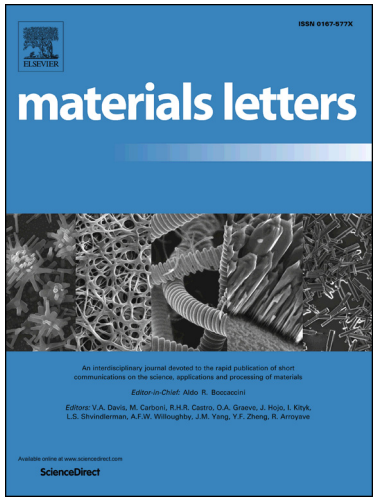

Formation of TiC-Cu nanocomposites by a reaction between $Ti_{25}Cu_{75}$ melt-spun alloy and carbon

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PII: S0167-577X(18)31566-0
DOI: https://doi.org/10.1016/j.matlet.2018.10.002
Reference: MLBLUE 25028

To appear in: *Materials Letters*

Received Date: 24 September 2018
Revised Date: 30 September 2018
Accepted Date: 1 October 2018

Please cite this article as: D.V. Dudina, M.A. Korchagin, A.I. Gavrilov, N.V. Bulina, I.S. Batraev, M.A. Esikov, K. Georgarakis, H. Kato, Formation of TiC-Cu nanocomposites by a reaction between $Ti_{25}Cu_{75}$ melt-spun alloy and carbon, *Materials Letters* (2018), doi: https://doi.org/10.1016/j.matlet.2018.10.002

Materials Letters, Volume 235, 15 January 2019, Pages 104-106
DOI:10.1016/j.matlet.2018.10.002

Formation of TiC-Cu nanocomposites by a reaction between $Ti_{25}Cu_{75}$ melt-spun alloy and carbon

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Abstract

In this work, $Ti_{25}Cu_{75}$ melt-spun partially amorphous alloy was used as a source of Ti and Cu to synthesize in-situ TiC-Cu nanocomposites. The reaction between the alloy and carbon started during ball milling and continued during Spark Plasma Sintering. At the same time, during ball milling, the alloy experienced phase transformations: crystallization of the amorphous phase was followed by decomposition of $TiCu_3$. Copper crystallites formed during the alloy transformations were the reason for the presence of copper regions 0.5-1 μm in size free from TiC nanoparticles in the sintered composites. The Ti-Cu intermetallics transformed into non-agglomerated TiC 10-20 nm in size distributed in the copper matrix. The hardness of the synthesized TiC-Cu nanocomposites exceeded that of composites obtained by conventional sintering of ball-milled Ti-C-Cu powders.

Keywords: nanoparticles; sintering; metals and alloys; microstructure.

Introduction

Metal matrix composites with nanoparticulate reinforcements attract a lot of attention due to possibilities of reaching strengthening by several mechanisms operating simultaneously [1]. The in-situ synthesis of ceramic nanoparticles in metallic matrices has been attempted in a large number of studies and is considered as a promising approach ensuring small size of inclusions [2]. When the metal to form a matrix and the metal to form a ceramic phase form an alloy, a ceramic particle-reinforced composite can be synthesized by creating conditions for the alloy to interact with an external non-metallic reagent. Recently, interaction of alloys with another metal has been used to induce dealloying via liquid/solid [3] or solid/solid [4] processes. The interaction of a metallic alloy with non-metallic reagent bears similarities with dealloying, as it leads to phase changes and disappearance of the alloy structure. In this work, a partially

amorphous $Ti_{25}Cu_{75}$ alloy was used as a precursor containing both the matrix metal and the reactant to participate in the formation of ceramic inclusions via a reactive processing. This work was aimed at tracking the phase and structural evolution of the $Ti_{25}Cu_{75}$+C system during transformations leading to the thermodynamically stable TiC and Cu phases.

Materials and Methods

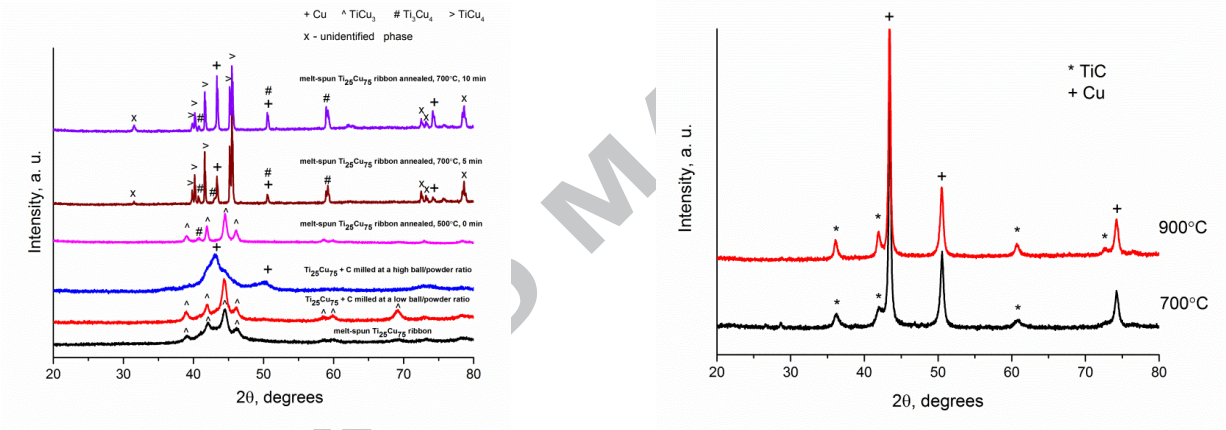
Titanium and copper (99.99%) were arc-melted in an argon atmosphere to prepare the master alloy. $Ti_{25}Cu_{75}$ ribbons were produced from the master alloy ingots by rapid quenching using the single roller melt-spinning technique. The ribbons were cut into pieces and milled together carbon (carbon black, 95% purity) in a high-energy planetary ball mill (milling time 5 min; composition of the mixture $Ti_{25}Cu_{75}$+25C). The ball/powder weight ratio used for the synthesis of composites was 180:5; a lower ratio of 180:10 was used for revealing the sequence of transformations during milling. Consolidation of the mixtures was carried out using a Spark Plasma Sintering (SPS) Labox 1575 apparatus (SINTER LAND Inc., Japan). The powders were sintered at 700, 800 and 900 °C. The samples were held at the maximum temperature for 3 min. A uniaxial pressure of 40 MPa was applied. For comparative purposes, pieces of the ribbons were annealed in the SPS chamber without applying any pressure at 500 and 700 °C. The heating rate in all SPS experiments was 70 °C min^{-1}.The phase composition of the samples was investigated by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with Cu Kα radiation. The ICDD PDF-4+ database was used for conducting the phase analysis. The microstructure of the sintered compacts was studied by Scanning Electron Microscopy (SEM) using a Hitachi TM-1000 Tabletop microscope (Japan). The fine structure of the sample was observed

by Transmission Electron Microscopy (TEM) using JEM-2000EX2 (JEOL) and EM-002B (TOPCON) microscopes working at 200 kV. Ion milling was used to prepare the samples of the sintered materials for TEM observations. In order to study the fine structure of TiC, Cu was selectively dissolved in concentrated HNO_3. Vickers hardness of the composites was measured using a Dura Scan 50 hardness testing machine with a load of 0.05 kg.

Results and Discussion

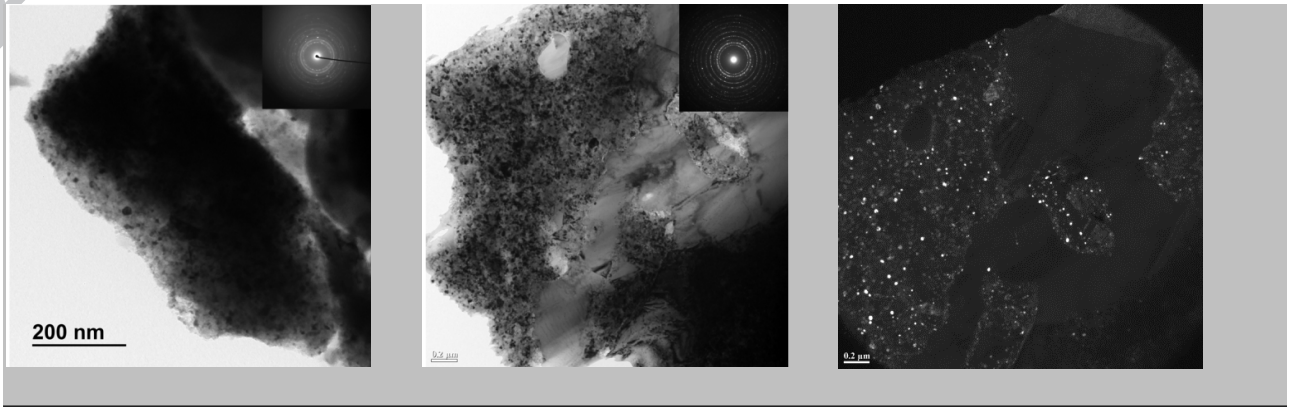
The melt-spun alloy is partially amorphous and contains nanocrystalline $TiCu_3$ (PDF card 00-025-316) intermetallic (Fig. 1(a)). During ball milling, metallic materials experience severe plastic deformation. Under these conditions, phase transformations in alloys can be expected [5-7], including decomposition of crystalline phases and crystallization of amorphous alloys. Indeed, during milling, the amorphous phase of the $Ti_{25}Cu_{75}$ alloy crystallized first and then decomposition of the alloy and its interaction with carbon started (Fig. 1 (a)) such that TiC, Cu and Ti_3Cu_4 phases formed (PDF cards 00-032-1383, 00-004-836, 00-018-460, respectively), as was confirmed by indexing the selected-area electron diffraction patterns (SAEDP) of the ball-milled powder (Fig. 2 (a)). Upon fast annealing, the same sequence of transformations occurred in the alloy: crystallization was followed by decomposition of $TiCu_3$ into Ti_3Cu_4, $TiCu_4$ (PDF card 00-020-370) and Cu. The presence of copper in the $Ti_{25}Cu_{75}$ alloy of non-equilibrium structure obtained in the course of fast crystallization agrees with results reported in ref. [8]. The reaction between the alloy and carbon continued during Spark Plasma Sintering, as was indicated by the results of XRD and TEM analyses (Fig. 1 (b), Fig. 2 (b-c)). Upon interaction with carbon, grains of Ti-Cu intermetallics transformed into composite areas consisting of non-agglomerated TiC 10-20 nm in size, as can be seen in

the bright- and dark-field (BF and DF) TEM images (Fig. 2 (b-c))), and the copper matrix, the other product of Ti_xCu_y+xC=xTiC+yCu reactions. Copper crystallites formed during the alloy transformations appear to be the reason for the presence of copper regions 0.5-1 μm in size free from TiC particles in the sintered composites (Fig. 2 (c)). The SEM microstructure of the sintered TiC-Cu composites is shown in Fig. 3 (a-b). With increasing sintering temperature, the material becomes denser, pieces of ribbons not full ground (bright particles) filling the pores between the composite agglomerates (including pores at triple junctions).



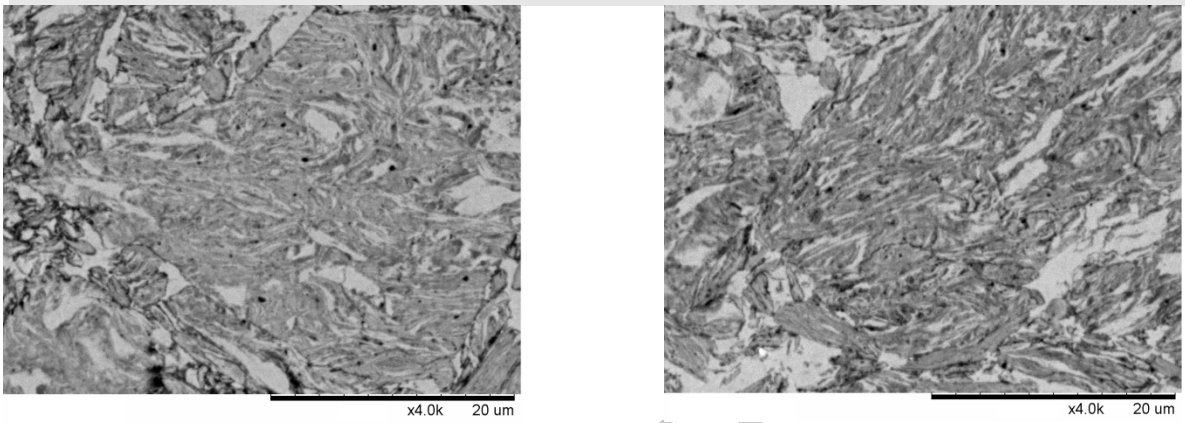
a b

Fig. 1. XRD patterns of (a) melt-spun $Ti_{25}Cu_{75}$ alloy ribbons, powders obtained by ball milling of the ribbons with carbon, and annealed ribbons (the holding time at the maximum temperature is given); (b) sintered TiC-Cu nanocomposites.



a b c

Fig. 2. TEM BF image/SAEDP of the powder obtained by ball milling of the ribbons with carbon (a), TEM BF/SAEDP (b) and DF in TiC (111) reflection (c) images of the TiC-Cu composite sintered at 900ºC.



a b

Fig. 3. Cross-sections of the sintered TiC-Cu nanocomposites: sintering at 700 ºC (a), 900 ºC (b), SEM images in the back-scattered electron mode.

After dissolution of copper from the sintered TiC-Cu nanocomposites in HNO_3, a TiC nanopowder was obtained, and its structure was analyzed by XRD and TEM (Fig. 4). No micrometer-sized TiC crystals were detected after dissolution, which indicated that a nano-sized TiC was a product of the interaction of the alloy with carbon.

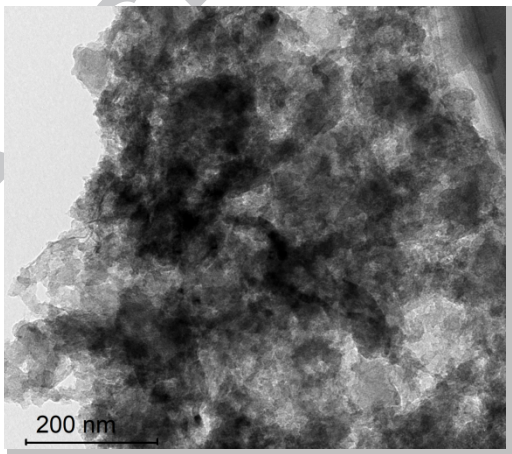


Fig. 4. TEM image of the TiC nanopowder obtained after copper has been selectively dissolved

from the TiC-Cu nanocomposite sintered at 900 ºC. The phase composition of the product – single phase TiC – was confirmed by XRD.

The relative density of the composites sintered at 700, 800 and 900 ºC is 85.0, 88.0 and 95.2%, respectively, while their Vickers hardness is 320±70, 310±70 and 440±30 HV, respectively. The synthesized nanocomposites exhibited high hardness exceeding that of composites of the same composition obtained by conventional sintering of Ti-C-Cu ball-milled powder mixtures (285 HV) [9]. Consequently, the presence of copper grains 0.5-1 μm in size free from TiC particles was not detrimental for the overall hardness of the composites.

We have found that solid-state processing of the TiC-Cu composites and their fast consolidation are crucial for maintaining their nanocomposite structure. When the alloy was heated up to 900 ºC in the SPS die and melted in contact with carbon, TiC crystals grew to sizes of 3-5 μm within 3 min of the holding time.

Conclusions

The phase and structural transformation during the interaction of the melt-spun $Ti_{25}Cu_{75}$ partially amorphous alloy with carbon have been elucidated. Ball milling of the alloy with carbon resulted in the formation of TiC, Cu and Ti_3Cu_4 phases in the mixture. Nearly fully dense TiC-Cu composites were obtained by SPS at 900 ºC. The TiC nanoparticles were distributed in the copper matrix; some Cu grains remained free from TiC particles. The use of an alloy instead of free metallic titanium allowed synthesizing very fine particles of TiC (10-20 nm). This work has shown that transformations in the alloy comprising both the matrix and the ceramic-forming element influence the structural features of the resultant composite obtained via the solid-state processing.

Acknowledgements

This research was funded by the Ministry of Science and Higher Education of the Russian Federation (project AAAA-A17-117030310277-6). Dina V. Dudina acknowledges support by the Cooperative Research and Development Center for Advanced Materials during her stay at the Institute for Materials Research, Tohoku University, as a visiting associate professor (July-August 2018). The authors are grateful to Mr. Shun Ito, Tohoku University, for his help in conducting TEM investigations and Prof. Boris B. Bokhonov, ISSCM SB RAS, for valuable discussions.

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Highlights

- $Ti_{25}Cu_{75}$ alloy was as a source of Ti and Cu to synthesize TiC-Cu nanocomposites
- During milling, the alloy experienced crystallization and decomposition
- In sintered composites, there were Cu regions 0.5-1 μm in size free from TiC
- Ti-Cu intermetallics transformed into non-agglomerated TiC 10-20 nm in size
- Hardness of nanocomposites exceeded that of conventional TiC-Cu composites

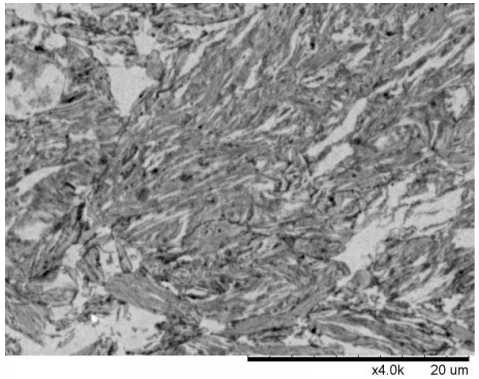
Graphical Abstract

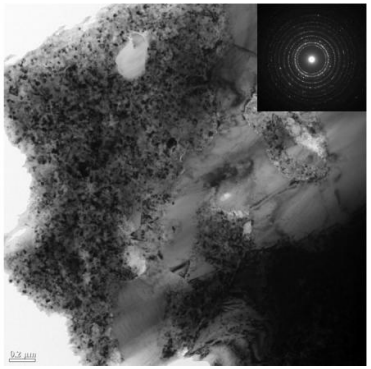
Ball milling, SPS

$Ti_{25}Cu_{75}$ + C → TiC + Cu

partially amorphous alloy

nano





Ball milling: ***partial reaction with carbon, alloy crystallization/decomposition***

SPS: ***completion of the reaction with carbon***