

Amorphization and solid solution formation in Sn modified Cu-Ag alloys produced by ball milling

L. Lyubenova, T. Spassov*, M. Spassova

*Faculty of Chemistry, University of Sofia "St.Kl.Ohridski", 1 James Bourchier str.
1164 Sofia, Bulgaria*

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The present work aims at studying the influence of Sn on the microstructure of Cu-Ag-based supersaturated solid solutions with potential application for fabrication of nanoporous structures. Nanocrystalline $\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ ($x=3, 6, 10$) fcc solid solutions are synthesized by high-energy ball milling under protective Ar atmosphere and liquid heptane as antisticking agent. Milling for 8h leads to formation of solid solution with fine nanocrystalline microstructure ($<10\text{--}15$ nm) in $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$. On the contrary, for the ternary systems with lower Sn concentration ($x=3$ and 6) only 5h of milling are necessary for complete alloying. Partial amorphization is also detected for all Sn containing alloys. The lattice constant of the fcc solid solution in the ternary systems is larger than that of $\text{Cu}_{50}\text{Ag}_{50}$, but slightly depends on the Sn concentration in the composition range of 3–10 at.% Sn.

Keywords: Cu-Ag alloys, solid solution, nanocrystalline, ball milling.

INTRODUCTION

Cu–Ag alloys are considered to be attractive for fabrication of nanoporous Ag structures for practical applications [1, 2]. A controlled thickness nanoporous Ag with desired pore and ligament size could be obtained easily after selective electrochemical dissolution of well-mixed and homogenized Cu–Ag solid solutions with proper composition.

Although Cu and Ag satisfy two of the Hume-Rothery rules for common solid-state solubility, equilibrium solid solutions in the Cu–Ag system are practically non-existing and the size factor is apparently not enough to contribute for easy amorphization in this system. However, formation of non-equilibrium supersaturated fcc Cu–Ag solid solutions by applying a variety of preparation methods has been reported: rapid quenching from a melt [3], splat quenching [3, 4] vapor deposition [5], mechanical alloying [1, 6, 7], cold rolling [8]. The microstructure of the Cu–Ag solid solutions with different composition prepared by these methods is most often nanocrystalline or composite, consisting of a mixture of nanocrystalline solid solution and

amorphous phases [3, 8, 9]. Formation of entirely amorphous Cu–Ag alloys exclusively by a vapor deposition technique has been reported only in a few papers [10, 11]. Repeatedly cold-rolled Cu–Ag alloys reveal also some local amorphous regions [8]. Mechanical alloying followed by annealing at 200°C was reported also to result in an amorphous phase formation [9]. Mechanical alloying of Ag-Cu-Sn powders, containing 10–20 wt.% Sn, caused a drastic decrease of their grain sizes. The formation of compounds like Ag_3Sn , Cu_6Sn_5 and $\text{Cu}_{10}\text{Sn}_3$ occurs after 1 hour of milling, but no amorphization up to 8 hours of milling was reported [12]. Nanocrystalline Ag_3Sn phase (~ 20 nm) was formed by ball milling for 1–2 h of Sn rich Sn-Cu-Ag alloys [13].

The present study aims at investigating the effect of Sn on the amorphization and formation of Cu-Ag-based solid solutions by mechanical alloying. The morphology and microstructure of the prepared solid solutions were also characterized. Due to the improved glass-forming ability of the ternary alloy containing Sn in comparison to the binary Cu-Ag, and the suitability of Sn for preparing nanoporous Ag by selective electrochemical dissolution of Cu-Ag-Sn, in the present study its concentration was varied in the range of 3–10 at.% (3, 6 and 10 at.% Sn).

* To whom all correspondence should be sent:
E-mail: tpassov@chem.uni-sofia.bg

EXPERIMENTAL PART

$\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ ($x=3, 6$ and 10) alloys were produced by milling Ag (99.99%), Cu (99.9%) and Sn (99.9%) using a planetary ball mill (Fritsch P6) with rotation velocity of 400 rpm, hardened Cr-steel vials and ball-to powder mass ratio of 9:1. Protective Ar atmosphere and liquid n-heptane were applied for the milling process. The regime of milling was: 30 min of continuous milling and 10 min relaxation time. **The milling time was varied** with the goal to produce powders with different morphology and microstructure.

The microstructure and morphology of the alloys were investigated by x-ray diffraction using Bruker D8 Advance diffractometer with Cu-K α radiation and Scanning electron microscopy (SEM, JEOL-5510). Thermal stability of the ball-milled samples was analyzed with a Perkin-Elmer DTA.

RESULT AND DISCUSSION

Electron microscopy analysis (Fig. 1) of the ball-milled powders showed similar particle size for all investigated materials. The average particle size of the alloy with lowest Sn content ($\sim 10 \mu\text{m}$) is only slightly larger than that of the Sn richer compositions (about $7.0 \mu\text{m}$) milled for the same time of 10 h. Extending the milling time up to 20 hours results in additional particle decrease: $6 \mu\text{m}$ for $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$. Similar particle size distribution was observed for all compositions.

X-ray diffraction of the two hours milled $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$ and $\text{Cu}_{50}\text{Ag}_{44}\text{Sn}_6$ (Fig. 2a) revealed the formation of Ag_3Sn and Cu_4Sn_5 phases, which were not observed at longer than 8 hours of milling. For $\text{Cu}_{50}\text{Ag}_{47}\text{Sn}_3$ formation of these phases was not detected by any duration of milling. Milling for a longer time shows obvious development of the phase composition and microstructure in the systems studied. After 8 hours of milling (Fig. 2 c,d) only the

solid solution formation was observed. In general, the diffraction peaks become slightly sharper (narrower), meaning that a process of nanograin growth takes place during the milling, Fig. 2. The position of the maximum of the main diffraction peak also does not change with milling time, revealing that the terminal solid solutions are already formed at 8 h of milling. It is seen that solid solution formation is faster for the alloy with 3 at.% Sn, i.e. this composition is close to the optimal for $\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ with respect to the solid solution formation ability. Furthermore, milling for 8 hours leads also to formation of amorphous phase in $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$, proved by DTA analyses of an as-milled alloy. Diffraction peaks of pure Cu and Ag at the longer milling times (> 8 h) were not detected, indicating a process of complete alloying.

The lattice parameters for the formed solid solutions are comparable with the data from our previous investigations on the Cu-Ag binary system (Fig. 3), [8]. It should be noted that unlike the binary Cu-Ag, the longer time of mechanical alloying does not lead to significant changes in the lattice parameter, **a**, of the three-component solid solutions, studied in this work. Generally, the increase of the Sn content in the alloy results in lattice parameter, **a**, enlargement, but for milling durations $t \geq 12$ h the alloys with 3 and 6 at.% Sn reveal almost the same **a**.

The three $\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ alloys studied show rather different development of the average grain size of the metastable fcc solid solutions with milling time. Whereas for $\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ ($x=3$ and 6) the grain size is more or less constant (4–5 nm) in the range of 5–15 h milling, for $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$ it initially decreases with milling time, reaching a value of 6 nm after 12 h of milling, Fig. 4, and then increases again to about 9 nm at $t=15$ h. The increase of the grain size at longer milling durations can be associated with a nanograin growth process.

DTA analysis reveals broad overlapped exothermic peaks starting at about 100°C for the ball milled

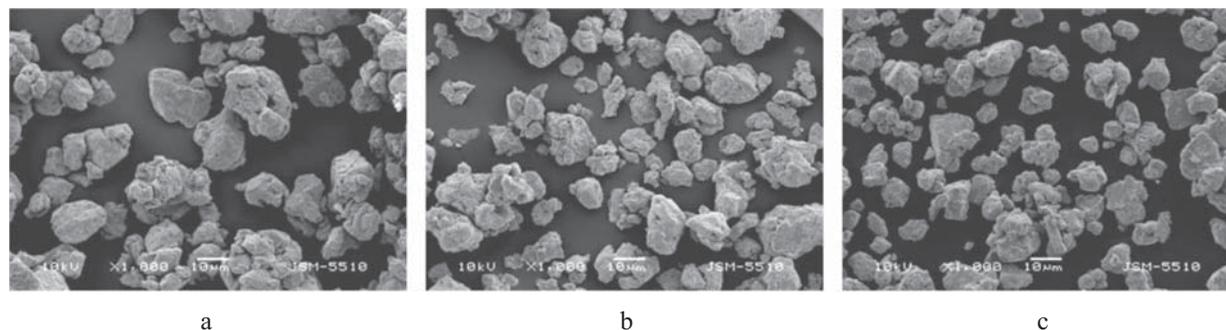


Fig. 1. SEM micrographs of: $\text{Cu}_{50}\text{Ag}_{47}\text{Sn}_3$ (a), $\text{Cu}_{50}\text{Ag}_{44}\text{Sn}_6$ (b) and $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$ (c) alloy powders ball-milled for 10 h

alloys, associated with the solid solution decomposition to terminal elemental Ag and Cu, as shown in our previous study [1]. XRD analysis of milled for 20 h and then annealed at 400 °C CuAgSn confirms the alloy decomposition, Fig. 2d (inset). As mentioned earlier [1] ball milled Cu-Ag-based solid solutions show somehow different thermal behavior compared to the cold-rolled and rapidly quenched Cu-Ag alloys

[8], expressed in the presence of exothermic peaks at lower temperatures, which could be associated with relaxation of microstresses created by milling. The thermal behavior of the ball milled Cu-Ag-Sn is different compared to the binary alloys. Generally, the major thermal peaks are shifted to higher temperatures (250–400 °C), implying higher thermal stability of the ternary solid solutions.

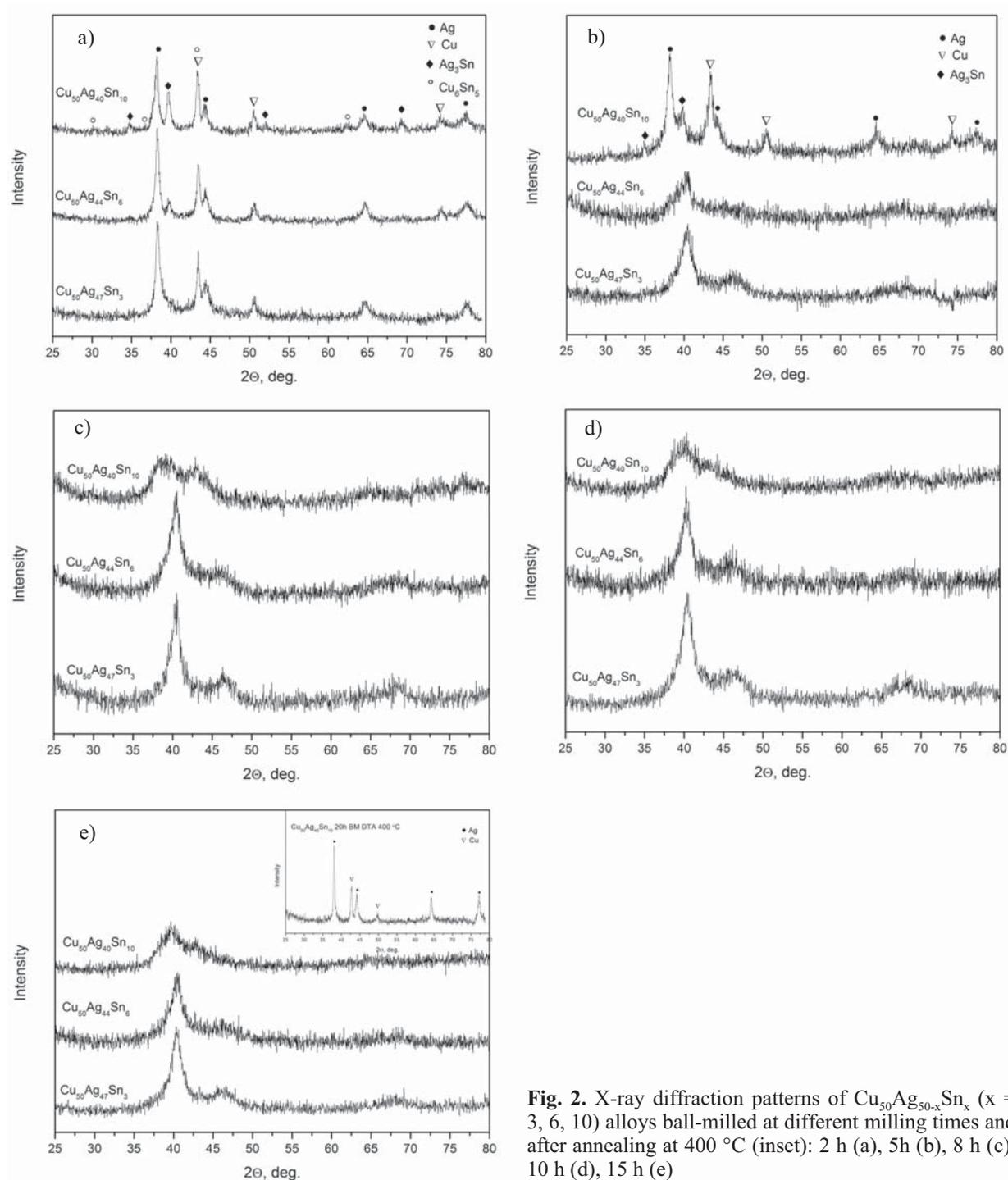


Fig. 2. X-ray diffraction patterns of $\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ ($x = 3, 6, 10$) alloys ball-milled at different milling times and after annealing at 400 °C (inset): 2 h (a), 5 h (b), 8 h (c), 10 h (d), 15 h (e)

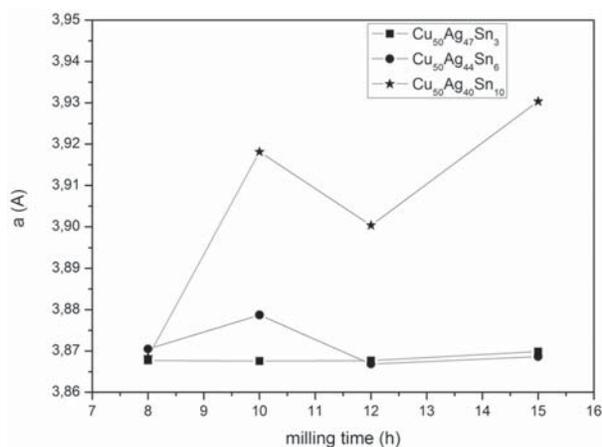


Fig. 3. Lattice parameters, a , for the alloys studied at various milling times

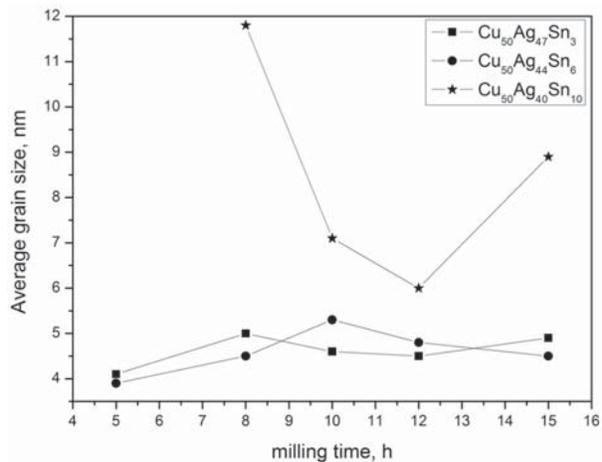


Fig. 4. Average grain size for the alloys studied as a function of milling time

In summary, the present study reveals an improved ability for metastable solid solution formation by ball milling of ternary Cu-Ag-Sn, compared to binary Cu-Ag alloys. The microstructure of the tin containing Cu-Ag fcc solid solutions is fine nanocrystalline (5–10 nm) with a presence of some amorphous phase and as a whole its thermal stability is higher than that of binary Cu-Ag alloys. It is expected that solid solutions with this microstructure would be attractive for preparing nanoporous Ag structures by selective electrochemical dissolution.

CONCLUSIONS

Supersaturated Cu₅₀Ag_{50-x}Sn_x ($x=3, 6, 10$) solid solutions were prepared by mechanical alloying for different milling times. For Cu₅₀Ag₄₀Sn₁₀ 8h of milling were enough to form homogeneous Cu-Ag-based fcc solid solutions, whereas for the ternary systems with lower Sn content even 5h were sufficient for complete alloying. The microstructure of the fcc solid solutions is fine nanocrystalline (< 10 nm) for the ternary system, as ball-milling results also in a better pronounced amorphous phase formation. The lattice constant of the fcc solid solution in the ternary systems is larger than that of Cu₅₀Ag₅₀, but slightly depends on the Sn concentration in the composition range of 3–6 at.% Sn. The alloy with 10 at.% Sn shows distinct increase of the lattice constant compared to the Sn deficient alloys at milling times larger than 8 h. Solid solution decomposition, grain growth process and crystallization of the amorphous phase formed during milling have been detected by DTA.

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АМОРФИЗАЦИЯ И ОБРАЗУВАНЕ НА ТВЪРДИ РАЗТВОРИ В ЛЕГИРАНИ С Sn Cu-Ag СПЛАВИ, ПОЛУЧЕНИ ПОСРЕДСТВОМ МЕХАНИЧНО СМИЛАНЕ

Л. Любенова, Т. Спасов, М. Спасова

Химически факултет, СУ „Св. Климент Охридски“, бул. „Дж. Баучър“ 1, 1164 София, България

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(Резюме)

Настоящата работа е насочена към изучаване влиянието на добавки от Sn върху микроструктурата на метастабилни твърди разтвори на основата на Cu-Ag с потенциално приложение за получаването на нанопорьозни структури. Нанокристални твърди разтвори със състав $\text{Cu}_{50}\text{Ag}_{50-x}\text{Sn}_x$ ($x = 3, 6, 10$) са получени посредством механохимично сплавяване във високо енергетична планетарна мелница в Ar-атмосфера и течен n-хептан. Образуването на фина нанокристална микроструктура ($<10\text{--}15\text{ nm}$) в проби от $\text{Cu}_{50}\text{Ag}_{40}\text{Sn}_{10}$ бе наблюдавано след смилане в продължение на 8 часа. Пълното сплавяване на компонентите в системите с по-малки количества Sn ($x = 3$ и 6) бе постигнато само за 5 часа синтез. Частична аморфизация бе наблюдавана при всички изследвани сплави, съдържащи Sn. Решетъчната константа на твърдия разтвор за трикомпонентните системи е по-голяма, отколкото тази на $\text{Cu}_{50}\text{Ag}_{50}$, но зависи слабо от концентрацията на Sn в интервала от 3–10 at.% Sn.