Association of Metallurgical Engineers of Serbia
AMES

Scientific paper
UDC: 669.35'295.018.9

HARDENING MECHANISMS IN Cu-Ti-TiB$_2$ COMPOSITES

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Received 15.09.2009
Accepted 28.09.2009.

Abstract

The multiple hardening mechanisms of a copper matrix have been presented and discussed. The gas atomized Cu-0.6 wt.%Ti-2.5 wt.%TiB$_2$ (Cu-Ti-TiB$_2$) powders have been used as starting materials. Dispersoid particles TiB$_2$ were formed *in situ* in the copper matrix during gas atomization. The powders have been consolidated by hot-isostatic pressing (HIP). Optical microscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) analysis were performed for microstructural characterization of powders and composite compacts. High strenthening of Cu-Ti-TiB$_2$ composite achieved by aging is a consequence of the simultaneous influence of the following factors: the development of modulated structure with metastable Cu$_4$Ti$_{(m)}$ particles and *in situ* formed TiB$_2$ dispersoid particles.

Key words: Cu-Ti-TiB$_2$, dispersoid hardening, precipitation and spinodal hardening, structure, microhardness

Introduction

Copper matrix composites have a wide range of applications because of the combination of high mechanical strength and electrical and thermal conductivity. To improve the interfacial compatibility and avoid serious interfacial reaction various new processing techniques are being used to fabricate ceramic particle-reinforced metal matrix composites (MMC**s**) [1-5]. The basic principle of this technique is that the fine and thermodynamically stable ceramic phases are formed *in situ* by exothermal reaction between elements or between element and intermetallic compound within a metal matrix. The formation of reinforcing particles as a result of reaction processes between structural components occurs in solid or liquid state [6]. The *in situ* composites exhibit improved mechanical strength, hardness as well as enhanced wear resistance [7].

The titanium diboride (TiB$_2$) particles are nowadays increasingly used for copper matrix strengthening. The TiB$_2$ is well known for its high stiffness, hardness and high

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mechanical strength. Furthermore, in contrast to most ceramics it is electrical and thermal conductive [8]. This suggests that TiB_2 is a potential reinforcing material for copper and its alloys in cases where high electrical conductivity is important. *In situ* formation of these particles in copper matrix, or copper alloys, is most frequently conducted in liquid state by spray forming process [9], reaction of B_2O_3, carbon and titanium in Cu-Ti melt [8], or gas atomization of Cu-Ti and Cu-B melt [10]. In this case, the size of formed TiB_2 particles is very small and it measures in nanometres.

The aim of the present work includes the strengthening of a copper alloy matrix by using powder metallurgy (PM) techniques, whereas a special attention was paid to a choice of alloying elements. Experimental methods for dispersoids formation were applied as well as analysis of their single or combined effects on the microhardness of obtained composite material at room and elevated temperatures.

Experimental

In the first step the master alloys were prepared. The starting material consisted of titanium chips and electrolytic copper mixed with amorphous boron as green samples. Cu-4 wt.%Ti and Cu-1.2 wt.%B alloys were separately vacuum induction melted at 1100°C, for 10 min. The heating and cooling rates during melting were 100 and 200 $Kmin^{-1}$, respectively, and casting in a copper mould was performed in an argon atmosphere. In the following procedure the gas atomization was applied in order to obtain powder particles with desired chemical composition. The master alloys were heated at a rate of 200 $Kmin^{-1}$. Atomization started at 1400°C and the homogenization time was 5 min. The argon pressure used was 3 MPa and the cooling rate of droplets was in the range from 10^3 to 10^6 Ks^{-1} [11].

Characterization of atomized powders included chemical analysis by means of atomic emission spectrometry, light and transmission electron microscope (TEM) examination, X-ray diffraction (XRD) analysis, sieving and microhardness measurements.

The atomized powders were consolidated by hot-isostatic pressing (HIP). The HIP-ing test tube was made of the thin-sided copper tube, 10 mm in diameter and 200 mm in length. Tube walls were 0.8 mm thick. At 40 mm of the tube length, tube diameter was reduced to 6 mm. Vacuuming of the tube, previously heated for 30 min at 580ºC, was conducted at 100ºC for 60 min. When vacuuming was completed tube was welded using the Cu-Ni electrode with the melting point in the temperature interval between 830ºC and 920ºC. HIP-ing was performed at 750ºC for 10 min in the argon protective atmosphere with 200 MPa maximal applied pressure, followed by the argon quenching to room temperature. Small specimens cut from compacts were solution treated under vacuum at 900°C for 1h, and immediately water quenched. These specimens were aged from 300 to 600°C in steps of 50°C for different times. All samples were metalographically prepared in the same manner, and KLEMM III solution (100 ml distilled water, 11 ml saturated $Na_2S_2O_5$, 40 g potassium disulfite) was used for etching.

The light microscope and transmission electron microscope (TEM) were used for the microstructural characterization of compacts. Cylindrical discs with thickness less than 100 μm were thinned by a double jet method with the same solution used for etching. The density of examined materials was determined using the standard

Archimedes method in xylene. The Vickers microhardness tester was utilized to determine microhardness of compacts, applying the 15 g load.

Results and discussion

Since it is well known that the melting temperature of the binary copper-based alloys is near 1000°C [12,13], this temperature was the basic parameter for the preparation of master alloys (Table 1). As-cast microstructure of master alloys is illustrated in Fig. 1. The presence of coarse equilibrium Cu_4Ti particles which are uniformly distributed in the Cu-Ti matrix (solid solution) is more or less unavoidable due to the low cooling rate during solidification.

Table 1. Basic characteristics of as cast master alloys used for composite production.

Composition of master alloys (wt.%)	Casting temperature (°C)	Holding duration at casting temperature (min)	Composition of as-cast material (wt. %)	Microhardness (HV)
Cu-4Ti	1100	10	Cu-3.8Ti	190
Cu-1.4B	1100	10	Cu-1.2B	117

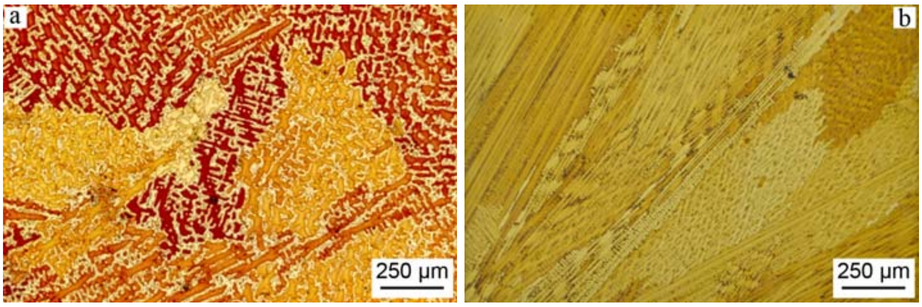

Figure 1. Light microscopy. Microstructure of as cast (a) Cu-3.8Ti (wt.%) and (b) Cu-1.2B (wt.%) master alloys

Using the as-cast master alloys the composite powder particles were produced by gas atomization according to the previously described procedure. The nominal chemical composition of powders obtained by gas atomization is Cu-0.6Ti-2.5TiB_2 (wt.%) and in the further text this material will be referred as Cu-Ti-TiB_2. The diameter of particles, d, was in the range $50 < d < 500$ μm. After completing the gas atomization, microstructural characterization of the obtained powder was undertaken.

The quantitative investigation of atomized Cu-Ti-TiB_2 powder particles obtained by XRD analysis and their microhardness as a function of their size are given in Table 2. The alloy particles are spherical in shape with homogenous structure and characteristic dendrite morphology. The homogenous distribution of TiB_2 particles in the microstructure could not be observed using light microscopy (Fig. 2), but its presence reflects to the michardness values. Namely, comparing the results of Tables 1 and 2 it is evident that the microhardness of gas atomized particles is higher than microhardness of as-cast master alloys.

Although the XRD analysis of atomized powders showed only the presence of TiB_2 phase in the copper matrix (Fig. 3), using an additional chemical analysis the presence of certain amount of titanium was identified (see Table 2), whereas the amount of boron may be regarded as negligible.

Table 2. Characteristics of Cu-Ti-B atomized powders (d-powder particles diameter)

Composition of as-cast master alloys (wt.%)	Microhardness (HV)				
	Ti	TiB_2	d<80μm	80<d<150μm	200 <d<500 μm
Cu-3.8Ti+Cu-1.2B	0.6	2.5	230	227	229

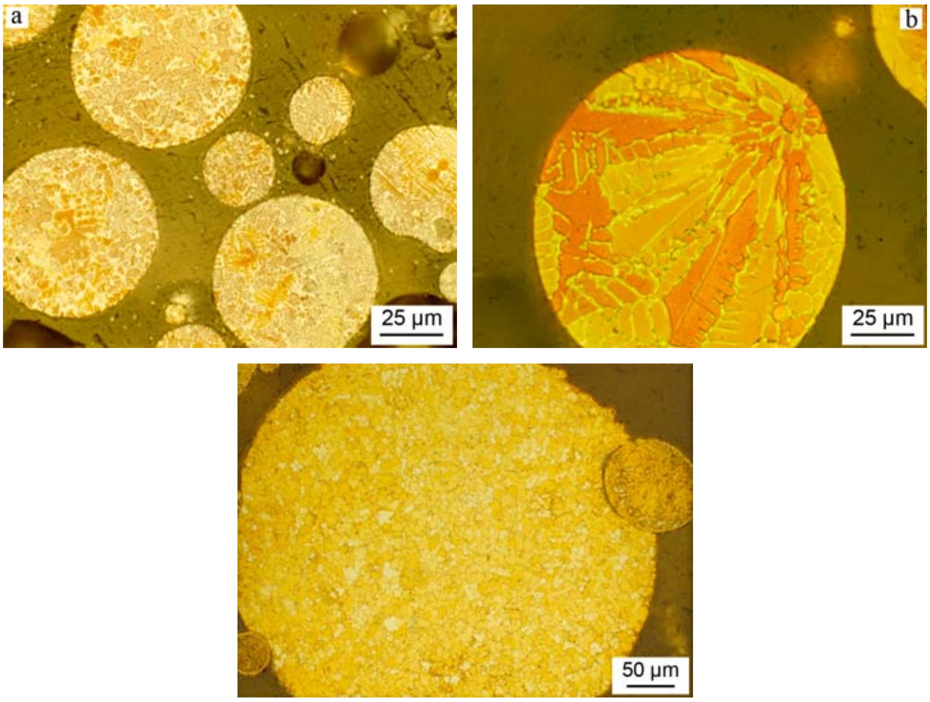

Figure 2. Light microscopy. Microstructure of different as-atomized Cu-0.6Ti-2.5TiB_2 (wt.%) alloy powder sieving fractions: (a) d < 80 µm, (b) 80 µm < d <150 µm and (c) 200 µm < d < 500 µm.

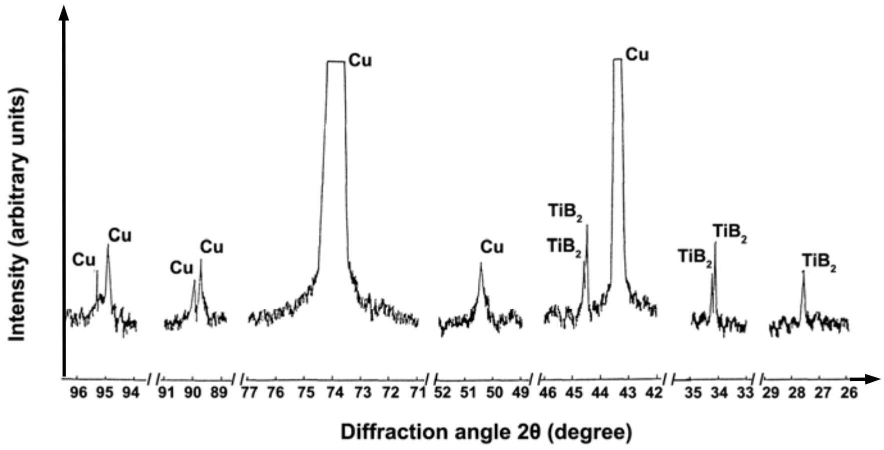

Figure 3. XRD pattern of the Cu-TiB$_2$ powder.

Diffusivities of titanium and boron in copper were calculated (Fig. 4) using the diffusion coefficients values for titanium and boron in copper at 800°C and 900°C reported in the literature [14], and an extrapolation of the literature data. It was shown that the convergence of the obtained results with the increase in temperature is a result of a lattice expansion [14]. The increase in the diffusion coefficients with increasing temperature points out that small concentrations of titanium and boron require longer times for formation of TiB$_2$ at lower temperatures, whereas the formation of dispersoids is very rapid (*in-situ*) during the atomization process (1400°C).

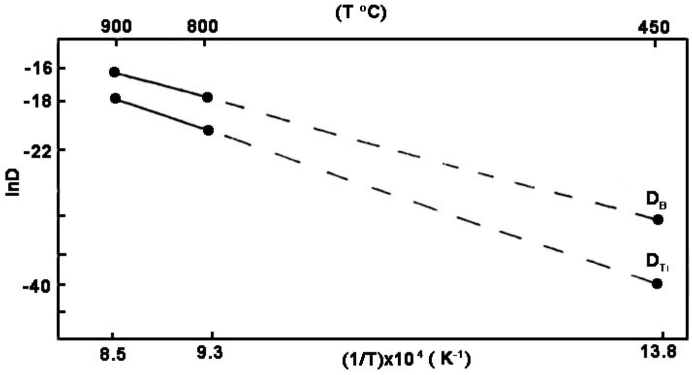

Figure 4. Calculated diffusion coefficients for titanium and boron in copper.

An increase of microhardness in the as-atomized powders should be explained by homogeneously distribution of very hard TiB$_2$ particles in the primary matrix (Table 2). The microhardness presented in Table 2 reveals the surprising fact that the decrease in powder particle size does not affect the microhardness values. From the present results it may be assumed that the distribution of dispersoids in the powder structure has a much greater influence on the powder particle microhardness than the particle size itself. This was the main reason why HIP-ing procedure was chosen as the powder compacting method in this study.

It is well known that compaction of spherical particles of different size results in lower compact porosity. Namely, during the compacting treatment smaller powder particles will fill in the empty spaces between larger neighbouring spherical particles [15]. In this way the powder apparent density can reach even 60% of the theoretical material density facilitating easier powder compaction. The powder mixture consisting of spherical particles of different size was used for compaction, without any concern that this may bring about the variation in the compact microhardness. This attitude was supported by the results presented in Table 2 clearly showing that the microhardness values are practically independent on powder fractions.

An investigation of Cu-Ti-TiB_2 composite produced by gas atomization and HIP-ing was a challenge because of the scarce literature data available. This is the reason why the main concern was directed to compaction of a composite with fine and hard dispersoid particles to near theoretical density with preserved the rapidly solidified microstructure.

Nearly nonporous compacts of Cu-Ti-TiB_2 composite were produced (see Fig. 5 and Table 3) by HIP-ing for 10 min at 750°C and applied argon pressure of 200 MPa. After HIP-ing, the compacts were rapidly quenched to room temperature.

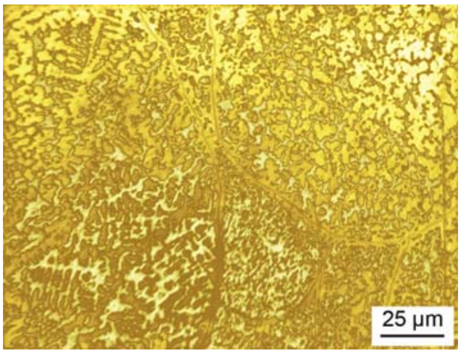

Figure 5. Light microscopy. Microstructure of HIP-ed Cu-Ti-TiB_2 composite compact

Table 3. HIP-ing parameters and properties of the obtained Cu-Ti-TiB_2 composite

Composition of as HIP-ed materials (wt.%)	Tempera -ture (°C)	Time (min)	Pressure (MPa)	Density (g/cm^{-3})	Open porosity (%)	Micro-hardness (HV)
Cu-0.6Ti-2.5TiB_2	750	10	200	8.43	0.05	210

During HIP-ing the densification occurs as a result of powder particles deformation near the surface of their contacts, power law creep and diffusion. The overall behaviour of materials under the influence of applied pressure and high temperature is very complex because all of the above mentioned densification mechanisms depend on the particle size, processing parameters and other material properties in a different way.

From Fig. 5 and the data presented in Table 3 one can conclude that parameters selected for the HIP-ing process provided sufficient atomic mobility, which is necessary for the high pressure sintering completion and elimination of porosity. At 750°C the material deformation induced by thermally activated dislocation movements is possible, and therefore time dependent densification mechanisms (above all, power law creep and diffusion) were significant in relation to the overall densification rate. It can also be noticed that the microstructure degradation and microhardness change of produced composite compacts did not occur.

Contrary to the rapidly solidified powders where only the presence of TiB_2 dispersoids was identified, in the TEM micrograph of HIP-ed compacts coarse particles of Cu_4Ti precipitates can also be distinguished (Fig. 6). This microstructure is a consequence of lower cooling rates after sintering, compared to cooling rates after atomization. The presence of Cu_4Ti precipitates causes a decrease of microhardness values (see Table 3). A uniform distribution of *in-situ* formed TiB_2 dispersoids in the metal matrix may be also observed in Fig. 6. This distribution of dispersoids which was achieved during the atomization processing was retained during the HIP-ing.

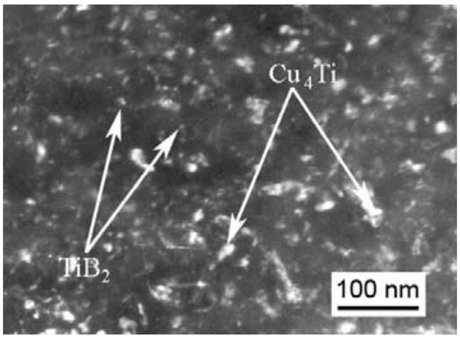

Figure 6. TEM. TiB_2 particles and Cu_4Ti equilibrium precipitates in the copper matrix.

The behaviour of HIP-ed composite compacts after solution treatment and aging is typical for alloys strengthened by spinodal decomposition [16-18]. The maximum appearing after aging at 350°C for 5 min (Fig. 7) is most likely due to precipitation of TiB_2 particles from the supersaturated solid solution and the presence of a modulated structure**.** The spinodal decomposition involves the continuous transformation of a disordered to an ordered $Cu_4Ti_{(m)}$ phase, which is in equilibrium with the fcc copper solid solution. Metastable $Cu_4Ti_{(m)}$ was formed is a result of modulation in structure and this phase should be distinguished from the equilibrium Cu_4Ti phase. The hardening effect in the early stage is due to effect**s** of internal stresses, the self-energy gradient, and chemical hardening. The motion of combined dislocations in the periodic deformation field is strongly dependent on the statistical configuration of obstacles present in the system. The structural ordering in the titanium rich regions causes the decrease or even disappearance of antiphase boundaries resulting from lattice misfit. In this case the easier dislocation motion through such an ordered structure was enabled leading to a hardness decrease (Fig. 7, aging between 5 and 15 min). However, with prolonged time of aging the hardening effect is due to the intensified coherent precipitation of $Cu_4Ti_{(m)}$ particles extending antiphase boundary formation [19].

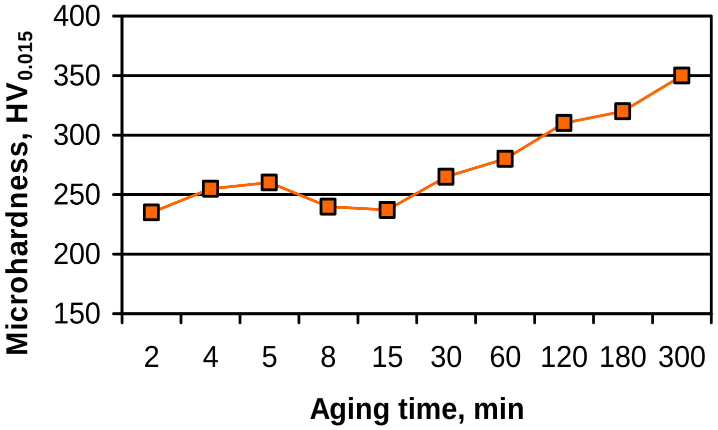

Figure 7. Microhardness of HIP-ed Cu-Ti-TiB_2 composite aged at 350°C vs. time of aging.

Compared to a binary Cu-Ti alloy with the similar titanium content (0.58 wt.% Ti [11]), the Cu-Ti-TiB_2 composite yields much higher microhardness values, owing to the presence of primary TiB_2 dispersions formed *in situ* during atomization. Thus, the multiple hardening mechanisms occur during precipitation from the supersaturated Cu-Ti-TiB_2 solid solution.

Except of increased starting microhardness value (which remains nearly unchanged at high annealing temperatures) and strengthening intensity after aging, the presence of finely distributed TiB_2 dispersoids shows a positive effect on the microhardness stability of matrix on higher precipitation temperatures (Fig. 8).

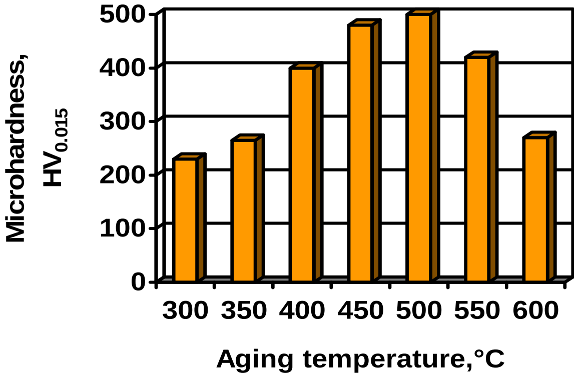

Figure 8. Microhardness of HIP-ed Cu-Ti-TiB_2 composite v.s. aging temperature.

Higher precipitation temperatures (e.g. 550 and 600°C) lead to a decrease of hardness because of coarsening of precipitates. However, the hardness decrease of the Cu-Ti-TiB_2 composite is smaller than that of the other alloys of the same type [10,20]. This behaviour can be explained by a retarding influence of the TiB_2 particles on the coarsening of the $Cu_4Ti_{(m)}$ phase.

Conclusions

The following conclusions can be drawn from the present study:

1. Successful preparation of the *in situ* formed TiB_2 dispersoids in copper matrix powders was achieved via argon atomization at 1400 ^{0}C.
2. Rapidly solidified Cu-Ti-TiB_2 powders are characterized by the presence of finely dispersed TiB_2 particles which are the main reason for the high microhardness values of Cu-Ti-TiB_2 powders.
3. Non-porous compacts of Cu-Ti-TiB_2 composite with homogenous microstructure and high microhardness values were obtained during 10 min of HIP-ing at 750°C under applied argon pressure of 200 MPa. Starting microstructure morphology of the rapidly solidified powder particles was not disturbed after HIP-ing, whereas a uniform distribution of the TiB_2 particles in the copper matrix was attained.
4. High strengthening of Cu-Ti-TiB_2 composite compacts was achieved by aging as a consequence of the simultaneous influence of the following factors: the development of modulated structure with metastable $Cu_4Ti_{(m)}$ particles and *in situ* formed TiB_2 dispersoid particles.

Acknowledgments

This work was financially supported by the Ministry of Science and Technological Development of the Republic of Serbia through the Project No. 142027.

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