Materials Letters 330 (2023) 133409

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Indentation size effect in exceptionally hard AlCu thin films

Dániel Olasz [a,b], György Sáfrán [b], Noémi Szász [b], Gabriella Huhn [a], Nguyen Quang Chinh [a,*]

[a] Department of Materials Physics, Eötvös Loránd University, 1117 Budapest, Pázmány Péter sétány 1/A, Hungary

[b] Institute for Technical Physics and Materials Science, Centre for Energy Research, Budapest, 1121 Budapest Konkoly-Thege út 29-33, Hungary

ARTICLE INFO

Keywords:
Al-Cu thin films
High strength
Indentation size effect
Fine-grained structure
Grain boundary sliding

ABSTRACT

Dual DC magnetron sputtered AlCu thin films representing the whole composition range were investigated by depth-sensing indentation (DSI), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Experimental results show exceptionally high hardness of ~16 GPa in the middle concentration range of ~40–70 at% Cu. Indentation tests also revealed phenomena related to indentation size-effect. At Al or Cu contents below 20 at%, the well-known size effect was not observed, which can be interpreted by the grain boundary sliding deformation mechanism of fine-grained films. In the middle range of the composition, the size effect can be clearly observed even against the fine grain structure. This is a consequence of the highly precipitated microstructure of these films, which leads to the indentation processes taking place in a manner more characteristic of amorphous materials.

1. Introduction:

Most of the research on Al-based thin film systems focuses on properties suitable for microelectronic, telecommunication and optical applications [1,2]. For the Al-Cu system, the scope of investigations is limited to cases with low Cu alloying concentrations [3,4]. For this type of applications, not only the electromigration but also the mechanical properties of the material used are critical aspects. Depth-sensing indentation is one of the most commonly used testing method for the mechanical properties of thin films [5,6]. An important phenomenon during indentation is the so-called indentation size effect (ISE), which describes the scale dependent behavior of the hardness, namely that smaller indentation forces, and thus smaller indentation depths, are associated with larger hardness values. The origin of ISE is not yet fully understood, as many factors such as the friction along the indented surface [7], imperfections in the tip of the indenter [8] and/or the occurrence of geometrically necessary dislocations [9] may result in similar effect. The latter is a widely accepted theory that is very well suited to the interpretation of ISE for pure Cu.

The motivation for this work is to investigate the microstructure and mechanical properties of Al-Cu thin films over a wide compositional range, which have applications in a variety of technological fields.

2. Experimental:

Al-Cu thin films of different compositions, 1 mm wide and ~ 1.7 m thick, were deposited by double DC magnetron sputtering on a single 12x25 mm2 Si substrate. Sputtering was performed through a 1 mm wide gap at room temperature at a deposition rate of 15.4 Å/s without substrate cooling, varying the target Al and Cu power according to the desired composition, similar to the previously used technique [10]. The base pressure of the vacuum chamber and that of the Ar sputtering gas was 5×10^{-8} and 3.6×10^{-3} mbar, respectively.

Mechanical properties of the films were investigated by depth-sensing indentation (DSI) measurements using a UMIS type instrument. Indentations were carried out with a Vickers indenter tip for maximum loads of 10, 20 and 50 mN. Hardness values were evaluated using the Oliver-Pharr method [11,12].

Analytical and structural characterization was performed by scanning (SEM- FEI Scios 2 Dual Beam) and transmission (TEM- FEI Themis 200) electron microscopy and energy dispersive spectroscopy (EDS-Oxford instruments X-MaxN).

Surface topography of the indented sample was also studied by atomic force microscopy (AFM) using a SmartSPM-1000 instrument with a 120–190 kHz resonant natural frequency and conductive silicon cantilevers operating in semi-contact mode.

* Corresponding author.
E-mail address: chinh@metal.elte.hu (N.Q. Chinh).

https://doi.org/10.1016/j.matlet.2022.133409
Received 17 September 2022; Received in revised form 21 October 2022; Accepted 24 October 2022
Available online 28 October 2022

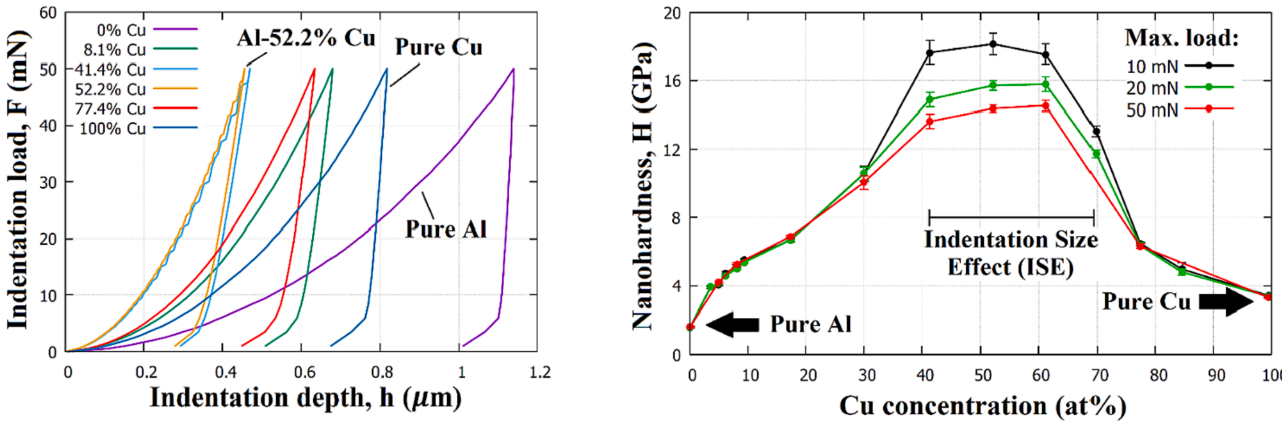
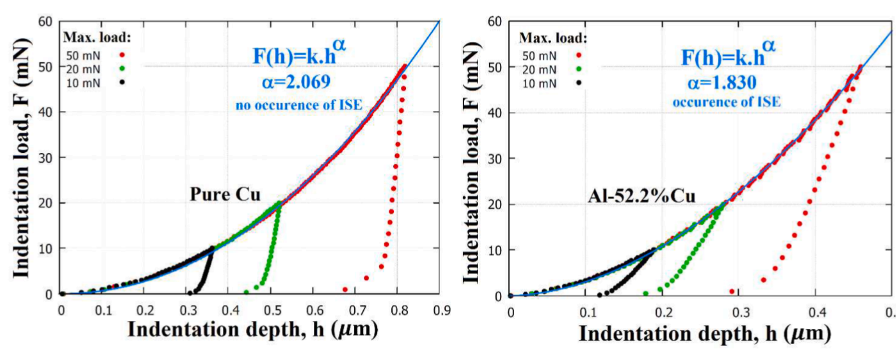


Fig. 1. Results of indentation tests, showing a) typical indentation depth-load (h-F) curves and b) nanohardness values, H of Al-Cu thin films over the whole range of Cu concentrations. The hardness values obtained at max. Load of 10, 20 and 50 mN are plotted together.



a)   b)

Fig. 2. Loading stage of indentation depth-load curves, fitted with power-law function for a) pure Cu and b) Al- 52.2 at% Cu thin films.

3. Results and discussion

Fig. 1a shows typical indentation depth-load (*h-F*) curves obtained on the investigated samples. The nanohardness, H of the samples over the full composition range (0–100 at% Cu) is shown in Fig. 1b, where the hardness values obtained for maximum loads of 10, 20 and 50 mN are plotted together. The hardness of pure Al and pure Cu films is 1.6 and 3.3 GPa, respectively. With increasing alloy concentration, the hardness increases and reaches a maximum of ~15–16 GPa around the equiatomic (~40–60 at% Cu) composition, which is almost twice the 8 GPa hardness previously reported in the Al_xCu_{1-x} system [13]. This indicates that extremely hard films can be prepared in the Al-Cu binary system, which increases the potential for using such materials as a protective coating with high strength and good corrosion resistance.

In addition to the exceptional hardness, another interesting behavior of AlCu films can be seen in Fig. 1b. Indentation measurements at different maximum loads of 10, 20 and 50 mN resulted in identical H values for thin films with low alloy concentrations, including pure Al and pure Cu samples (see H values on the left and right side of Fig. 1b). This indicates that the Al_xCu_{1-x} thin film system is not sensitive to the indentation size effect (ISE) at either low (≤0.2) or high (≥0.8) values of x. It is worth noting that these observations are in contrast to those described for conventional pure Al [7] and Cu [9], where ISE is a known phenomenon. Around the equiatomic composition (~40–70 at% Cu), however, the ISE is clearly observed in Fig. 1b, where the hardness, H, decreases with increasing maximum strain (i.e., increasing indentation).

In the light of the above results, important questions arise, such as: i) why no size effect is observed for the pure Al and Cu samples, where the phenomenon is widely accepted? and ii) why is there an ISE for samples in the middle range of composition? To the best of the authors' knowledge, similar behavior and phenomena have not been observed for Al-based thin films.

Table 1
Fitting parameters of the $F(h) = k \bullet h^{\alpha}$ power law function fitted to the loading stage of indentation depth-load (h-F) curves for different compositions.

Cu concentration (at%)	Value of *k* (±1.6)	Value of *α* (±0.009)	Occurrence of ISE?
0 (pure Al)	37.4	2.097	no
3.7	83.0	2.023	no
5.0	91.6	2.062	no
6.2	93.6	2.006	no
8.1	109.6	2.075	no
9.4	104.0	1.990	no
17.4	134.5	2.018	no
30.0	176.6	1.966	poorely
41.4	198.5	1.860	yes
52.2	205.7	1.830	yes
61.3	223.1	1.876	yes
69.8	167.1	1.845	yes
77.4	127.2	2.042	no
84.5	101.3	2.182	no
100 (pure Cu)	74.7	2.069	no

When studying the ISE phenomenon, it is useful to examine the course of the indentation curves. For this purpose, the loading part of all indentation depth-load (*h-F*) curves is fitted by a power law function, $F(h) = kh^{\alpha}$, as shown, for examples, in Fig. 2 for pure Cu (see Fig. 2a) and for Al-52 at% Cu sample (see Fig. 2b). Careful analysis shows that in every case, the indentation curve can be very well-fitted by a power law

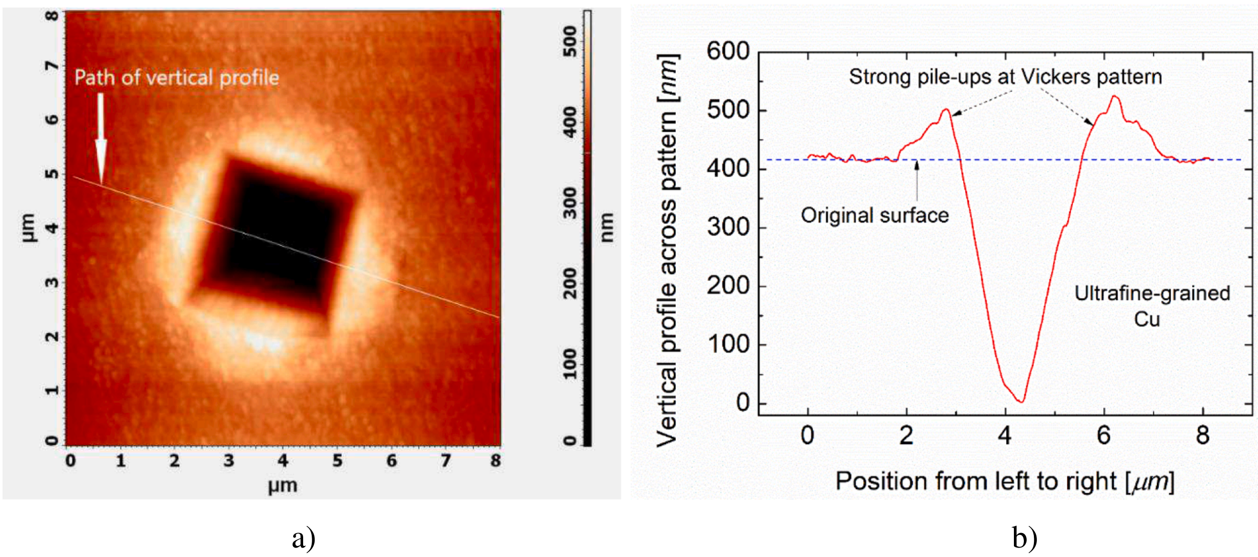


Fig. 3. Characterization of the microstructure of pure Cu film by 3D AFM with a) observation of indented surface and b) analysis of the vertical profile through Vickers pattern.

function. The values of the fitting parameters, k and α are given in Table 1, in which the presence of ISE is also indicated for each sample.

Comparing the data in Table 1, there is a clear correlation between the occurrence of the α exponent and the indentation size effect. If the loading part of the indentation curve is characterized by a function with $\alpha < 2$, then ISE is clearly present, while in cases of $\alpha \approx 2$ there is no sign of the phenomenon.

As to the the first question why the size effect is not observed in the pure Cu film, while the phenomenon is widely accepted for conventional Cu, the deformation mechanism in the pure Cu film was investigated by atomic force microscopy.

Characteristics of microstructure and indentation behaviour of pure Cu sample by 3D AFM are represented in Fig. 3. Fig. 3a and 3b show the morphology of the surface around a Vickers pattern and the corresponding vertical profile across the pattern, respectively. In Fig. 3a, very fine grains between 100 and 120 *nm* are clearly visible on the surface of the sample. In addition, well-developed pile-ups form around the Vickers pattern on this ultrafine-grained film. Similar to the previous calculations for ultrafine-grained Al [14], the analysis of the height of the of the pile-ups (Fig. 3b) suggests that the grain boundary sliding (GBS) mechanism contributes at least 50–60 % of the total deformation during indentation, emphasizing the important role of submicron fine grains. In the present submicron-grained structure, the effect of intragrain dislocations, including geometrically necessary dislocations [9], is no longer significant due to intense grain boundary sliding. Therefore, the size effect is not observed.

Concerning the second question, it should be noted that the ISE phenomenon is observed only for the four exceptionally hard films in the middle range of the composition (~40–70 at% Cu), where the film is composed of narrow nanoscale crystalline columns containing very finely distributed particles of Al_2Cu_3 and Al_4Cu_9 phase, as observed by TEM. TEM investigations also revealed the formation of deformation bands under the Vickers pattern. Although further studies are needed to clarify the details of this phenomenon, it can be assumed that due to the significant strengthening effect of highly precipitated, nanocrystalline structure, the indentation process occurs with the formation and progression of deformation bands, a mechanism typical of amorphous materials.

4. Conclusions

Mechanical and plastic properties of AlCu thin films were investigated over a wide compositional range by depth-sensing indentation, TEM and AFM. The main results are followings:

i) Exceptionally high hardness of up to16 GPa can be achieved, making this system suitable for a wide range of technological applications.

ii) It was found that the occurrence of indentation size effect can be predicted by analyzing the indentation curves. No ISE was observed for the highly different Al and Cu component films, due to significant grain boundary sliding in submicron-grained films.

iii) The size effect was clearly observed around the equiatomic (40–70 at% Cu) composition, as the indentation process in these highly precipitated films follows the deformation band formation and progression mechanism typical of amorphous materials.

CRediT authorship contribution statement

Dániel Olasz: Conceptualization, Formal analysis, Writing – original draft. **György Sáfrán:** Conceptualization, Investigation, Writing – review & editing. **Noémi Szász:** Investigation, Data curation. **Gabriella Huhn:** Investigation, Data curation. **Nguyen Quang Chinh:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the KDP-2021 Program of the Ministry of Innovation and Technology from the source of the National Research, Development and Innovation Fund. Research of NQC, DO, GS was also supported by the Hungarian-Russian Research program (TÉT) No. 2021-

1.2.5-TÉT-IPARI-RU-2021-00001. Support from Hungarian Scientific Research Fund OTKA, Grant numbers: K129009 and K143216 is also greatly acknowledged.

References

[1] F.M. Mwema, O.P. Oladijo, S.A. Akinlabi, E.T. Akinlabi, J. All. Comp. 747 (2018) 306-323. (Review). https://doi.org/10.1016/j.jallcom.2018.03.006.
[2] A. Kumar, R. Jayaganthan, R. Chandra, V. Chawla, A.A.O. Tay, 8th Electronics Packaging Technology Conference, (2006) 560-564. https://doi.org/10.1109/EPTC.2006.342774.
[3] Y. Joo, Met Mater 4 (1998) 1033–1039, https://doi.org/10.1007/BF03025973.
[4] L.J.C. Bergers, J.T.M. De Hosson, M.G.D. Geers, J.P.M. Hoefnagels, Mater. Sci. Eng. A 722 (2018) 37–46, https://doi.org/10.1016/j.msea.2018.02.083.
[5] D. Olasz, J. Lendvai, A. Szállás, G. Gulyás, N.Q. Chinh, Micromachines 11 (2020) 1023–1044, https://doi.org/10.3390/mi11111023.
[6] N.Q. Chinh, J. Gubicza, Z. Kovács, J. Lendvai, J. Mater. Res. 19 (2004) 31–45, https://doi.org/10.1557/jmr.2004.19.1.31.
[7] M. Atkinson, J. Mater. Res. 10 (1995) 2908–2915, https://doi.org/10.1557/JMR.1995.2908.
[8] J. Menčík, M.V. Swain, J. Mater. Res. 10 (1995) 1491–1501, https://doi.org/10.1557/JMR.1995.1491.
[9] W.D. Nix, H. Gao, J. Mech. Phys. Solids 46 (1998) 411–425, https://doi.org/10.1016/S0022-5096(97)00086-0.
[10] N.Q. Chinh, G. Sáfrán, MRS Commun 9 (2019) 1111–1114, https://doi.org/10.1557/mrc.2019.108.
[11] G.M. Pharr, W.C. Oliver, F.R. Brotzen, J. Mater. Res. 7 (1992) 613–617, https://doi.org/10.1557/JMR.1992.0613.
[12] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564–1583, https://doi.org/10.1557/JMR.1992.1564.
[13] M. Draissia, H. Boudemagh, M.Y. Debili, Phys. Scr. 69 (2004) 348–350, https://doi.org/10.1238/Physica.Regular.069a00348.
[14] N.Q. Chinh, P. Szommer, Z. Horita, T.G. Langdon, Adv. Mater. 18 (2005) 34–39, https://doi.org/10.1002/adma.200501232.