

CHAPTER – 3

Al-Cu-Fe Quasicrystalline Matrix Composite Reinforced with Sn

Al-Cu-Fe QUASICRYSTALLINE MATRIX COMPOSITE REINFORCED with Sn

The Al-Cu-Fe alloy in a desired compositional space shows icosahedral diffraction symmetry. The Al-Cu-Fe IQC alloy having a nominal composition of $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ (at%) has a stable icosahedral phase [357]. These IQC alloys have the perfect combination of hardness, corrosion resistance, excellent wear resistance, and low co-efficient friction. These lucrative properties of Al-Cu-Fe IQC alloys have justified its usage as candidate materials for coatings. This kind of IQC alloy is commercially used as a coating material for non-sticking frying pans. However, the inherent room temperature brittleness restricts its usage for coating application of engineering components. The fracture toughness of quasicrystals can either be enhanced by nanostructuring or by reinforcing them with immiscible phased like Sn, Pb, FeAl or Carbon [125,358,367,359–366]. The early investigation on toughening of quasicrystals dealt with reinforcing them with Sn particles through liquid metallurgy routes. However, the low melting point of Sn limits its homogenous distribution in the Al-Cu-Fe IQC matrix. For overcoming the difficulty for uniform distribution of Sn particles in the Al-Cu-Fe quasicrystalline matrix, a hybrid strategy has been employed. The high energy planetary ball milling has been used to synthesize Al-Cu-Fe quasicrystalline matrix nanocomposite with uniformly distributed Sn particles through mechanical milling (MM).

In the present investigation, efforts were given to study the effect MM on structural transformation, thermal stability, and indentation behavior of Al-Cu-Fe IQC matrix nanocomposite powder and sintered compact reinforced with a varying volume fraction of Sn. The duration of MM and volume fraction of Sn particles affects the structural transformation of IQC phases of the matrix to various crystalline phases. The purpose of this study is to investigate the mechanically driven structural change during MM of IQC-Sn nanocomposite powder and phase evolution during thermal treatment. Further attempts

were made to correlate the grain refinement and phase evolution during mechanical milling with indentation behavior and hardness of IQC-Sn nanocomposite powder. The toughening behavior of IQC-Sn composite was studied in detail for nanocomposite powders and bulk samples compacted through spark plasma sintering (SPS), hot pressing (HP), and pressure-less sintering.

3.1 Structural transformation of IQC-Sn milled powder

The $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ (at %) IQC alloy was prepared by vacuum induction melting followed by annealing, as briefly mentioned in section 2.2.1 of Chapter 2. The Al-Cu-Fe alloy was further crushed to a size of $\leq 100 \mu\text{m}$ with a vibratory ball mill as described in section 2.3.1 of Chapter 2. The powder X-ray diffraction (XRD) patterns of as-received as-cast and annealed IQC and as-received Sn powder particles are shown in Figure 3.1 (a) and (b), respectively. From Figure 3.1 (a), it is evident that the $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ (at %) ternary alloy have IQC phase as the major constituent phase with the presence of crystalline phases of B2-type/ β -Al (Cu, Fe) [$a=0.29 \text{ nm}$; cP2; $\text{Pm}\bar{3}\text{m}$; JCPDS card no.: 65-3201] & $\text{Al}_{13}\text{Fe}_4$ [C2/m, $a=1.548 \text{ nm}$, $b=0.80831$, $c=1.2476 \text{ nm}$; JCDPS card no.: 65-1257] phase. The phase fraction of crystalline phases is 4% and 12% for the B2-type/ β -Al (Cu, Fe) and $\text{Al}_{13}\text{Fe}_4$ phase. The XRD patterns display sharp diffraction peaks that can be indexed following the Elser indexing scheme [40]. The major reflection of the IQC phase corresponding to 2-fold (2-f), 3-fold (3-f), and the 5-fold (5-f) axis of symmetry along with face-centered ordering can be discerned from Figure 3.1 (a). The (311111) peak of the IQC phase is the signature reflection for face-centered ordering in Al-Cu-Fe alloys. The XRD pattern of as-received Sn particles in Figure 3.1 (b), shows all the major reflection corresponding to β -Sn i.e. (200), (101), (220), (211), having tetragonal crystal structure [$a=b=0.58 \text{ nm}$, $c=0.3182 \text{ nm}$; tI4; I41/amd; JCPDS data card no.: 00-004-0673]. The IQC alloy and Sn particles used in the present investigation have particle sizes $\leq 100 \mu\text{m}$ and

~20 μm , respectively, as shown in Figure 3.1 (c & d). Further, it can be observed that the as-received Sn powder particles are not spherical in shape and are elongated in one dimension (Figure 3.1 (d)).

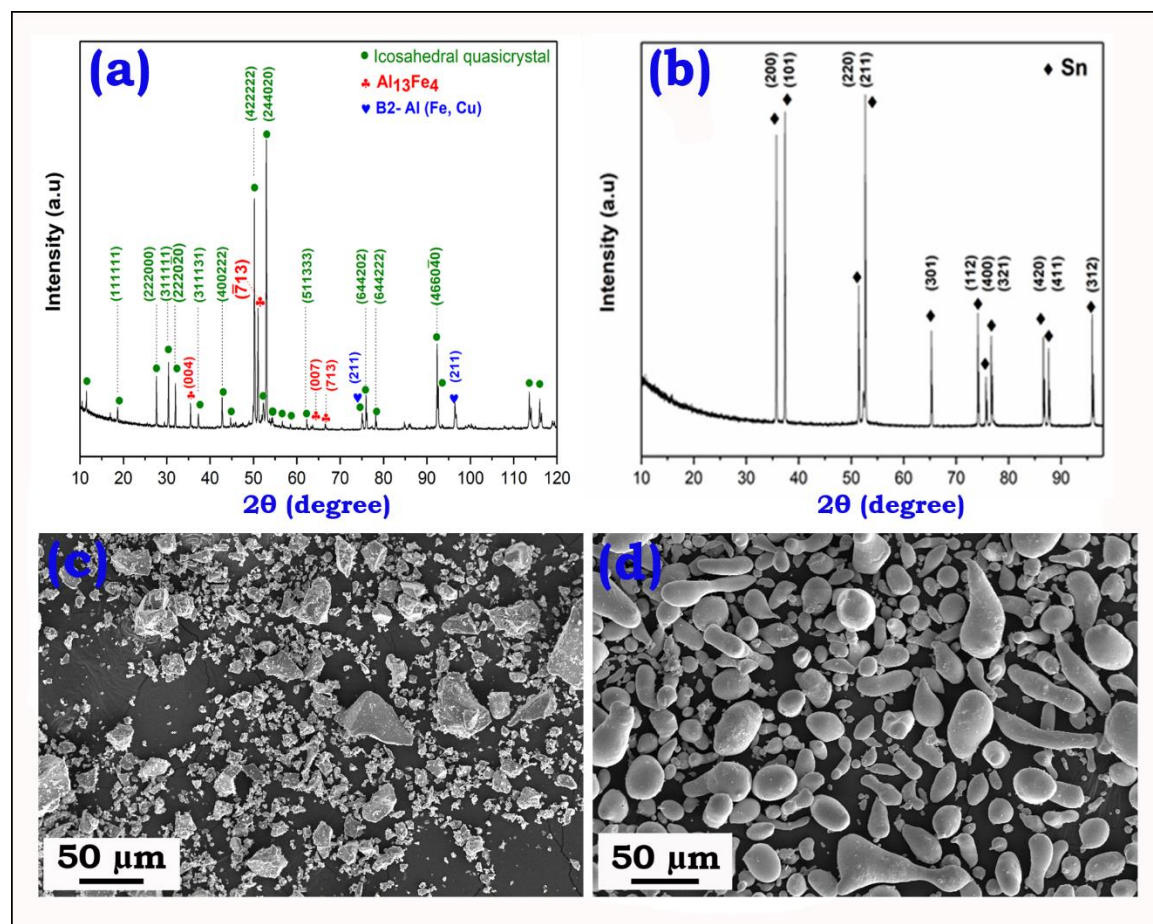


Figure 3. 1: Phase analysis of (a) as-cast and annealed $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ (at %) IQC alloy and (b) as-received Sn powder; (c) SEM micrograph of as-cast and annealed $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ (at %) IQC alloy and (d) as-received Sn powder.

3.1.1 XRD analysis of IQC-Sn milled powder

The powder XRD patterns show the sequence of structural change during MM of IQC-10Sn, IQC-20Sn, and IQC-30Sn as evident from Figure 3.2 (a, b, c), Figure 3.3 (a, b, c), and Figure 3.4 (a, b, c) respectively. The IQC-Sn nanocomposite powder shows all the primary reflections corresponding to the ordered IQC phase at MM's starting.

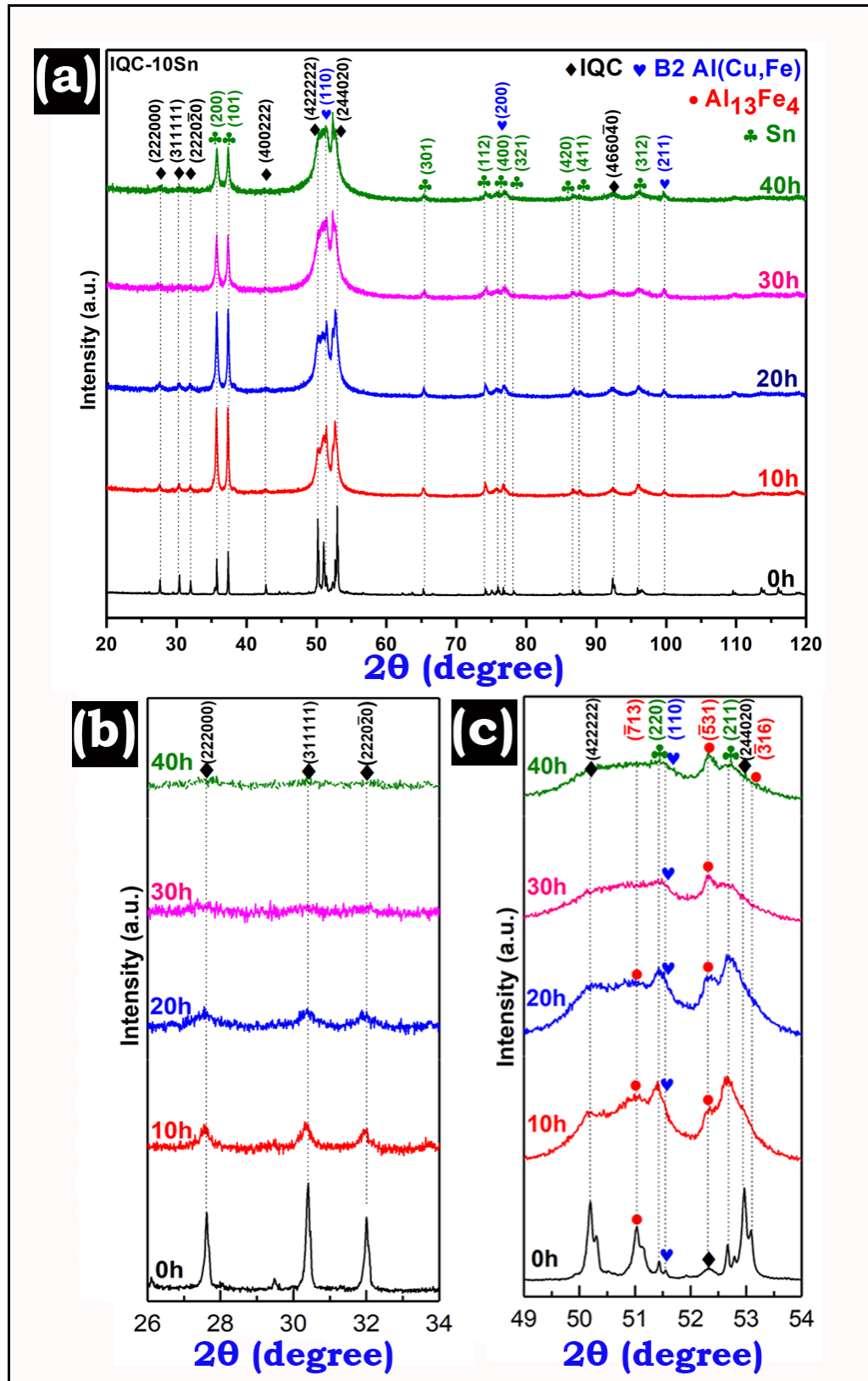


Figure 3. 2: Phase transformation during MM of IQC-10Sn (a); Changes in the superlattice (311111) peak in FCI quasicrystal during MM in IQC-10Sn (b); Structural transformation of IQC to crystalline phases (c).

The major diffraction peak corresponds to (222000) ($d \sim 3.748 \text{ \AA}$), (311111) ($d \sim 3.415 \text{ \AA}$), (2220 $\bar{2}$ 0) ($d \sim 3.224 \text{ \AA}$), (400222) ($d \sim 2.456 \text{ \AA}$), (422222) ($d \sim 2.111 \text{ \AA}$), (244020) ($d \sim 2.007 \text{ \AA}$) & (4660 $\bar{4}$ 0) ($d \sim 1.240 \text{ \AA}$) in IQC-10, 20 & 30Sn as evident from Figure 3.2, 3.3, and 3.4 respectively for 0 h MM. Apart from all the major peak of IQC phases, minor phase fraction corresponding to crystalline phases, i.e., $\text{Al}_{13}\text{Fe}_4$ and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ are also seen from Figure 3.2 (a, b, c), Figure 3.3 (a, b, c) and Figure 3.4 (a, b, c) respectively. The existence of the IQC phase and the crystalline phases and Sn reinforcement were also understood by deconvoluting the peak profile in the vicinity of intense reflection of IQC as illustrated in Figure 3.5.

The deconvoluted profile depicts crystalline phases along with the significant IQC phase as a function of milling duration for IQC-10Sn nanocomposite powder. The variation of the intensity of phases in the deconvoluted profiles illustrates the structural transformation taking place in IQC-10Sn during MM. The prominent diffraction peak ($\bar{7}13$) (marked in red colour) in Figure 3.2 (a & c), 3.3 (a & c), and 3.4 (a & c) corresponds to that of the $\text{Al}_{13}\text{Fe}_4$ ($d \sim 2.0778 \text{ \AA}$). Similarly, the diffraction peak (110) ($d \sim 2.056 \text{ \AA}$) and (200) ($d \sim 1.447 \text{ \AA}$) (marked in blue color) correspond to B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase. Figures 3.2, 3.3, and 3.4 clearly show the sequence of structural transformation of the IQC matrix to crystalline phases as a function of volume fraction of Sn reinforcement particles and MM duration. It is evident from Figures 3.2, 3.3, and 3.3 that the ordered face-centered IQC (FCI) phase is the primary phase with minor phase fraction corresponding to $\text{Al}_{13}\text{Fe}_4$ and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ crystalline phases. The sharp diffraction peak corresponding to (311111) reflection of IQC phase ($d \sim 3.415 \text{ \AA}$) in IQC-10, 20, and 30Sn composite powder are shown in Figure 3.2 (a, b), Figure 3.3 (a, b), and Figure 3.4 (a, b) respectively.

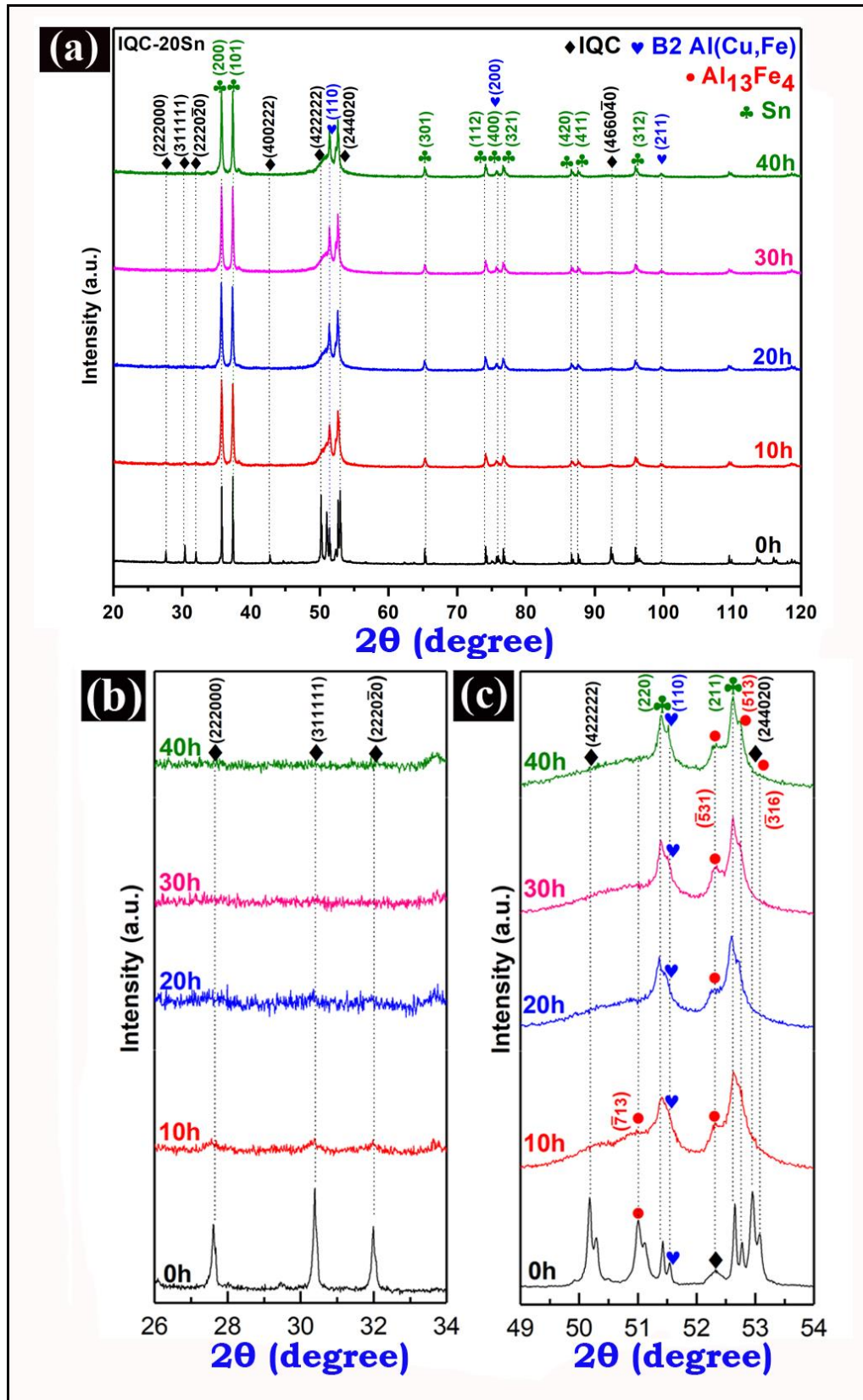


Figure 3. 3: Phase transformation during MM of IQC-20Sn (a); Changes in the superlattice (311111) peak in FCI quasicrystal during MM in IQC-20Sn (b); Structural transformation of IQC to crystalline phases (c).

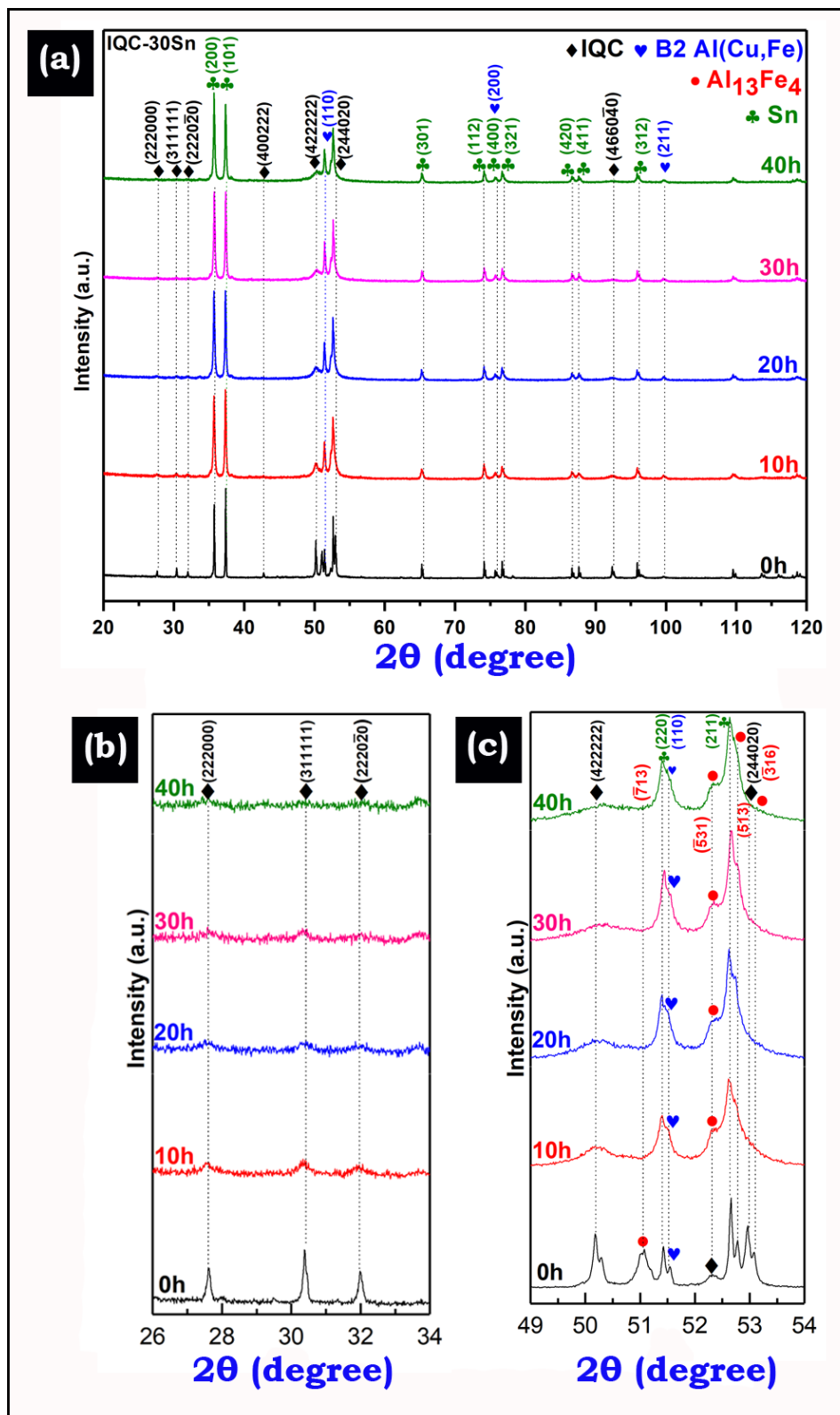


Figure 3. 4: Phase transformation during MM of IQC-30Sn (a); Changes in the superlattice (311111) peak in FCI quasicrystal during MM in IQC-30Sn (b); Structural transformation of IQC to crystalline phases (c).

This establishes that the IQC matrix in IQC-Sn composite powder at the starting of MM is necessarily ordered in nature. The order-disorder structural transformation during MM of IQC-Sn nanocomposite is evident from Figures 3.2, 3.3, and 3.4. It is evident that the (311111) superlattice peak of the IQC phase maintains its identity up to 20 h of MM for IQC-10 and 20Sn as seen in Figure 3.2 (b) and Figure 3.3 (b), respectively. However, in the case of IQC-30Sn nanocomposite powder, the (311111) peak of the IQC phase maintained its identity up to 30 h of MM, and its intensity diminished afterward, as evident from Figure 3.4 (b).

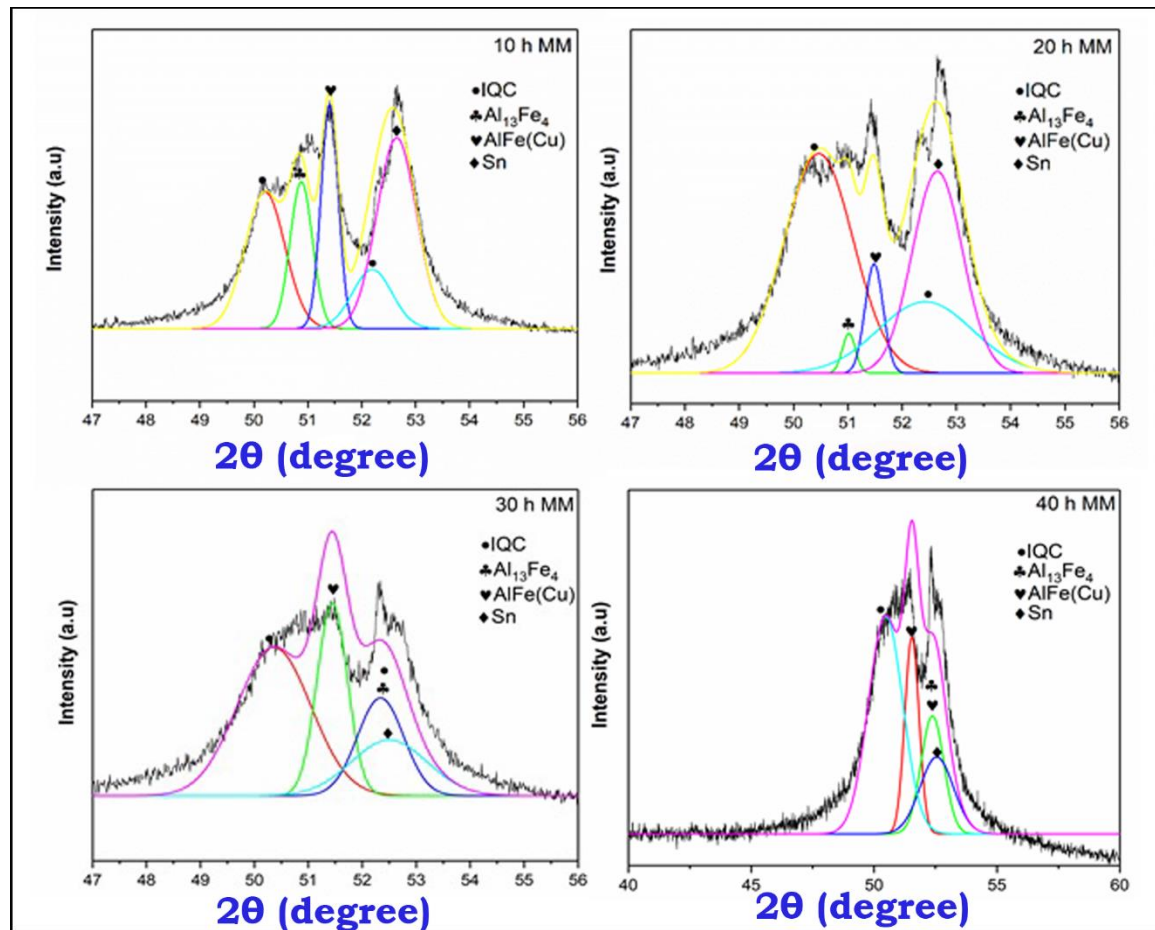


Figure 3. 5: Deconvolution of IQC-10Sn nanocomposite powder during MM showing the existence of IQC, Sn, and crystalline phase.

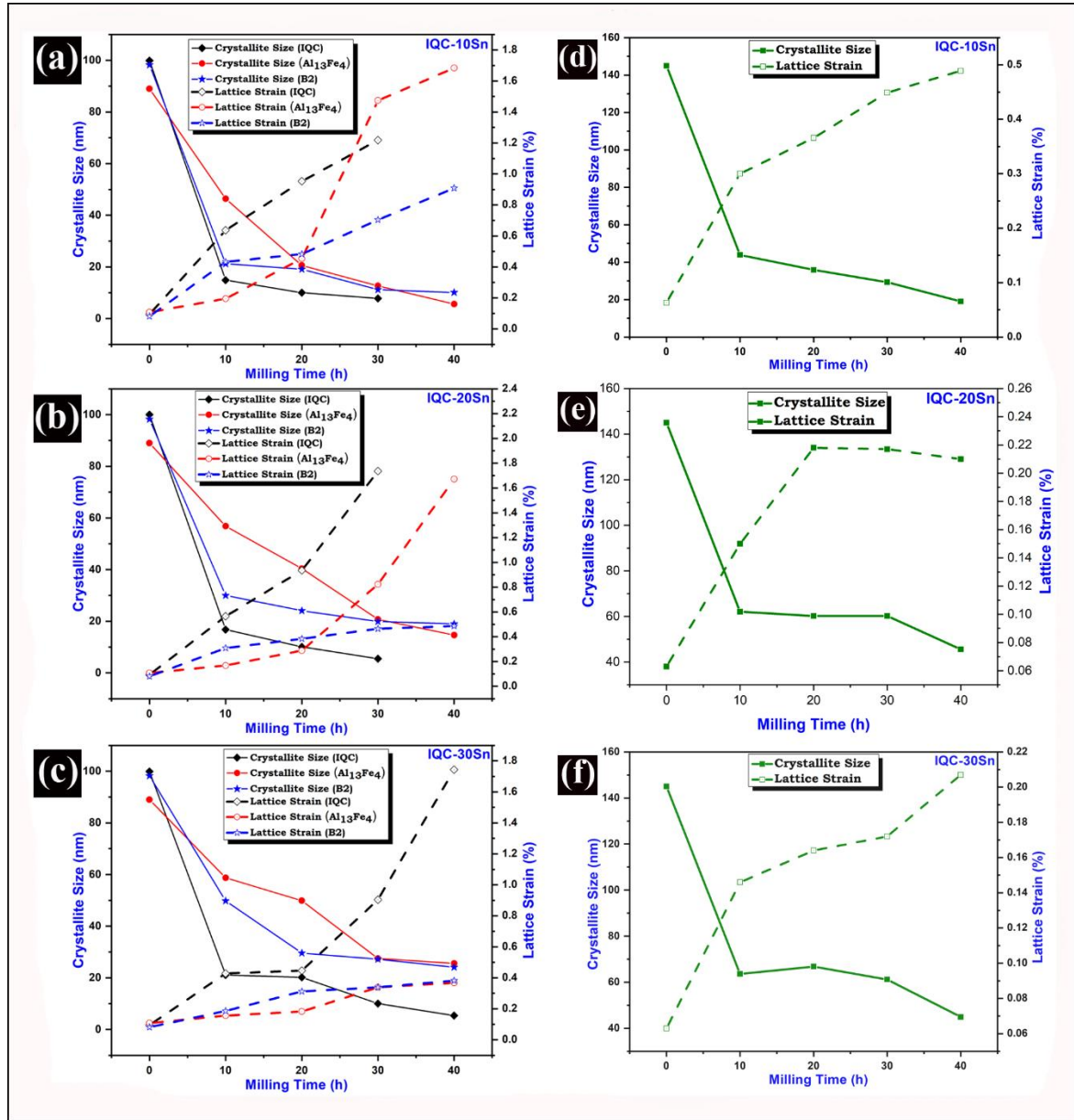


Figure 3. 6: Variation of crystallite size and lattice strain of icosahedral quasicrystal and approximant phases i.e. $Al_{13}Fe_4$ and B2-type $Al(Cu, Fe)$ as a function of milling time in IQC-10Sn (a), IQC-20Sn (b), IQC-30Sn (c); Variation of crystallite size and lattice strain of Sn reinforcement in IQC-10Sn (d), IQC-20Sn (e) and IQC-30Sn (f) as a function of milling time respectively.

Therefore, it can be stated that the IQC-10, 20 Sn remains ordered up to 20 h of MM. However, due to an increase in the volume fraction of Sn, the IQC matrix maintains its FCI ordering structure up to 30 h of MM. The major and most intense diffraction peak corresponds to the (422222) and (244020) reflection of IQC with 5-f and 2-f axis of

rotation. The MM intensity and the volume fraction of the Sn influence the changes of these significant peaks, as shown in Figure 3.2 (c), 3.3 (c), and 3.4 (c). In the case of IQC-10Sn, the (422222) peak maintains its identity up to 20 h of MM, and then after its phase fraction reduces considerably, as evident from Figure 3.2 (c). A similar observation is made for the (244020) plane of IQC, which sustains up to 20 h of MM, and phase fraction reduces considerably on further continuation of MM up to 40 h.

Table 3. 1: Variation of Crystallite size and lattice strain in IQC-Sn nanocomposites.

Sample designation	Mill-ing Time (h)	Phases present during MM of IQC-Sn nanocomposite							
		IQC		Al ₁₃ Fe ₄		B2-type Al(Cu, Fe)		Sn	
		CS (nm)	LS (%)	CS (nm)	LS (%)	CS (nm)	LS (%)	CS (nm)	LS (%)
IQC-10Sn	0	99	0.095	89	0.108	98	0.081	145	0.063
	10	15	0.637	46	0.195	21	0.433	44	0.300
	20	10	0.953	20	0.454	19	0.483	36	0.366
	30	8	1.218	13	1.474	11	0.704	29	0.449
	40	-	-	6	1.684	10	0.909	19	0.489
IQC-20Sn	0	100	0.094	89	0.108	98	0.081	145	0.063
	10	17	0.565	57	0.168	30	0.309	62	0.150
	20	10	0.935	40	0.288	24	0.384	60	0.218
	30	6	1.736	20	0.823	19	0.464	60	0.217
	40	-	-	15	1.671	19	0.486	46	0.210
IQC-30Sn	0	100	0.095	89	0.108	98	0.081	145	0.063
	10	21	0.428	59	0.156	80	0.186	64	0.146
	20	20	0.447	50	0.183	30	0.312	67	0.164
	30	10	0.904	28	0.339	27	0.339	61	0.172
	40	5	1.744	26	0.367	24	0.382	50	0.207
Crystallite size (CS); Lattice strain (LS)									

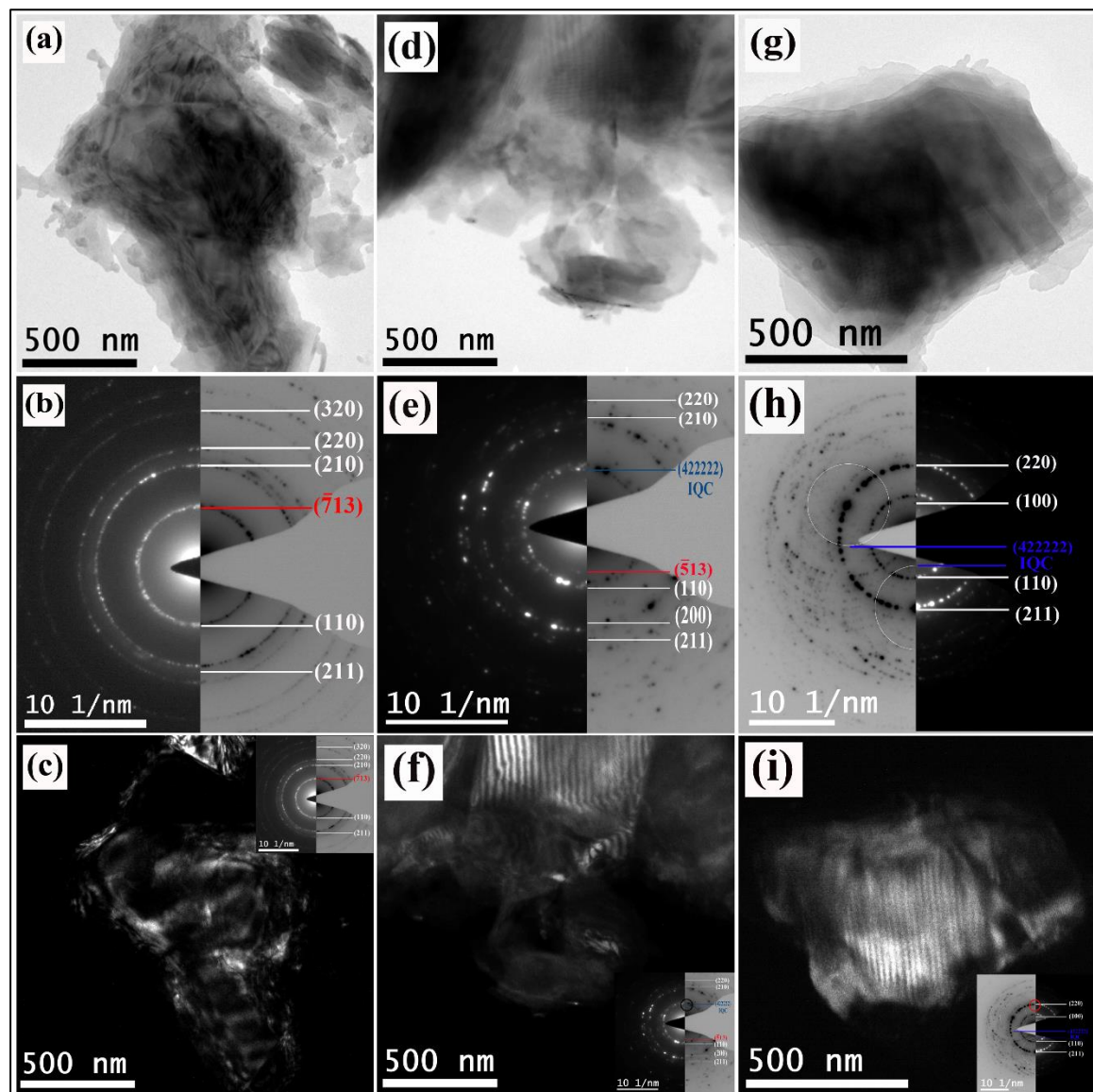


Figure 3. 7: Diffraction contrast images of IQC-10 Sn (a-c), IQC-20Sn (d-f) and IQC-30Sn (g-i); Bright field image of IQC matrix MM for 40h in IQC-10Sn (a), IQC-20Sn (d) and IQC-30Sn (g); Selected area diffraction pattern of IQC-10Sn (b), IQC-20Sn (e) and IQC-30Sn (h) corresponding to BF as shown in (a), (d) and (g) respectively; Darkfield images of IQC matrix MM for 40h in IQC-10Sn (c), IQC-20Sn (f) and IQC-30Sn (i).

Similar structural stability of (422222) and (244020) plane IQC is also observed for IQC-20Sn nanocomposite powder, as evident from Figure 3.3 (a). However, the sequence of structural stability for the major reflections of IQC phase in IQC-30Sn is not similar as in the previous two cases. The 5-f (422222) peak of IQC can sustain up to 40 h MM. However, the (244020) peak can withstand only upto 20 h of MM. In all the three cases,

i.e., IQC-10, 20, and 30 Sn, the minor IQC phase at $d \sim 2.029 \text{ \AA}$ transforms to $\text{Al}_{13}\text{Fe}_4$ phase, which can be identified from the appearance of $(\bar{5}31)$ ($d \sim 2.031 \text{ \AA}$) after 10 h of MM regardless of the volume fraction of Sn reinforcement particles in IQC-Sn nanocomposite powder.

In the present investigation, considerable efforts were also made to investigate Sn particles' effect on the structural transformation of minor crystalline phases during MM. The IQC phase coexists with the minor fraction of crystalline phases of $\text{Al}_{13}\text{Fe}_4$ and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ up to $\sim 12\%$ and 4% , respectively. At the beginning of MM, the $(\bar{7}13)$ and $(\bar{3}16)$ reflection of $\text{Al}_{13}\text{Fe}_4$ phase ($d \sim 2.0778 \text{ \AA}$) and ($d \sim 2.0037 \text{ \AA}$) respectively, are the major peaks for the phase as evident from Figures 3.2, 3.3, and 3.4. Similarly, the (513) reflection of the $\text{Al}_{13}\text{Fe}_4$ phase ($d \sim 2.0153 \text{ \AA}$) is a minor peak corresponding to this phase (Figure 3.2 (c), 3.3 (c), 3.4 (c)). In the case of IQC-10Sn, the $(\bar{7}13)$ maintains its identity upto 40 h of MM and becomes more intense as compared to (422222) and (244020) reflection of IQC phase after 10 h of MM. The $(\bar{5}31)$ reflection of $\text{Al}_{13}\text{Fe}_4$ phase fraction increases considerably after 10 h of MM. After 40 h of MM, the phase fraction of IQC is relatively minimal compared to that of the $(\bar{7}13)$ and $(\bar{5}31)$ reflection of $\text{Al}_{13}\text{Fe}_4$. The $(\bar{7}13)$ principal reflection of $\text{Al}_{13}\text{Fe}_4$ phases starts losing its identity after 20 h and 10 h of MM for IQC-20Sn and IQC-30Sn, respectively.

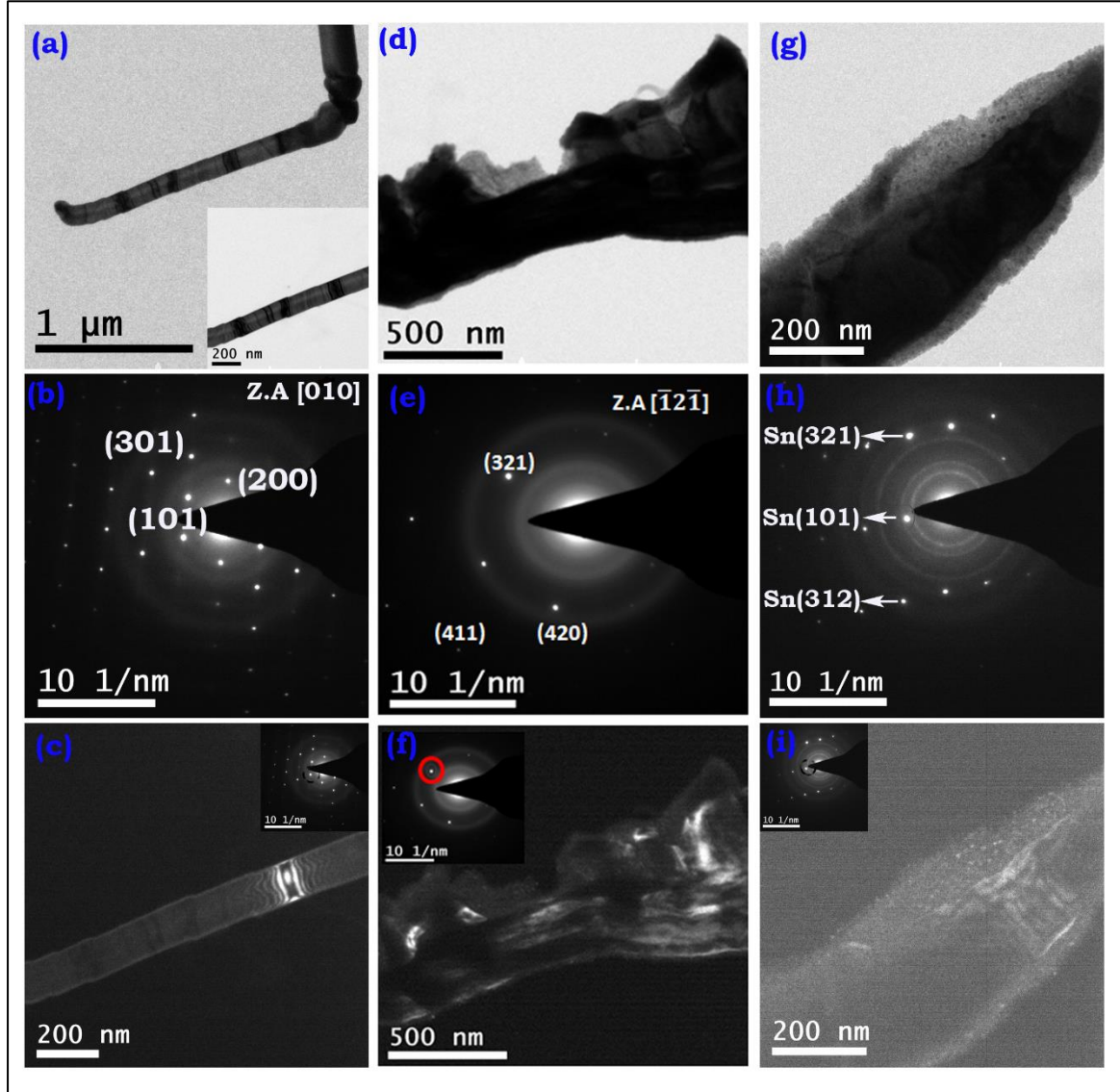


Figure 3. 8: Diffraction contrast images of IQC – Sn nanocomposite showing the rod like Sn particles; (a), (d), and (g) bright-field image of Sn particle in IQC-10Sn, IQC-20Sn and IQC-30Sn respectively; (b), (e), and (h) SADP corresponding to BF image of Sn in IQC-10Sn, IQC-20Sn, IQC-30Sn respectively; (c), (f), and (i) dark-field image of Sn particles in IQC-10Sn, IQC-20Sn, and IQC-30Sn respectively.

The structural transformation of the IQC phase to the B2-type Al(Cu, Fe) phase is also dependant on the MM duration and the volume fraction of Sn reinforcement in the IQC matrix. B2-type Al(Cu, Fe) phase has only 4% phase fraction in IQC matrix at MM's starting. However, the MM duration induces the transformation of IQC to a B2-type phase, and the phase fraction of the B2-type phase depends upon the varying volume fraction of Sn. In IQC-10Sn, the phase fraction of the B2-type phase is comparatively less than that

of the $\text{Al}_{13}\text{Fe}_4$ phase, as evident from Figure 3.2 (c). However, in the case of IQC-20Sn and IQC-30Sn, the phase fraction of B2-type phases increases considerably after 20 h and 10 h of MM, respectively.

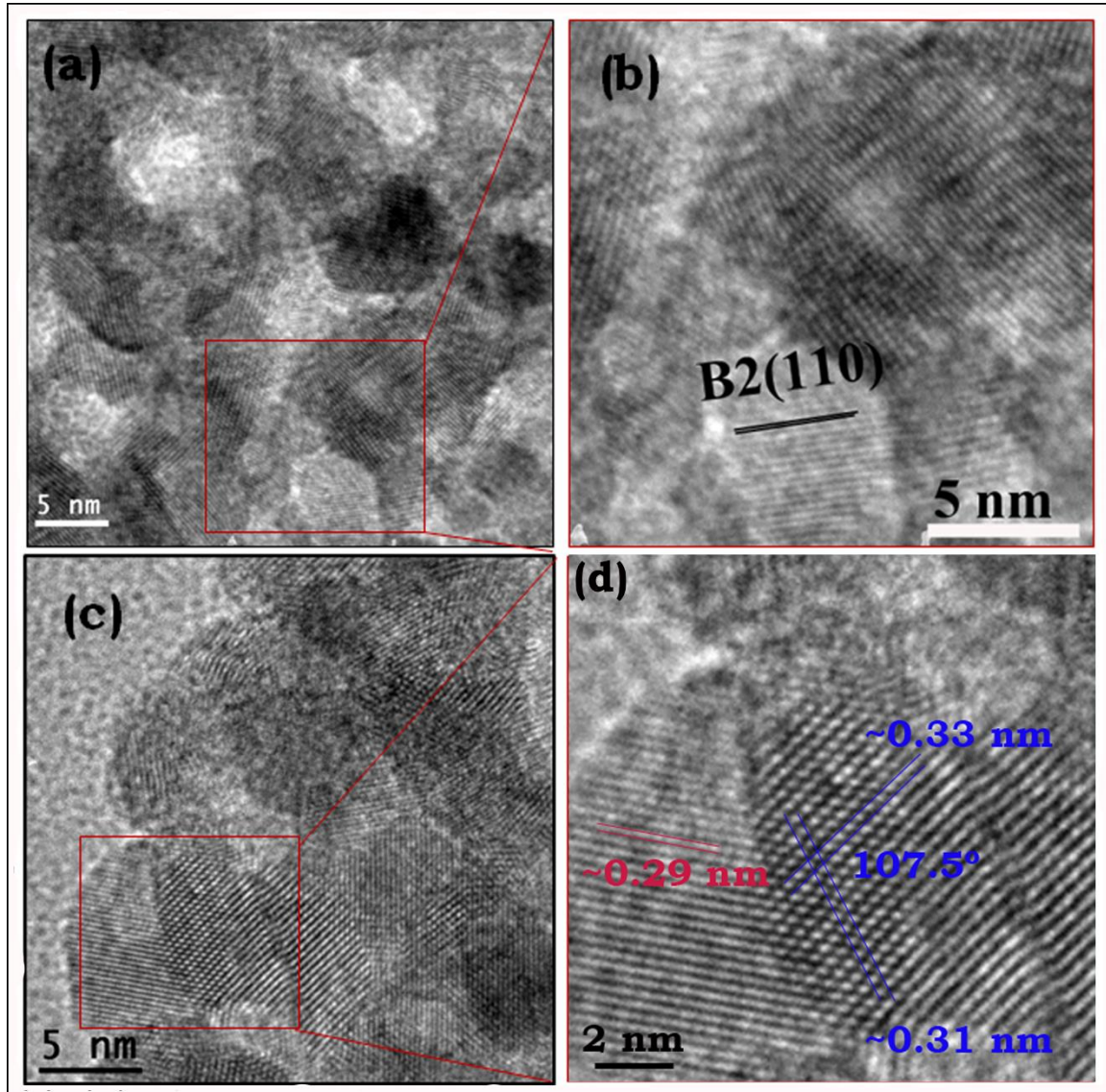


Figure 3. 9: Phase contrast images of IQC-30Sn nanocomposite powder showing the presence of nanocrystalline B2-type phases (a & b); and co-existence of B2-type phase with $\text{Al}_{13}\text{Fe}_4$ phase (c & d).

In both the IQC-20 & 30Sn, the preferential increase in the intensity of (110) reflection of B2-type phase is associated with a decrease in the intensity of $(\bar{7}13)$ principal reflection of $\text{Al}_{13}\text{Fe}_4$ phase after 20 h and 10h of MM, respectively. However, merely from

the XRD pattern of IQC-Sn nanocomposite powder, it is challenging to predict the ordering in B2-type Al(Cu, Fe) phase formed during MM. This may be indicated with the help of a TEM micrograph.

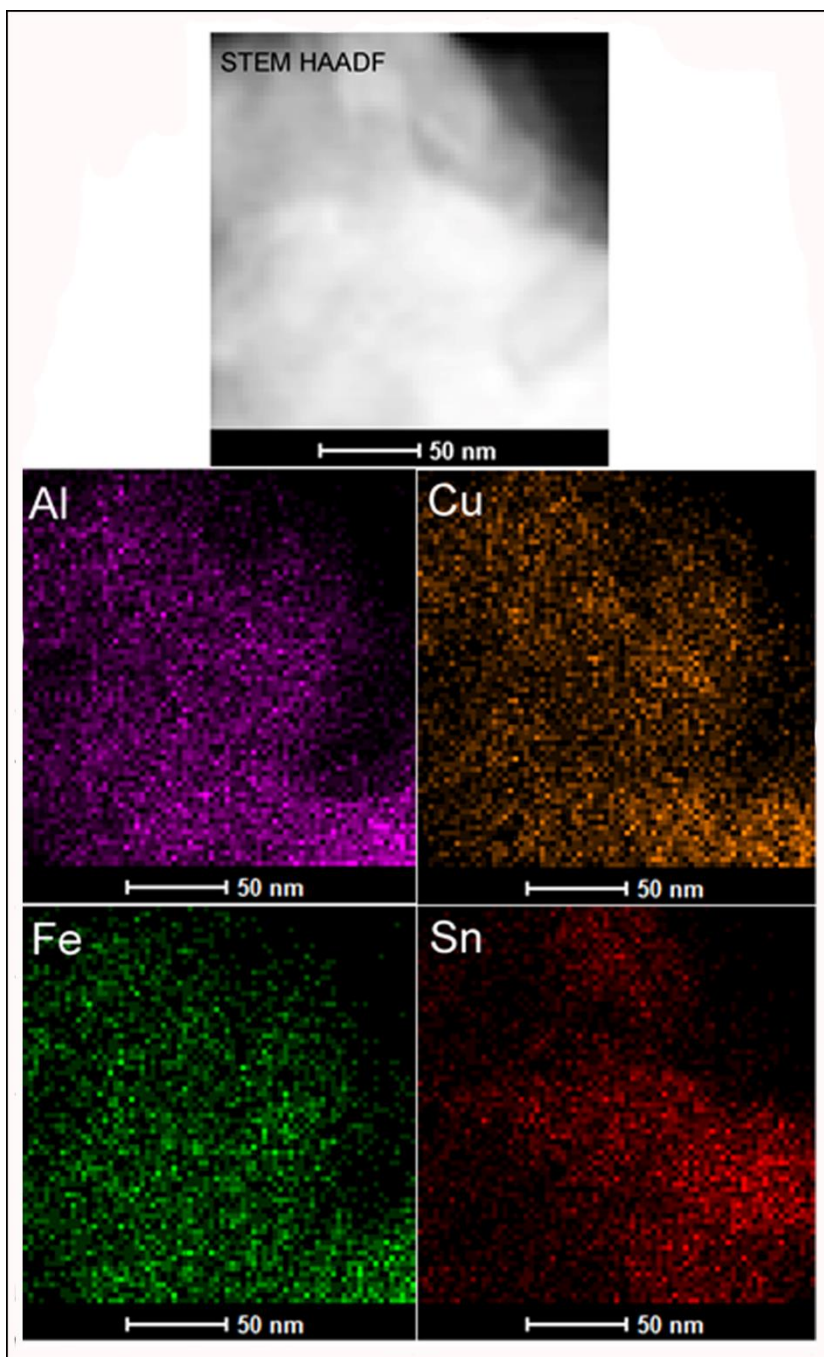


Figure 3. 10: STEM – EDS mapping of IQC – 30Sn nanocomposite powder.

The crystallite size and lattice strain for IQC-Sn nanocomposite powder are reported in Table 3.1. Efforts were made to compute the crystallite size and lattice strain of the IQC

phase, and crystalline phases evolved during MM and the Sn reinforcement particles as evident from Figure 3.6. The crystallite size and lattice strain are also dependent on the MM duration and the volume fraction of Sn reinforcement in the IQC matrix. The variation of crystallite size and lattice strain of the matrix consisting of the IQC phase along with $\text{Al}_{13}\text{Fe}_4$ and B2-type crystalline phases in IQC-10Sn, IQC-20Sn, and IQC-30Sn is evident from Figure 3.6 (a), Figure 3.6 (b), and Figure 3.6 (c) respectively.

Similarly, the crystallite size and lattice strain of Sn reinforcement particle during MM upto 40 h, in IQC-10Sn, IQC-20Sn and IQC-30Sn are shown in Figure 3.6 (d), Figure 3.6 (e), and Figure 3.6 (f), respectively. It was observed from Figure 3.6 and Table 3.1 that the degree of grain refinement is dependent on the volume fraction of Sn. The crystallite size $\sim 5\text{-}6$ nm of IQC phase in IQC-20Sn MM upto 30 h, is almost comparable to IQC-30Sn MM upto 40h. In the case of IQC-10Sn and IQC-20Sn, the crystallite size and lattice strain for 40 h MM were complicated to be computed due to its minor phase fraction of IQC phase, as evident in Figure 3.2 (c) and Figure 3.3 (c), respectively. The crystallite size significantly increases, and lattice strain considerably decreases for crystalline phases and Sn reinforcement particles, increasing the volume fraction of Sn (Table 3.1).

3.1.2 TEM investigation of IQC-Sn milled powder

The diffraction contrast image of IQC-10Sn, IQC-20Sn, and IQC-30Sn are shown in Figure 3.7 (a-c), Figure 3.7 (d-f), and Figure 3.7 (g-i), respectively for the IQC matrix. The structural and microstructural features of Sn reinforcement particles in IQC-10Sn, IQC-20Sn and IQC-30Sn can be discerned from the TEM micrographs shown in Figure 3.8 (a-c), 3.8 (d-f), 3.8 (g-i) respectively. The bright-field (BF) image and corresponding selected area diffraction (SAD) pattern along with the dark field (DF) image are shown in Figure 3.7 (a), 3.7 (b), and 3.7 (c), respectively for IQC-10Sn. The BF image of IQC-10Sn shows the flaky type of nanocomposite powder particles, which seems to be elongated

during 40 h MM. There are dark patches also observed in the BF images of IQC-10Sn, which may be attributed to strain accumulation during MM up to 40 h. It is also evident from Table 3.1 that the lattice strain for crystalline phases is relatively high ~ 1.68 and 0.91 for $\text{Al}_{13}\text{Fe}_4$ and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase, respectively. The SAD pattern of IQC-10Sn represents the polycrystalline rings corresponding to both $\text{Al}_{13}\text{Fe}_4$ and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase. The polycrystalline ring ascertains the fact that phases formed after 40 h of MM are randomly oriented. The composite nature of the SAD pattern substantiates XRD results, showing the co-existence of the $\text{Al}_{13}\text{Fe}_4$ phase along with the B2-type phase, as evident from Figure 3.2 (c). In the SAD pattern, no spot or ring corresponding to the (100) reflection of the ordered B2-type phase is seen. This confirms that the B2-type phase formed during MM of IQC-10Sn is disordered without any superlattice reflection of (100) peak of the B2-type phase ($d \sim 2.90 \text{ \AA}$). The DF image corresponding to $(\bar{7}13)$ reflection of $\text{Al}_{13}\text{Fe}_4$ and (110) reflection of B2-type phase shows the nanocrystalline nature of the IQC-10Sn nanocomposite powder.

For IQC-20Sn, the BF, SAD pattern and DF image are shown in Figure 3.7 (d), Figure 3.7 (e) and Figure 3.7 (f), respectively. In a similar line to IQC-10Sn, the BF image of IQC-20Sn shows strain localization and the flaky elongated particles. Additionally, feeble contribution appearing like moiré fringes due to localized layering may also be evident from Figure 3.7 (d). The SAD pattern of IQC-20Sn represents the polycrystalline rings corresponding to both (422222) reflection of IQC and (110) reflection of B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase and a feeble diffraction spot corresponding to $(\bar{5}13)$ of $\text{Al}_{13}\text{Fe}_4$ phase ($d \sim 2.6556 \text{ \AA}$). The polycrystalline ring ascertains the fact that phases formed after 40 h of MM are randomly oriented. The composite nature of the SAD pattern substantiate the results of XRD, showing the co-existence of IQC, $\text{Al}_{13}\text{Fe}_4$ phase along with B2-type phase as evident from Figure 3.3 (c).

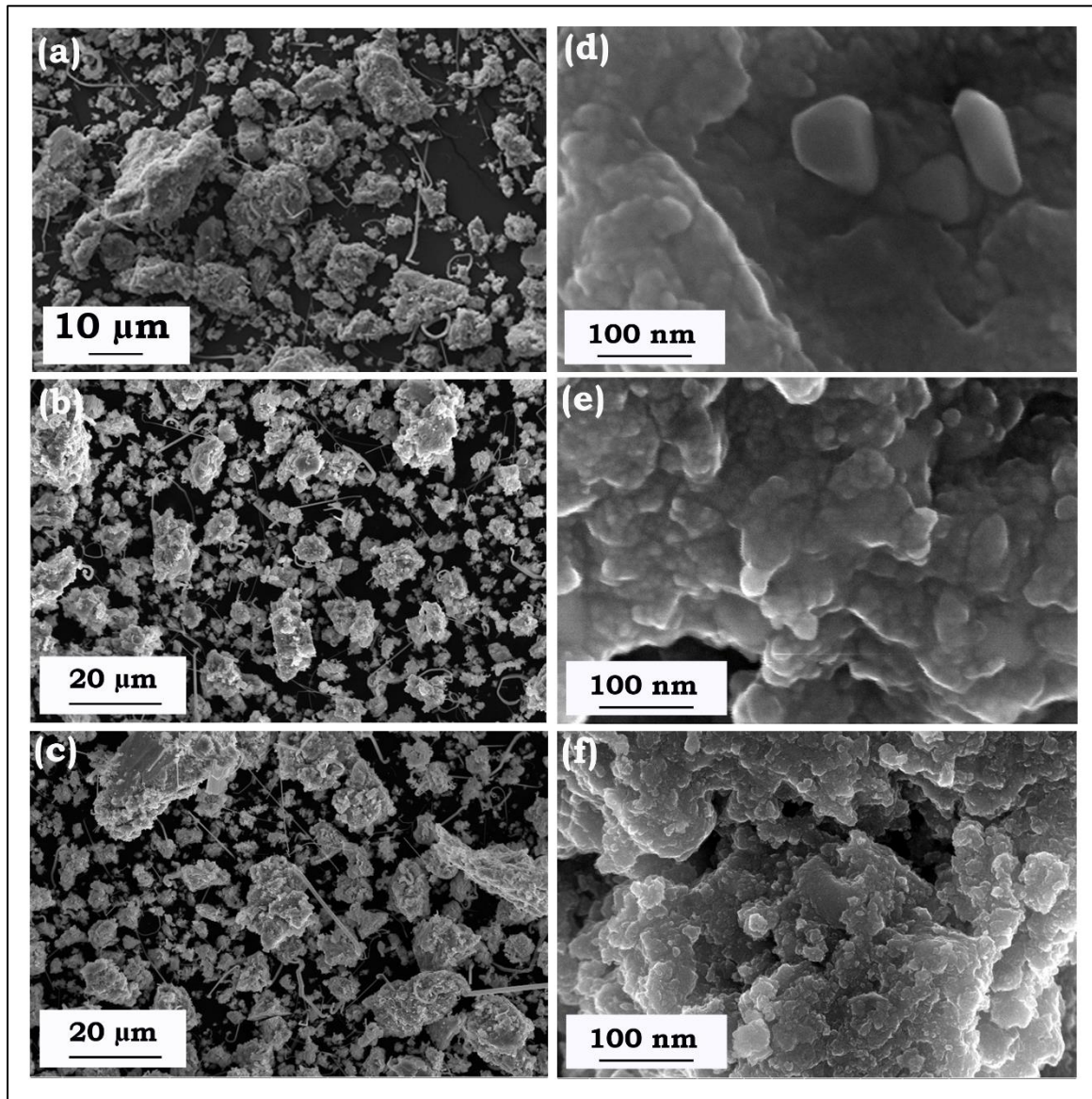


Figure 3. 11: SEM micrograph of IQC-10Sn (a, d), IQC-20Sn (b, e), and IQC-30Sn (c, f).

In the SAD pattern, no spot or ring corresponding to the (100) reflection of the ordered B2-type phase is seen. This confirms that the B2-type phase formed during MM of IQC-20Sn is disordered without any superlattice reflection of (100) peak of the B2-type phase ($d \sim 2.90 \text{ \AA}$). The DF image corresponding to (422222) reflection of IQC and (110) reflection of the B2-type phase shows the layering of IQC and B2-type phase having a thickness in the range of nanometer and length the ultra-fine grain regime.

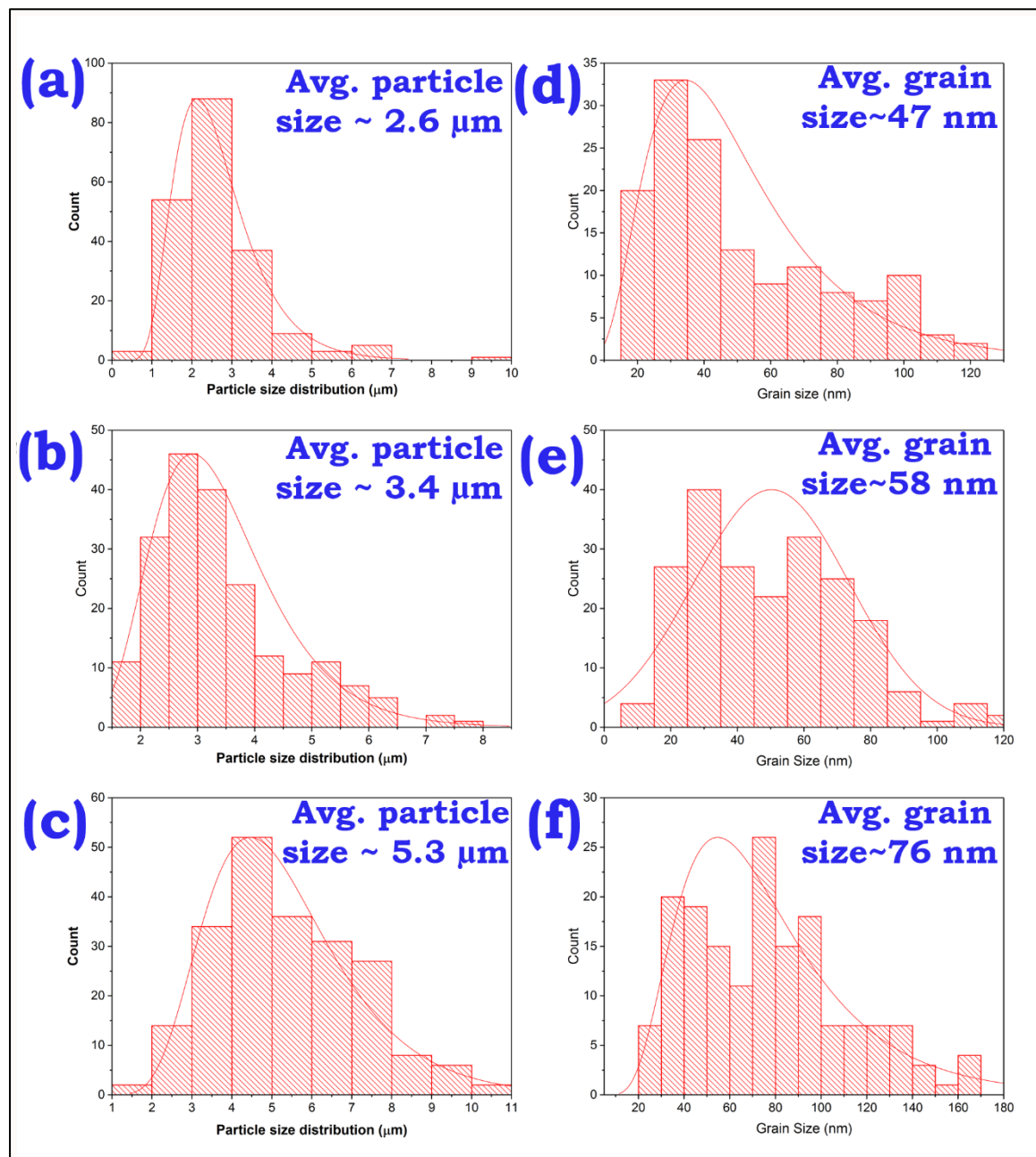


Figure 3. 12: Particle size distribution of IQC matrix MM for 40 h (a) IQC-10Sn, (b) IQC-20Sn, (c) IQC-30Sn; Grain size distribution of IQC matrix MM for 40 h in (d) IQC-10Sn, (e) IQC-20Sn, (f) IQC-30Sn.

For IQC-30Sn, the BF, SAD pattern, and DF image are shown in Figure 3.7 (g), Figure 3.7 (h), and Figure 3.7 (i), respectively. The BF image of IQC-30Sn shows strain localization and the flaky layered particles instead of flaky elongated particles as observed for IQC-10 & 20Sn. The BF images show the moiré fringes due to the layering of the IQC phase and B2-type phase. The SAD pattern of IQC-30Sn represents the polycrystalline

rings corresponding to both (422222) reflection of IQC and (110) reflection of B2-type Al(Cu, Fe) phase and a feeble diffraction spot corresponding to (100) reflection of B2-type Al(Cu, Fe) phase ($d \sim 2.90 \text{ \AA}$). The SAD pattern of the IQC-30Sn prominently shows double diffraction due to layering or juxtaposition of IQC and ordered B2-type Al(Cu, Fe) phase. It is evident from Figure 3.7 (h) that layering or juxtaposition of the B2-type phase on the IQC phase takes place during the process of MM.

The polycrystalline ring ascertains that phases formed after 40 h of MM are randomly oriented and are nanocrystalline and nano-quasicrystalline. The double diffracted SAD pattern substantiates XRD results, showing the co-existence of IQC along with the B2-type phase as evident from Figure 3.4 (c). In the SAD pattern, feeble spot corresponding to the (100) reflection of the ordered B2-type phase was observed. This confirms that the B2-type phase formed during MM of IQC-30Sn may be locally ordered, having a very small fraction. The DF image corresponding to (422222) reflection of IQC and (110) reflection of the B2-type phase shows the layering of IQC and B2-type phase having a thickness in the range of nanometer and length the ultra-fine grain regime are even more significant than the IQC-20Sn.

Figure 3.8 (a-i) shows the diffraction contrast images of IQC-Sn nanocomposite powder showing the Sn reinforcement particles structural and microstructural feature embedded in the IQC matrix. It can be observed from Figure 3.8 that the refinement of Sn reinforcement is more in IQC-10Sn compared to that of the IQC-20 and 30 Sn. From the BF images of IQC-10Sn, it is evident from Figure 3.8 (a) that the Sn particles are in an ultra-fine grain regime, having a diameter of $\sim 127 \text{ nm}$. The diffraction pattern (DP) of the rod-like Sn particle corresponds to [010] zone axis of Sn (Figure 3.8 (b)) and are oriented along the (101) plane. The DF image is recorded from the (101) spot in Figure 3.8 (c), shows a bright contrast, which may be attributed to defects after 40 h of MM.

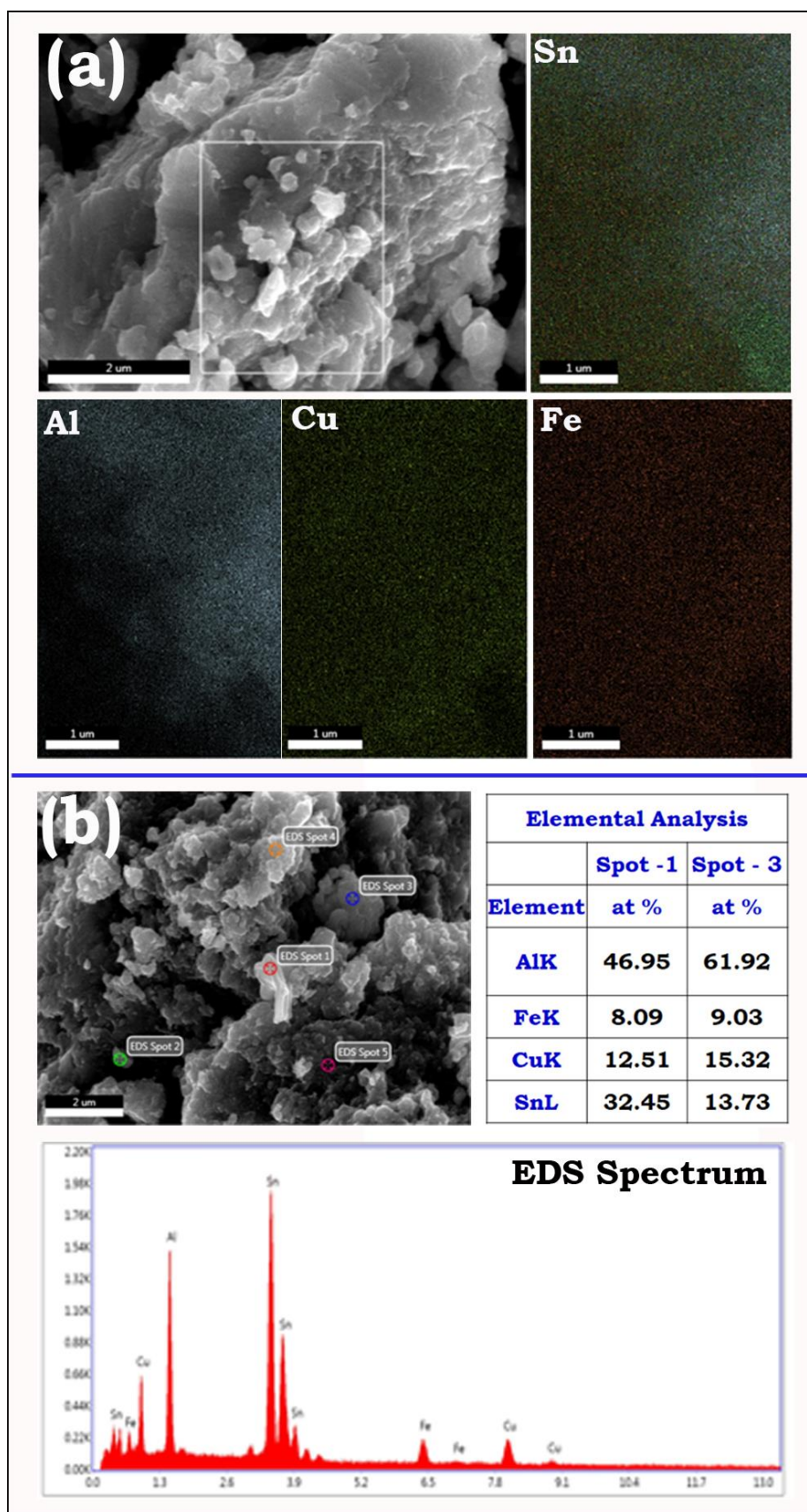


Figure 3. 13: SEM-EDS mapping of IQC-30Sn nanocomposite powder (a); Point EDS analysis, nominal composition, and the EDS spectrum of IQC – 30Sn (b).

Figure 3.8 (d) shows the Sn particles having a dark contrast are embedded in the IQC matrix with light contrast for the case of IQC-20Sn. The Sn particles in IQC-20Sn have a thickness of ~ 200 nm and are surrounded by the IQC matrix. The DP corresponding to the Sn particle in IQC-20Sn corresponds to the $[\bar{1}2\bar{1}]$ zone axis as evident from Figure 3.8 (e). The DF image of Sn particles in IQC-20Sn shows the grain refinement of Sn particle during MM for 40 as depicted in Figure 3.8 (f). During MM, ultrafine grains with a thickness of ~ 60 -70 nm and length of ~ 250 nm are observed from the DF image corresponding to the (321) Sn reinforcement particles plane. On increasing MM's duration, it was observed that the grain refinement of Sn particles decreases, as shown in Figure 3.8 (g-i). The Sn particles in IQC-30Sn are also surrounded by IQC matrix; however, the thickness of Sn particle ~ 250 nm as can be discerned from Figure 3.8 (g). The diffraction pattern of IQC-3Sn confirms Sn reinforcement's presence surrounded by IQC/ B2-type phases (Figure 3.8 (h)). The DF image of the Sn particles corresponding to the (101) plane of Sn particle confirms the refinement of the Sn particle and is observed to be in an ultrafine regime (Figure 3.8 (i)). Further, Sn particles refinement was found to be less in comparison to the Sn particles in IQC-10Sn and 20Sn.

The high-resolution phase-contrast images of IQC-30Sn is shown in Figure 3.9 (a-d). The MM has influenced the IQC matrix's significant refinement, as shown in Figure 3.9 (a & c). The HRTEM images show the presence of grains having the size of $\sim 10 - 15$ nm. The crystallite size of the crystalline phases observed through XRD is also in line with the grains observed through HRTEM. Further, the enlarged HRTEM image of crystalline phases are shown in Figure 3.9 (b & d). Figure 3.9 (b) lattice fringes corresponding to the (110) plane of the B2-type phase having d spacing of ~ 2.05 Å can be affirmed. The HRTEM phase contrast image of Figure 3.9 (d) represents B2-type Al(Cu, Fe) phase and $\text{Al}_{13}\text{Fe}_4$ phase. The lattice fringes corresponding to the (100) plane of B2-type phase can

be observed from Figure 3.9 (d), having d-spacing ~ 2.90 Å. The HRTEM images further represent the lattice fringes corresponding to the minor monoclinic $\text{Al}_{13}\text{Fe}_4$ phase having an angle between lattice fringes equivalent to $\sim 107.5^\circ$. Additionally, from Figure 3.9 (d) it can be discerned that the interface between the planes of two crystalline phases are also coherent. The crystalline and IQC phase's co-existence and juxtaposition were also observed through the diffraction contrast images of Figure 3.7.

It is known that the Sn particles are immiscible in the Al-Cu-Fe IQC alloys. However, in the present investigation, it was observed that the Sn particles either are embedded in the IQC matrix or are surrounded by the IQC particles. The distribution of the elements and Sn reinforcement in the nanocomposite powder can be discerned through the STEM – EDS elemental mapping of IQC-30Sn, as illustrated in Figure 3.10. The STEM-EDS elemental mapping of IQC-30Sn shows the homogenous distribution of Al, Cu, and Fe uniformly in the matrix. Simultaneously, the Sn particles are embedded in the Al, Cu, and Fe are uniformly distributed. The Sn particles having a size of ~ 50 nm are embedded in the IQC matrix, and a few regions rich in the Sn can be observed from the STEM – HAADF and elemental map of Sn particle in the IQC-30Sn. The regions showing the high-intensity corresponding to Sn are lean in Al, Cu, and Fe as it can be discerned from their intensity. Apart from this, at a few regions, minor fluctuation in these elements' intensity corresponds to the variation in thickness, size, the shape of the IQC-Sn nanocomposite powder particles due to repetitive cold welding and fracturing. The Sn particles are embedded inside and on the surface of IQC matrix (as evident from Figure 3.8), therefore the variation in the intensity of Sn throughout the IQC matrix was observed. These parameters influence the electron beam interaction with the IQC-Sn powder particle being investigated, leading to a minor fluctuation in the intensity at a few localized regions. Thus, it can be discerned that the Sn particles are not soluble in the IQC matrix.

3.2 Morphology of IQC–Sn milled powder

The SEM micrograph as shown in Figure 3.11 (a, d), (b, e), and (c, f) represents the morphology, shape, size, and distribution of Sn and IQC matrix in IQC-10, 20 & 30Sn respectively. The as-received Sn particles have a dumbbell-shaped morphology Figure 3.1 (d). The MM of the Sn particles in the IQC-Sn nanocomposites for 40 h leads to the rod-like morphology. Sn particles' morphology can be attributed to the preferential deformation of the Sn reinforcement entrapped between the repetitively colliding balls during high-energy ball milling. Similar kinds of observations were made during diffraction contrast imaging of IQC-Sn nanocomposite powder, as shown in Figure 3.8. Due to 40 h of MM, the Sn reinforcement particles are homogeneously dispersed in the IQC matrix on a micron level length scale as illustrated in Figure 3.11 (a), (b), and (c) for IQC – 10Sn, 20Sn, and 30Sn respectively. The refinement of the powder particles and grains are found to be dependent on the volume fraction of the Sn reinforcement in the IQC-Sn nanocomposite powder. It was observed from Figure 3.11 (d), (e), and (f) that the extent of the grain size refinement of the IQC matrix decreases with increasing the volume fraction of Sn in IQC-10Sn, 20Sn, and 30Sn, respectively.

Table 3. 2: Variation of particle size and grain size in IQC-Sn nanocomposite powder.

Average particle size of IQC matrix (μm)			Average grain size of IQC matrix (nm)		
IQC-10Sn	IQC-20Sn	IQC-30Sn	IQC-10Sn	IQC-20Sn	IQC-30Sn
2.60 ± 0.16	3.43 ± 0.12	5.32 ± 0.27	47 ± 2.75	58 ± 3.92	76 ± 3.25

The average particle size and grain size of the matrix (B2 + IQC phase) for IQC-10, 20 & 30Sn are shown in Figure 3.12 (a, d), (b, e), and (c, f) respectively, and the values are reported in Table 3.2. It is evident from Figure 3.11, Figure 3.12, and Table 3.2 that with increasing the volume fraction of Sn, the propensity for refinement of particle and

grain decreases. It is also evident that the grain size for IQC-10, 20 & 30Sn was found to be 47 nm, 58 nm & 76 nm, respectively. The increase in the grain size with increasing the volume fraction of Sn may have attributed to the change in MM's mechanism. The size of the grains seen through SEM is in good accordance with the crystallite size. Additionally, SEM micrograph reveals that the Sn particles are well embedded in the matrix after 40 h of MM. The chemical composition of IQC-Sn nanocomposite powder is mentioned in Table 3.3.

Table 3. 3: Chemical composition of IQC-Sn nanocomposite powder derived from SEM-EDS.

Elements	IQC-10Sn	IQC-20Sn	IQC-30Sn
Al	59.63 ± 7.72%	46.90 ± 8.61%	51.43 ± 8.33%
Cu	22.52 ± 4.12%	27.50 ± 4.62%	22.50 ± 4.85%
Fe	12.57 ± 4.63%	13.51 ± 5.63%	12.02 ± 5.55%
Sn	5.28 ± 5.47%	12.08 ± 4.22%	14.05 ± 3.24%

The SEM-EDS mapping shown in Figure 3.13 (b) of the IQC-30Sn nanocomposite powder further ascertain the claim made by the STEM – EDS mapping of the same. It was observed to have a few Sn rich regions having a very low intensity corresponding Al, Cu, Fe elements constituting the IQC matrix. Further, point EDS analysis was carried out to ascertain rods' chemical composition like Sn rich region and the region's deficit in Sn particles. The EDS spot – 1 having rod-like morphology have are rich in Sn, and the other particles are lean (EDS spot – 3). This further substantiates the fact that particles having rod-like morphology are Sn-rich. The EDS spectrum of IQC-30Sn nanocomposite powders also affirms no significant signature of either oxidation or carbon contamination during MM.

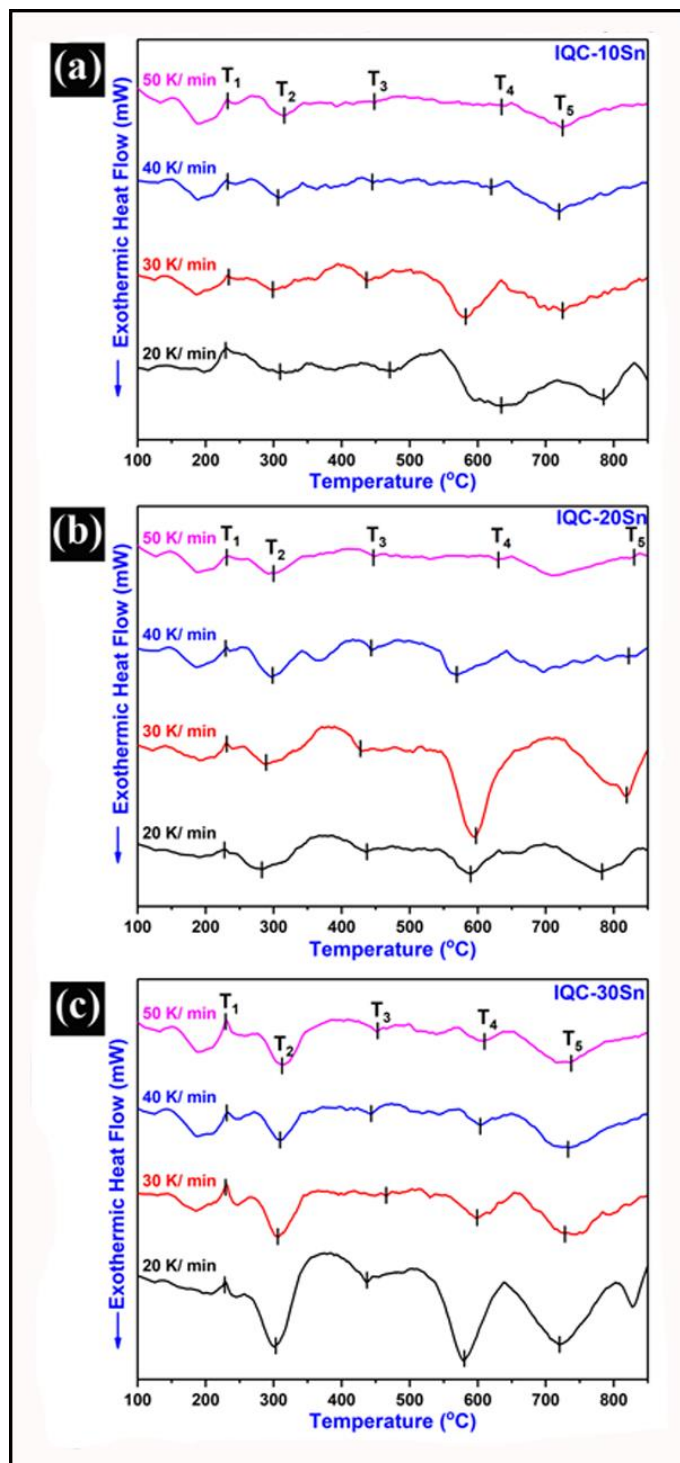


Figure 3. 14: Dynamic differential scanning calorimetry thermogram of IQC-10Sn (a), IQC-20Sn (b) and IQC-30Sn (c) at a heating rate of 20 K/min, 30 K/min, 40 K/min and 50 K/min.

3.3 Thermal stability of IQC–Sn milled powder

The thermal stability and phase evolution during heating of IQC-Sn nanocomposite powder have been investigated through dynamic DSC at different heating rates of 20

K/min, 30 K/min, 40 K/min, and 50 K/min. The dynamic DSC thermogram for IQC-10Sn, IQC-20Sn, and IQC-30Sn are shown in Figure 3.14 (a), Figure 3.14 (b), and Figure 3.14 (c), respectively. The DSC thermograms show the five heating events in the temperature range of 100 °C (373 K) to 850 °C (1123 K). The endothermic heating event is marked as T1 and T2, T3, T4 & T5 belongs to exothermic heating event depicting the phase transformation as a function of temperature. It is evident from the dynamic DSC thermogram that it lowers the phase transformation temperature at a lower heating rate due to sufficient time for conversion. As the heating events are not very much dependant on the characteristics temperature, this implies that the transformation occurring during heating events is diffusive.

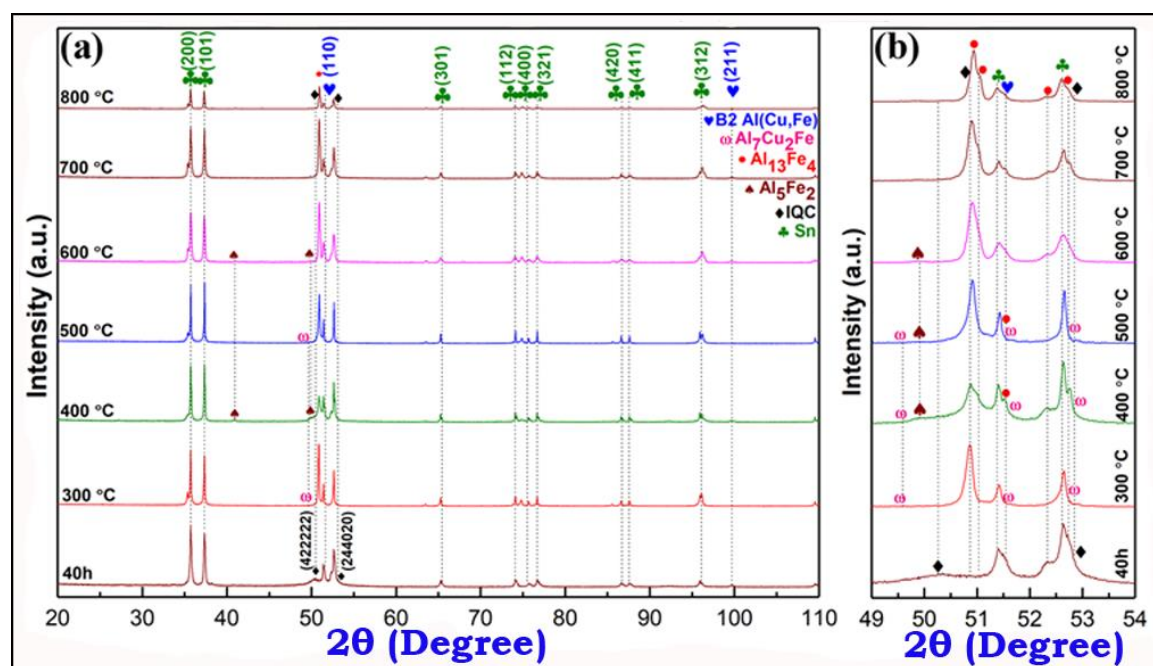


Figure 3. 15: Phase evolution during annealing of IQC-30Sn 40 h MM powder in the temperature range of 300 °C to 800 °C for 10h (a); Blown-up image showing phase evolution of crystalline phases of IQC during annealing of IQC-30Sn 40 h MM powder in the temperature range of 300 °C to 800 °C for 10h (b).

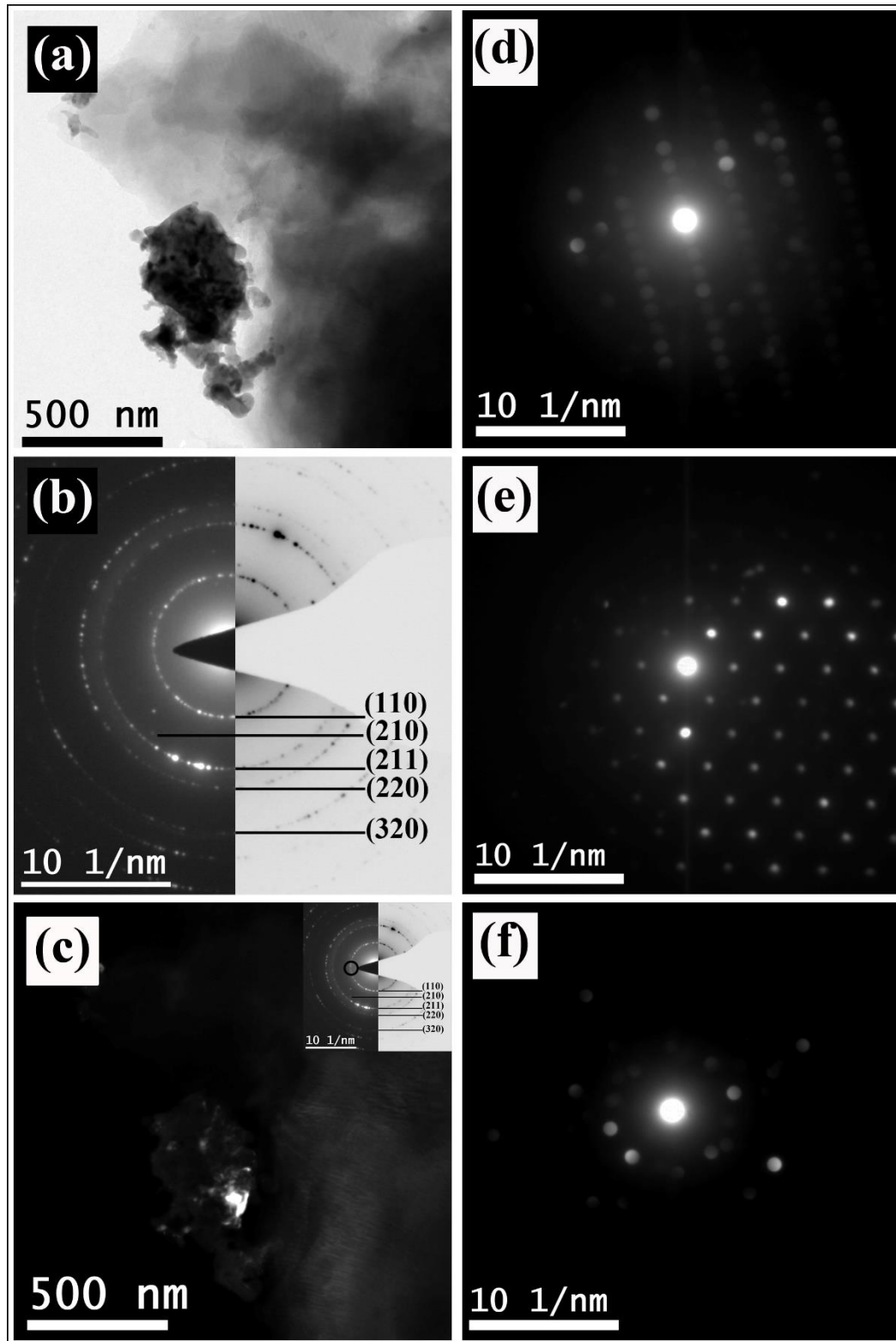


Figure 3. 16: Diffraction contrast images and nano-beam diffraction (NBD) of IQC-30 Sn MM for 40h followed by annealing at 800 °C for 10h (a-c) and (d-f) respectively. Bright-field image of annealed IQC-30Sn (a); selected area diffraction pattern of annealed IQC-30Sn (b); Dark field images of annealed IQC-30Sn (c). NBD is showing (d) $\text{Al}_{13}\text{Fe}_4$ phase, (e) B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase and (f) pseudo-five fold (5-f) axis of symmetry.

However, to substantiate the transformation corresponding to each heating event, ex-situ heat treatment of IQC-30Sn nanocomposite powder was conducted between 300 °C to 800 °C with an interval of 100 °C. Further, structural characterization was performed to ascertain the sequence of phase evolution corresponding to each heating event. The structural characterization of IQC-30Sn nanocomposite powder heat-treated at different temperatures is shown in Figure 5. The endothermic heating event at temperature T1~ 231 °C (504 K), 229 °C (502 K), and 228 °C (501 K) in IQC-10Sn, IQC-20Sn, and IQC-30Sn correspond to the melting of Sn reinforcement particles respectively, in the matrix. The exothermic heating event at temperature T2~306 °C (579 K), 290 °C (563 K) and 307 °C (580 K) in IQC-10Sn, IQC-20Sn, and IQC-30Sn correspond formation of ω -Al₇Cu₂Fe phase. The exothermic heating event at temperature T3 ~ 449 °C (722 K), 439 °C (712 K), and 449 °C (722 K) in IQC-10Sn, IQC-20Sn, and IQC-30Sn correspond formation of the Al₅Fe₂ phase. The exothermic heating event at temperature T4 ~ 617 °C (890 K), 595 °C (868 K), and 597 °C (870 K) in IQC-10Sn, IQC-20Sn, and IQC-30Sn correspond to the formation of the ordered IQC phase. The exothermic heating event at temperature T5 ~ 739 °C (1012 K), 814 °C (1087 K), and 729 °C (1002 K) in IQC-10Sn, IQC-20Sn, and IQC-30Sn correspond formation of the B2-type phase.

The activation energy calculation for the phase transformation events occurred, as shown in Figure 4 for IQC-Sn nanocomposite powder MM up to 40 h has been done through Kissinger [368] and Ozawa models [369]. The detailed procedure used for the calculation of activation energy is mentioned elsewhere [370,371]. The activation energy associated with phase transformation is mentioned in Table 3.4.

Table 3. 4: Activation energy calculation for phase evolution during heating of IQC-Sn milled powder.

Sample designation	Peak Temperature (K)	Activation Energy (kJ/mol-K)	
		Kissinger	Ozawa
IQC-10Sn	579	~46	~56
	722	~142	~154
	890	~46	~60
	1012	~297	~314
IQC-20Sn	563	~114	~123
	712	~183	~195
	868	~118	~132
	1087	~352	~370
IQC-30Sn	580	~314	~324
	722	~290	~302
	870	~159	~173
	1002	~422	~439

The value obtained from the Kissinger model and the Ozawa model are relatively close to each other. Moreover, the activation energies of any particular composite monotonically increase with the temperature of the heat events. It might be pointed out here that all the transformations are diffusive. However, higher temperature transformation events are mostly ordering transformations, which require a very specific type of diffusive jumps. Intermediate temperature events are mostly nucleation events, and the lower temperature event is the melting of Sn. This distinction qualitatively explains as to why the activation energies may exhibit a monotonically increasing trend. The structural characterization of IQC-30Sn annealed for 10 h at 800 °C was carried out using transmission electron microscopy. The BF, SAD pattern, and DF image of IQC-30Sn annealed at 800 °C for 10 h is shown in Figure 3.16 (a), Figure 3.16 (b), and Figure 3.16 (c), respectively.

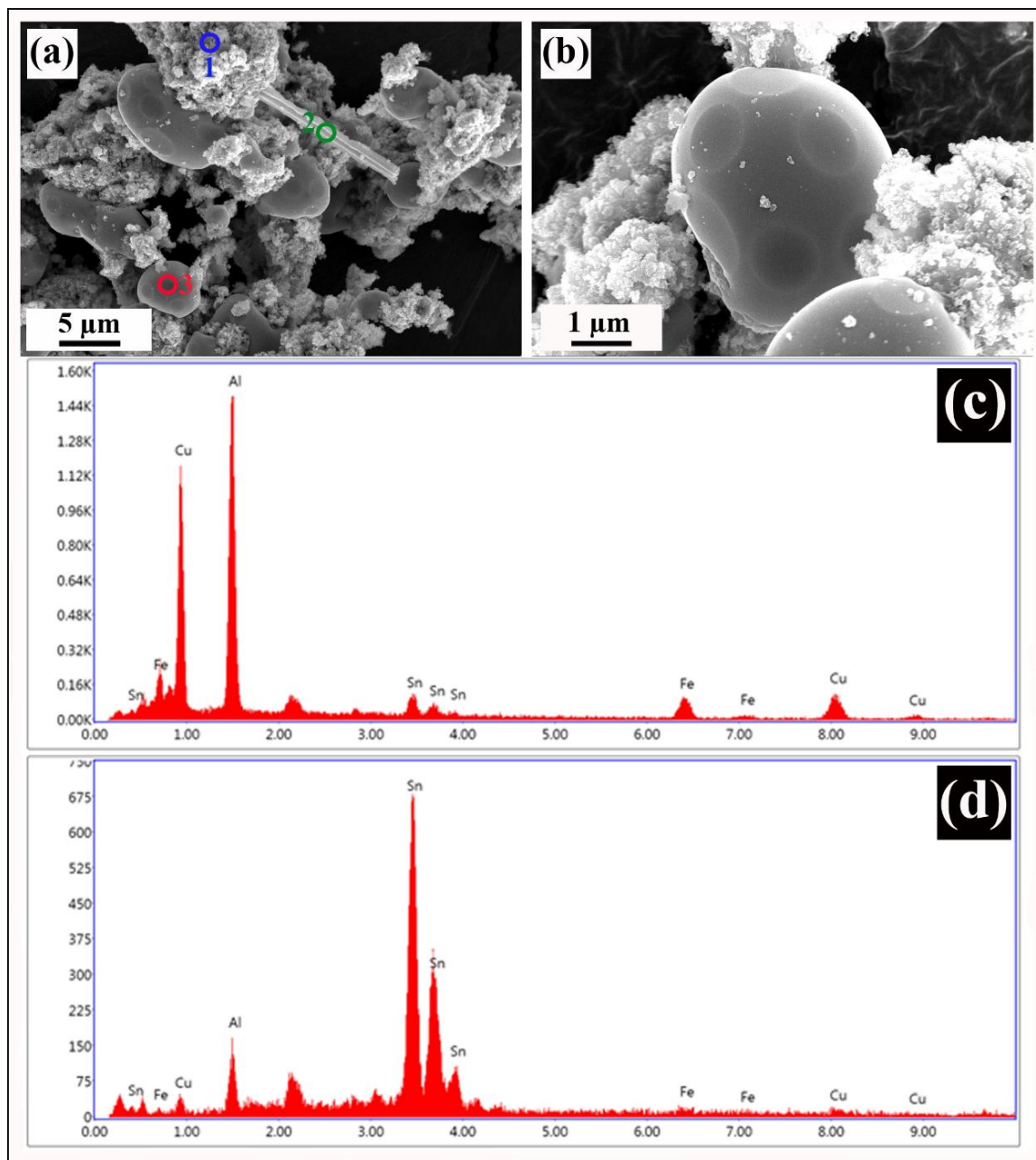


Figure 3. 17: SEM micrograph of IQC-30Sn MM for 40 h followed by annealing treatment at 800 °C for 10 h. The distribution of IQC phases along with Sn particles and approximant phases (a); IQC phase along with crystalline phases at higher magnification (b); EDS spectrum of point-1 (marked in blue) in Figure 3.17 (a) representing composition near to IQC phase (c); EDS spectrum of point-3 (marked in green) in Figure 3.17 (a) representing existence of rod-like Sn particle (d).

Table 3. 5: Chemical composition of corresponding to point-1, 2, and 3 as marked in Figure 3.17 (a) with blue, green, and red circles, respectively.

Element	Spot-1		Spot-2		Spot-3	
	weight %	atomic %	weight %	atomic %	weight %	atomic %
Al	36.11	57.82	3.93	14.11	34.58	54.75
Cu	41.03	27.90	6.50	9.93	45.23	30.40
Fe	14.54	11.25	2.98	5.18	18.70	14.31
Sn	8.32	3.03	86.59	70.78	1.49	0.53

The BF image of IQC-30Sn + annealed particle still depicts the particles' flaky nature comparatively strain-free after annealing for a prolonged duration. The SAD pattern, as seen in Figure 3.16 (b) represents the polycrystalline ring corresponding to the B2-type Al(Cu, Fe) phase. In the SAD pattern, diffraction spots corresponding to (100) superlattice reflection are not seen, substantiating that the B2-type phase is disordered. The DF images show the distribution of nanocrystalline grains corresponding to the (110) plane of the B2-type phase (Figure 3.16 (c)). The nanobeam diffraction (NBD) of the IQC-30Sn + annealed nanocomposite powder particle was conducted to ascertain the IQC phase's presence in the matrix annealed for 10 h. NBD was done randomly on the powder particles to observe the 2-f, 3-f, and 5-f axis of rotation for the IQC phase. However, the Figure 3.16 (d), 3.16 (e), and 3.16 (f) represent the NBD pattern corresponding to $\text{Al}_{13}\text{Fe}_4$ phase, B2-type phase and the pseudo-5-f axis of rotation symmetry for IQC-30Sn+annealed nanocomposite powder. Due to difficulty capturing the NBD pattern at the exact 5-f axis of rotation, the NBD pattern near the 5-f axis of rotation was captured.

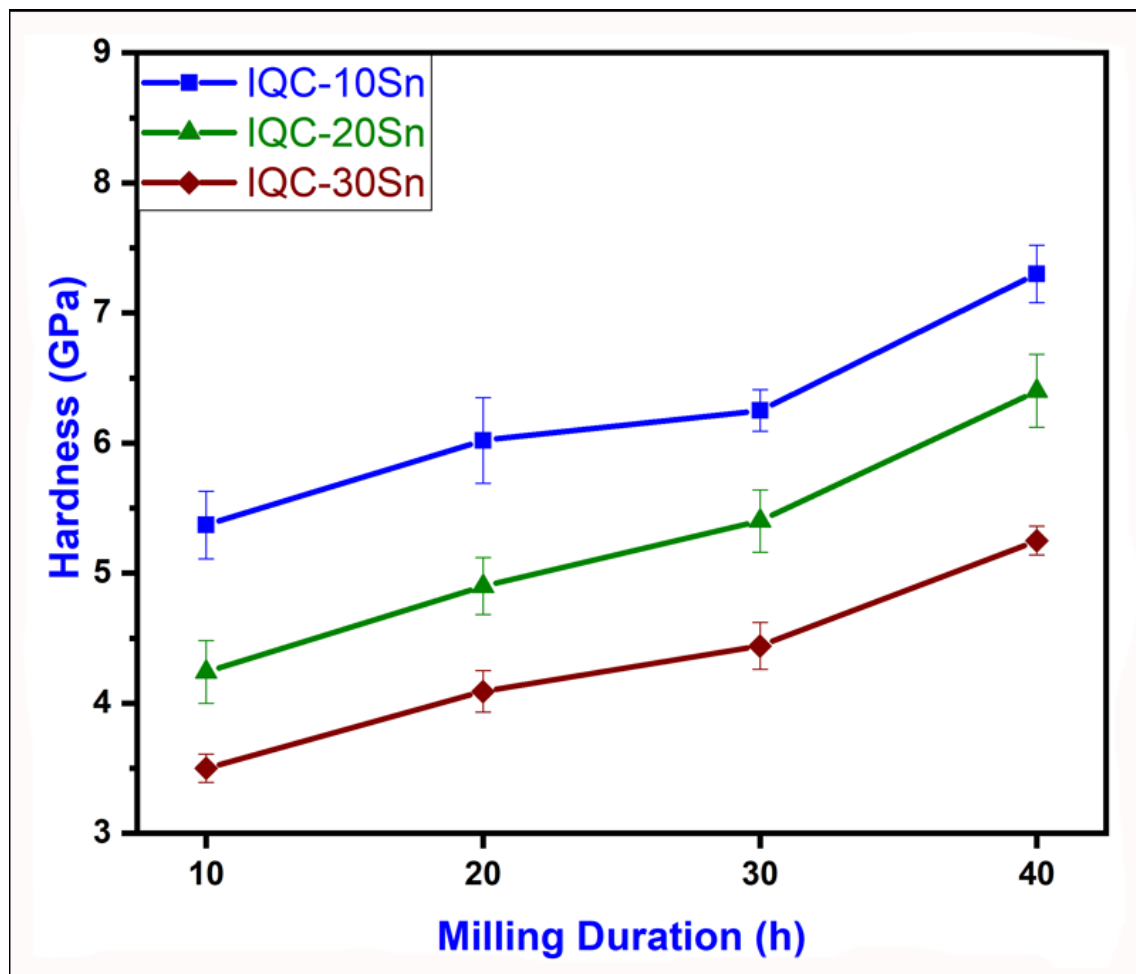


Figure 3. 18: Microhardness (at an indentation load of 10 g) of IQC – Sn nanocomposite powders as a function of the duration of mechanical milling.

The EDS spectrum of the spot-1 and spot-2 marked in Figure 3.17 (a) are shown in Figure 3.17 (c) and Figure 3.17 (d). The chemical composition of spot-1, 2 and 3 are mentioned in Table 3.5. Figure 3.17 (a, b) and Table 3.5 show that the chemical composition of Spot-1, Spot-2, and Spot-3 is very close to the chemical composition of IQC phase, Sn reinforcement particle, and B2-type Al(Cu, Fe) phase, respectively. Apart from the chemical composition, it is also certain that the particles having composition closer to the IQC phase are in the ultra-fine grain regime. However, the particles having a chemical composition closer to B2-type are mostly in the micron size regime. Figure 3.17 shows the morphology of IQC-30Sn nanocomposite powder annealed at 800 °C for 10 h. Figure 3.17 (a) represents the morphology of the IQC phase and crystalline phase along

with the distribution of rod-like Sn reinforcement particles. Figure 3.17 (b) illustrates the morphology of the matrix phases at higher magnification. The chemical composition of the particles of different morphology was ascertained through SEM-EDS compositional analysis.

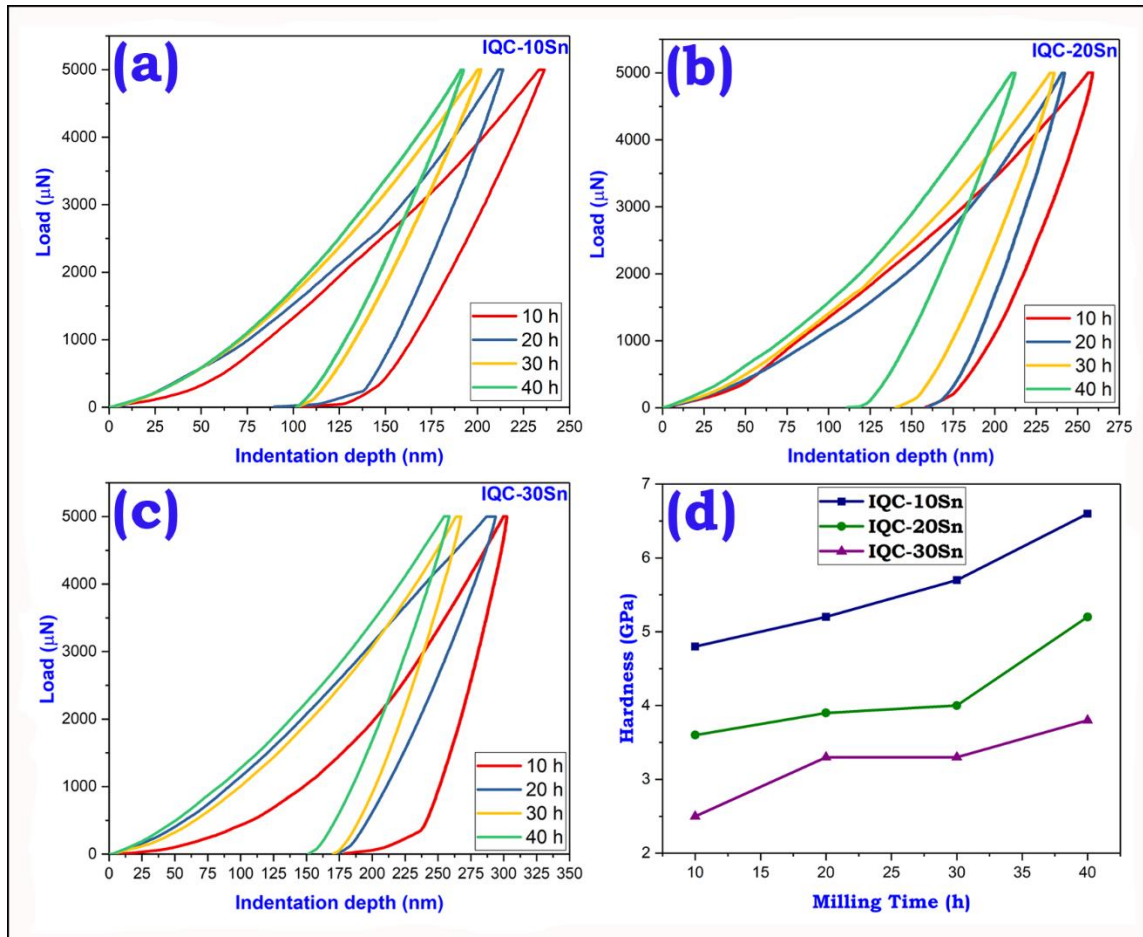


Figure 3. 19: Load versus depth of indentation plot for IQC-10Sn (a), IQC-20Sn (b) and IQC-30Sn (c) as a function of milling duration; Variation of Hardness with milling time for IQC-10, 20 & 30Sn (d).

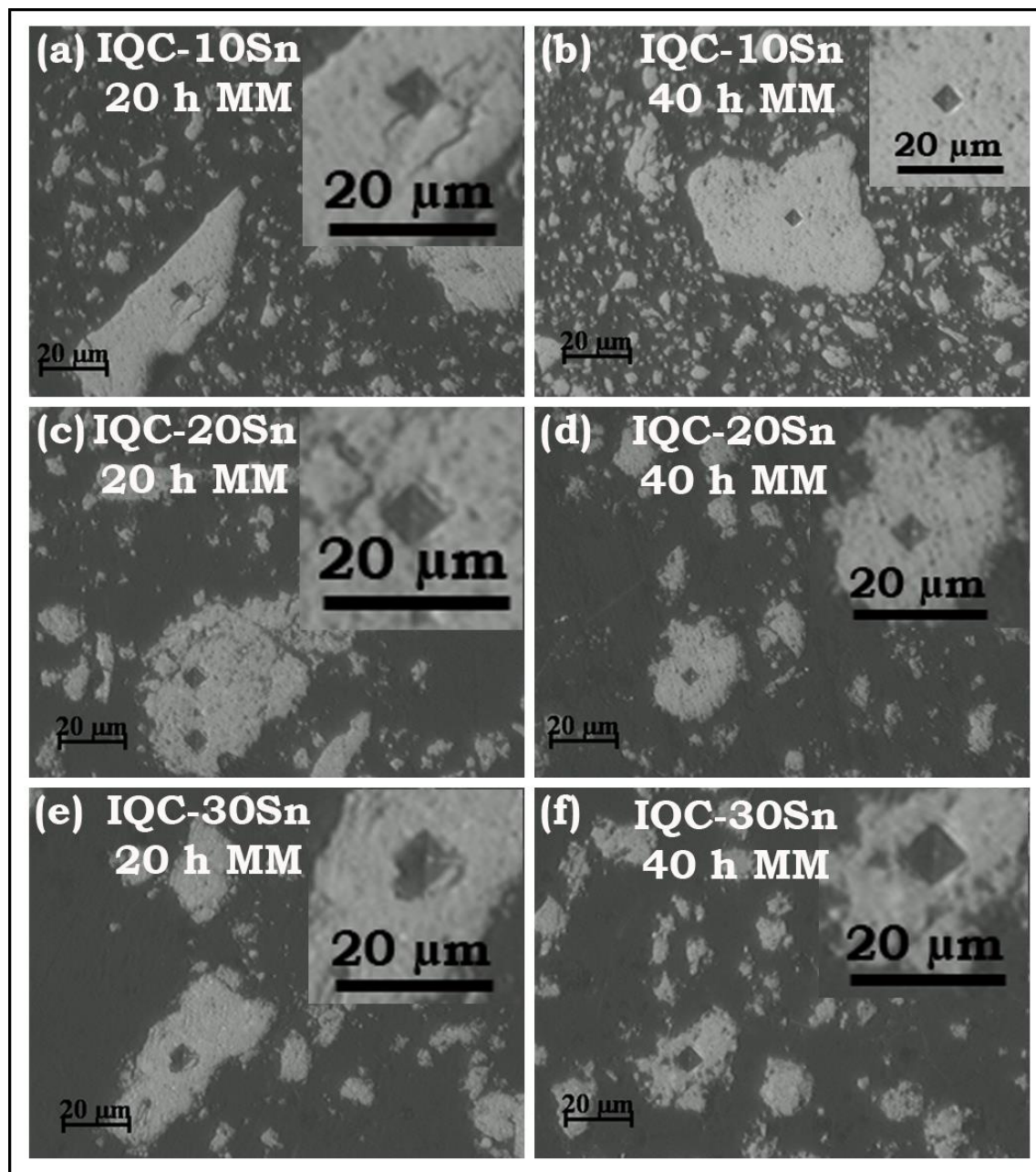


Figure 3. 20: Optical micrograph showing indentation mark on the IQC – 10Sn (a, b), IQC – 20Sn (c, d), and IQC – 30 Sn nanocomposite powder MM for 20 h and 40 h (e, f).

3.4 Indentation behavior of IQC–Sn milled powder

The indentation behavior of IQC – Sn nanocomposite powders were observed through microindentation and nanoindentation techniques. The indentation of the nanocomposite powder was carried out for samples milled up to 40 h of MM. The variation of microhardness and nanohardness (H) with milling time for the varying volume fraction

of Sn in IQC-Sn nanocomposite powder is shown in Figure 3.18 and Figure 3.19. The value of nanohardness is also mentioned in Table 3.6.

Table 3. 6: The hardness of IQC-Sn milled powder.

Milling duration	IQC-10Sn	IQC-20Sn	IQC-30Sn
	H (GPa)	H (GPa)	H (GPa)
10 h	4.8	3.6	2.5
20 h	5.2	3.9	3.3
30 h	5.7	4.0	3.3
40 h	6.6	5.2	3.8

It can be discerned from Figure 3.18 that the microhardness of IQC – Sn nanocomposite powder increases with increasing the duration of MM up to 40 h. However, the volume fraction of Sn reinforcement in the IQC matrix decreases the nanocomposite powder's microhardness. The peak microhardness observed for IQC – 10Sn, 20 Sn, and 30 Sn was found out to be 7.3 ± 0.22 GPa, 6.4 ± 0.28 GPa, and 5.25 ± 0.11 GPa, respectively. The increase in the microhardness from 20 h to 30 h of MM is not very significant as compared to the 10-20 h and 30-40h. Figure 3.19 (a), Figure 3.19 (b), Figure 3.19 (c) represents the load versus indentation depth plot for IQC-10Sn, IQC-20Sn, and IQC-30Sn, respectively. Figure 3.19 (a, b & c) clarifies that the indentation depth increases with increasing the volume fraction of Sn reinforcement from 10 to 30 volume fraction. It is seen from Figure 3.19 (d) and Table 3.6 that the hardness increases with increasing the milling duration and decreases with the increasing the volume fraction of the Sn reinforcement, similar to the observation made during micro indentation of IQC – Sn nanocomposite powders. The

increase in hardness upto 20 h of MM is significant. However, there was a slower rate of increase in hardness from 20 h to 30 h of milling. However, an overall rise of hardness was observed due to grain refinement by MM. The increase in hardness may be well explained and are in accordance with the crystallite size, as mentioned in Table 3.1.

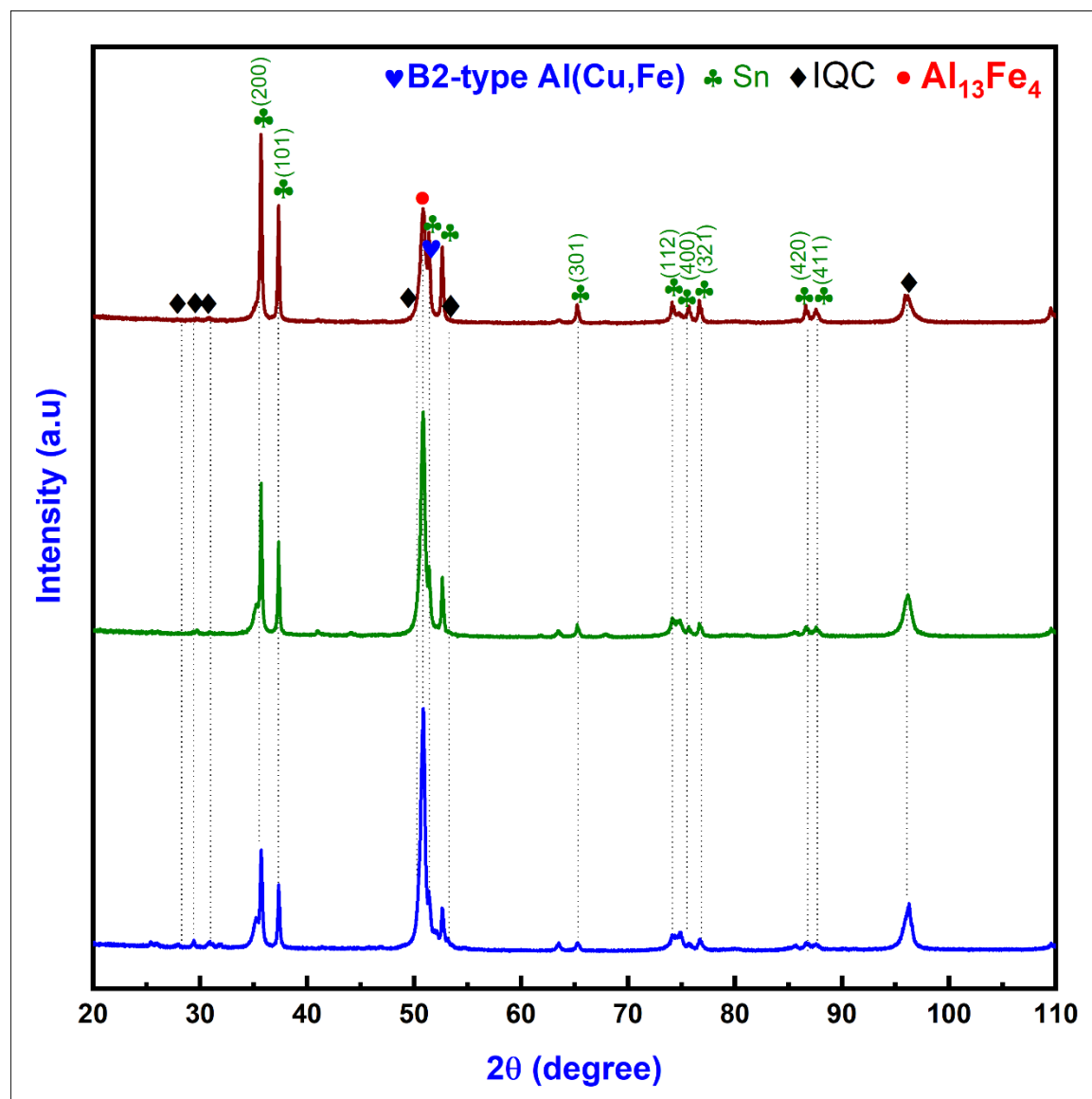


Figure 3. 21: Phase analysis of IQC – Sn composite SPSed at 800 °C (1073 K).

The optical micrographs of Figure 3.20 show the indentation marks of the 20 h and 40 h MM powders of IQC – 10Sn, IQC – 20 Sn, and IQC – 30Sn. It can be discerned from Figure 3.20 (a), (b), and (c) that the crack length after indentation at a load of 10 g is highest

for IQC – 10Sn followed by IQC – 20Sn and 30 Sn. The inhibition of cracks during indentation varies as a function of the volume fraction of Sn and duration of MM. On increasing the time of MM to 40 h, the crack length of IQC – 10Sn, 20Sn, and 30Sn after indentation decreases as shown in Figure 3.20 (a), (b), and (c), respectively. After 40 h of MM, no significant marks of indentation cracks were observed for IQC – 10Sn, 20Sn, and 30Sn nanocomposite powder. However, the case is not the same for 20 h MM IQC – Sn nanocomposite powder. The crack length for 20 h MM IQC – 10Sn, 20Sn and 30Sn was found to $\sim 11.5 \mu\text{m}$, $\sim 6.5 \mu\text{m}$, and $\sim 4.2 \mu\text{m}$, respectively.

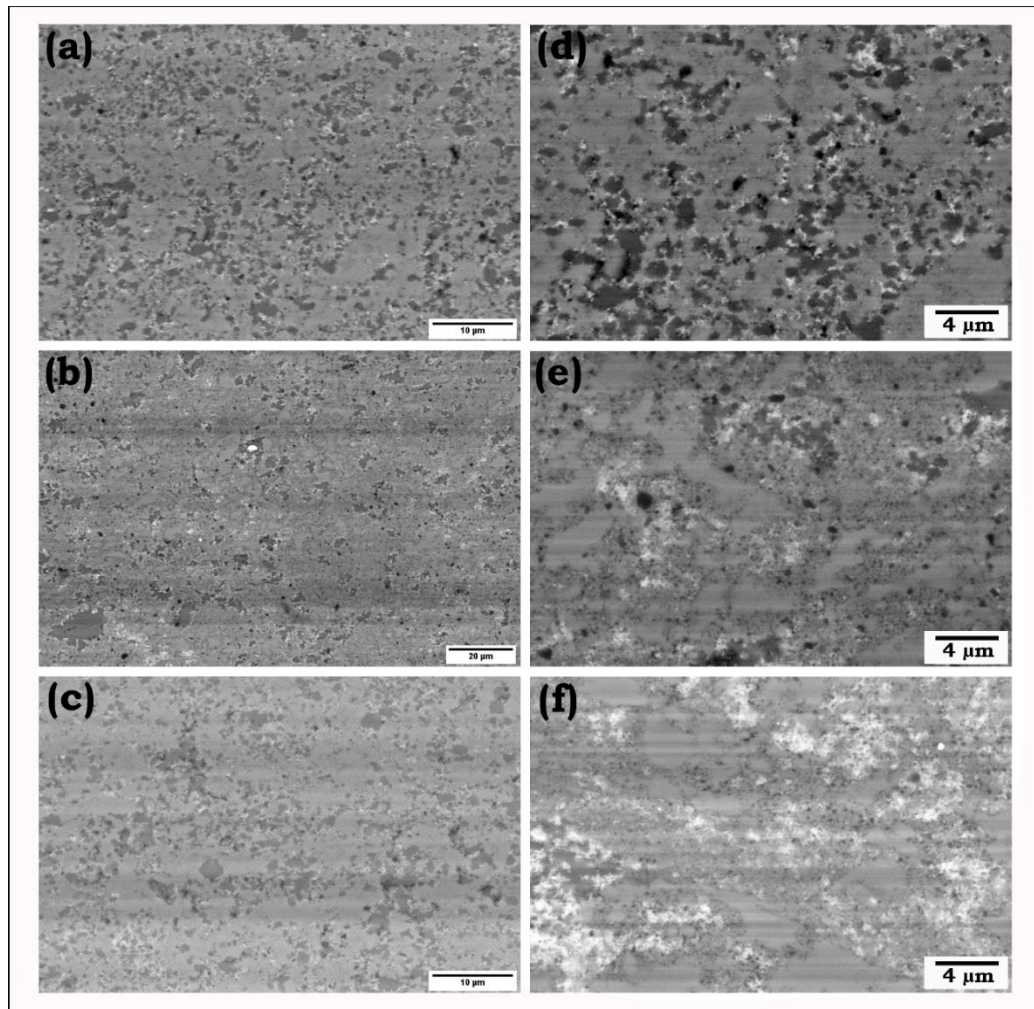


Figure 3. 22: SEM micrograph of (a, d) IQC – 10Sn, (b, e) IQC – 20Sn, (c, f) IQC – 30Sn bulk composite SPSed at 800 °C (1073 K) at different magnification.

3.5 Microstructure and mechanical properties of IQC–Sn bulk composite

The bulk composite of IQC–Sn was prepared by spark plasma sintering (SPS) and hot-pressing (HP) as per the procedure and parameters defined in Chapter 2.

3.5.1 IQC-Sn composite consolidated by SPS

The IQC – Sn composite was SPSed at 800 °C (1073 K) for 15 min with a pressure of 50 MPa. The XRD pattern of IQC – Sn composite powder is shown in Figure 3.21. The phase formed in the IQC – Sn composite sample comprises both IQC and crystalline phase, i.e., the $\text{Al}_{13}\text{Fe}_4$ and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase. The IQC phases formed in the bulk composite samples face face-centered ordering, as evident from the existence of the (311111) reflection of IQC at $d \sim 3.45 \text{ \AA}$. However, the intensity of the reflection depicting the IQC phase's ordering gradually decreases with increasing the volume fraction of the Sn as evident from the Figure 3.21. The intensity of the most intense reflection of the IQC phase (422222) ($d \sim 2.11 \text{ \AA}$) and (244020) ($d \sim 2.005 \text{ \AA}$) having 5-f and 2-f axis of rotation respectively, also decreases with increasing the volume fraction of Sn as observed in the Figure 3.21. The phase fraction of crystalline phases formed after SPS of the IQC–Sn bulk composite varies as a function of the Sn reinforcement particle volume fraction. The phase fraction of the $\text{Al}_{13}\text{Fe}_4$ phase is more compared to the B2-type $\text{Al}(\text{Cu}, \text{Fe})$ as discerned from the intensity of $(\bar{7}13)$ ($d \sim 2.0778 \text{ \AA}$) plane of $\text{Al}_{13}\text{Fe}_4$ phase for IQC–10Sn. However, the fraction of the B2-type phase is more in the case of IQC–30Sn as observed from the intensity of the (110) ($d \sim 2.056 \text{ \AA}$) plane of B2-type phase. Even after the SPS of IQC – Sn bulk composite, Sn reinforcement particle was found to maintain its structural integrity and are immiscible in the Al-Cu-Fe IQC. The observation made for phases evolved after SPS is in line with the phases observed for IQC–Sn nanocomposite powder MM for 40 h, as shown in Figure 3.2, Figure 3.3, and Figure 3.3.

The Back-scattered SEM micrograph of IQC–Sn bulk composite prepared by SPS shows the appearance of phases uniformly distributed in the matrix of IQC. From Figure 3.22 (a, b, and c) it can be discerned that the IQC–Sn bulk composite do not have any significant signs of pores after spark plasma sintering at 800 °C (1073 K) for 15 min. Further, the shape, size, and distribution of the phases are also discerned to be uniform in the IQC matrix. Figure 3.22 (d), (e), and (f) represents the back-scattered SEM micrograph of IQC-10Sn, 20Sn, and 30Sn at higher magnification. It was observed from these micrographs that the composite consists of three types of phases based on the contrast. There are mainly three types of contrast that can be observed from Figure 3.22, i.e., dark grey contrast, light grey contrast, and white contrast.

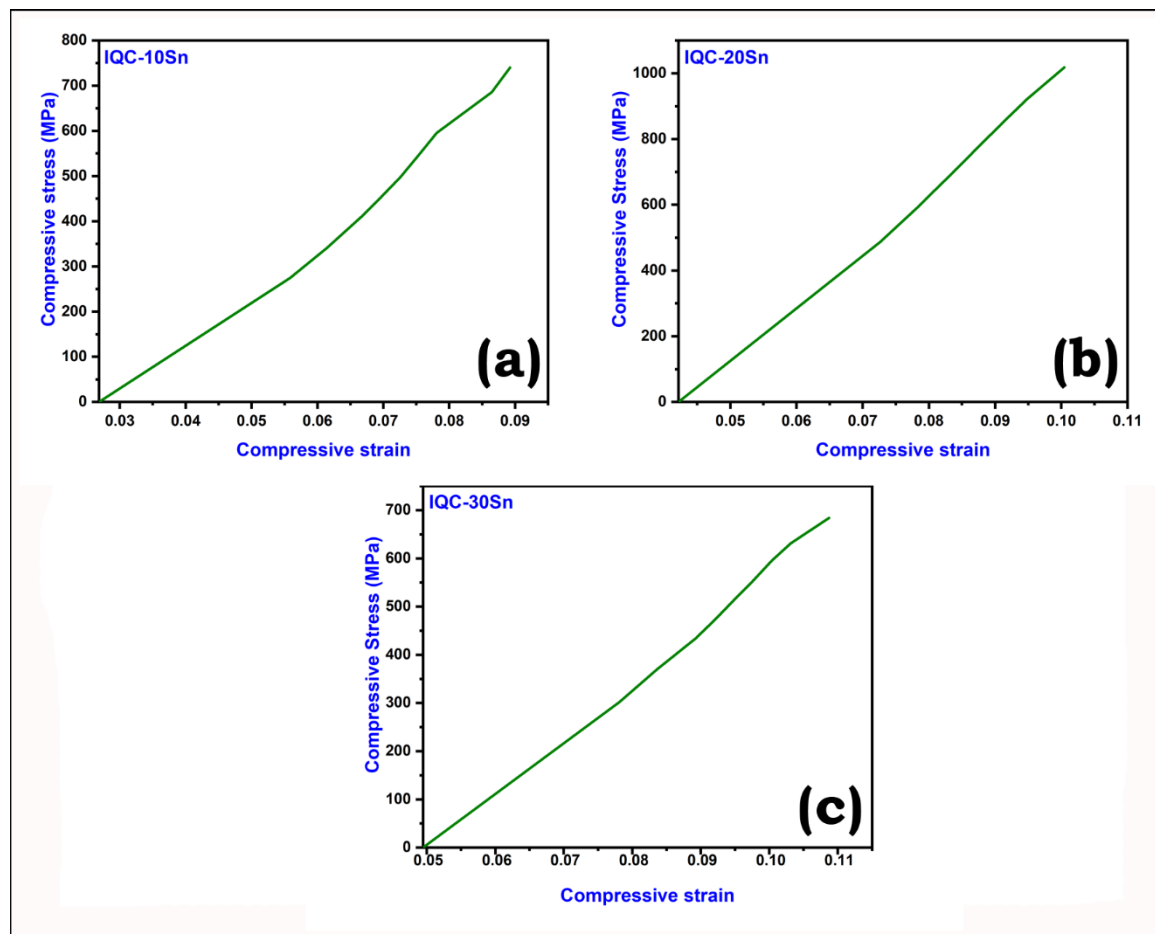


Figure 3. 23: Compressive stress-strain plot for (a) IQC – 10Sn, (b) IQC – 20Sn, (c) IQC – 30Sn bulk SPSed composite.

To ascertain the nominal chemical composition of the phases corresponding to each of these contrast, systematic point EDS analysis of these particles was done. From the EDS point analysis, it was discerned that the particles having dark grey contrast have nominal composition closed to the crystalline $\text{Al}_{13}\text{Fe}_4$ crystalline phase. The white or the bright contrast appearing in the microstructure corresponds to that of the Sn reinforcement particles. The light grey contrast has a nominal composition close to that of the IQC phase at some regions and is comparable to that of the B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phases at a few parts. These ambiguities, in contrast arise due to the atomic scattering factor, which is ought to be very close for IQC and B2-type phase having the composition of $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ (at%) and $\text{Al}_{50}(\text{Cu}, \text{Fe})_{50}$ (at%) respectively.

Table 3. 7: Physical and mechanical properties of IQC – Sn bulk SPSed composite.

Sample	Density			Mechanical properties		
	Experimental density (g.cm^{-3})	Theoretical density (g.cm^{-3})	Relative density (%)	Compressive Yield Strength (MPa)	Compressive Ultimate Strength (MPa)	Failure strain (%)
IQC	-	-	-		250 [372]	-
IQC-10Sn	4.52	4.49	~100	~544	~745	~ 9
IQC-20Sn	4.82	4.81	~100	~880	~1018	~ 10
IQC-30Sn	5.12	5.11	~100	~500	~683	~ 11

The various contrast appearing during imaging backscattered mode is dependent on the atomic number of the element being scanned. Therefore, distinguishing between the IQC phase and B2-type $\text{Al}(\text{Cu}, \text{Fe})$ phase is very difficult based on their contrast. Further, it was observed from Figure 3.22 that the contrast appearing for a particular phase are also

dependent on the volume fraction of the Sn reinforcement particles. From Figure 3.22, it was evident that the dark grey contrast corresponding to the $\text{Al}_{13}\text{Fe}_4$ crystalline phase decreases on increasing the volume fraction of Sn.

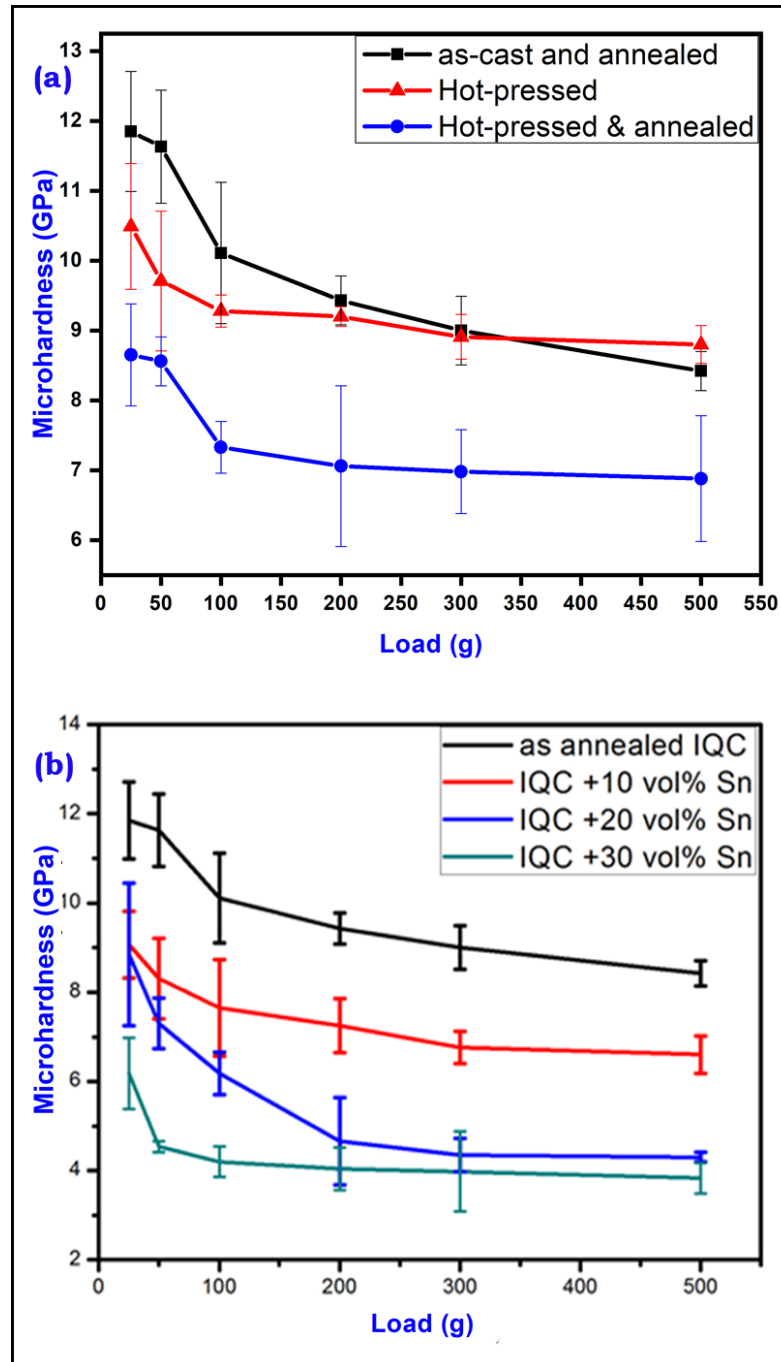


Figure 3. 24: Hardness value of (a) hot-pressed and (b) pressure-less sintered IQC-Sn bulk composite at different indentation loads.

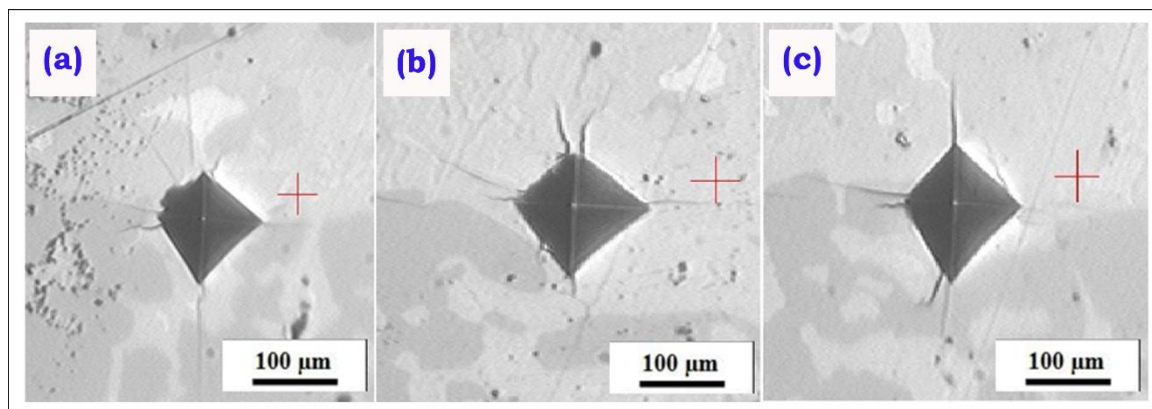


Figure 3. 25: Optical micrograph showing indentation marks on as-cast and annealed IQC at a load of (a) 200 g and (b, c) 500 g.

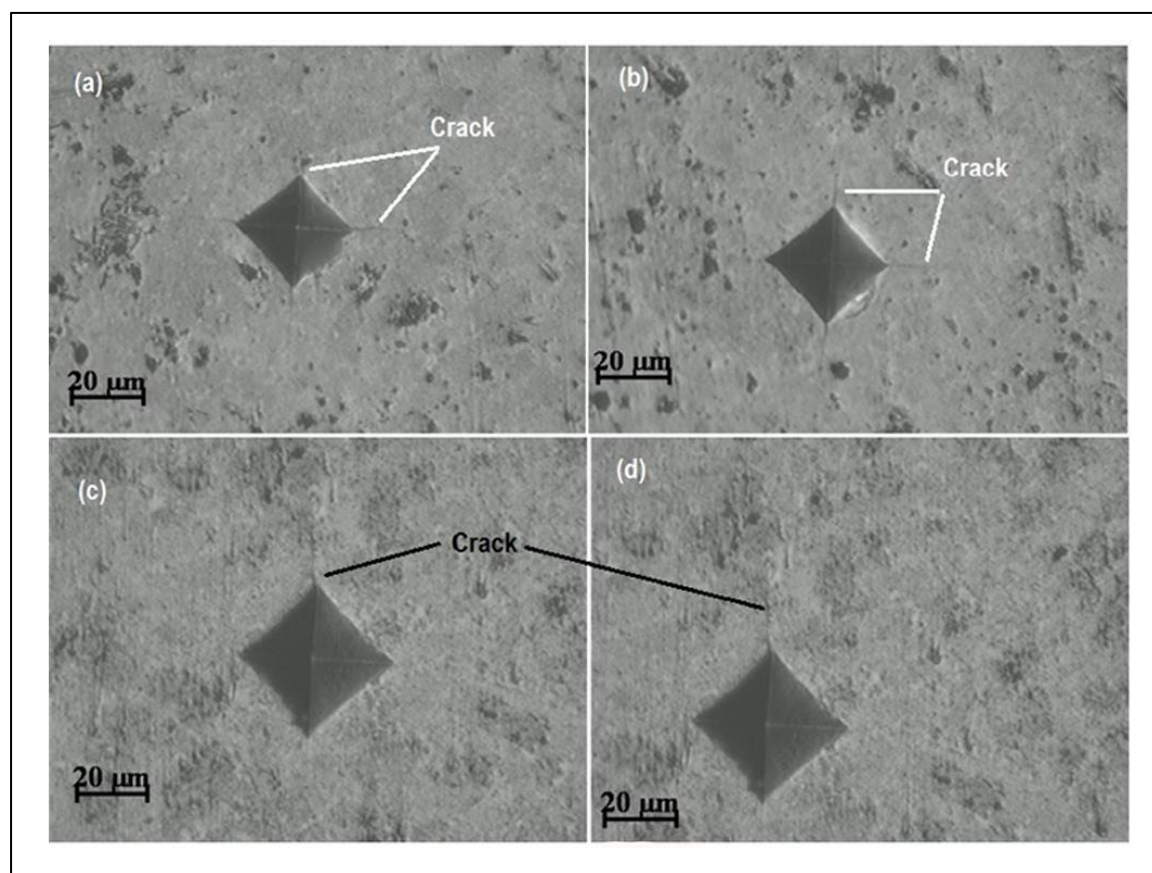


Figure 3. 26: Optical micrograph showing indentation cracks in IQC – 10Sn hot-pressed composite; (a) sintered at 650 °C (923 K) (b) sintered at 650 °C (923 K) and (c & d) hot-pressed and annealed at 800 °C (1023 K).

However, the phase fraction of the B2-type phase showed a reverse trend. There was also evidence from Figure 3.21 showing the variation of phase fraction of IQC and crystalline phases on increasing the phase fraction of Sn. The grain size $\text{Al}_{13}\text{Fe}_4$, B2-type/

IQC phase, and Sn reinforcement was found to be around $\sim 1.0 - 1.5 \mu\text{m}$, $2.0 - 2.5 \mu\text{m}$, and $\leq 1.0 \mu\text{m}$, respectively, for IQC – 10Sn bulk SPSed composite. The grain size $\text{Al}_{13}\text{Fe}_4$, B2-type/ IQC phase, and Sn reinforcement were found to be around $\sim 2.0 - 3.5 \mu\text{m}$, $4.0 - 4.5 \mu\text{m}$, and $1.5 - 2.0 \mu\text{m}$, respectively, for IQC-30Sn bulk SPSed composite. Similar observations were also made for particle size and the grain size distribution of the IQC matrix and Sn reinforcement, as illustrated in Figure 3.12.

The compressive testing of IQC–Sn bulk SPSed composite was done to ascertain the mechanical properties. For this, cylindrical samples of these composite were prepared by wire-EDM technique as described in Chapter 2. The compressive stress-strain diagram for IQC–Sn bulk composite is shown in Figure 3.23. Figure 3.23 and Table 3.7 shows that the compressive yield strength and ultimate strength increase up to 20 vol% of Sn in IQC matrix. However, the strength for IQC-30Sn decrease in comparison to the IQC-10Sn and IQC-30Sn. The incorporation of Sn reinforcement in the IQC matrix inhibits the IQC-Sn bulk composite's catastrophic failure synthesized by SPS. The optimum mechanical properties were observed for IQC-20Sn composite with high compressive yield strength and ultimate strength of $\sim 880 \text{ MPa}$ and 1018 MPa . The synergy of strength and ductility is also maintained as these bulk composites have failure strain $\sim 10\%$. The enormous rise in the strength and increase in the failure strain of bulk IQC-Sn SPSed composite can be attributed to the inhibition of cracks by soft Sn particles reinforced in the IQC matrix.

3.5.2 IQC-Sn composite consolidated by hot pressing

Attempts were also made to investigate the formation of bulk IQC – Sn composite through hot-pressing and pressure-less sintering. The microstructural features for IQC – Sn hot-pressed composite was similar to that observed in bulk SPSed composite. The indentation behavior of IQC – 10Sn composite was prepared by hot-pressing at 650°C (923 K) and subsequently annealed at 800°C (1073 K) for 4 h. The indentation was carried out

at different loads for IQC–Sn hot-pressed composite and compared to the pressure-less sintered composite as shown in Figure 3.24 (a) and 3.24 (b). In both the condition, indentation size effect (ISE) was evident. However, in the case of the hot-pressed samples, the ISE can be seen only upto the load of ~100 g, however in case of pressure-less sintering, ISE was evident upto a load of ~ 200 g. The ISE was observed mainly due to the elastic recovery and low tendency for crack formation at small indentation loads. Increasing the indentation load above a specific limit, the bulk composite hardness becomes constant as observed from Figure 3.24 (a & b).

The hardness for IQC – 10Sn hot-pressed and hotpressed + annealed composite was found to be ~9.3 GPa and 7.3 GPa, respectively. On the other hand, the pressure-less sintered bulk composite shows a minor decrease in the hardness, as shown in Figure 3.24 (b). The hardness for IQC -10Sn, 20Sn, and 30Sn was found to be ~4.0 GPa, 4.5GPa and 7.5 GPa. The decrease in the hardness of pressure-less sintered compact may be attributed to the sintering mechanism in contrast to the hot-pressed samples. Further efforts were also made to investigate the fracture toughness of the as-cast+annealed IQC and hot-pressed IQC–10Sn composite. For evaluating the fracture toughness of these materials, the Palmqvist method was used. The fracture toughness of any brittle material can be computed by using equation 3.1 mentioned below:

$$K_{IC} = 0.035 * \Phi^{(-\frac{3}{5})} * H * \left(\frac{d/2}{\sqrt{l}}\right) * \left(\frac{H}{E}\right)^{(-\frac{2}{5})} \dots\dots\dots(3.1)$$

where K_{IC} = Fracture toughness, Φ = Constraint factor, H = Microhardness, E = Young's modulus, d = diagonal length of indentation, L = length of the Palmqvist crack.

Table 3. 8: Fracture toughness of IQC–Sn hot-pressed composite.

Sample specification	Fracture toughness MPa. (m) ^{1/2}	Enhancement (%)
As cast and annealed Al-Cu-Fe IQC	1.58 ± 0.27	--
Hot pressed 10 vol% Sn IQC at 650 °C for 5 min	1.92 ± 0.12	22%
Hot pressed 10 vol% Sn IQC at 650 °C for 5 min along with annealing at 800 °C for 4 h	1.81 ± 0.16	15%

The various factor considered for computing the fracture toughness using the Palmqvist crack method is reported elsewhere [373,374]. The fracture toughness of the as-cast plus annealed IQC and IQC-10Sn hot-pressed composite are mentioned in Table 3.8. The increase in the fracture toughness of the IQC-10Sn hot-pressed composite can be attributed to the inhibition of cracks due to soft Sn reinforcement particles. From Figure 3.25 and Figure 3.26, it can be discerned that the length of the crack in IQC is ~10 times more than that observed for IQC-10Sn hot-pressed composite. These lead a significant increase in the fracture toughness of these composite, as reported in Table 3.8.

3.6 Discussion

As described in Chapter 1, the Al-Cu-Fe IQC is the potential candidate for engineering structural material as a coating or reinforcement in aluminum matrix composite. However, the inherent room temperature brittleness of these Al-Cu-Fe IQC limits its application as a candidate material for coating applications to enhance the wear resistance and reduce friction. There are various strategies and methodologies for encountering the problem associated with room temperature brittleness of Al-Cu-Fe IQC. The fracture toughness of these IQC can be enhanced either by nanostructuring [282] or by incorporation of secondary immiscible phases in the IQC matrix [358,364,366,367].

Although nanostructuring induces softening of these alloys, however, this is associated with structural transformation of IQC to crystalline phases as described by Mukhopadhyay et al. [282,375]. The other method used for the IQC toughening is to incorporate the soft Sn particles, immiscible in the Al-Cu-Fe IQC matrix, enhancing the fracture toughness by arresting the crack by soft Sn particles. Most of the investigation carried to date uses the melting and solidification techniques for incorporating soft Sn phases in the IQC matrix. However, melting and solidification are associated with the difficulty of homogenous distribution of low melting Sn phases in the IQC matrix due to the vast difference in the melting point of both.

3.6.1 Structural transformation during mechanical milling

The synthesis of IQC-Sn nanocomposite powder through MM mainly offers two advantages, i.e. homogenous distribution of Sn particles in IQC matrix and nanostructuring of both IQC matrix and Sn reinforcement. Therefore, it is essential to study the sequence of structural transformation in IQC-Sn nanocomposite powder as a function volume fraction of Sn and milling duration.

The sequence of structural transformation during MM of IQC-10Sn and 20 Sn nanocomposite powder upto 40 h may be summarized as below:

The sequence of structural transformation during MM of IQC-10Sn:

- **0 h** Ordered quasicrystalline (major)+Crystalline ($\text{Al}_{13}\text{Fe}_4$ +B2 type Al(Cu, Fe)) (minor).
- **10 h** Ordered nano-quasicrystalline (major)+Nano-crystalline ($\text{Al}_{13}\text{Fe}_4$ +B2 type Al(Cu, Fe)) (minor).
- **20 h** Ordered nano-quasicrystalline (major)+Nano-crystalline ($\text{Al}_{13}\text{Fe}_4$ +B2 type Al(Cu, Fe)) (minor).

-
- **30 h** Disordered nano-quasicrystalline (major)+ Nano-crystalline $\text{Al}_{13}\text{Fe}_4$ (minor)+Nano-crystalline B2 type Al(Cu, Fe).
 - **40 h** Disordered nano-quasicrystalline (minor)+ Nano-crystalline $\text{Al}_{13}\text{Fe}_4$ (major)+Nano-crystalline B2 type Al(Cu, Fe) (minor).

However, the sequence of structural transformation during MM of IQC-30Sn NC powder upto 40 h is different from that of the IQC-10Sn and 20Sn, which may be summarized as below:

The sequence of structural transformation during MM of IQC-30Sn:

- **0 h** Ordered quasicrystalline (major)+Crystalline ($\text{Al}_{13}\text{Fe}_4$ +B2 type Al(Cu, Fe)) (minor).
- **10 h** Ordered nano-quasicrystalline (major)+Nano-crystalline ($\text{Al}_{13}\text{Fe}_4$ +B2 type Al(Cu, Fe)) (minor).
- **20 h** Ordered nano-quasicrystalline (major)+Nano-crystalline ($\text{Al}_{13}\text{Fe}_4$ +B2 type Al(Cu, Fe)) (minor)+ (713) peak of $\text{Al}_{13}\text{Fe}_4$ loses identity.
- **30 h** Ordered nano-quasicrystalline (major)+ Nano-crystalline $\text{Al}_{13}\text{Fe}_4$ (minor)+Nano-crystalline B2 type Al(Cu, Fe).
- **40 h** Disordered nano-quasicrystalline (minor)+ Nano-crystalline $\text{Al}_{13}\text{Fe}_4$ (minor)+Nano-crystalline B2 type Al(Cu, Fe) (major)+Ordered nanocrystalline B2 type Al(Cu, Fe) phase (very minor fraction in localized regions).

The ballistic movement of atoms due to high shear stresses generated during MM because of the collision between balls and powder particle leads to the structural transformation of these IQC. These may be corroborated by the broadening of IQC and crystalline phases after MM, as shown in Figures 3.2, 3.3, 3.4, and Table 3.1. During MM of IQC-Sn, the nanocomposite powder's structural transformation depends on the volume fraction of Sn reinforcement. As described in Figures 3.2, 3.3, and 3.4, the phase fraction

of $\text{Al}_{13}\text{Fe}_4$ is more compared to that of the disordered B2-type Al (Cu, Fe) phase in IQC-10Sn and vice versa for IQC-30Sn. The transformation of the IQC phase to the $\text{Al}_{13}\text{Fe}_4$ phase was described in Cheng et al. [376]. They have explained the transformation of IQC to $\text{Al}_{13}\text{Fe}_4$ based on the combination of physical space rotation and projection strip rotation having equivalence with special linear phason strain [376]. In line with the present investigation, Mukhopadhyay et al. [377] have described the transformation of IQC phase with minor $\text{Al}_{13}\text{Fe}_4$ phase at 400 r.p.m and BPR of 40:1. After MM for 60 min, the IQC transforms to $\text{Al}_{13}\text{Fe}_4$ as a significant phase with a minor phase fraction of disordered B2-type Al(Cu, Fe) and IQC phase. Although the structural transformation of IQC to $\text{Al}_{13}\text{Fe}_4$ phase is related to linear phason strain; however, the change of the IQC phase to B2-type phase may be either due to compositional fluctuation or strain-induced transformation. The contamination of Fe and Cr from the steel balls and vials, during MM of Al-Cu-Fe IQC phase, leads to the transformation to B2-type Al (Cu, Fe) phase as described by Mukhopadhyay et al. [378]. On further annealing of the phase formed after MM, an ordered B2-type phase was formed. In the present investigation, MM was carried out in WC vials and with WC balls; therefore, the chances of structural transformation due to compositional fluctuation may be ruled out. The reduction in crystallite size and increase in lattice strain as a function of milling intensity and volume fraction of Sn is quite evident from Figures 3.2, 3.3, 3.4, and Table 3.1. The MM process generated a defect structure in the Al-Cu-Fe IQC phase, responsible for its structural transformation. Mukhopadhyay et al. [375], have described in detail the structural transformation of pure Al-Cu-Fe IQC phase to B2-type phase due to quasilattice strain, i.e. phason strain and phonon strain component. The structural transformation of IQC phase to the B2-type phase is due to phason strain. In the present investigation, it may be seen that in IQC-30Sn nanocomposite powder, the lattice strain for IQC phase is ~ 1.74 , comparatively less than that in IQC-10Sn and IQC-20Sn.

Therefore, the phase fraction of the IQC phase in IQC-30Sn nanocomposite powder is significant, and (422222) reflection of IQC can retain its identity even after 40 h of MM. The incomplete transformation of the Al-Cu-Fe IQC phase to B2-type may be due to MM's mechanism change.

In IQC-30Sn, due to an increase in the volume fraction of soft Sn particle, the mechanism from brittle-brittle milling changes to brittle-ductile kind of milling. The various modes of MM are also explained in details in review papers by Suryanarayana [345]. The increase in the phase fraction of B2-type phase in contrast to $\text{Al}_{13}\text{Fe}_4$ phase in IQC-30Sn nanocomposite powder may be due to Sn, which acts as a β / B2 stabilizer. An investigation carried out by Srivastava et al. [364] and Mukhopadhyay et al. [358] have reported the coexistence of minor B2-type phase along with IQC phase due to the addition of Sn, which acts a β stabilizer during spray forming of the Al-Cu-Fe composite reinforced with Sn. The increase in the volume fraction of Sn also enhances the layering of IQC and B2-type phase in IQC-20Sn and IQC-30Sn as evident from the TEM micrograph in Figure 3.7. There is the localized formation of ordered B2-type phase in the IQC-30Sn nanocomposite powder. This may be due to insufficient strain required for complete disordering of B2-type phases in localized regions due to soft Sn reinforcement.

3.6.2 Theoretical estimation of grain size during mechanical milling

The TEM and SEM micrograph showed in Figure 3.8 and Figure 3.11, respectively, confirms the presence of elongated or rod-like Sn reinforcement particles in the IQC – Sn nanocomposite powder. Although the IQC matrix was refined significantly, however the level of refinement for Sn particles was not that significant. It was reported by Ali et al. [350] that the rise in temperature during MM of Al-Cu-Fe IQC alloy was $\sim 100 - 200$ K. Therefore, the Sn particles are thought to be milled at a temperature above $0.5T_m$ (where, T_m =melting point of bulk material). This was confirmed with the TEM and SEM

micrograph showing the Sn particles in the ultra-fine grain regime. Therefore, it is essential to consider the theoretical estimation for computing the Sn particles' minimum grain size and sintering temperature in the IQC – Sn nanocomposite powders. The minimum grain size ($d_{\min}$) is estimated using the Mohamed et al. model [379] as per equation 3.2.

$$\frac{d_{\min}}{b} = A \left(\exp \left(\frac{-\beta Q}{4RT} \right) \right) \left\{ \frac{D_{po} G b^2}{v_o k T} \right\}^{0.25} \left(\frac{\gamma}{G b} \right)^{0.5} \left(\frac{G}{H} \right)^{1.25} \dots\dots\dots (3.2)$$

where, $d_{\min}$ is the minimum crystallite/grain size, D_{po} is the diffusion coefficient for pipe diffusion, G is the shear modulus, b is the magnitude of Burgers vector, V_o is the Poisson's ratio, H is the hardness, k is the Boltzmann constant, Q is the activation energy for thermal recovery, γ is the stacking fault energy, R is the universal gas constant, β is the constant, T is the absolute temperature.

In the present investigation, the mechanical milling was carried out at room temperature. However, Ali et al. [350] have shown a localized increase in the temperature during MM of Al-Cu-Fe IQC due to the balls collision. During the MM, the temperature rise was not ascertained through any experimental technique. Therefore, Schwarz and Koch [380] model was used to estimate the increase in temperature (ΔT) during MM, as described by equation 3.3 mentioned below.

$$\Delta T = \frac{F}{2} \left(\frac{\Delta t}{\pi k_p C_p \rho} \right)^{\frac{1}{2}} \dots\dots\dots (3.3)$$

where, F is the dissipated energy flux $= \sigma \cdot V$, σ is the normal stress caused by a head-on collision, V is the relative velocity of the ball before impact, ΔT is the stress state lifetime, ρ is the powder density, K_p is the thermal conductivity of powder, C_p is the heat capacity of the powder.

The maximum compressive stress generated by head-on collision of balls having diameter 'd' is considered normal stress and can be described by equation 3.4.

$$\sigma = \sigma_c = 0.616 \left(PE^2 \left(\frac{2}{d} \right)^2 \right)^{1/3} \dots\dots\dots (3.4)$$

where, P is the load, E is the elastic modulus of the balls.

The details of the milling ball dimensions and material are mentioned in Chapter 2. The parameters required for estimating the minimum grain size/ crystallite size for Sn reinforcement particles are mentioned in Table 3.9.

Table 3. 9: Parameters for estimating minimum grain/crystallite size during MM.

Parameters	Al _{62.5} Cu ₂₅ Fe _{12.5} (at %)	Sn
D _{po} is the diffusion coefficient for pipe diffusion	-	12.8 cm ² /s
G is the shear modulus,	-	18 GPa
b is the magnitude of Burgers vector,	-	0.3172 nm
ν _o is the Poisson's ratio,	-	0.37
H is the Vickers hardness,	-	0.088 GPa
k is the Boltzmann constant,	0.0083144 kJ/mol.K	
K is the thermal conductivity	1.8 W/m.K	64 W/m.K
ρ is the density	4.18 g.cm ⁻³	7.31 g.cm ⁻³
C _p is the specific heat	600 J/kg.K	218 J/kg.K
Q is the activation energy for thermal recovery	173.6 kJ/mol	107.2 kJ/mol
γ is the stacking fault energy,	-	3 mJ/m ²
R is the universal gas constant,	-	0.0083 kJ/mol K
β is the constant,	-	0.04
T is the absolute temperature for IQC–10Sn during mechanical milling	782 K	

The minimum grain size estimated of Sn in IQC–10Sn nanocomposite powder was estimated to be in the ~15 nm respectively. The minimum grain size estimated in the present investigation is in line with the findings reported by Khan et al. [360]. Their study reported the minimum grain size of 14 nm for Sn embedded in the Al matrix. In their

investigation, the estimated grain size was close to the experimental findings for embedded Sn particles. However, there is a disparity between the theoretical and the observed values in the present investigation, as observed in Table 3.1. This discrepancy in the results corresponds to the sintering of the Sn particles during MM. The temperature of the sintering during MM can be predicted with the help of Alymov et al. model [380]. As per the Alymov et al. [380], the minimum temperature for sintering of Sn particles during mechanical milling of IQC-Sn nanocomposite was estimated to be ~ 352 K. It is clear from Table 3.9 that the rise in temperature during MM of IQC-10Sn was ~ 782 K. This temperature rise is significantly higher than the minimum temperature required for the Sn particle's sintering, leading to the sintering of Sn powder particles during MM. This can be correlated with the sintered Sn powder particle observed in the bright-field image shown in Figure 3.8 (a), which illustrates the sintering of two-fragmented Sn particles after MM for 40 h.

3.6.3 Thermal stability of IQC-Sn milled powder

The phase evolution during dynamic DSC at different heating rates may be evident from Figure 4. The DSC thermogram shows one endothermic followed by four exothermic events during heating of IQC-Sn nanocomposite powder. For correlating the phases evolved during heating events, particularly to IQC-30Sn, phase analysis of IQC-30Sn at different temperatures is carried out as evident from Figure 3.14. As per the DSC thermogram and phase analysis of the heat-treated sample, the sequence of phase evolution during heating may be stated as described below:

Disordered B2 [Al (Cu, Fe)] (major) + Disordered IQC (minor) (IQC-30Sn MM for 40 h)

- (~ 239 °C): Melting of Sn reinforcement
- (~ 300 °C): $\text{Al}_{13}\text{Fe}_4$ (major) + Disordered IQC (minor) + (B2 + ω - $\text{Al}_7\text{Cu}_2\text{Fe}$) (minor)

- (~ 439 °C): $\text{Al}_{13}\text{Fe}_4$ (major) + Disordered IQC (minor) + (B2 + ω - $\text{Al}_7\text{Cu}_2\text{Fe}$ + Al_5Fe_2) (minor)
- (~ 579 °C): $\text{Al}_{13}\text{Fe}_4$ (major) + Ordered IQC (minor) + (B2 + Al_5Fe_2) (minor)
- (~ 721 °C): ($\text{Al}_{13}\text{Fe}_4$ + B2) (major) + Ordered IQC (minor)

The B2-type phase appears to be stable even after annealing of IQC-30Sn after 10 h at 800 °C. An investigation by Mukhopadhyay et al. reports a minor phase fraction of the B2-type phase along with a major IQC phase after annealing at 800 °C [375]. Similarly, Srivastava et al. have described the formation of the B2-type phase in the Al-Cu-Fe IQC matrix reinforced with Sn phase [364]. An investigation carried out by Salimon et al. reports the formation of ω phase in the temperature range of 400-600 °C, and in the range of 500-700 °C IQC phase co-exist with ω phase [381].

3.6.4 Toughening behavior of IQC-Sn composite

The hardness for IQC-Sn nanocomposite powders is reported in Table 3.6. The peak hardness of IQC-10Sn ~ 6.6 GPa, due to grain refinement and the homogenous distribution of Sn reinforcement in the nanocomposite powder. The hardness of the IQC-10Sn is comparable to that of the pure IQC, milled at various milling intensities reported by Ali et al. [350]. The MM technique is instrumental in synthesizing IQC-Sn nanocomposite powder with hardness comparable to that of MM pure IQC (~ 7 GPa). An investigation by Srivastava et al. [364] used spray forming to synthesize 10 wt % Sn reinforced IQC composite with a 6.0 GPa. The bulk IQC – Sn composite prepared by SPS and hot-pressing shows a significant rise in the strength and fracture toughness, respectively. The strength increase upto IQC – 20Sn SPSed composite and then decreases for IQC – 30Sn. A similar kind of behavior was observed by Fleury et al. [372] for Al-Cu-Fe, and Al-Cu-Fe-B reinforced with Sn through melting and solidification routes. They

have reported an increase in the strength of IQC from ~250 MPa to ~550 MPa with addition of 20 vol% of Sn. This huge increase in the strength was attributed to the soft Sn particles that restricts the propagation of cracks. However, in the present investigation due to implication of hybrid strategy (i.e. nanostructuring as well as homogenous distribution of Sn) for toughening of IQC resulted in enormous increase in the yield strength having synergy with failure strain as evident from Figure 3.23 and Table 3.7. Due to homogenous distribution and liquid phase sintering of Sn particles in the IQC matrix (Figure 3.22) during MM and SPS, results in significant enhancement in the strength of IQC–Sn composites to those reported by other investigators and co-workers [358,362,364]. The high hardness and strength of the IQC-Sn nanocomposite powder bulk composite may help design potential coating material with excellent fracture toughness as a structural material for engineering applications.

3.7 Conclusions

The mechanically driven structural transformation of IQC-Sn nanocomposite powder as a function of milling duration and volume fraction of Sn have been analyzed in details. The sequence of structural change was co-related with the hardness of IQC-Sn nanocomposite powder MM upto 40 h. Further, efforts were made to study the toughening behavior of bulk IQC–Sn composite prepared by SPS and HP. It can be concluded from the present work that

1. The structural transformation of the Al-Cu-Fe IQC phase (with a minor phase fraction of crystalline phases) transforms to $\text{Al}_{13}\text{Fe}_4$ and B2-type Al (Cu, Fe) phase as the major phase after MM. However, the phase fraction of $\text{Al}_{13}\text{Fe}_4$ and B2-type phases formed after MM is dependent on the volume fraction of Sn reinforcement in the IQC-Sn nanocomposite powder.

2. The order-disorder transformation of the IQC phase in the IQC-Sn nanocomposite powder is dependent on the volume fraction of Sn reinforcement. The MM of IQC-Sn nanocomposite powder upto 40 h leads to the structural transformation of ordered face-centered IQC to disordered face-centered IQC phase i.e, simple icosahedral phase. The IQC phases in IQC-10Sn & 20Sn are ordered upto 20 h of MM, while for IQC-30Sn, the IQC phase is ordered upto 30 h of MM. This may be attributed to the change in MM's mechanism leading to disordering among the atoms in the IQC phase.
3. The disordered B2-type Al (Cu, Fe) phase, i.e., BCC phase, is formed after milling of IQC-Sn upto 40 h. Increasing the volume fraction of Sn also enhances the layering of crystalline phases (for IQC-10Sn) and B2-type Al (Cu, Fe) phase on IQC phase (for IQC-30Sn).
4. The heating events in IQC-Sn nanocomposite powder are associated with the phase evolution of crystalline phases of IQC. The Sn reinforcement in IQC-Sn nanocomposite powder enhances the structural stability of the B2-type phase even after annealing at 800 °C.
5. The structural transformation induced by MM in IQC-Sn nanocomposite powder affects the indentation behavior and hardness to the tune of ~ 4 to 7 GPa, as a function of MM duration and volume fraction of Sn reinforcement.
6. The IQC-Sn bulk composite prepared through SPS and HP shows a significant increase in strength and hardness. The increase in the strength of SPSed IQC-10Sn, 20Sn, and 30Sn bulk composite was $\sim 65\%$, 75% and 63% , respectively due to the homogenous distribution and inhibition of cracks by Sn particles.

7. The hardness of hot-pressed IQC–10Sn at 50 g load was reported to be ~ 9.7 GPa. However, the pressure-less sintered composite has an inferior value of hardness compared to that of the HPed sample at 50 g load.
8. The overall increase in the fracture toughness of IQC–10Sn HPed composite was $\sim 22\%$ due to the significant reduction in the indentation crack length ($\sim 15\text{ }\mu\text{m}$). This reduction in the crack length was attributed to Sn particles' homogenous distribution in the IQC matrix, thereby enhancing its propensity for arresting the cracks. This offers the possibility of synthesizing nanocomposite powders and bulk composite by SPS and HP with suitable processing treatments for having good fracture toughness and optimal strength required for application, such as coating materials for bearing application.