In-situ formation of 2D-TiC_x in Cu-Ti_2AlC composites: an interface reaction study

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Abstract

We have explored to fabricate Cu based Ti_2AlC composite focusing on the processing method and the reaction which takes place at the matrix-reinforcement interface to yield 2D TiC_x. In due course of consolidation of Cu-Ti_2AlC; the formation of 2D TiC_x via the reaction between Cu and Ti_2AlC by forming solid solution between $CuAl_x$ was facilitated. This reaction has been elaborated and analyzed in the light of corroborated results.

Keywords: Microstructure; Powder Technology; Ti_2AlC; 2D TiC_x; Interface; Reaction

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1. Introduction

MAX phases are a class of materials which are layered ceramics, with a generic formula of $M_{n+1}AX_n$ [1]. In this formula M stands for an early transition metal, while A represents an element from the IIIA or IVA groups, and X is representative of carbon and/or nitrogen [2]. Depending on the value of n index, the MAX phases are divided to three general categories, namely 211, 312 and 413 groups. $M_{n+1}AX_n$ phases (with n = 1–3) form a wide class of nano-laminated ternary carbides or nitrides, with a hexagonal crystal structure. MAX phases have equivalent or superior electrical and thermal conductivity as compared to the corresponding metallic element M [3].

Copper based metal matrix composites (MMC) are a class of materials which combine the electrical properties of Cu and the mechanical properties of the reinforcements like ceramics particles. MAX phase-based Cu MMC offers the possibility of a tough material without a profound loss in electrical conductivity. Peng et al. showed that Ti_3AlC_2 reinforced Cu exhibits a lower electrical conductivity but a much higher flexural strength without the loss in fracture toughness [4]. Cu is also used as an interphase to stop the reaction between Al and Ti_3AlC_2 for MMC applications [5]. Hence Cu is a suitable candidate for the matrix with Ti-Al based MAX phase as the reinforcement.

$(Ti_xCu_{1-x})_3(Al,Cu)C_2$ MAX phase solid solution was synthesized by sintering at 760 °C by compacting Ti_3AlC_2-40 vol.% Cu composite particles mixed by mechanical milling [6]. The reaction between Ti_3AlC_2 and Cu is elaborated by some research groups showing that when Cu enters the Ti_3AlC_2 crystal structure it yields a defective Ti_3AlC_2 which is $TiC_{0.67}$ with layers of Cu-Al alloy within a Ti_3AlC_2 grain [7]. The reports till date have emerged from high amount of Ti_3AlC_2 phase being added [7–11], but in the present work we have used only 1 and 3 vol.% of Ti_2AlC phase to establish that in-situ 2D TiC_x reinforced Cu composites can be fabricated with certain desirable properties by tailoring the processing conditions. The properties of 2D materials are typically superior to their bulk counterparts and this motivation led to numerous researches in graphene and subsequently MXene [12–14]. MXenes are 2D structures composed of only M and X elements and is synthesized from MAX phases by acid etching of the A element [14].

The schematic representation in Fig. 1 represents the concept behind the in-situ formation of 2D TiC_x taking place in the Cu matrix reinforced with MAX phase in this experiment. The idea of this experiment was to choose a matrix which could form a solid solution with the A element of the MAX phase. This solid solution formation would deplete the MAX phase of A element thereby creating MX_n layers. The underlying principle to solid solution formation of A element with the matrix element was the eutectic reaction of Al and Cu thereby providing enough time for Al atoms to diffuse out of the MAX phase and react with the Cu matrix. This concept can be extended to important systems; the eutectic solid solution formation would provide additional strengthening to the material. The gradient kind of microstructure distributed around with solid solution formation, 2D TiC_x and Cu matrix provides ample scope to engineer the material to obtain desirable properties.

2. Materials and Methods

Copper (Alfa Aesar, 325 mesh) was blended with 1 and 3 vol. % Ti_2AlC (synthesized from elemental precursors [15][16]) agglomerate size ~40 μm) powder followed by uniaxial cold compaction (700 MPa) and sintering in vacuum furnace (Thermal Technologies, USA) at 900ºC for 2 h. The consolidated specimens were studied for microstructural characteristics and phase distribution using field emission scanning electron microscopy (FEI Quanta) and electron probe micro-analyzer (EPMA). Transmission electron microscopy (TEM) (FEI T20) has been performed to study the interaction of Cu with the Ti_2AlC phase.

3. Results and discussion

The X-ray diffraction pattern of Ti_2AlC powder has been shown in Fig. 2(a) which contains Ti_2AlC and traces of Ti_3AlC_2. Fig. 2(b) shows the Ti_2AlC powder with an inset of higher magnification, the layers of Ti_2AlC stacked together.

The microstructure of the sintered specimens reveals near-uniform distribution of Ti_2AlC in copper matrix (Fig. 2(c)). Three phases by contrast which indicates Cu, $CuAl_x$ partial solid solution and Ti_2AlC particles can be seen. Ti_2AlC is present on the grain boundaries and has pinning effect on the Cu matrix, in Fig. 2(d). Formation of sheet like loose ends at the grain boundary regions labelled by arrows in Fig. 2(d) suggest structure like 2D sheets. Fig. 2(e) reveals sub layer structure in the Ti_2AlC particle. Zhang et al. [7] suggested that Cu and Ti_3AlC_2 reacts above 850°C to form a layer at the interface. Molten Cu triggers the exfoliation of Ti_3AlC_2 via its decomposition yielding $TiC_{0.67}$ layers and Cu-Al alloy layers within Ti_3AlC_2 grains[10]. In Fig.2(d) well-defined grain boundaries visible indicate complete wetting of Cu by Ti_2AlC and vice-versa[17]. The layer-like morphology of intergranular phase shown with arrows renders hindrance to the crack propagation in the material, whereas the particle-like morphology would contribute to resistance in plastic deformation[18].

Fig. 3 shows that the Al in the Ti_2AlC phase has interacted with the Cu matrix to form a partial solid solution. The core of the particle shows lower concentration (atomic%) of Al in accordance with the Al content in Ti_2AlC phase, as it has interacted with copper and has diffused into the matrix region. The periphery of the interphase region is Al rich indicating the onset of formation of a Cu-Al solid solution.

It is observed that Cu has entered the core of Ti_2AlC phase which proves the reaction taking place between Cu and Ti_2AlC phase result in a partial Cu-Al solid solution. The Cu map indicates the inward diffusion of Cu from the matrix into the Ti_2AlC particle substituting in the Ti atomic position as well[6]. The presence of Cu alters the decomposition temperature of Ti_2AlC, i.e. stability of Ti_2AlC ranges from 1100 to 1200°C, but Cu decreases the stability temperature considerably by reacting with Ti_2AlC at 900°C [7]. The diffusion reaction can be formulated as

$$xTi_2AlC + Cu \longrightarrow 2xTiC_x + CuAl_x \quad (1)$$

Cu and Ti_2AlC have been reported to have a good wettability with each other. The de-intercalation of Al in MAX phase is most viable as the M-A bond is quite weak. A mild reaction between Cu and Ti_2AlC starts at 850-950°C, the reaction becomes strong above 950°C. Above 1000°C, total decomposition occurs with sub-stoichiometric TiC_x and CuAlx solid solution formation in Cu-Ti_3AlC_2[7].

Cu-Ti_2AlC composite reveals dislocation tangles in the Cu matrix (Fig.4(a)); as the Ti_2AlC is layered, showing dislocation arrays in Fig.4(b); inset showing the SAD pattern. The bright field micrographs in Fig.4(c&d) shows two distinct regions of interest. i.e. near the Cu-Ti_2AlC phase interface and away from the interface. The region near the interface exhibits a sub-grain boundary pattern which can be marked as the reaction layer between Cu and Ti_2AlC. In due course Cu has entered the Ti_2AlC phase and formed partial solid solution of Cu-Al (Fig.4(d)). The region farther from the interface shows some precipitates which can be identified by viewing the bright and dark field images (Fig.4(c)). These precipitates denote the formation of solid solution between Cu-Al. Cu was found within the defective Ti_3AlC_2 and a crystallographic relationships ½1210 Ti_3AlC_2 ½111Cu and (0001) Ti_3AlC_2 (111) Cu was established [7].

Single sheets of 2D TiC_x are present in the matrix Fig.4(e&f) showing electronically transparent area of TiC_x of 50 nm in average width. The TiC_x nanosheets can be seen at the grain boundaries of Cu matrix indicating the reaction between Ti_2AlC and Cu. SEM microstructures corroborates; 2D entities being present at the grain boundaries. The SAD pattern of these transparent flakes shows (0002) ring present in them (Fig.4(g)). TiC_x flakes are fragmented during the diffusion reaction process mentioned above, hence show size in nanometer scale. The formation of TiC_x is anticipated to have been taken place partially i.e.

localized in the periphery of Ti_2AlC phase regions. This fact could be attributed to the partial solid solution formation between Cu and Al from the Ti_2AlC phase yielding 2D TiC_x.

4. Conclusion

The fabrication of in-situ 2D TiC_x in the Cu matrix with partial $CuAl_x$ solid solution has been reported. The microstructure of the composites showed a graded characteristic of three phases Ti_2AlC in the copper matrix. The reaction between Cu and Ti_2AlC shows that Cu diffuses into the Ti_2AlC and forms a partial solid solution of $CuAl_x$ and 2D TiC_x. Formation of 2D TiC_x occurs at grain boundaries. Single flakes of 2D TiC_x were formed at the grain boundaries.

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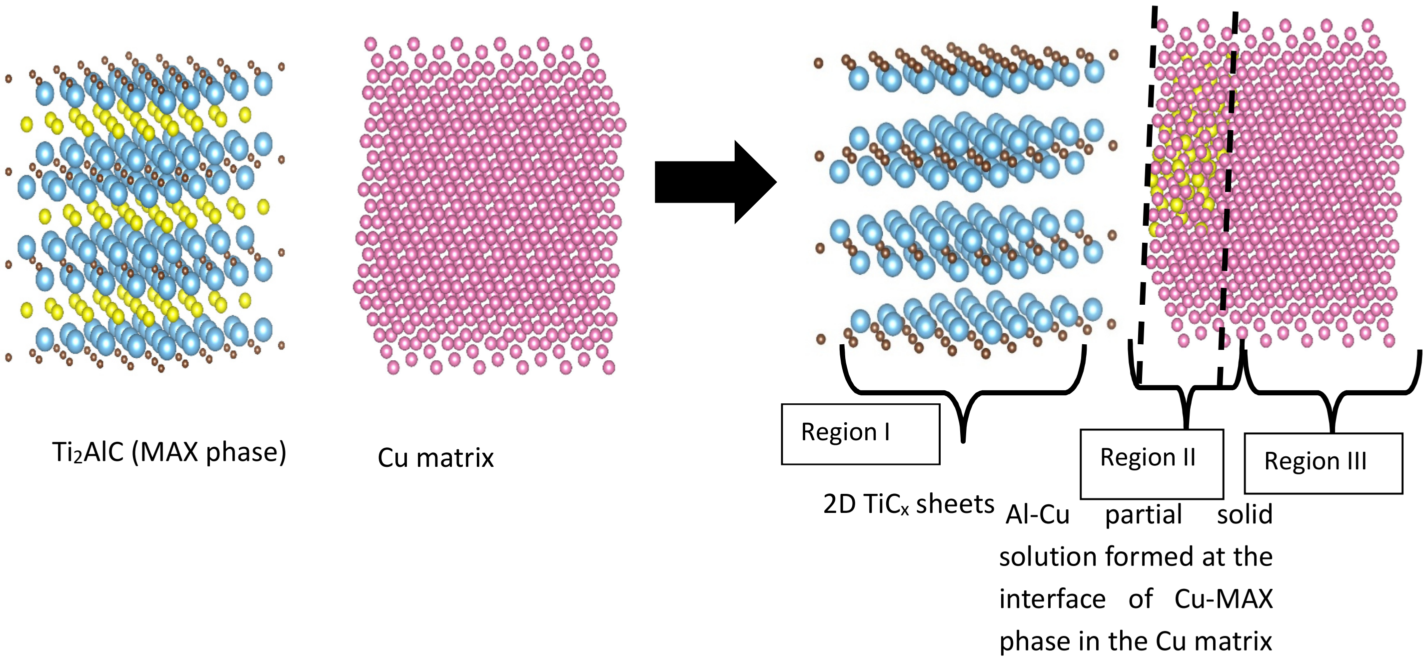


Fig.1 Schematic representation of the in-situ reaction in the process of sintering

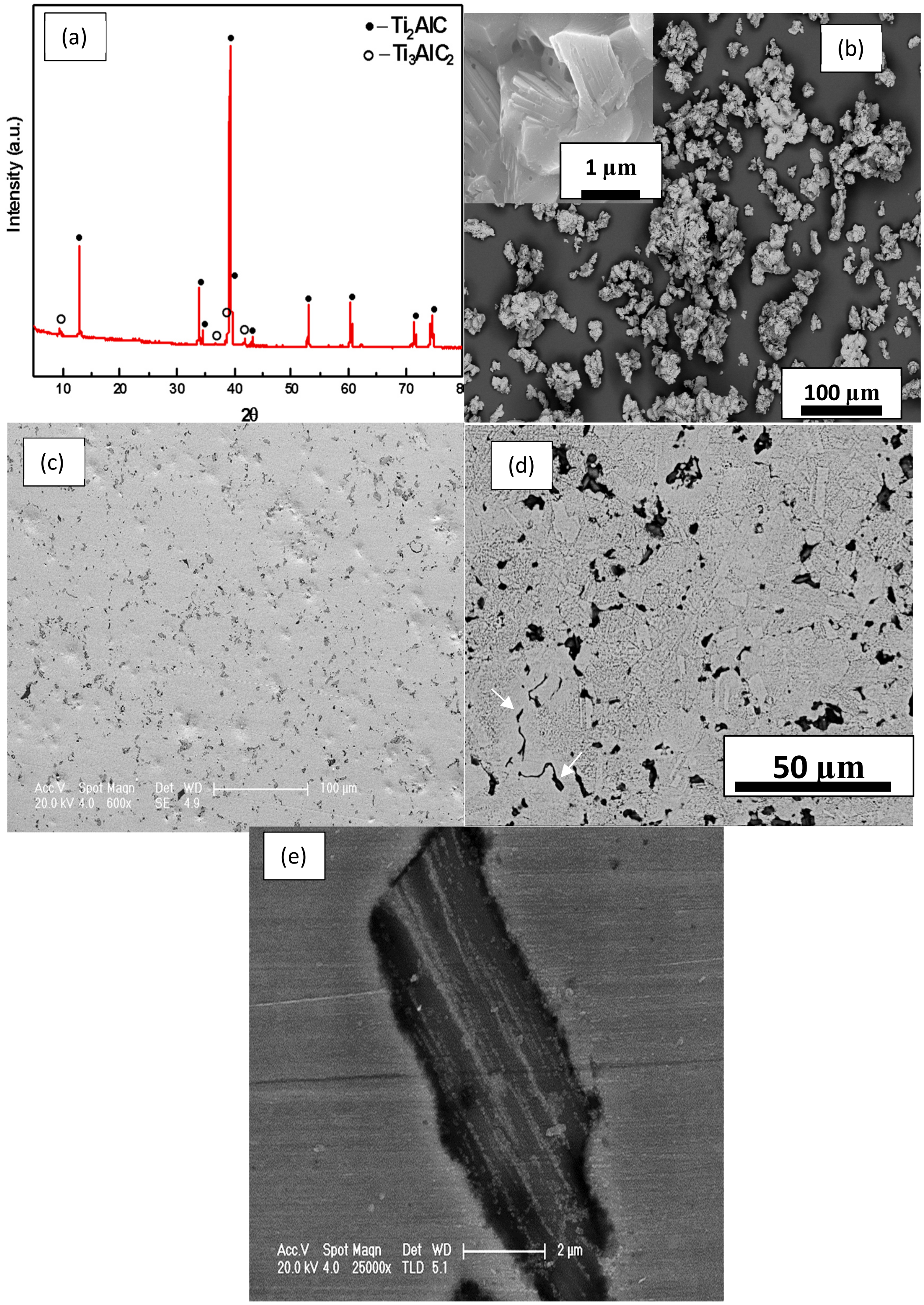
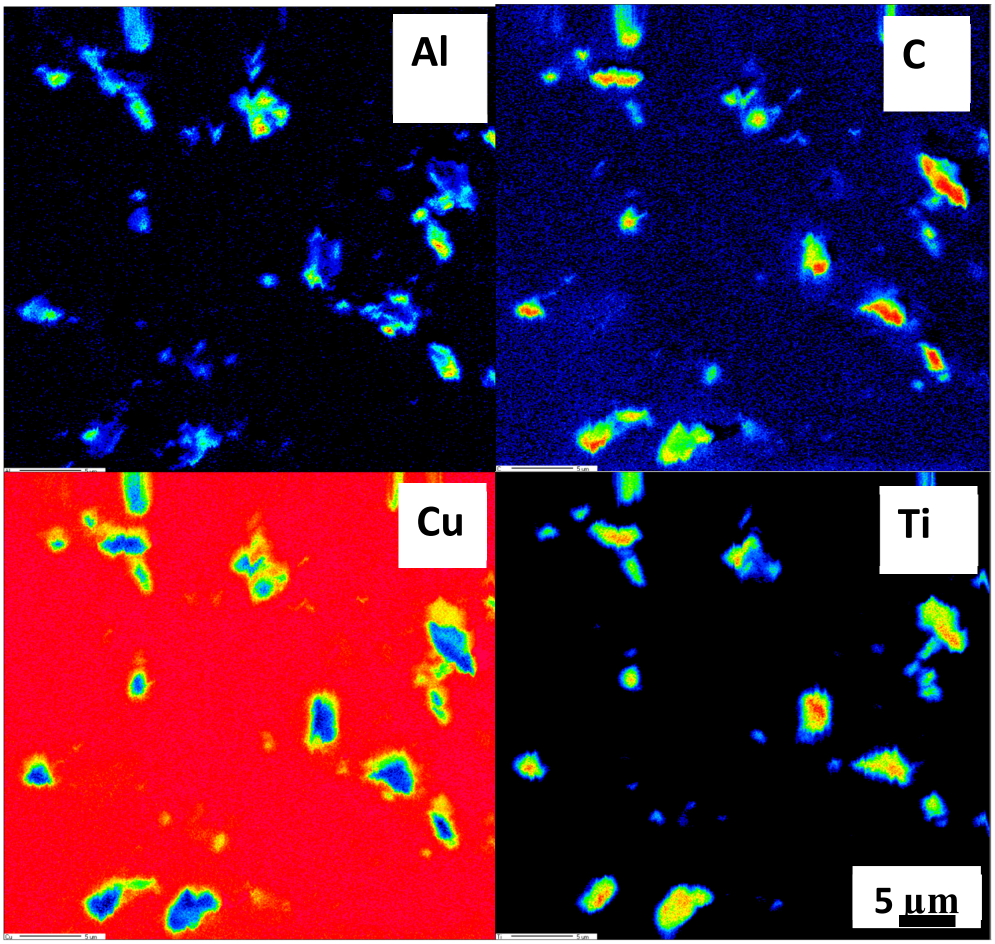


Fig.2 (a) XRD plot of starting Ti_2AlC powder (b) Microstructure of Ti_2AlC powder, (c-e) microstructure of Cu-1&3 and 3vol.% (high magnification) Ti_2AlC composite respectively



Al
C
Cu
Ti
5 µm

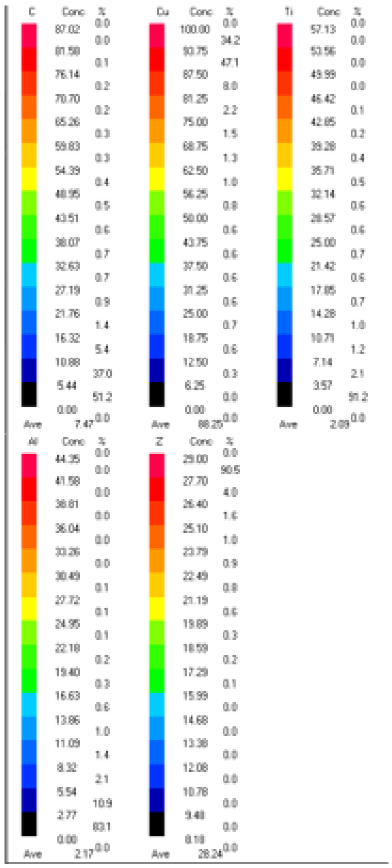
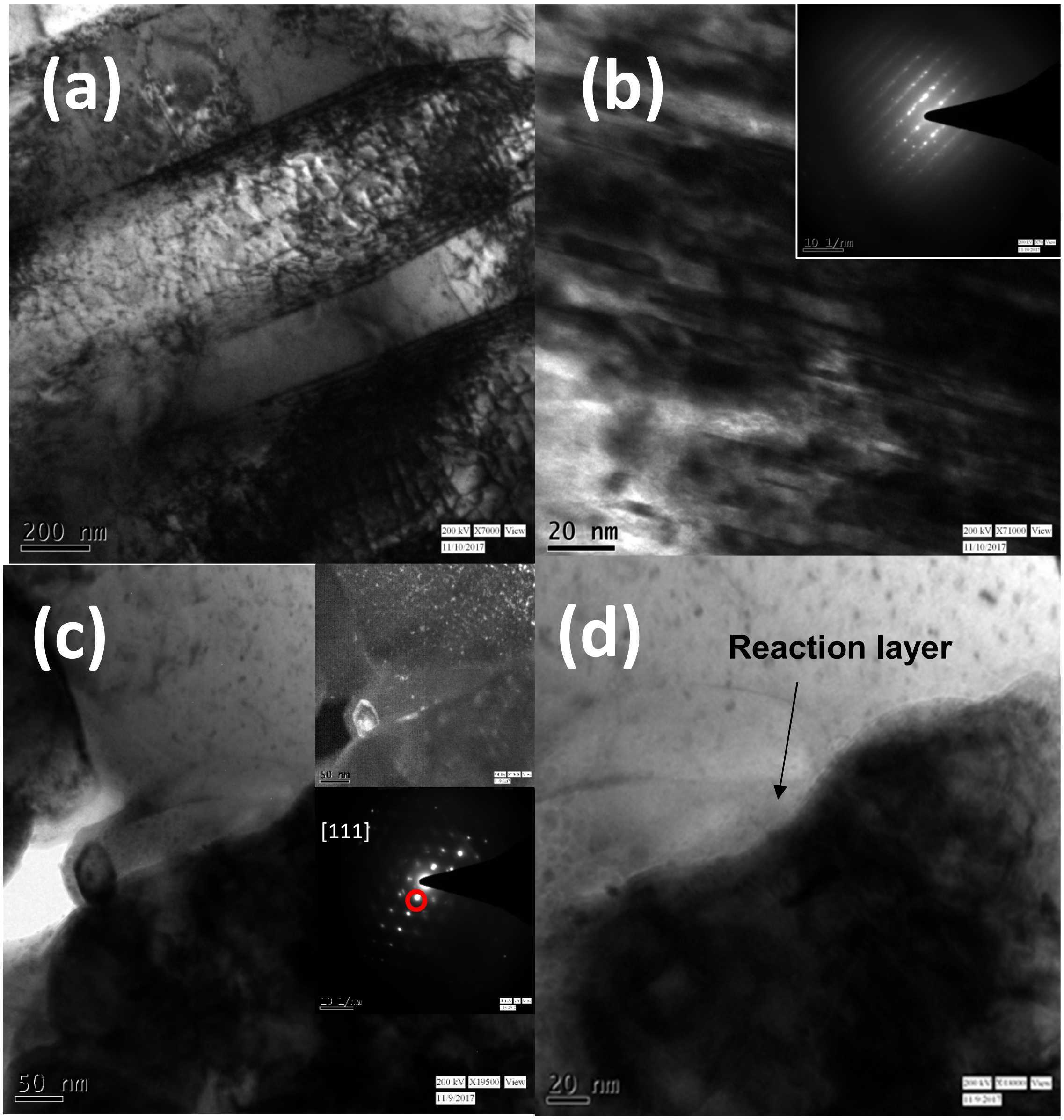


Fig.3. Elemental mapping of (a) Al, (b) C, (c) Cu and (d) Ti in Cu-3 vol.% Ti_2AlC MMC


(a)
200 nm
200 kV X7000 View
11/10/2017
(b)
10 1/nm
20 nm
200 kV X71000 View
11/10/2017
(c)
50 nm
[111]
50 nm
200 kV X19500 View
11/9/2017
(d)
Reaction layer
20 nm
11/9/2017

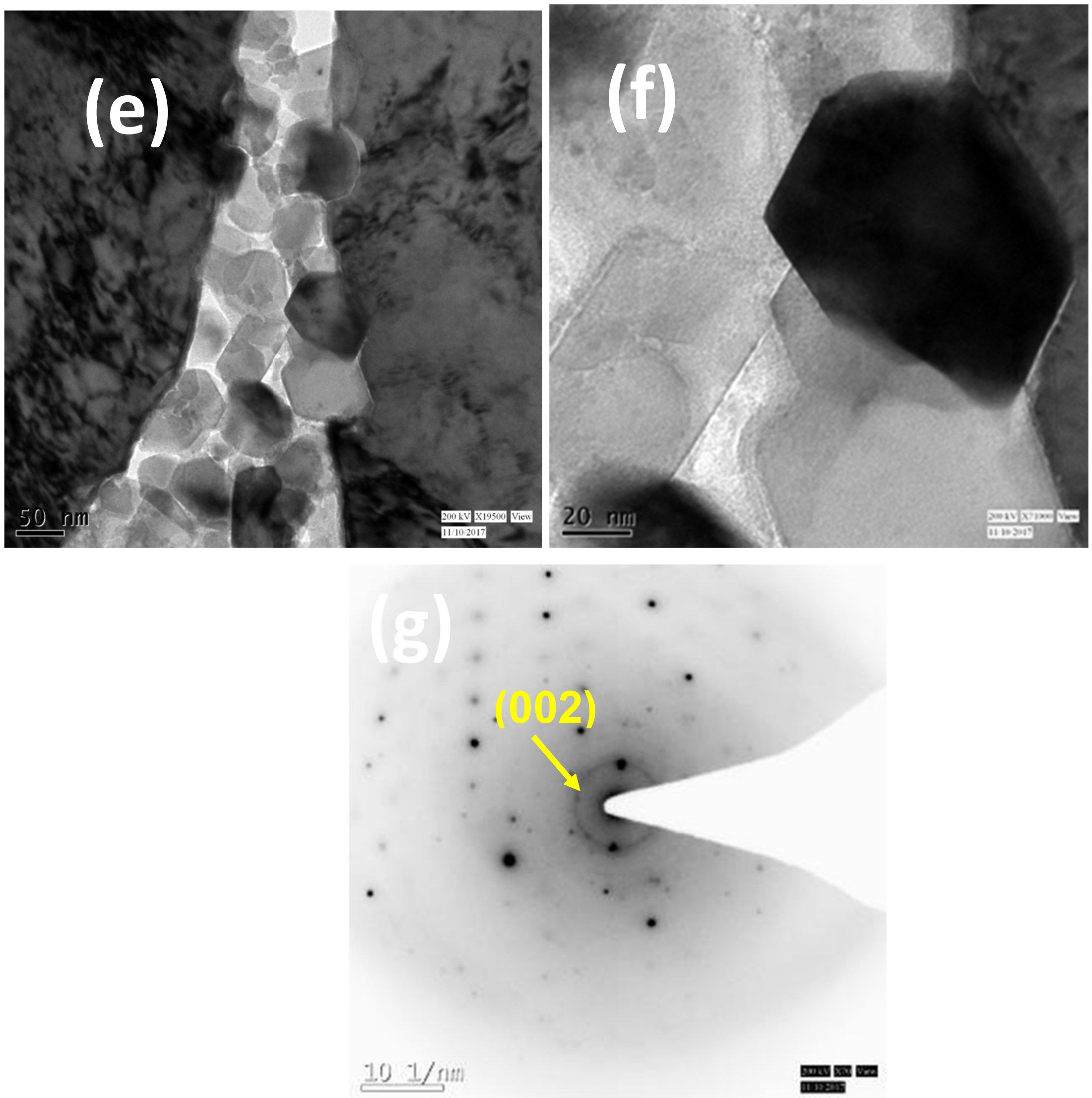


Fig.4 TEM micrographs of Cu-3 vol.% Ti_2AlC composite illustrating (a) dislocation in layers (b) layered stacked together (inset SAD pattern) (c) interaction between Cu and Ti_2AlC phase and (d) reaction layer (e) 2D TiC_x at the grain boundary (f) single flakes of 2D TiC_x (g) SAD pattern of 2D TiC_x