

Microstructure and dispersion of Cu-TiC_x master alloys into molten Cu and the relation to contact angle data

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Cu-TiC_x composites have been made self-propagating high temperature synthesis of Cu-Ti-C mixtures. It was found that as the C/Ti ratio decreases, wetting of the carbide, by what is effectively a molten Cu-Ti alloy, is improved and the distribution of the carbides in the master-alloy becomes ideal for subsequent dispersion, i.e. discrete particles are formed. Increasing quantity of Cu in the reactants from 10 to 50 wt% Cu had a similar effect to decreasing the C/Ti ratio and enabled the size of the TiC_x particles to be varied in the approximate range 20–0.5 μm. Incorporation and dispersion of the master alloy into molten copper was possible when the C/Ti ratio in the products was below approximately 0.73, which agreed well with contact angle data in the literature.

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1. Introduction

Self-propagating High temperature Synthesis (SHS) is an attractive alternative to conventional processing methods for the production of engineering materials such as ceramics, composites and intermetallics. Advantages of SHS include the generation of high reaction temperatures, high thermal gradients and rapid cooling rates, resulting in high purity products and the formation of fine, non-equilibrium or metastable phases. The main commercial advantage of processing by this route is that the short reaction times and high temperatures, minimise operating and processing costs and avoid the need for expensive processing facilities. These advantages have encouraged researchers to become active in exploring SHS of new and improved materials such as abrasives, cutting tools, polishing powders, shape memory alloys, high temperature intermetallics, metal and ceramic matrix composites and functionally graded materials [1].

Reaction between Cu, Ti and C can be used to make high volume fraction composites consisting of hard titanium carbide particles dispersed in a metallic Cu matrix [2, 3]. Applications for this material include master alloy additives for making metal matrix composites. Poor wetting between molten copper and most ceramics makes copper-based composites difficult to produce by traditional infiltration or dispersion methods [4]. This poor wettability is attributed to the stable electron configuration of copper which has a full “3d” orbital. According to the Ti-C phase diagram, titanium carbide, TiC_x, has a wide stoichiometry, from $x = 0.47$ to 0.98

[5]. Although the modulus and hardness of TiC_x both decrease as the C/Ti ratio decreases [6], the ability of molten metals to wet the carbide increases [7, 8]. Since reaction between Ti and C is sufficiently energetic for synthesis via an SHS or reactive synthesis route, this offers the opportunity to tailor the stoichiometry of the carbide and improve the likelihood of successful composite manufacture.

The aims of this study are to react Cu, Ti and C powders to produce Cu-TiC_x master alloys, to tailor the stoichiometry of the carbide formed so that it can be dispersed in molten Cu and to relate the resulting behaviour to wetting data in the literature.

2. Materials and experimental procedures

The reactant powders used were; titanium, >99.5 wt% pure, particle size between 125–180 μm; graphite, >98 wt% pure, <10 μm in size and copper, >98.5 wt% pure, <75 μm in size. The powders were accurately weighed and mixed to attain different C/Ti ratios and different Cu contents. The powder mixtures were pressed in a 13 mm diameter die to a pressure of 200 MPa, to produce compacts approximately 4 g in mass. The compacts were placed in an induction melting furnace and, in order to reduce carbon and titanium losses through oxidation, the furnace chamber was evacuated and flushed with argon several times before being filled with argon to a pressure of 1 atmosphere. In order to react the samples to produce Cu-TiC_x master alloy pellets, the compacted powders were rapidly heated in the induction field to the SHS ignition

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TABLE IA The C/Ti ratios applied with constant Cu content of 30 wt%

30 wt% Cu	C/Ti = 1	C/Ti = 0.9	C/Ti = 0.8	C/Ti = 0.7	C/Ti = 0.6	C/Ti = 0.5	C/Ti = 0.4
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TABLE IB The Cu contents (wt%) applied with constant C/Ti ratio of 0.6

C/Ti = 0.6	10 wt% Cu	20 wt% Cu	30 wt% Cu	40 wt% Cu	50 wt% Cu
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temperature. Table I shows the reactant compositions investigated.

The microstructure of the master-alloys was characterised using scanning electron microscopy (SEM) on polished sections and the phases present were identified using X-ray diffraction (XRD). The lattice parameter of TiC_x in the master-alloy was determined from XRD reflections between 30° and 80° using established methods [9]. In order to measure the lattice parameter with the required accuracy, a step size of 0.01° (2 s/step) was used.

Master alloy pellets produced by SHS, were placed in a graphite crucible and to this >99.3 wt% pure copper pieces were added so that dilution would result in a composite with 10 wt% or approximately 18 vol% of TiC_x particles. The graphite crucible and its contents were heated in an induction furnace, again under argon, to $1200^\circ C$ to melt the copper pieces and the master alloy. Once the copper was molten it was stirred manually using a graphite rod that passed through a hole in the lid of the furnace chamber. After 10 min, power to the furnace was switched off and the metal was allowed to freeze in the crucible. The microstructures of the resulting composite materials were also characterised using scanning electron microscopy.

3. Results and discussion

The measured lattice parameters for the carbides produced by SHS reactions, as a function of C/Ti ratio and Cu content, are shown in Fig. 1 and are compared with those for samples without Cu [3], which are in close agreement with the work of Storms [5]. An increase in lattice parameter is observed with Cu present and the difference in lattice parameter increases with decreasing C/Ti ratio in the reactant mixture. The re-

lationship between lattice parameter and stoichiometry in the binary Ti-C system can be used to determine the stoichiometry of the carbide in the master alloys produced in this study. Table II presents the estimated C/Ti ratio in the carbide reaction products. By considering the difference between the C/Ti ratio in the reactant mixture and that in the product, the amount of Ti in the matrix can also be estimated and this value is also included in Table II.

In all instances, the actual C/Ti ratio in the carbides produced after SHS is higher than that in the reactant mixture. Table II also indicates that the C/Ti ratio in the carbide deviates more strongly from that in the reactant mixture with decreasing C/Ti ratio and with increasing Cu content, although the deviation for the later case is less strong. The increase in C/Ti ratio in the products is a result of the dissolution of titanium in copper. It has been found that as the C/Ti ratio decreases, the Ti concentration in the Cu-Ti alloy in equilibrium with TiC_x increases [9,10], reducing the tendency for the formation of carbides with lower C/Ti ratios. Increasing the amount of Cu in the reactant mixture has a similar effect. Although SHS processing conditions are far from equilibrium, this explanation goes towards accounting for the differences observed in this work. Dissolved titanium forms intermetallic compounds on cooling and is evidenced by XRD analysis, which is also shown in Table II. The table indicates very high levels of Ti in the master alloy matrix are expected, and indeed observed, for lower C/Ti ratios in the reactant mixtures.

The C/Ti ratio in the reactant mixture also affects the microstructure of the master alloys and examples are shown in Fig. 2. All the samples are, however, characterised by the presence of high levels of porosity, the large black areas in the micrographs, a result of the evolution of gases, associated with adsorbed moisture and surface contaminants and oxides that are vapourised during SHS reaction at high temperatures [8]. For C/Ti ratios close to unity, networks of coarse, agglomerated TiC_x particles are observed, the darker grey phase shown in the micrographs, but as the C/Ti ratio is reduced, a more even dispersion of smaller, isolated particles is obtained. For a constant C/Ti ratio, as the quantity of Cu in the matrix increases, the particles decrease in size with little effect on their distribution in the matrix. Higher C/Ti ratios and lower Cu contents lead to increased reaction temperatures and as a result, the carbides formed are coarser [8, 10]. Variation in the quantity of Cu in the reactants enables the size of the TiC_x particles to be varied, in this case for 10 to 50 wt% Cu in the approximate range 20 to $0.5 \mu m$. It should be noted that although intermetallic phases were detected using XRD, their low contrast makes them difficult to observe in backscattered mode in the SEM.

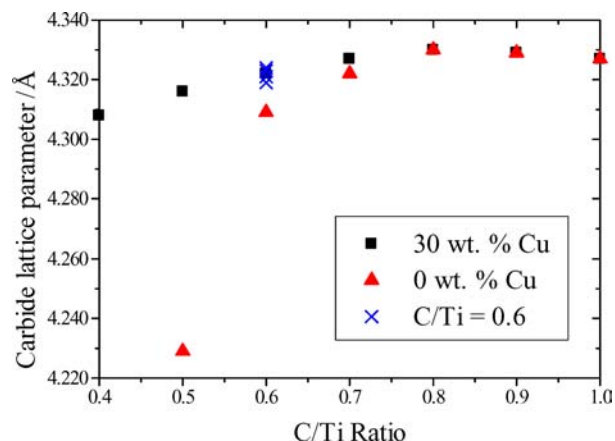


Figure 1 Lattice parameter changes as a function of C/Ti ratio and Cu content.

TABLE 2 Composition data for the master alloys

Reactant composition wt%Cu C/Ti	TiC _x lattice parameter /Å	C/Ti in products	wt% Ti in binder	Phases detected by XRD	Dispersion behaviour	
30	0.4	4.308	0.59	40	Ti ₃ Cu ₄ ,TiCu ₃ ,TiCu	○
30	0.5	4.316	0.66	34	Ti ₃ Cu ₄ ,TiCu ₃ ,TiCu	○
30	0.6	4.322	0.70	23	TiCu ₃ ,Cu	○
30	0.7	4.327	0.78	14	TiCu ₃ ,Cu	
30	0.8	4.330	0.80	–	Cu	
30	0.9	4.329	0.90	–	Cu	
30	1	4.327	1.00	–	Cu	
10	0.6	4.319	0.68	48	Ti ₂ Cu	○
20	0.6	4.321	0.69	33	Ti ₃ Cu ₄ ,TiCu ₃ ,TiCu	○
30	0.6	4.322	0.70	23	TiCu ₃ ,Cu	○
40	0.6	4.323	0.71	21	TiCu ₃ ,Cu	○
50	0.6	4.324	0.73	16	TiCu ₃ ,Cu	○

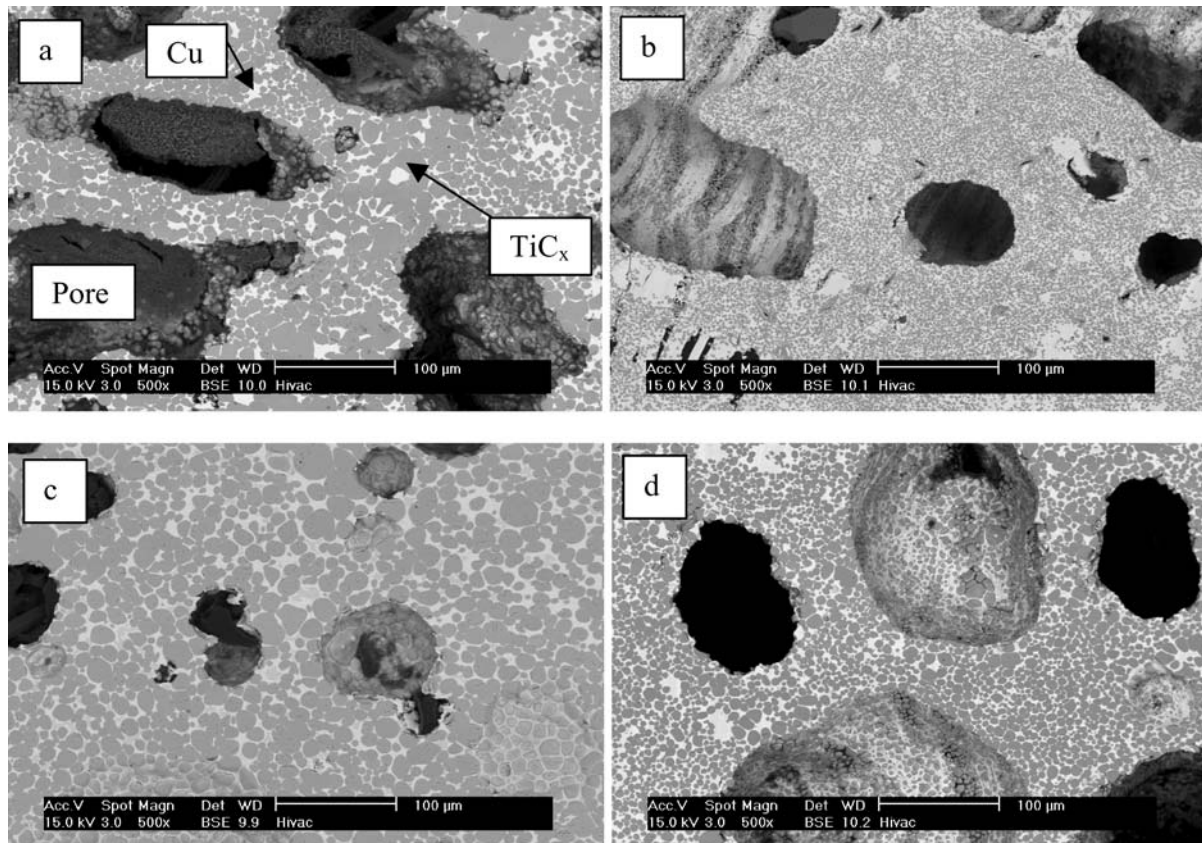


Figure 2 Comparison of the microstructures of the master alloys, (a) 30 wt% Cu, C/Ti = 0.8, (b) 30 wt% Cu, C/Ti = 0.4, (c) 10 wt% Cu, C/Ti = 0.6, and (d) 30 wt% Cu, C/Ti = 0.6.

Chemical etching can be used to reveal these phases [3].

When adding the master alloys to pure Cu it was found that for C/Ti carbide ratios greater than or equal to 0.78, the master alloys could not be incorporated. For reactant C/Ti ratios below this value, it was possible to incorporate the master alloy into the molten Cu and disperse the TiC_x particles throughout the matrix. Table II shows a summary of the dispersion behaviour, ticks indicating successful incorporation and dispersion. Fig. 3 clearly shows that the master alloys have broken up, resulting in dispersion of the carbide particles fairly evenly throughout the copper matrix. These micrographs also show that some of the particles formed are porous, as evidenced by a speckled appearance, and that Ti has been transferred to the melt to

form Cu-Ti intermetallics. The Ti content in the melt varies with master alloy composition, but is estimated to be no more than 2 wt%.

Contact angle data for pure Cu on TiC_x in the region 1100–1200°C, in vacuum, [7, 11–15], indicate that the transition between non-wetting and wetting behaviour, characterised by a contact angle less than 90°, is observed for a C/Ti ratio in the region 0.8–0.6. Although the presence of dissolved Ti in conjunction with TiC_x was not considered, in the presence of stoichiometric TiC, Ti was found to lead to a significant reduction in contact angle for as little as 1–2 wt% additions [15, 16].

As the particles form during SHS processing, for high C/Ti ratios, wetting is poor and the particles preferentially agglomerate and sinter to produce a master alloy that has no possibility of breaking-up even if it can be

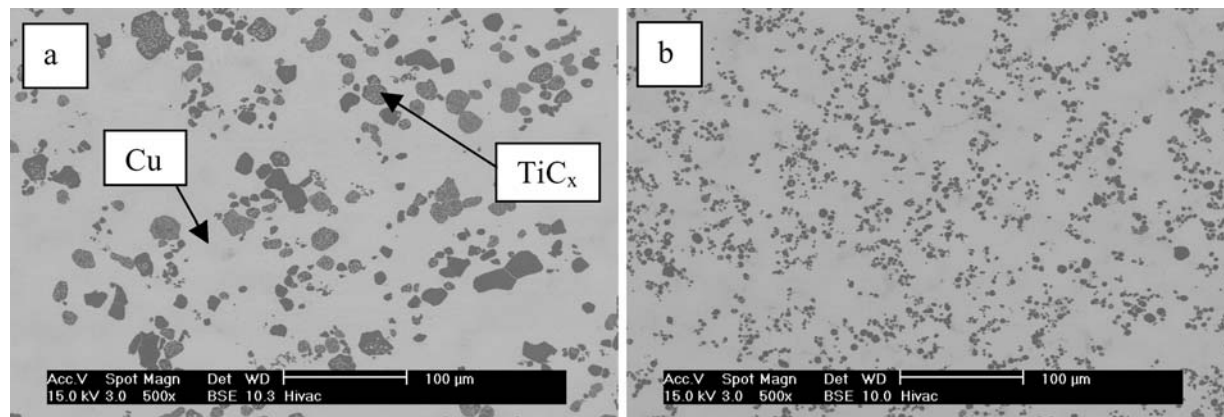


Figure 3 Microstructure of master alloys with (a) 10 wt% Cu, $C/Ti = 0.6$ and (b) 30 wt% Cu, $C/Ti = 0.4$, after incorporation and dispersion into molten Cu at 1200°C .

incorporated into molten Cu. As the C/Ti ratio in the reactants decreases, the molten Cu-Ti alloy is able to wet the TiC_x particles, eliminating the formation of particle clusters. Examination of samples with variable Cu contents and a constant C/Ti ratio suggests that reaction temperature is less influential than the C/Ti ratio in determining the distribution of the particles in the matrix. Although the formation of isolated particles occurs for C/Ti ratios between 0.8 and 0.6 and the values are similar to those for the wetting transition as determined by contact angle experiments, the presence of high levels of Ti in molten Cu, as indicated in the table, are likely to have significantly enhanced wetting.

This study has also shown that a reaction product with stoichiometry $TiC_{0.73}$ or below can be readily incorporated into molten Cu and will disperse to provide individual particles in the matrix. This observation is also in close agreement with the wetting transition observed during contact angle experiments. It should be noted that the presence of Ti as an alloying element in the copper-based master alloy is expected to have assisted its break-up and dispersion. Ti not only improves wetting, but alloying within the range 14 to 47 wt% Ti results in more than a 200°C reduction in the melting point of the Cu-rich phase binding the particles together [17].

4. Conclusions

During SHS reaction in the Cu-Ti-C system, as the C/Ti ratio in the TiC_x reaction product decreases, wetting by what is effectively a molten Cu-Ti alloy, is improved. The size of the particles formed decreases and their distribution in the master alloy becomes ideal for subsequent dispersion, i.e. discrete particles are formed.

Increasing the amount of Cu in the reactant mixture has a similar effect to decreasing the C/Ti ratio in terms of both the particle size and the stoichiometry of the product. Variation in the quantity of Cu in the reactant mixture from 10 to 50 wt% Cu, enables the size of the TiC_x particles to be varied in the approximate range 20 to $0.5\ \mu\text{m}$.

Incorporation of the master alloy into molten copper was possible when the C/Ti ratio in the products was below approximately 0.73. When this occurred, the master alloy dispersed to produce a fairly even distribution of isolated particles. The wetting behaviour associated with both particle formation during SHS and incorporation and dispersion into molten Cu, agreed well with contact angle data in the literature.

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