] but can efficiently map [87] the presence of different phases (of distinct crystal structure) [82] in a bulk of material [97] and compare them with existing crystal structures in international crystallographic diffraction database. With the augmentation of energy dispersive X-ray spectroscopy (EDS) detector, it can also generate elemental maps which can serve as input for back scatter diffraction data collection [94, 98]. It also generates pole figures and grain size histograms which again can be used to determine mechanical properties of material. Application of post processing techniques [99], also help to generate more detailed information about crystal structure of material. In present study, which is part two of two-part study, author aim to bridge this gap. A comprehensive electron back scatter diffraction study is carried out with the help of modern Hiraki electron diffraction detector. Resulting kikuchi patterns are captured on the phosphorus screen. These captured patterns are corrected, converted to Hough space transform and then indexed by comparison with well-known and defined patterns in international crystallographic diffraction database. This is postulated and observed to cast effect on resulting phase identification in microstructure of material.

1. Experimental procedure

Melting and casting: Melting and casting of small ingots in the form of wedge [22] was performed at CSIRO – Manufacturing, Clayton, Victoria, Australia by employing vacuum arc melting and

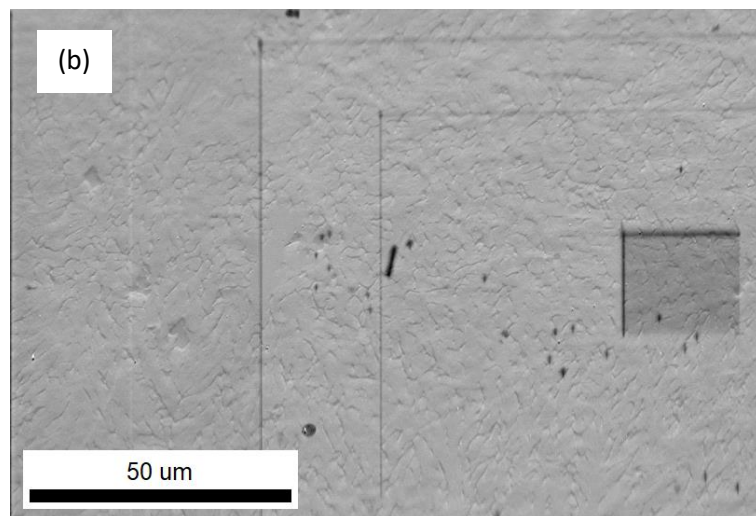
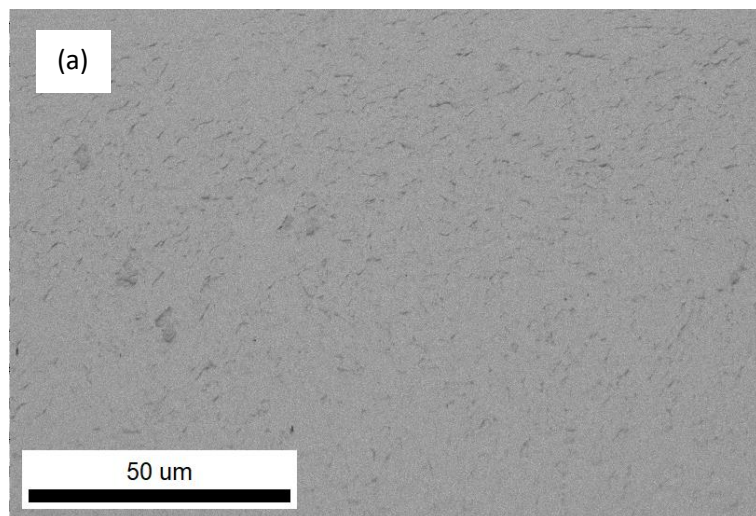
suction casting button furnace. Alloying elements including major (Zr) and minor (Al, Cu, Co) were premixed in appropriate amounts with Aluminium foil serving the purpose of wrapper as well as alloying element. A detailed procedure of melting, casting and metallographic sample preparation can be found in a previous study [100]. *Electron back scatter diffraction*: Electron back scatter diffraction was performed using field emission Teneo microscope at EDAX Laboratories, Draper, Utah. Microscope was equipped with thermally assisted Schottky type field emission gun. Operating voltage was 30 KV while working distance was kept at 25 mm. Microstructure mapping was carried out using Hiraki EBSD detector with maximum speed (count) of 600 indexed points per second. Scan area / area of interest selected was 150 x 130 microns while step size was kept at 0.1 microns. From this, an indexed point per second of around 200 was calculated which was operating parameter in present case. Camera binning of 2 x 2 was used. Time taken for one scan was around 3 hours. EBSD detector was operated at lower counts per second to avoid any damage to its phosphorous screen. For proper pattern capture, first, series of EDS mapping for individual elements Zr, Cu, Al and Oxygen was carried out which generated enough data point on which further back scatter diffraction mapping was based. These were converted to Hough transform and indexed with well-known crystal information files present in database of software of machine.

2. Results and discussion

Simultaneous energy dispersive spectroscopy (EDS) and electron back scatter diffraction (EBSD) performed on bulk metallic glass matrix composite samples with the help of EDS and EBSD detectors attached with high speed digital cameras enables both to be used as imaging devices. This enables acquisition of images exhibiting topographic, atomic density and orientation contrast. Resulting images and their details are described below

2.1 ZrC = zero percent

Figure 1 (a) shows image quality map of sample with zero percent inoculant. It clearly indicates that there is no crystallinity in material. Background is placid with no precipitation and it indicates formation of 100 % monolithic glassy structure. Similar type of behaviour and effect is observed in scanning electron microscope image of material (Figure 1 (b)). These facts are reinforced by diffraction scattering map shown in Figure 1 (c).



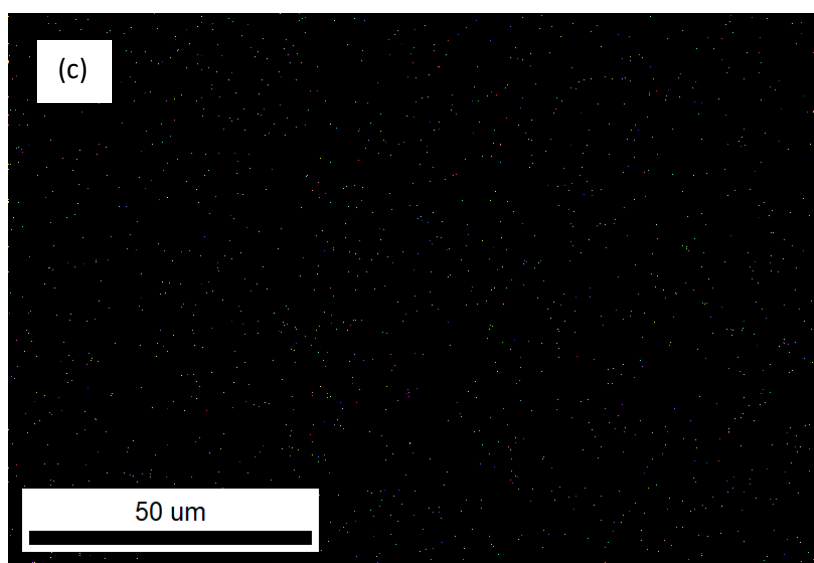


Figure 1: (a) Image quality map of sample with zero percent inoculant, (b) scanning electron microscopy image, (c) phase identification map with crystal orientation

2.2 ZrC = 0.25%

Microstructural features developed in bulk metallic glass matrix composite with inoculant percentage 0.25% are shown in Figure 2 (a) – (p). Simultaneous EDS and EBSD mapping were carried out. First EDS mapping was conducted to generate enough data set which is present in the form of congregation of points on the microstructure. These points serve as input for further crystal structure mapping and determination of orientations in them. This was followed by EBSD mapping at binning of 2×2 and speed of 200 indexed points per second in an area of $130 \mu\text{m} \times 150 \mu\text{m}$. This methodology generated a very good data set and speed which were adequate for appropriate mapping. Microstructure was depicted in the form of colour coded micrographs. Evidently, it showed eight types of microstructures. These are;

1. CuZr B2

Structure: Primitive simple cubic (like CsCl) [39]. **Morphology,** Spherical to Spheroidal with the inclination to get spheroidal as the time for diffusion is provided. They are soft in nature (Hardness: 3.5 GPa) while matrix (glass) is hard (4.9 GPa). That is, as the time for diffusion increases alloy tends to form large spheroidal particles. This spheroidal shape is not only the function of diffusion but is also formed as a result of considerable change in kinetics. Higher cooling rates tends to form finely dispersed needle like morphology while at slow cooling rates, sphere tends to form their ideal spherical morphology. These are brittle in nature and are formed because of Aluminium which is β – destabilizer.

2. Ductile small body centred cubic (bcc) dendrites

Structure: These are body centered cubic in nature. They have yield strength in the range from 900 – 1000 MPa [101]. **Morphology:** They were identified to have body centered cubic β dendrite structure primarily as β -Ti because of Ti in 2003 [101]. Further research in 2008 showed them to exhibit body centered cubic solid solution dendrites [7]. These are preferably observed along [111] zone axis of one of dendrites which confirms they are body centered cubic. In conclusion, these are body centered cubic dendrites. These are neither Cu Zr B2 nor β phase.

3. Face centred cubic (fcc)

Most likely, they are aluminium crystals as shown by strong signal of Aluminium in EDS maps (Figure 2 and 3 (c)). These may have been brittle Al_2Zr phase [71] (point 5 below). However, further research is needed to probe this effect and their exact nature.

4. Small Zr_2Cu dendrites

These are cubic (Fd – 3m) [58]. These are brittle intermetallic and are formed at the interface of glass and CuZr B2. These are not observed at 6500 – 7500 x. These are not observed by XRD alone. Only EBSD or TEM can reveal them at 15,000 – 20,000 x. These are primary sites of heterogeneous nucleation of Cu_2Zr in addition to homogeneous nucleation directly from glass [58].

5. Brittle Al_2Zr

These are formed in CuZrAl ternary alloy in the presence of Nb [71]. These are evidently observed at 2.0% Nb as characterised by XRD. Below 2.0% their formation is not observed. Further, with the addition of Nb with the application of tensile force, deformation induced martensitic transformation of CuZr B2 (primitive simple cubic) to B19' (monoclinic) is observed.

6. Brittle Ni_2Zr

This is evidently observed in alloys having Ni only [58]. In present alloy, a phase resembling them is observed. However, as the alloy does not have exact chemistry, this phase can not be ascertained to have exact Ni_2Zr nature. Further research is needed to determine its exact nature.

7. Cu_2Zr (hexagonal)

This is typical phase observed in CuZrAl ternary alloy having nickel. These have symmetry $P6_3/nmc$ [58]. This is because of stabilizing effect of Oxygen. They are observed in a recent study by author [100]. However, in alloys having Cobalt, their emergence is not clearly witnessed. Only their resemblance could be ascertained. Further research is needed to verify their presence.

8. $Cu_{10}Zr_7$ small plates

Very recently, a report has been published [102] which identify a new phase named as $Cu_{10}Zr_7$. However, this is reported to be predominantly emerging only in the presence of Be (which is original Viterloy 1). This is intermetallic phase which nucleate and grow at the surface of already precipitated β -Zr dendrite. In present alloy, their presence could be ascertained as β stabilizers is present. However, it cannot be justified as chemistry of alloy is not exactly Vit 1. Further, research is required to ascertain and quantify its presence.

Note:

1. Bcc dendrites only form when there is Be (e.g. Vit1) [7, 101].. If dendrites are forming in the absence of Be, it means both process and chemistry control are excellent.
2. Why fcc dendrites are appearing? (these could be Al₂Zr [71] as during EDS mapping Al is shown to form majority of these long dendrites and Al has fcc structure).

In alloy inoculated with 0.25% ZrC, microstructures observed are shown in figures below. EDS maps show two types of behaviours. (a) A continuous map consisting of individual elements and (b) spots in continuous map. Spot is characterised as white in Cu map, dark green in Zr, blue around previous two regions and green in oxygen map. This may be identified as unmelted ZrC inoculant around which heterogeneous nucleation start. An evidence for this may be inferred from the fact that a lot of footprint of Al is observed around this point while the centre is rich in Zr. This points towards the fact that Al₂Zr [71] is formed as Zr tends to seep away from ZrC and preferably reacts with aluminium to form primary nucleation site.

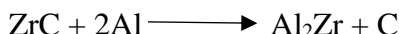
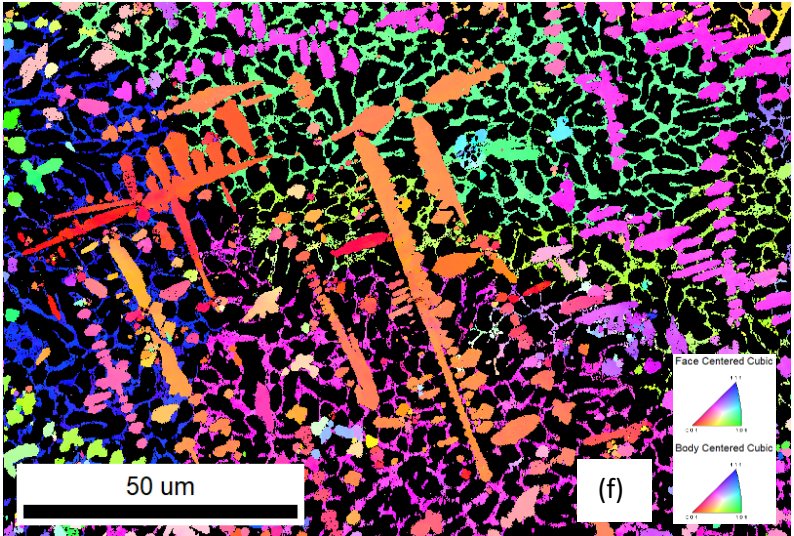
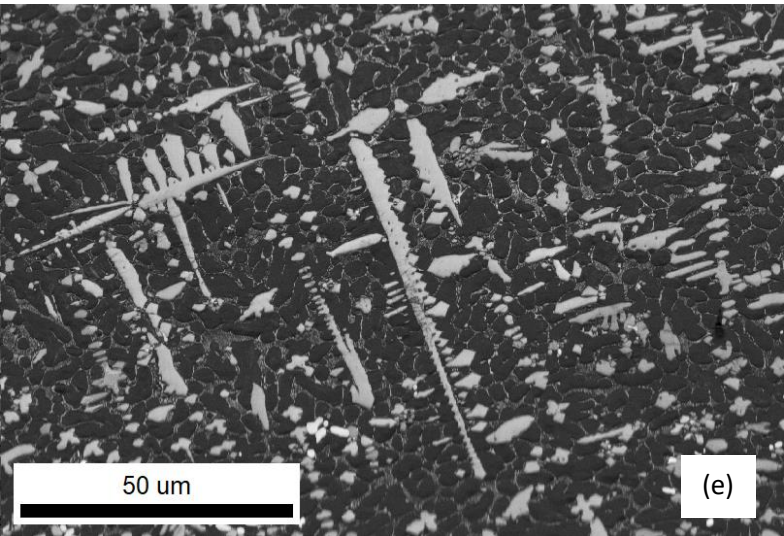
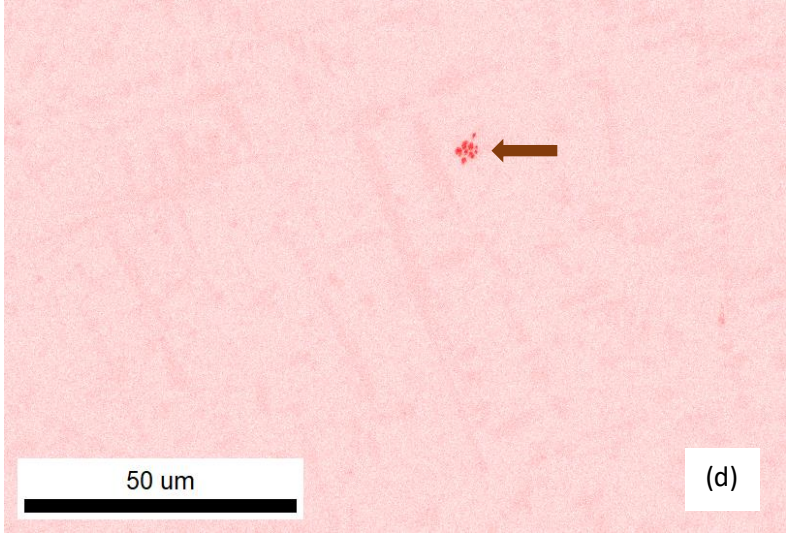
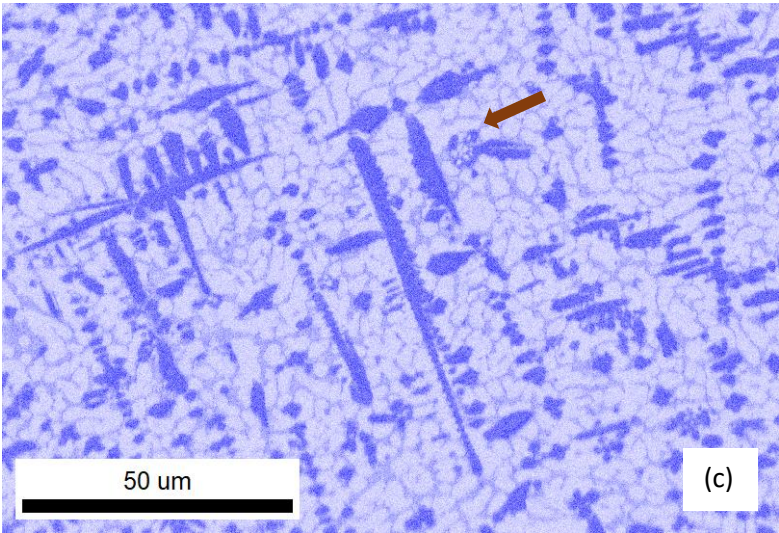
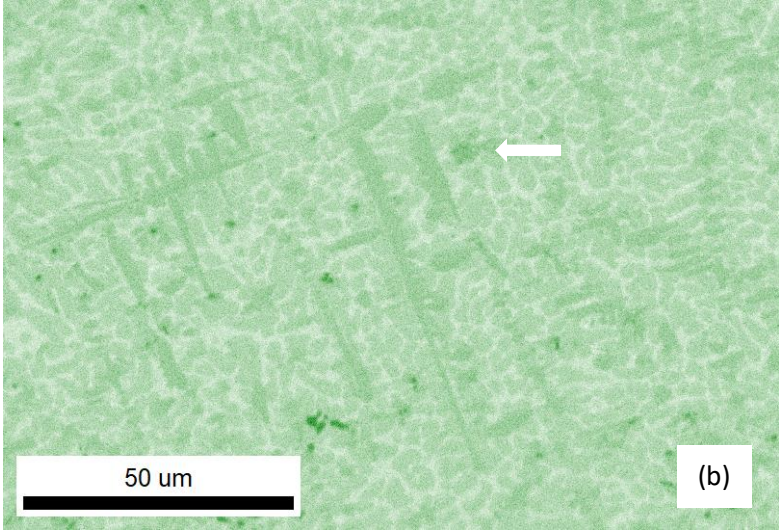
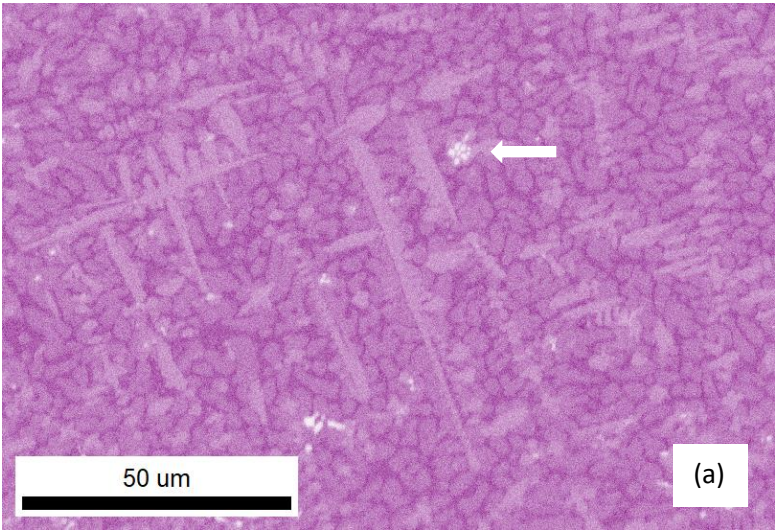


Figure 2 (e) shows image quality map of Zr_{47.5}Cu_{45.5}Al₅Co₂ while Figure 2 (f) shows colour coded orientation map of Zr_{47.5}Cu_{45.5}Al₅Co₂ with 0.25% ZrC. These maps clearly show difference from previous maps when percentage of inoculant is zero percent. Marked crystallinity is observed. Primarily two types of phases are identified in these orientation maps. (a) face centred cubic phase and (b) body centred cubic phase. As described earlier, fcc phase may be identified as long dendrites of Al or Al₂Zr [71] with branches of small dendrites protruding as off shots from main dendrite. Difference of colour in these dendrites (Figure 2 (g)) points towards orientation change. That is, there are certain regions in the micrograph which are oriented at different angles to each other. These angles may be read in detail from associated pole figures. Grain size histograms show average size to be around 1.2742 µm. Similarly, a careful analysis of colour coded orientation map of body centred cubic phase show mostly small grains spread all throughout the matrix as three-dimensional network. Their size is around 4 – 6 µm. They are shown to possess a certain definite orientation relationship between different grains of same phase. Grain size histogram show their size to be 0.6853 µm.



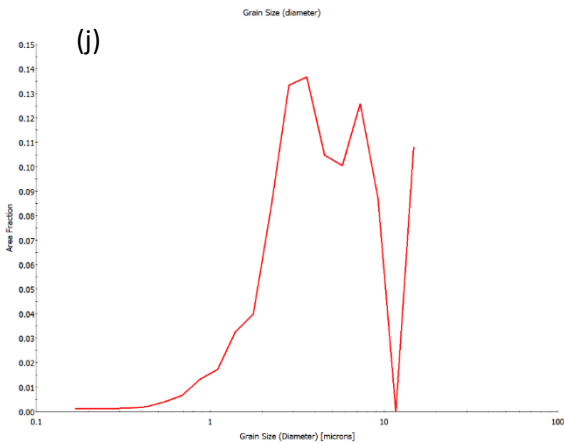
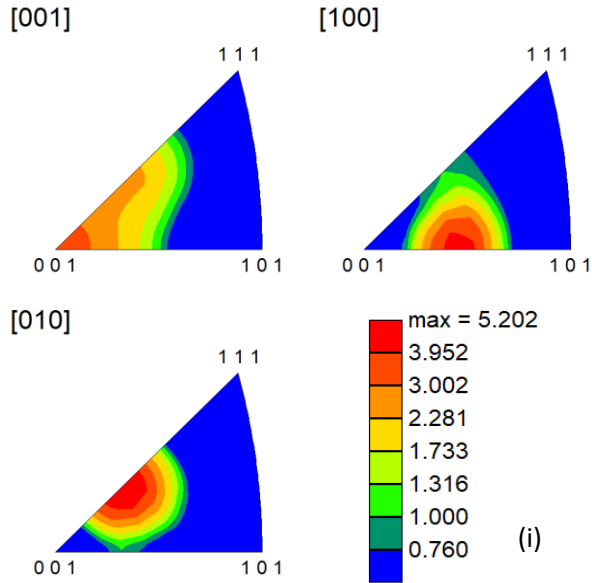
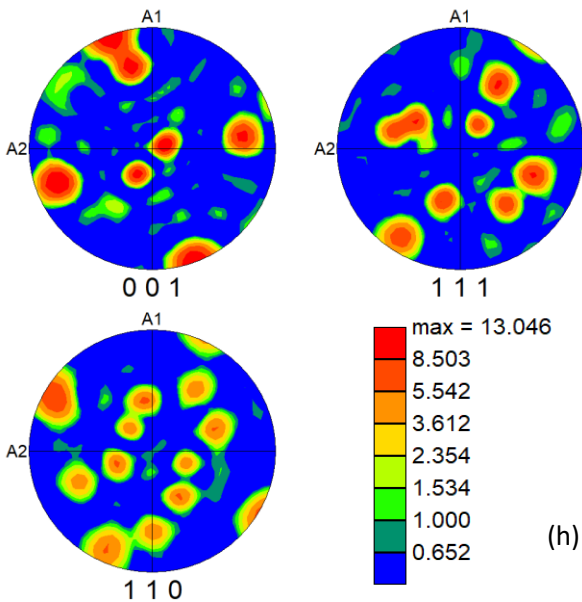
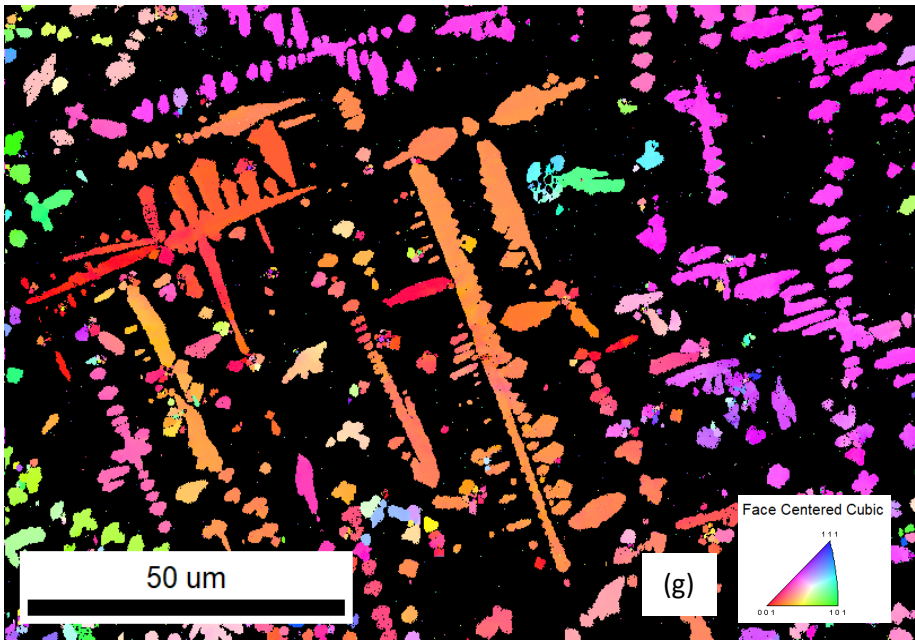


Chart: Grain Size (diameter)

Edge grains included in analysis

Diameter [microns]	Area Fraction
0.187103	0.00115951
0.211583	0.00122815
0.287903	0.00133111
0.339215	0.00144142
0.429509	0.00190964
0.543839	0.00390753
0.6886	0.00665065
0.871895	0.0131273
1.10398	0.0171745
1.39784	0.0326943
1.76993	0.0397789
2.24106	0.0834972
2.83759	0.133231
3.59292	0.136766
4.5493	0.104685
5.76026	0.100404
7.29355	0.125836
9.23499	0.0869631
11.8932	0
14.8058	0.108095

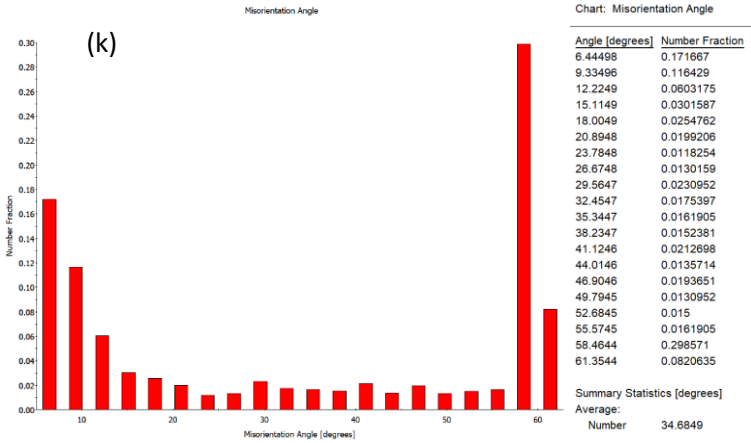
Summary Statistics [microns]

Average: 1.27423

Number: 5.64678

Standard Deviation: 1.55794

Number: 4.17178



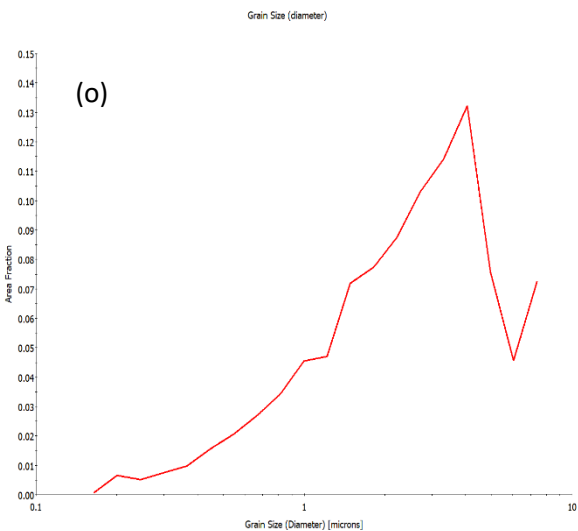
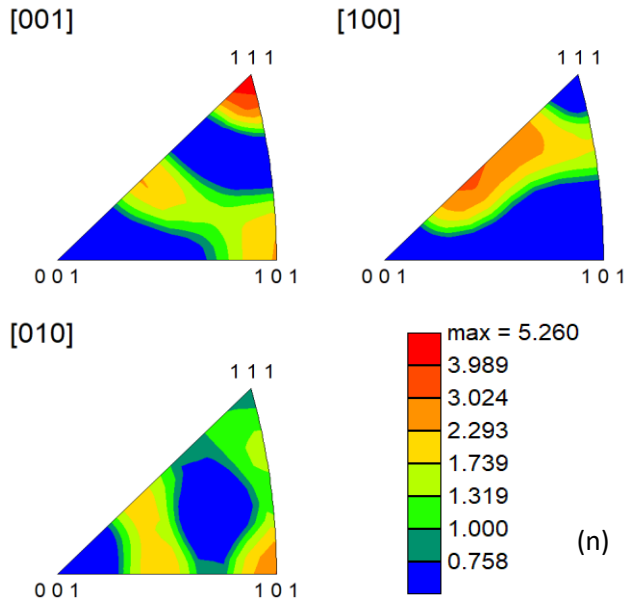
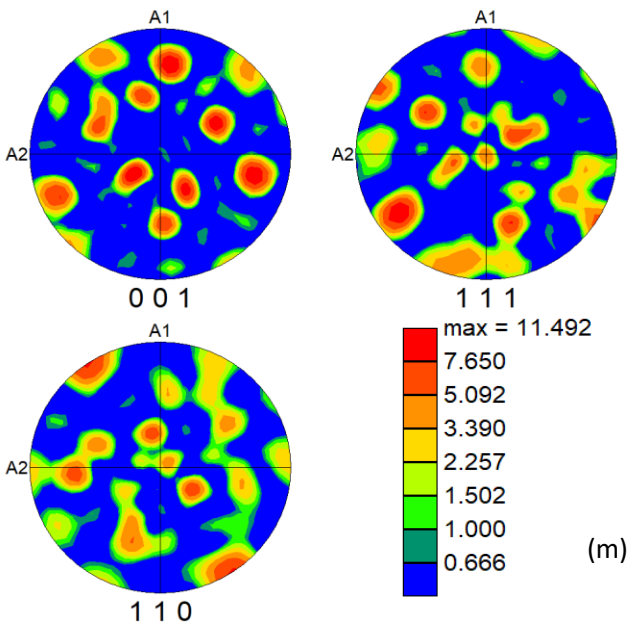
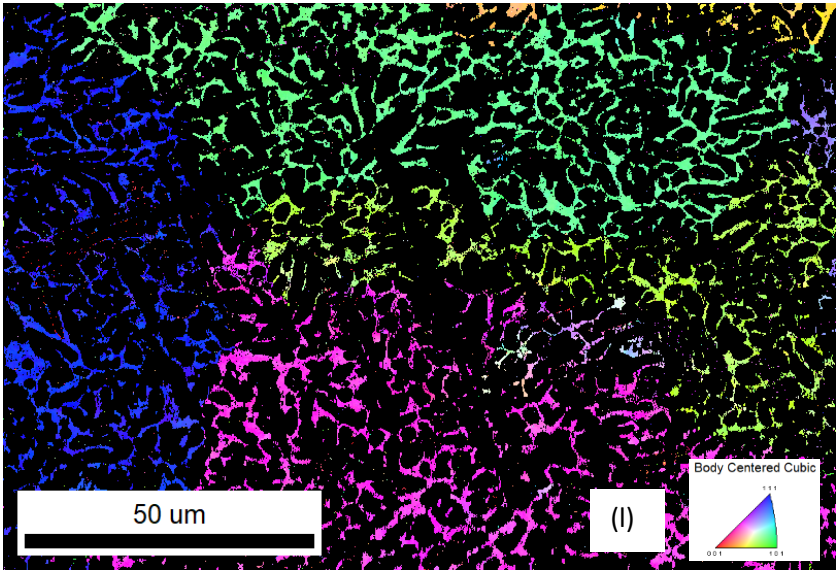


Chart: Grain Size (diameter)

Edge grains included in analysis

Diameter [microns]	Area Fraction
0.164153	0.000782328
0.200575	0.00652888
0.245077	0.00522026
0.299454	0.00741433
0.365896	0.00973287
0.447079	0.0158621
0.546275	0.0205894
0.667481	0.0270045
0.815579	0.0342304
0.996536	0.0454355
1.21764	0.0471139
1.48781	0.0719279
1.81792	0.0774469
2.22127	0.0874607
2.71412	0.103072
3.31631	0.11417
4.05212	0.132203
4.95119	0.0757649
6.04974	0.0455635
7.39203	0.0726569

Summary Statistics [microns]

Average:	
Number	0.685344
Area	3.00369
Standard Deviation:	
Number	0.798475
Area	1.95013

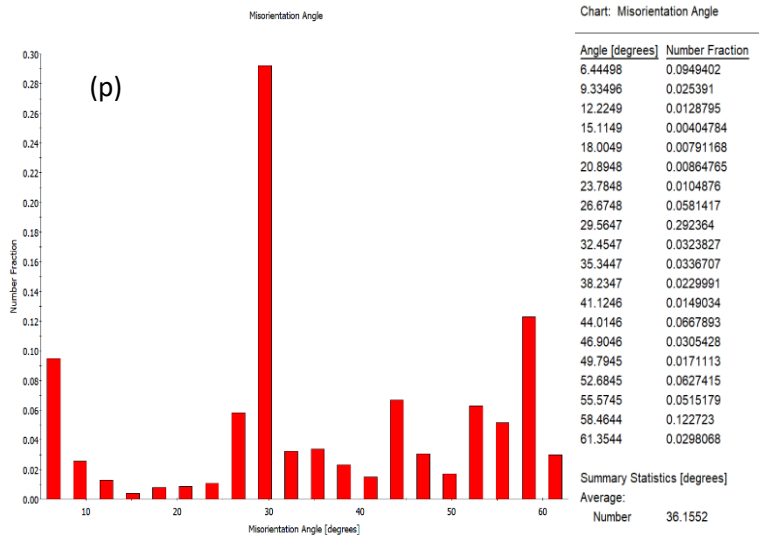
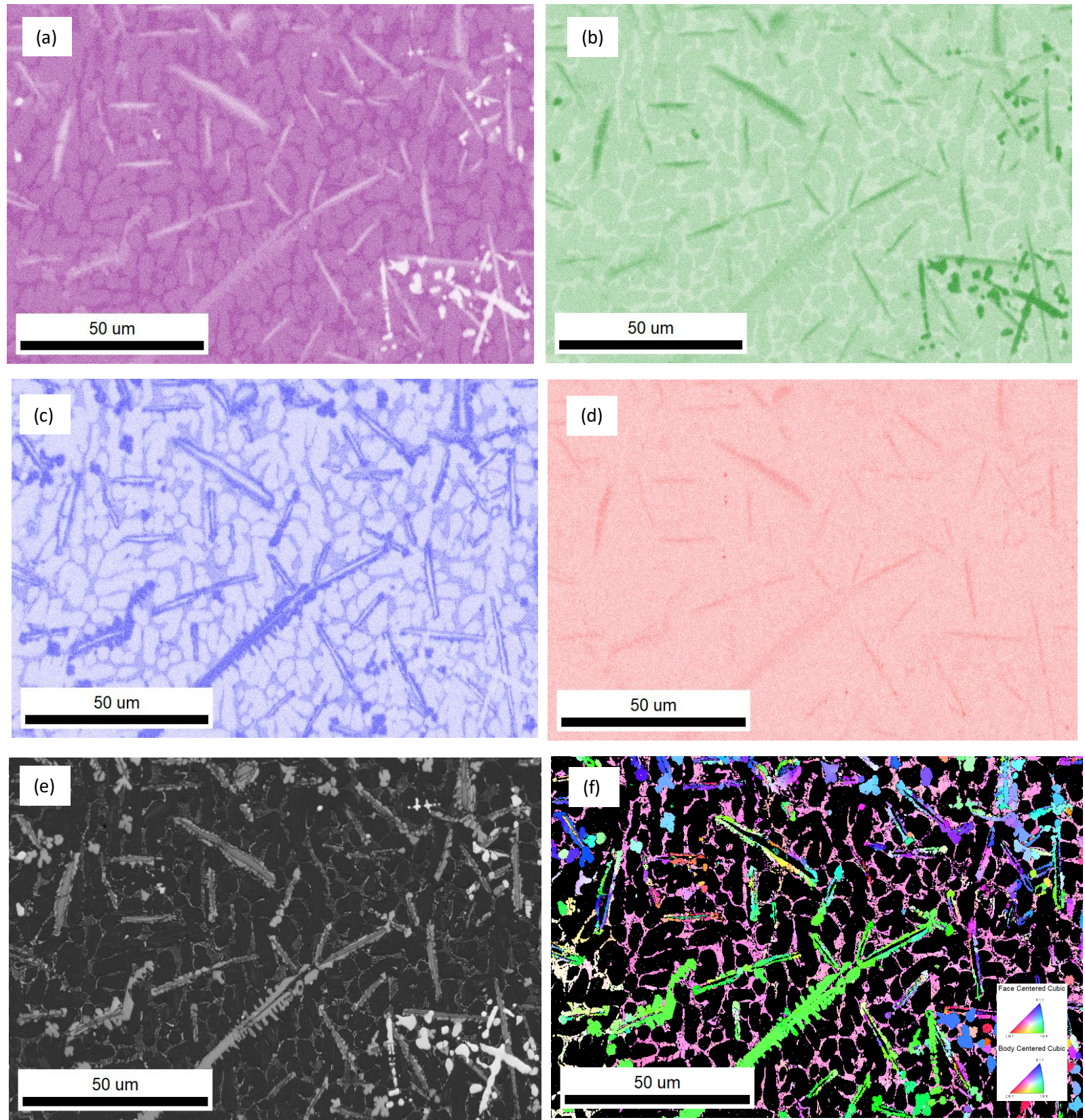
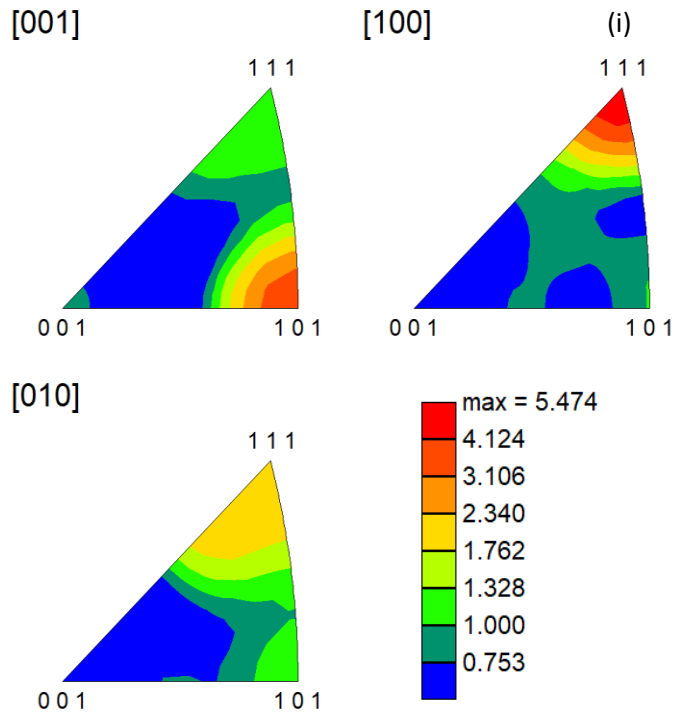
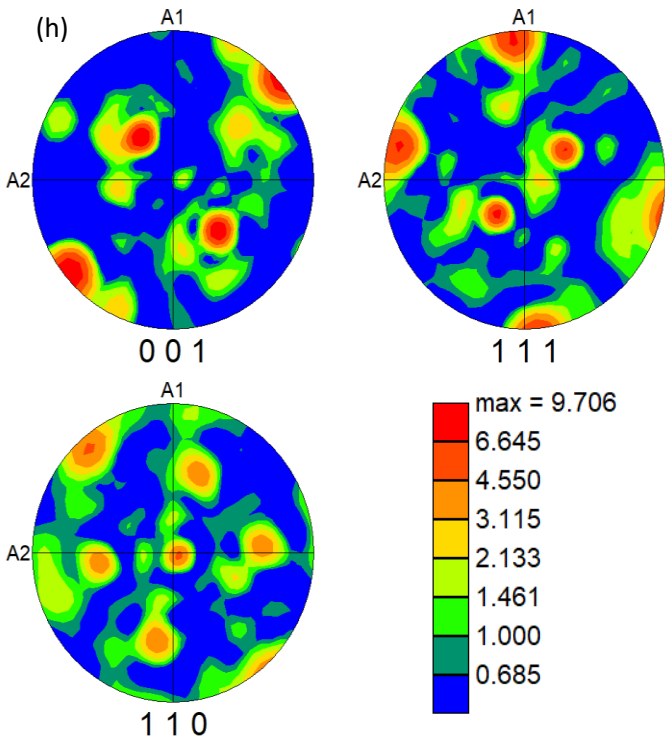
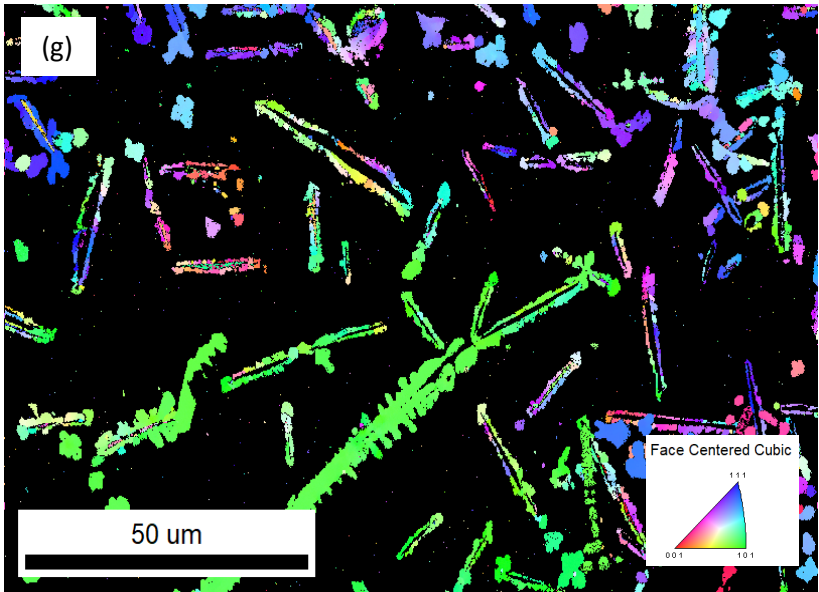


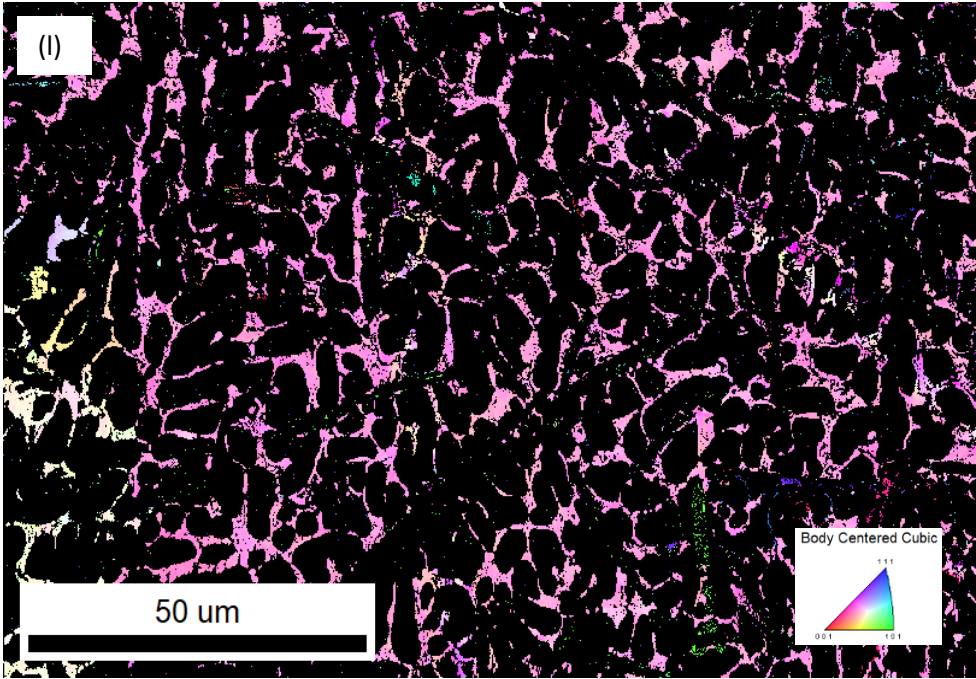
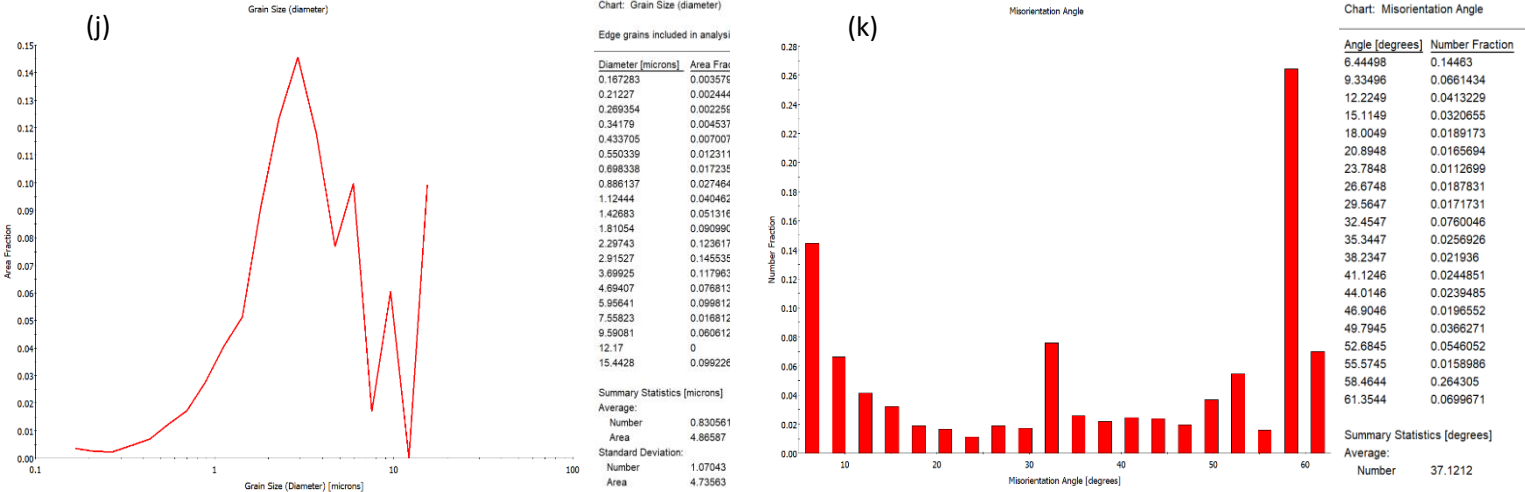
Figure 2 (a) – (p): (a) – (d) Elemental maps of Copper, Zirconium, Aluminium and Oxygen, (e) Image quality of map of $\text{Zr}_{47.5}\text{Cu}_{45.5}\text{Al}_5\text{Co}_2$ (0.25% ZrC) (f) Colour coded orientation map of $\text{Zr}_{47.5}\text{Cu}_{45.5}\text{Al}_5\text{Co}_2$ (0.25% ZrC) (g) Colour coded orientation map of Al_2Zr FCC phase [71], (h) and (i) Pole figures of Al_2Zr FCC phase, (j) – (k) grain size histograms of Al_2Zr FCC phase, (l) Colour coded orientation map of BCC phase [71], (m) and (n) Pole figures of BCC phase, (o) – (p) grain size histograms of BCC phase.

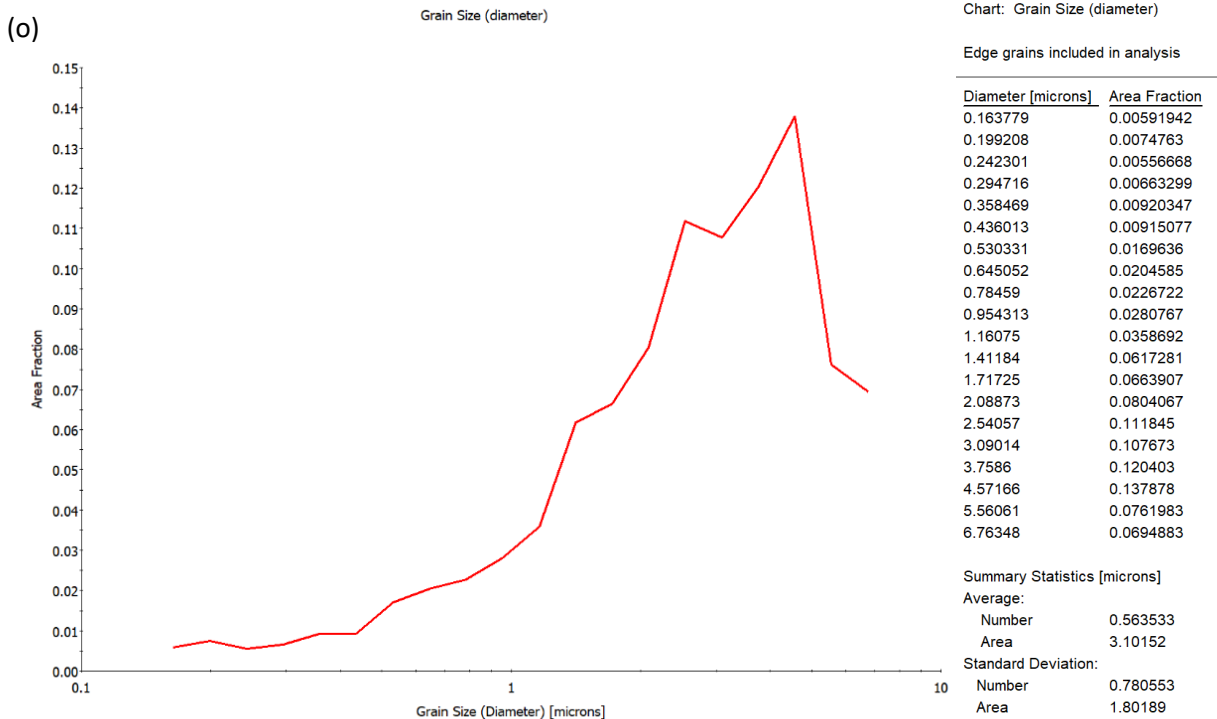
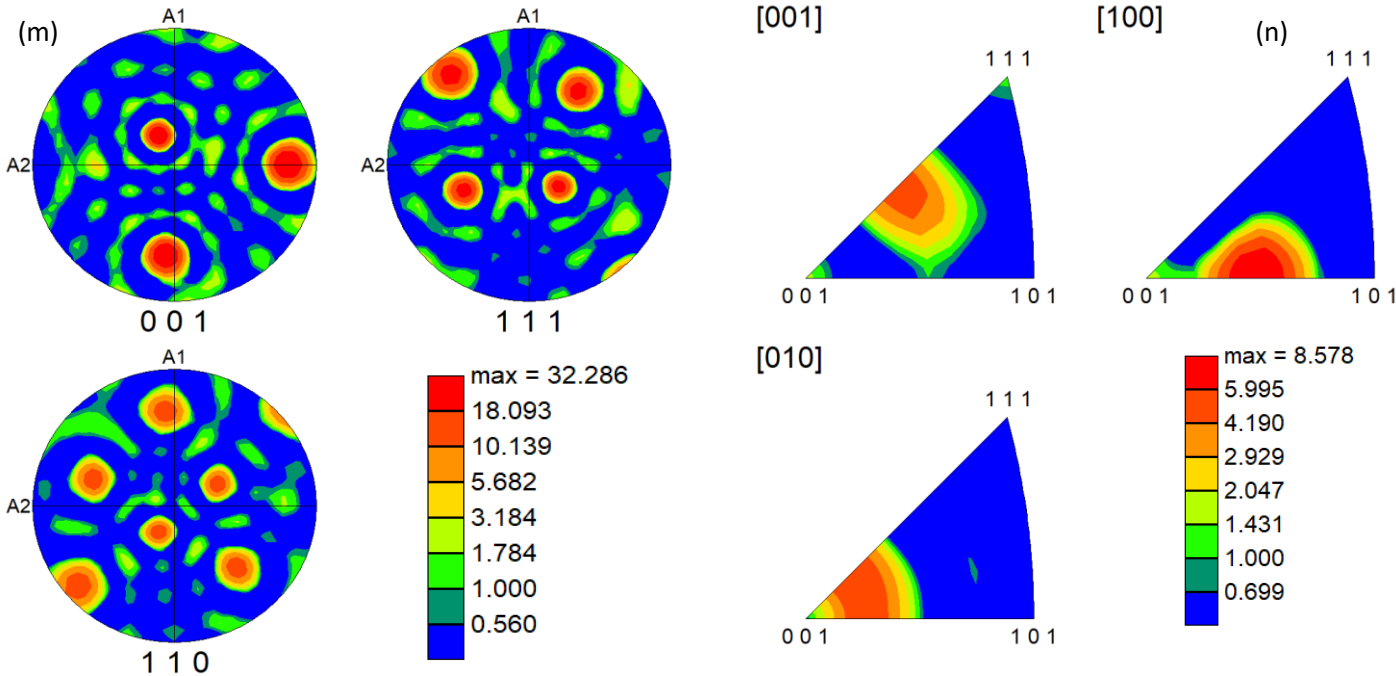
2.3 ZrC = 0.50 %

As the percentage of inoculant increase from 0.25 to 0.5%, microstructure evolved and as observed via EBSD mapping is shown in figure 3 (a) – (p). As can be easily seen that with increase of percentage of inoculant, length of fcc dendrites increase while their width decrease. They tend to form more of needle like or acicular type structure. This is clear indication of profound effect of inoculation towards promoting crystallinity. They are more closely spaced and have evolved to have more compact morphology. This may have been the reason for increased toughness at this inoculant percentage. Colour coded EDS maps clearly show the evolution of Cu, Zr, Al and oxygen. However, this time any presence of unmelted inoculant is not detected. This may be due to the reason that higher temperatures maintained during this casting [22] promote proper dissolution. As was the case previously, colour coded orientation map can be split for two individual phases. That is face centred cubic (fcc) (Figure 3 (g)) and body centred cubic (bcc) (Figure 3 (l)). Difference of colour once gain indicates presence of grains having different orientations with respect to plane of observation. Size of fcc dendrites can be further divided into three types. Small, medium and large. Size of small dendrites range from average 2 μm wide to average 6 μm long. Medium dendrites maintain same width while their length increase to 24 – 26 μm . Lastly, only one large dendrite is observed in the lower middle portion of figure 3 (g). This is prominent indication of proper and complete diffusion. Its width has increased to 4 μm while its length ranges from 130 – 140 μm . Emergence of further small secondary dendrites can also be witnessed from its main trunk specially from thick region where profound diffusion has occurred. It also indicates that there is optimal size (around 4 μm) at which this dendrite tends to stabilize and beyond which it tends to protrude into small branches forming secondary dendrite arms. Further close observation reveals that both very small and one large dendrite are oriented along same direction while medium ones (having blue colour) have different orientation. There is another small fat and short dendrite found in the lower left region of micrograph. It indicates initial stage of development of long dendrite but due to suppressed kinetics, it remained unsuccessful in growing into full dendrite. Grain size histogram (figure 3 (k)) shows average grain size to be 0.5635 μm . Similarly, a careful analysis of colour coded orientation map of body centred cubic phase show mostly small grains spread all throughout the matrix as three-dimensional network. Their spreading indicates jelly type honeycomb structure. Mostly their size is around 1 μm wide to 3.2 μm long. However, they tend to maintain a lower aspect ratio. Also, mostly they are oriented along one crystallographic direction. Only one area is observed in the middle left of micrograph which has different colour. Thus, indicates presence of different orientations. Their average grain size is 0.8305 μm .









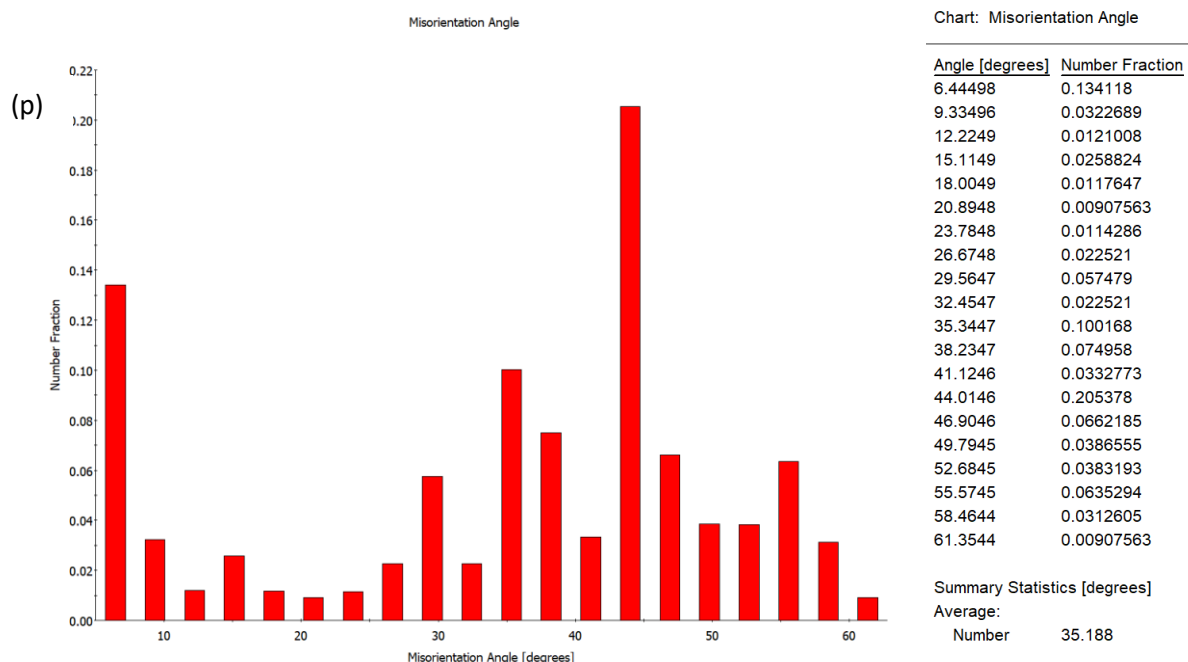


Figure 3 (a) – (p): (a) – (d) Elemental maps of Copper, Zirconium, Aluminium and Oxygen, (e) Image quality of map of $\text{Zr}_{47.5}\text{Cu}_{45.5}\text{Al}_5\text{Co}_2$ (0.5% ZrC) (f) Colour coded orientation map of $\text{Zr}_{47.5}\text{Cu}_{45.5}\text{Al}_5\text{Co}_2$ (0.5% ZrC) (g) Colour coded orientation map of Al_2Zr FCC phase [71], (h) and (i) Pole figures of Al_2Zr FCC phase, (j) – (k) Grain size histograms of Al_2Zr FCC phase, (l) Colour coded orientation map of BCC phase [71], (m) and (n) Pole figures of BCC phase, (o) – (p) Grain size histograms of BCC phase.

2.4 ZrC = 0.75% and 1.0%

Alloys with 0.75% and 1.0 % ZrC are tested at The University of New South Wales, Sydney, Australia. Unfortunately, improper patterns were captured due to poor workmanship skill which subsequently did not result in good Hough Space Transform, indexing and matching with crystal information files. Only color-coded orientation maps are presented (Figure 4 and 5) to give an image of outcome. Most of the data consisted of background noise without detecting any crystallinity. One of the reasons attributed to this is the absence of simultaneous EDS mapping prior EBSD mapping. That is, not enough data points from EDS were available to provide a feedstock for EBSD. Thus, no useful information could be extracted from these maps. These results proved out to be erroneous. An attempt is underway to repeat the same at EDAX Laboratories, Utah and will be presented in subsequent reports.

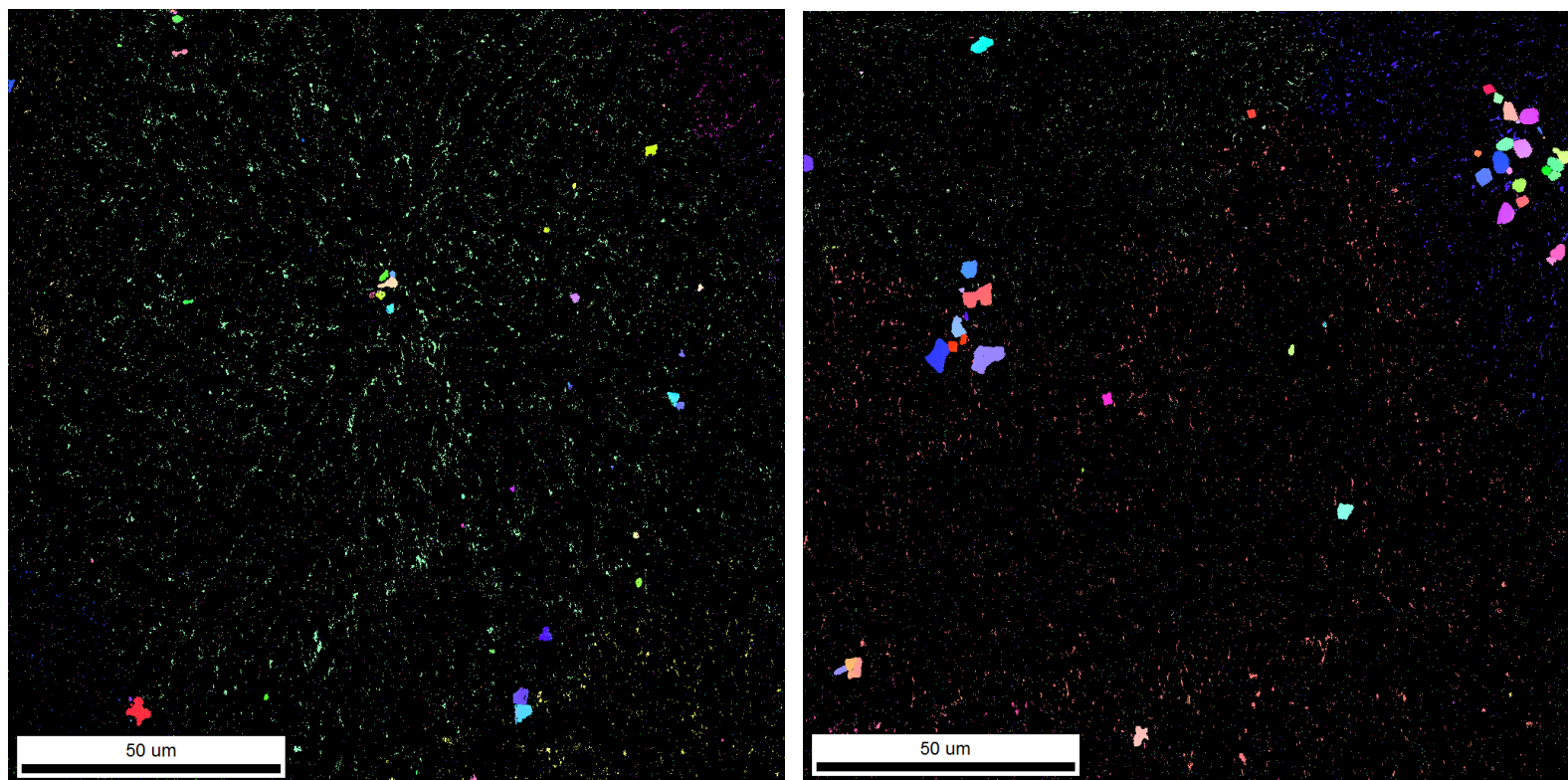


Figure 4 (left) and 5 (right): (Left) Colour coded EBSD map of $\text{Zr}_{47.5}\text{Cu}_{45.5}\text{Al}_5\text{Co}_2$ (0.75% ZrC), (right) Colour coded EBSD map of $\text{Zr}_{47.5}\text{Cu}_{45.5}\text{Al}_5\text{Co}_2$ (1.0% ZrC),

2.5 Acknowledgements

Author would like to thank the support, encouragement, patience and perseverance of his supervisors (specially Prof. Milan Brandt and Mrs. Lina Bubic). He would also like to thank Mr. Ron Witt of EBSD Analytical Inc. for help in carrying out quick EBSD scans.

2.6 Conclusions

Following conclusions could be drawn from this study;

1. Electron back scatter diffraction shows the effect of inoculation in promoting crystallinity.
2. Eight types of phases may be observed in this family of composites.
3. Unmelted ZrC is observed at the center of nucleating grain in element maps of Cu, Zr, Al and Oxygen indicating incomplete mixing and heterogeneous nucleation at ZrC = 0.25%.
4. Size and morphology of fcc dendrites at ZrC = 0.25% indicates improper to proper diffusion. On average their size is around 4 μm wide to 120 μm long (long dendrites).
5. At ZrC = 0.25%, there is definite orientation relationship between fcc grains in one micrograph and bcc in other indicated by difference of color.
6. Three types of fcc grains namely large, medium and small with needle like or acicular morphology are observed at ZrC = 0.5% with an orientation relationship between small

and large dendrites (same color) and a different relationship for medium size dendrites (different blue color). Their average size is around 0.5635 μm

7. No unmelted ZrC is observed at the center of nucleating grain indicating complete melting at high temperature, mixing, homogenization and rapid solidification at ZrC = 0.5%
8. At inoculant percentage of 0.5% ZrC, almost all grains of body centered cubic phase are found to lie along one crystallographic plane. Their average grain size is 0.8305 μm .

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