

Cu-Hf-Al amorphous/nanocrystalline composite particles produced by milling

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Abstract

$\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ amorphous/nanocrystalline composite particles were prepared by ball-milling. Crystalline master alloys were prepared by induction melting under purified argon atmosphere. During the mechanical amorphization the grinded ingots were milled for different durations of time and with several interruptions in order to analyse the structure of the powders. The mechanical milling was performed in a Pulverisette5 high energy planetary ball-mill under argon atmosphere using stainless vial and balls with diameters of about 3 mm, 5 mm and 10 mm. The ball-to-powder ratio was 20:1. The milled powders were analyzed by XRD to determine the amorphous fraction, by SEM to characterize the microstructure and by DSC to observe processes in the powders during heating. After milling for 20 h, an amorphous structure appeared and the amorphous fraction was 95%.

Keywords: amorphisation, milling, planetary ball-mill

1. Introduction

The materials of bulk metallic glasses (BMG) attract tremendous attention because they offer unique mechanical properties such as ultrahigh strength or high hardness [1-5]. Copper-based amorphous alloys are particularly interesting for practical applications as new structural materials due to their significant advantages, including their low cost, high fracture strength of around 2 GPa, often coexisting with visible ductility, and feasibility for the formation of BMG based composites [5-10].

The new types of Cu-Hf-Al alloys are suitable structural materials in engineering and motorcar industry owing to their excellent mechanical properties such as strength as well as corrosion and wear resistance. The $\text{Cu}_{49}\text{Hf}_{42}\text{Al}_9$ alloy was developed by Jia et al. [6] and shows a critical diameter value higher than the values obtained earlier, that is, it can be cast in a bulk amorphous form with a diameter of 10 mm. Ball-milling (BM) is a well-known process producing a wide range of materials with unique properties [12].

The present work reports about $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ amorphous/nanocrystalline composite particles prepared by ball-milling.

2. Experimental

The crystalline master alloys were prepared by induction melting under purified argon atmosphere. The master alloy ingots were grinded to particles with size below 320 μm before the mechanical milling. The particles were milled for different periods of time during the mechanical amorphization.

The procedure was interrupted after arbitrarily selected milling times in order to analyze the structure of the powders. The mechanical milling was performed in a Pulverisette 5

high-energy planetary ball-mill under argon atmosphere using stainless steel vial and balls with diameters of 3 mm, 5 mm and 10 mm. The ball-to-powder ratio was 20:1. The optimal parameters of the milling were determined in a previewed work of the Materials Science Research Group [1-2].

The microstructure of the powders was characterized using a 1830 I Amray Scanning Electron Microscope equipped with an EDX DX4 and a Zeiss EVO MA Scanning Electron Microscope. The ball-milled powders were analyzed by X-ray diffraction (XRD) using a Philips PW 1830 diffractometer with Cu K α radiation ($\lambda = 0.1542$ nm). The glass transition and crystallization temperatures of the amorphous phase were measured with a Netzsch 204 DSC with alumina container. The particle size was measured by a Quantimet Image Analyzer using Leica Software.

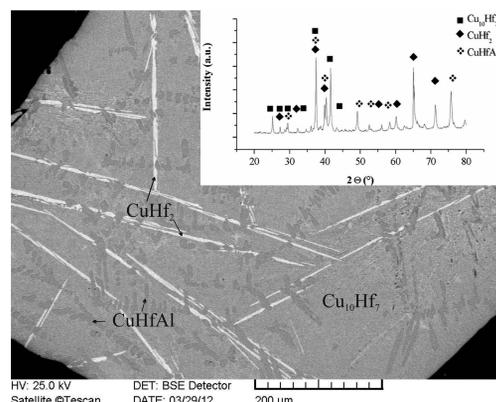


Fig. 1. Backscattered SEM image of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ master alloy with the XRD diffractogram

1. ábra A $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ alapötözet elektronmikroszkópos képe és röntgendiffraktogramja

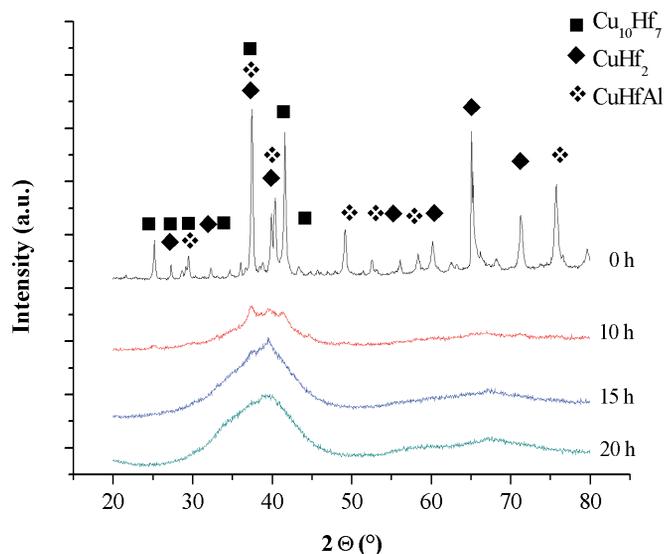


Fig. 2. XRD diffractograms of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ powders as function of milling time
2. ábra $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ porok röntgendiffraktogramjai az őrlési idő függvényében

3. Results and discussion

Figure 1 shows the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ crystalline master alloy with three identified intermetallic compounds: $\text{Cu}_{10}\text{Hf}_7$ (orthorhombic, $a = 1.2587$ nm, $b = 0.9238$ nm, $c = 0.9265$ nm [13]), CuHf_2 (tetragonal, $a = 0.3170$ nm, $c = 1.1133$ nm [14]) and the ternary compound CuHfAl (hexagonal, MgZn₂-type Laves-phase, $a = 0.5155$ nm, $c = 0.8381$ nm [15]). Confirmed by element analysis using EDX, the needle shape crystalline phases

(lighter) were identified as CuHf_2 , the dendrites (dark gray) as CuHfAl and the matrix $\text{Cu}_{10}\text{Hf}_7$ intermetallic compounds, respectively.

Figure 2 shows the XRD patterns of $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ powders after different milling times. 10 h milling resulted in broadening the crystalline diffraction peaks and reduction of their intensity; however, there was no significant change in the position of diffraction peaks. Increasing the milling time beyond 10 hours led to the appearance of a broad diffuse diffraction maximum between $2\theta = 32^\circ$ and 46° , which implies the formation of an amorphous phase. After milling for 20 h, an amorphous structure appeared and the amorphous fraction was 95%.

The scanning electron images show the structure of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ powders as a function of milling time (Figure 3). After 10 hours milling CuHf_2 phase remains in the powder, as seen in Figure 3 (a). Figure 3 (b) shows 15 hours milled powder. The needle shape crystalline phases (lighter) were identified as CuHf_2 . The particles are coalescent with gaps encompassed between them. Figure 3 (c) shows 20 h milled powder in lower magnification, while Figure 3 (d) – in higher magnification. The structure of the particles can not be observed, an amorphous structure appears and the amorphous fraction is 95%. During the high-energy milling the particles were repeatedly attended, cold welded, fractured and rewelded. Figure 4 shows the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ particle size distribution as a function of milling time measured by Quantimet Image Analyzer. The average size of the particles decreases with increasing milling time. The majority of the particles in the starting powder were 200 μm in size. As the milling time increases, the range of particles size distribution narrows. While the average particle size in the starting powder was 200 μm , after 20 hours of milling it was only ~ 10 μm .

Thermal data of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ alloy were obtained by DSC measurements with the first crystallization temperature at $T_x = 572$ °C and the crystallization peak temperature being at $T_p = 618$ °C.

4. Conclusions

Within the frames of this work $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ powders were produced by ball-milling with the milling time varying between 5 and 20 h.

The results can be summarized as follows: increasing the milling time resulted in an increase of the amorphous fraction. After milling for 20 h, an amorphous structure appeared and the amorphous fraction was 95%. Thermal data of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ alloy were obtained by DSC measurements with the first crystallization temperature at $T_x = 572$ °C and the crystallization peak temperature being at $T_p = 618$ °C.

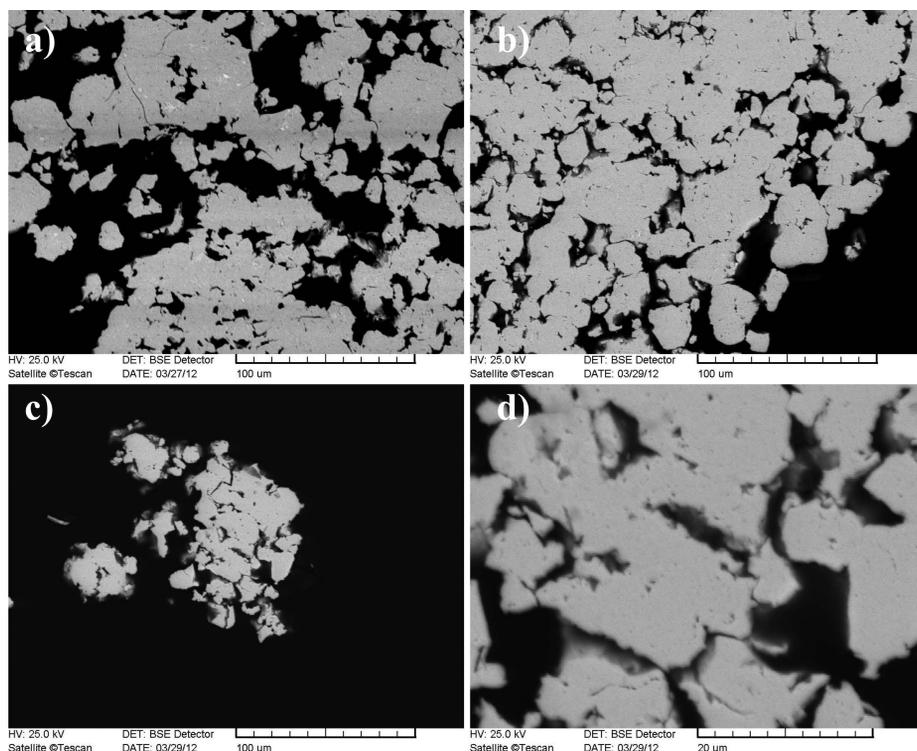


Fig. 3. Backscattered SEM images of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ powder as function of milling time:
a) 10 h, b) 15 h, c) 20 h, d) the same as c) in higher magnification
3. ábra $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ porok elektronmikroszkópos képei az őrlési idő függvényében:
a) 10 h, b) 15 h, c) 20 h, d) nagyobb felbontású képen

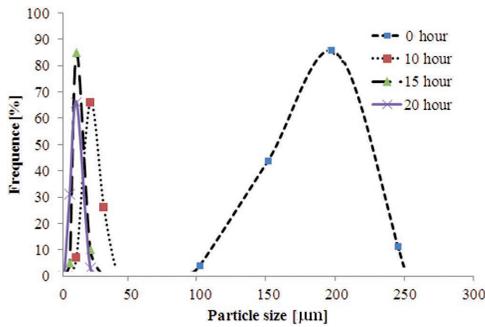


Figure 4. $Cu_{54}Hf_{36}Al_{10}$ particle size distribution
4. ábra $Cu_{54}Hf_{36}Al_{10}$ szemcseméret eloszlás

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References

- [1] Tomolya K. – Janovszky D. – Sveda M. – Hegman N. – Solyom J. – Roosz A.: *CuZrAl Amorphous Alloys Prepared by Casting and Milling*. Journal of Physics: Conference Series. **144**(1), 2009; pp. 012032 1-5. <http://dx.doi.org/10.1088/1742-6596/144/1/012032>
- [2] Tomolya K. – Janovszky D. – Janvari T. – Sycheva A. – Tranta F. – Solyom J. – Ferenczi T. – Roosz A.: *Consolidation of $Cu_{58}Zr_{42}$ amorphous/nanocrystalline powders by PM*. Journal of Alloys and Compounds. **536**(1), 25 September 2012, pp. S154-S158., <http://dx.doi.org/10.1016/j.jallcom.2011.12.107>
- [3] Zhang, W. – Inoue, A.: *Thermal Stability and Mechanical Properties of Cu-Based Bulk Glassy Alloys in $Cu_{50}(Zr_{1-x}Hf_x)_{45}Al_5$ System*. Materials Transactions, **44**(10), 2003, pp. 2220-2223.
- [4] Jia, P. – Xu, J.: *Comparison of bulk metallic glass formation between Cu-Hf binary and Cu-Hf-Al ternary alloys*. Journal of Materials Research. **24**(1), 2009 No. 1, pp. 96-106., <http://dx.doi.org/10.1557/JMR.2009.0014>
- [5] Jia, P. – Zhu, Z.-D. – Zuo, X.-W. – Wang, E.-G. – He, J.-C.: *Investigations of compressive strength on Cu-Hf-Al bulk metallic glasses: Compositional dependence of malleability and Weibull statistics*. Intermetallics **19**(12), December 2011, pp. 1902–1907., <http://dx.doi.org/10.1016/j.intermet.2011.07.031>
- [6] Jia, P. – Guo, H. – Li, Y. – Xu, J. – Ma, E.: *A new Cu-Hf-Al ternary bulk metallic glass with high glassforming ability and ductility 2006*. Scripta Materialia **54**(12), June 2006, pp. 2165–2168. <http://dx.doi.org/10.1016/j.scriptamat.2006.02.042>

- [7] Cai, A.-H. – Xiong, X. – Liu, Y. – Zhou, Y. – An, W.-K. – Luo, Y.: *Regular Cu based amorphous alloy powder*. Journal of Alloys and Compounds **497**(1-2), 14 May 2010, pp. 234-238., <http://dx.doi.org/10.1016/j.jallcom.2010.03.018>
- [8] Wang, Y.-Y. – Bian, X.-F. – Ran, J.: *Effects of cooling rate on thermal expansion of $Cu_{49}Hf_{42}Al_9$ metallic glass*. Transactions of Nonferrous Metals Society of China **21**(9), September 2011, pp. 2031–2036. [http://dx.doi.org/10.1016/S1003-6326\(11\)60968-0](http://dx.doi.org/10.1016/S1003-6326(11)60968-0)
- [9] Madge, S. V. – Wada, T. – Louzguine-Luzgin, D.V. – Greer, A.L. – Inoue, A.: *Oxygen embrittlement in a Cu-Hf-Al bulk metallic glass*. Scripta Materialia **61**(5), September 2009, pp. 540–543. <http://dx.doi.org/10.1016/j.scriptamat.2009.05.018>
- [10] Maddala, D. – Hebert, R. J.: *Effect of notch toughness and hardness on sliding wear of $Cu_{50}Hf_{41.5}Al_{8.5}$ bulk metallic glass*. Scripta Materialia **65**(7), October 2011, pp. 630–633., <http://dx.doi.org/10.1016/j.scriptamat.2011.06.046>
- [11] Choi-Yim, H.: *Thermal and Elastic Properties of Cu-Hf-Al Bulk Metallic Glasses*. Journal of the Korean Physical Society **60**(3), February 2012, pp. 485-487., <http://dx.doi.org/10.3938/jkps.60.485>
- [12] Inoue, A. – Zhang, W.: *Bulk glassy Cu-based alloys with a large supercooled liquid region of 110 K*. Applied Physics Letters **83**(12), 2003, 2351-2353., <http://dx.doi.org/10.1063/1.1613813>
- [13] Bsenko, L.: *Crystallographic data for intermediate phases in the copper-zirconium and copper-hafnium systems*. Journal of the Less Common Metals **40**(3), May 1975, pp. 365–366., [http://dx.doi.org/10.1016/0022-5088\(75\)90085-5](http://dx.doi.org/10.1016/0022-5088(75)90085-5)
- [14] JCPDS 1995No. 18-0440. International Center for Diffraction Data: Newton Square, PA
- [15] Handbook of Ternary Alloy Phase Diagrams, edited by P. Villars, A. Prince, and H. Okamoto (ASM International Publishing, (1995), p. 3219.

Ref.:

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Cu-Hf-Al amorf/nanokristályos szerkezetű por előállításával

$Cu_{54}Hf_{36}Al_{10}$ amorf/nanokristályos szerkezetű port állítottunk elő golyós malomban. Kristályos mesterötvözetet készítettünk indukciós olvasztás alatt argon atmoszférában. Az őrléshez Fritsch által gyártott Pulverisette 5 golyós-malmot használtunk, amelybe golyókat tettünk, amelyek átmérője 5, 7 és 10 mm volt. Argonnal feltölthető, saválló acél téglébe saválló acélból kísérletezve 20:1 golyó/őrleendő anyagarányban dolgoztunk. Az őrlött porok szerkezetét röntgendiffrakciós (XRD) vizsgálatokkal tanulmányoztuk és meghatároztuk a fázisokat illetve az amorf térfogathányadot. A mikroszerkezet jellemzésére pásztázó elektronmikroszkópos (SEM) vizsgálatokat alkalmaztunk. 20 órás őrlést követően a kapott amorf térfogathányad 95%-os volt.
Kulcsszavak: amorfizálás, őrlés, golyós malom

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structures. Urban heat island reduction, light colored pavements, green roofs and cool communities.

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New Concrete Technology: Durability, extended service life models and validation, performance based specifications to foster sustainability. Innovative concrete production methods.

Sustainability Initiatives: Green building codes and standards adopted by building owners, designers, contractors and product manufacturers. Economic incentives and legislation.

Functional Resilience: High performance concrete applications in buildings and infrastructure, fortified building codes, and community initiatives focusing on disaster resistance and adaptive reuse.