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Fabrication of copper-titanium powders prepared by mechanical alloying

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Mechanical alloying is an innovative method of fabricating bulk metallic glasses. Produced powders can be sintered by using one of the modern methods such as spark plasma sintering. Cu-based amorphous alloys have high strength, ductility, fracture toughness, fatigue strength and corrosion resistance. The aim of the present study is to fabricate, investigate and compare the structure, size and shape and microhardness of the $Cu_{50}Ti_{50}$ powders depending of the milling time. $Cu_{50}Ti_{50}$ powders are prepared by mechanical alloying. Mechanical allyoing is carried out in a high energy ball mill SPEX 8000. The structures of nanocrystalline and amorphous alloy powders are examined by X-ray diffraction. Chemical composition, particle size and shape of the powders are tested by scanning electron microscopy. Microhardness is measured by using Vickers hardness testing machine. The results demonstrated that amorphous Cu-Ti alloy can be prepared by mechanical alloying. The amorphous phase of $Cu_{50}Ti_{50}$ has occurred after 8 h of milling.

Keywords: Mechanical alloying, Nanocrystalline, Amorphous materials, Cu-Ti powders, X-ray diffraction, Scaning electron microscopy

The latest group of amorphous materials are materials based on the late transition metals (LTM), e. g., Fe, Co, Ni, Cu, Pd, Pt. The materials containing more than 50% copper and titanium were made in 2001, so there are modern materials. Fundamental properties of Cu-based amorphous alloys are: high strength, ductility, fracture toughness, fatigue strength and corrosion resistance in different aggresisive environments, including in acidic and salt solution, at ambient and elevated temperatures and in humid air. In comparison to other LTM-based alloys of Cu-based amorphous alloy are characterized by glass – forming ability: $d_{max} \geq 5$ mm (Pd; Pt >> Cu > Ni > Fe > Co), temperature interval of supercooled liquid: $\Delta T_x = 60$-90 K (Cu > Fe; Ni; Pd; Pt > Co), reduce glass transition temperature: $T_x/T_l \geq 0{,}60$ (Pd > Pt > Fe; Co; Ni; Cu), static mechanical strength ≥ 2000 MPa (Co > Fe > Ni > Cu > Pd > Pt), compressive ductility: $\varepsilon_f = 0.02$ with plastic strain (Cu; Ni > Pd; Pt; Fe > Co)[1,2]. Cu-based amorphous materials can be used as marine application[3], efficient catalysts[4,5], construction material (significant interest due to low cost), surgery instruments[3]. A typical method for preparation of amorphous Cu-Ti-based alloys is the pressure die casting method in form of rods and the rapid solidification from liquid phase on a copper wheel rotating in the form of ribbons. Dimensions of samples are only a few millimeters. Mechanical alloying (MA) is an innovative method of fabricating bulk metallic glasses. Mechanical alloying is definied as a high energy milling process during which particles are subjected to multiple cold welding, cracking and rewelding[6]. Mechanical alloying is utilized to prepare the following bulk materials: oxide dispersion strengthened materials, intermetallic, nanomaterials, composites, ceramics, polymers, amorphous, hydrogen storage and extended solid solutions[7]. The following amorphous Cu-Ti powders were prepared: $Cu_{45+x}Ti_{55-x}$ after 6 h milling[8] and $Cu_{64}Ti_{36}$ after 9 h milling[9]. Produced powders can be sintered by using one of the modern methods such as spark plasma sintering. This method only slightly changes the structure of amorphous powders, because current flow and temperature rise are momentary. Moreover, materials by larger size can be prepared with this method than by casting methods. Until now compacts of diameter 20 mm were prepared. Compacts sintered by spark plasma method are characterized by better mechanical properties than cast rods. Furthermore, these products demonstrate higher density than conventional sintered powders[10,11].

In this paper authors report fabrication and investigation of $Cu_{50}Ti_{50}$ powders prepared by mechanical alloying. The obtained amorphous powders

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are being sintered. The chemical composition of the Cu-Ti based alloy may be improved.

Experimental Procedure

Six samples (Table 1) with composition $Cu_{50}Ti_{50}$ were prepared using elemental powders of copper (99.5 % purity, < 325 mesh) and titanium (99.5 % purity, < 325 mesh). Each sample was prepared with 8 g properly weighed compound powders. Mass of elements were copper – 4.5629 g and titanium – 3.4371 g. Powder blend was weighed on an analytical high precision balance AS/X (four digits). Cr steel balls of 13 mm diameter were used. The weight ratio of balls to milled material was 5:1. The powder mixture together with Cr steel balls were placed in austenitic steel crucible under argon atmosphere within a glove bag.

Ball milling process was carried out in a vibratory mill type SPEX 8000 CertiPrep Mixer/Mill for six different milling times: 5 h, 6 h, 7 h, 8 h, 9 h and 10 h under argon atmosphere. The mill generated vibrations of the balls and the material inside the container[12,13]. At the first hour of milling 30 min breaks occurred every 15 min. In the next hours of mechanical alloying every 30 min milling were interrupted for 30 min break. The long break during milling did not allow too hot crucible and powders. Low temperature favors amorphization process.

Table 1—Identification of the specimens prepared to testing after different time of milling

Milling time (h)]	0	5	6	7	8	9	10
Number of sample	0	1	2	3	4	5	6

X-ray diffractometer X'Pert Pro Panalytical with Cu Kα radiation (λ=0.15418 nm) was used to study structure of fabricated powders. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 20° to 80° and 0.05° step. Program PCPDFWIN v. 2.1 was used in order to identify phases formed.

Particles size and shape of studied amorphous and nanocrystalline powders were characterized by using the scanning electron microscopy (SEM) SUPRA 35 ZEISS with magnification up to 100×.

Chemical characterization of a sample was analyzed by means of analytical technique – energy dispersive X-ray spectroscopy (EDS). EDS analyzer is part of the SEM. Energy dispersive X-ray analysis (EDS) was performed from area of selected particles after different milling times.

Microhardness of particles was measured by using Vickers hardness testing machine with automatic track measurement using image analysis FUTURE-TECH FM-ARS 9000. Microhardness measurements were made under load 0.97 N. In each of the prepared samples five particles were tested.

Results and Discussion

XRD analysis

The XRD patterns of the $Cu_{50}Ti_{50}$ powders after different six milling times (5 h, 6 h, 7 h, 8 h, 9 h and 10 h) with interval time 30 min were appeared in Figs 1-6. X-ray diffraction analysis has revealed that the samples after 8 h milling with 30 min interruptions was amorphous. In Fig. 4, the diffraction pattern shows a single broad diffraction halo with the 2θ range of 37º-48º from the amorphous phase only.

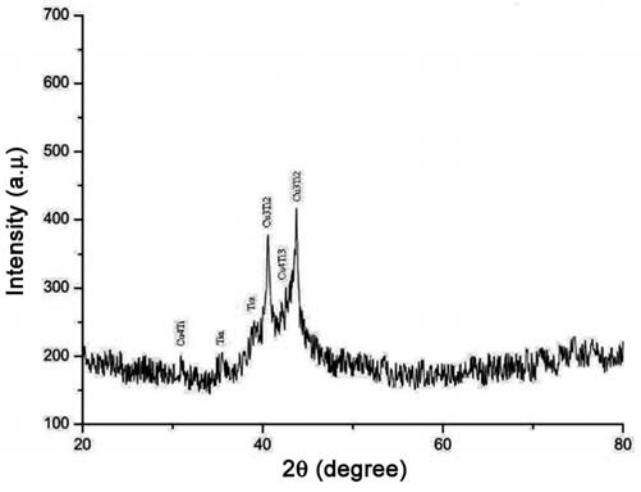

Fig. 1—X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 5 h of mechanical alloying

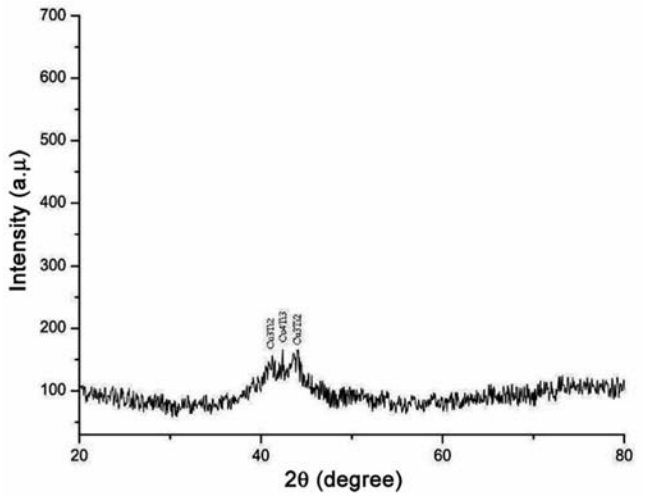

Fig. 2—X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 6 h of mechanical alloying

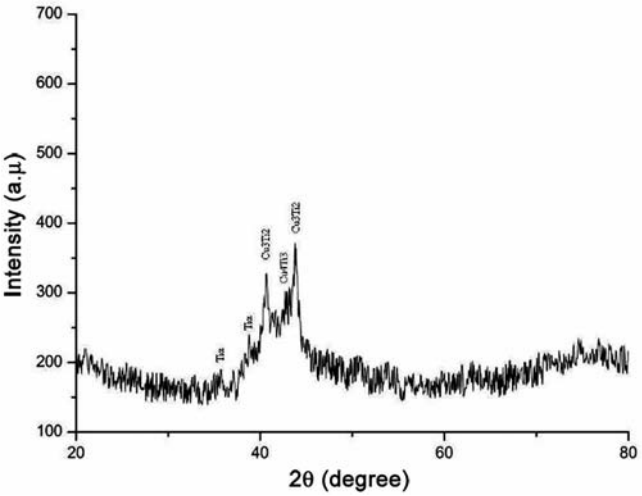

Fig. 3—X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 7 h of mechanical alloying

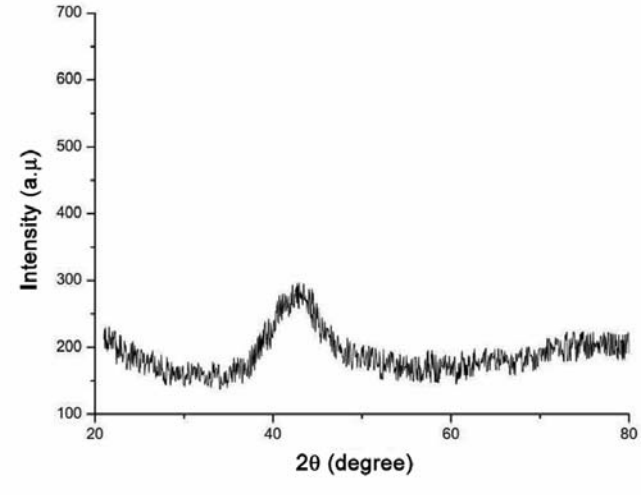

Fig. 4—X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 8 h of mechanical alloying

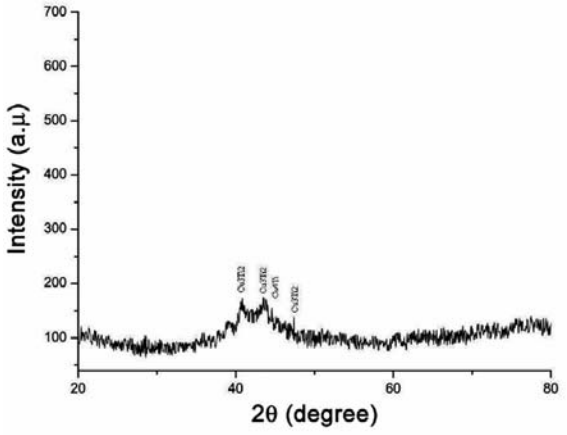

Fig. 5—X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 9 h of mechanical alloying

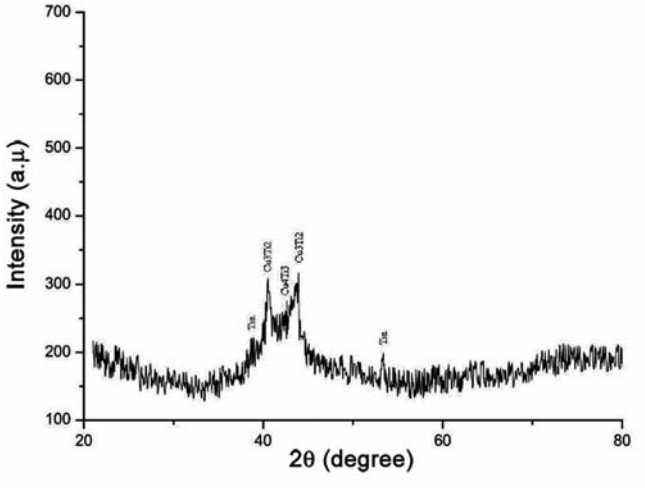

Fig. 6—X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 10 h of mechanical alloying

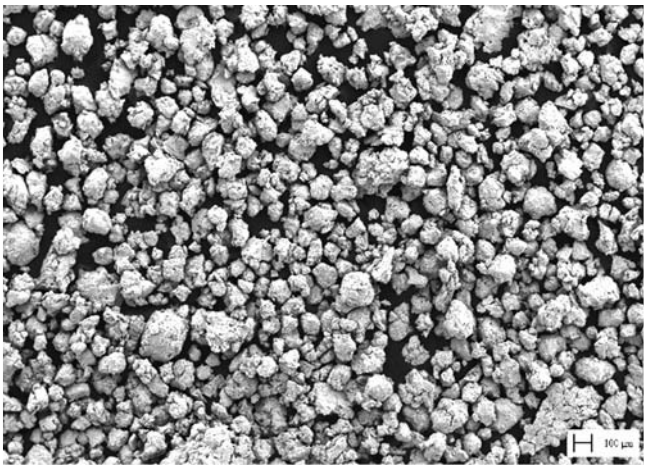

Fig. 7—Structure of powder $Cu_{50}Ti_{50}$ after 5 h of mechanical alloying, SEM images at 100 magnifications

Fig. 8—Structure of powder $Cu_{50}Ti_{50}$ after 6 h of mechanical alloying, SEM images at 100 magnifications

Al-Assiri and co-worker[8] received amorphous powders after a shorter time of mechanical alloying – after 6 h, than in earlier reported experiments[8] – after 8 h. The difference of time milling after which obtained an amorphous structure may result from several reasons. Details of cycle milling (milling time and interruption time) were not specified in the cited article. Certainly, Al-Assiri and co-worker[8] used less material – 4 g, and put it in the crucible of only two balls. The weight ratio of balls to milled material was 4.15:1 and in this paper 5:1. However, purity of starting elements were the same (99.5%). The maximum of the amorphous halo is around 43° in the present work and in the article of Al-Assiri *et al*.[8]

Remaining X-ray diffraction patterns were made the identification of phases. For identifying PCPDFWIN program v. 2.1 was used. In the test samples presence of the following phases were identified: Cu_3Ti_2, Tiα, Cu_4Ti, Cu_4Ti_3. Identified phases are the same as phases occurring in a two-component system Cu-Ti.

In the accompanying X-ray diffraction pattern showing that the structure of two-phase alloys – Cu-Ti easily alters under the influence of mechanical alloying. Therefore, mechanical alloying must be carried out very carefully.

Microstructure

Figures 7-12 represent the SEM micrographs of tested powders after different times of milling at 100× magnifications. Starting powders had size 325 mesh (44 μm). The increasing of particle size was observed after each mechanical alloying process. Average particle size of the powders is given Table 2. After five hours of mechanical alloying the particle size increased three times (from 44×44 μm to 112×123 μm),

Fig. 9—Structure of powder $Cu_{50}Ti_{50}$ after 7 h of mechanical alloying, SEM images at 100 magnifications

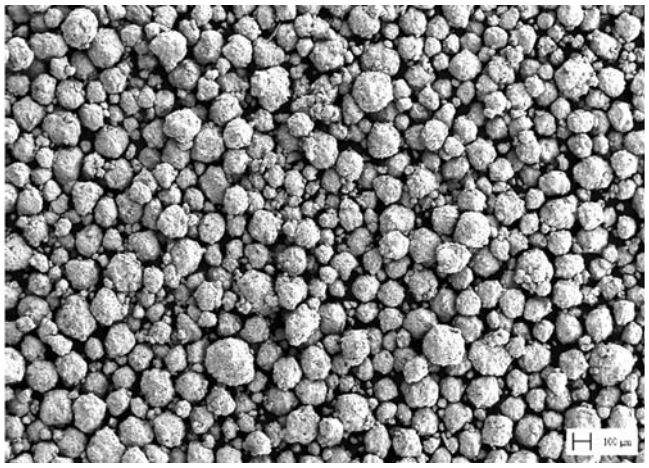

Fig. 10—Structure of powder $Cu_{50}Ti_{50}$ after 8 h of mechanical alloying, SEM images at 100 magnifications

Fig. 11—Structure of powder $Cu_{50}Ti_{50}$ after 9 h of mechanical alloying, SEM images at 100 magnifications

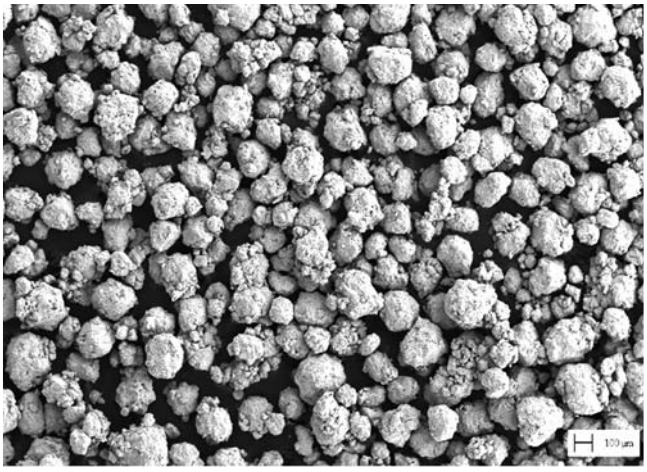

Fig. 12—Structure of powder $Cu_{50}Ti_{50}$ after 10 h of mechanical alloying, SEM images at 100 magnification

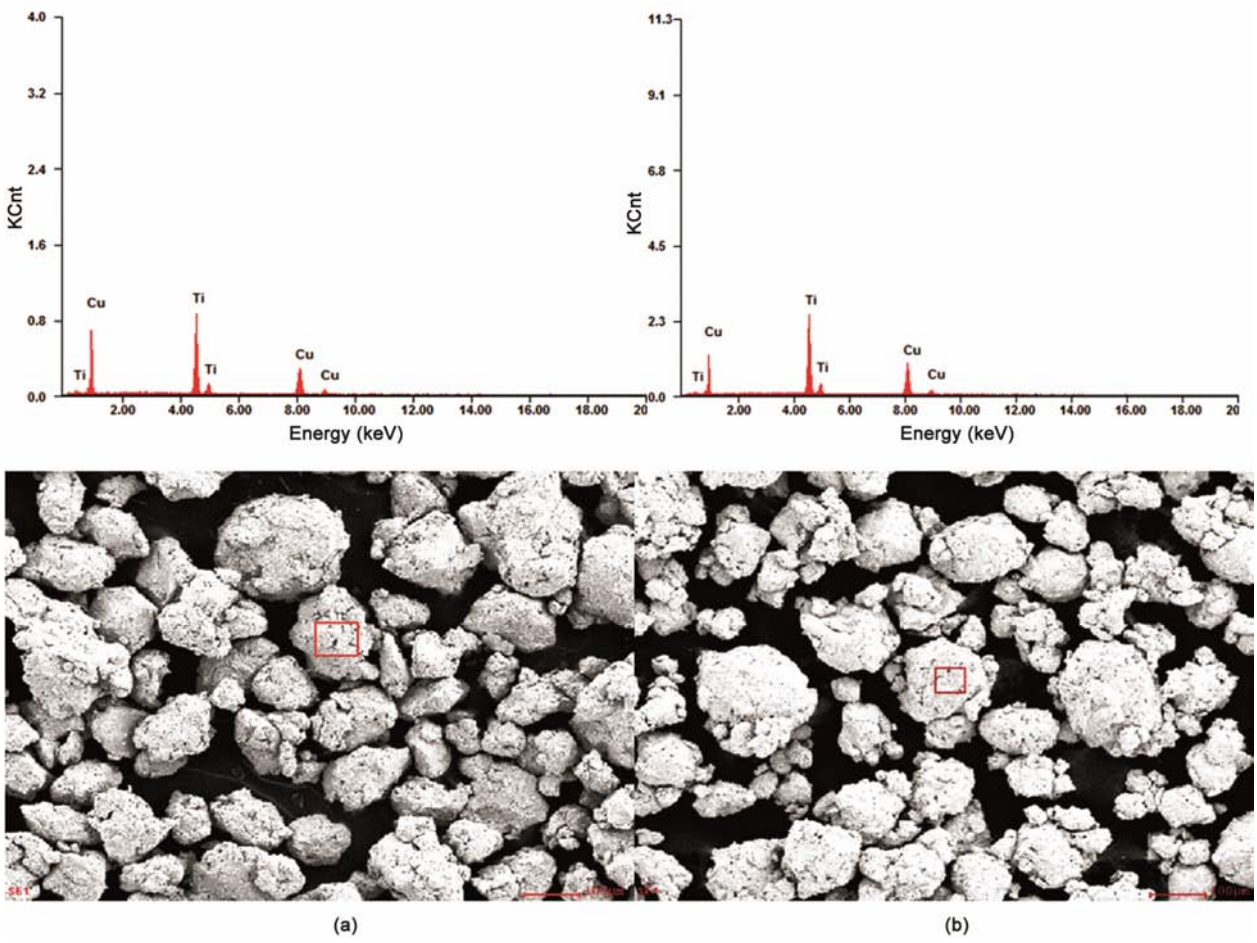

Fig. 13—SEM micrographs of $Cu_{50}Ti_{50}$ powders after mechanical alloying with 30 min interruption with marked area for which energy dispersive X-ray analysis (EDS) was performed (a) after 5 h mechanical alloying and (b) after 10 h mechanical alloying

Table 2—Results of chemical analysis from the powder surface and average particle size of the starting powders and after mechanical alloying

Sample	Element	At. (%)	Wt. (%)	Average particle size of the powders (μm)
0	Ti	50	43	44×44
	Cu	50	57	
1	Ti	50.67	43.64	112×123
	Cu	49.33	56.36	
2	Ti	49.15	42.15	160×165
	Cu	50.85	57.85	
3	Ti	48.72	41.73	140×154
	Cu	51.28	58.27	
4	Ti	49.41	42.40	158×166
	Cu	50.59	57.60	
5	Ti	48.96	42,11	175×165
	Cu	51.04	57,89	
6	Ti	48.85	41.86	192×173
	Cu	51.15	58.14	

and after ten hours of milling the particles increased many as five times (from 44×44 μm to 192×173 μm). In conclusion with increasing time of mechanical alloying the increased of particle size were observed.

In samples 1-3 were observed variety of particles (small and large), whereas powders in sample 4 and sample 5 were homogeneous (of similar size). The shape of the particles was very close to spherical. However, sample 6 shows the particles in the shape of agglomerates. Clearly seen in this picture are stuck together particles (large with small). Figure 13 presented microanalysis of $Cu_{50}Ti_{50}$ powders after 5 h milling and after 10 h with marked area. Energy dispersive X-ray analysis EDS showed existence of copper and titanium elements in studied sample. The chemical composition analysis was only a qualitative test and confirmed existing of main elements in alloy.

The amount of atomic share of copper and titanium depends on the time of milling. Table 2 gives the detailed results of the chemical analysis for every

Table 3—Results of measured microhardness samples after different time of milling

Sample	Measured microhardness of the grains (HV)	The average measured microhardness (HV)]
	412	
	438	
1	463	455.4
	485	
	479	
	412	
	405	
2	482	438.8
	452	
	443	
	446	
	431	
3	471	472
	518	
	494	
	528	
	557	
4	561	542
	539	
	525	
	528	
	549	
5	521	534.2
	532	
	541	
	523	
	533	
6	544	532.6
	527	
	536	

sample. In each of the particles were only basic components (Ti and Cu). The starting atomic percentage of Cu equals 50% and Ti 50%. The investigation result has shown that the obtained powder particles after alloying process have very similar atomic composition to initial one. The chemical composition of milled powders confirms the possibility of existence of the phases which were identified by the XRD analysis.

Microhardness

Microhardness measurement results of received powders are given in Table 3. In each of the powders sample prepared (different milling times) five particles were examined. The largest difference of microhardness of particles occurred in sample 1 (73 HV), sample 2 (77 HV) and sample 3 (87 HV). These results indicate a high heterogeneity of particles due to short milling time (5 h, 6 h and 7 h). After a longer time of milling the microhardness gradually became more homogeneous. The differences in microhardness of particles amounted for sample 4 (36 HV), Sample 5 (28 HV) and sample 6 (21 HV). The average microhardness change versus time of mechanical alloying is shown in Fig. 14.

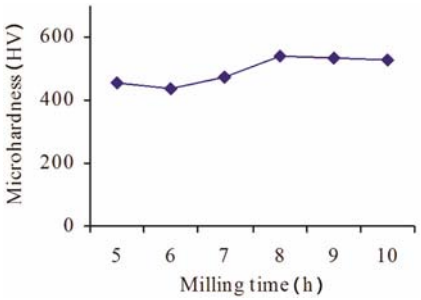

Fig. 14—Avarage microhardness changes versus time of mechanicall alloying

Conclusions

The following conclusion can be drawn from the investigations performed on the samples of the $Cu_{50}Ti_{50}$ powders:

Powder milling time has influence on the forming of structure, shape and size of particles and their microhardness.

The X-ray diffraction investigations have revealed that the studied $Cu_{50}Ti_{50}$ powders after 8 h mechanical alloying were amorphous.

Energy dispersive X-ray analysis EDX showed existence of copper and titanium elements in studied alloy, so samples did not undergo contamination and oxidation.

Scanning electron microscopy (SEM) demonstrated that with the increase of milling time increased the particle size of powders. After 10 h milling the particle size were over five times greater than the base elements.

The highest average microhardness (542 HV) revealed amorphous powders. The smallest variation in microhardness (21 HV) demonstrated the particles which were the longest milling (afret 10 h).

The success in preparation of the studied $Cu_{50}Ti_{50}$ amorphous alloy in form of the powders is important for the future progress in research and amorphous powders processing, e.g., spark plasma sintering, which will produce a larger than present dimensions of bulk amorphous samples.

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