Nanomechanical properties and thermal decomposition of Cu-Al$_2$O$_3$ composites for FGM applications

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Abstract – It is widely reported that copper-alumina (Cu-Al$_2$O$_3$) nanocomposite materials exhibit high potential for use in structural applications in which enhanced mechanical characteristics are required. The investigation of Cu-Al$_2$O$_3$ nanocomposites which are to form a functionally graded material (FGM) structure in terms of nanomechanical/structural integrity and thermal stability is still scarce. In this work, fully characterized nanosized Al$_2$O$_3$ powder has been incorporated in Cu matrix in various compositions (2, 5 and 10 wt.% of Al$_2$O$_3$ content). The produced composites were evaluated in terms of their morphology, structural analysis, thermal behavior, nanomechanical properties and their extent of viscoplasticity. The results reveal that all nanocomposites degrade at elevated temperatures; increased surface mass gain with decreasing Al$_2$O$_3$ content was observed, while no such difference of % mass gain in 5 and 10 wt.% of Al and Al$_2$O$_3$ content in Cu was observed. The increase of Al$_2$O$_3$ wt.% content results in thermal stability enhancement of the nanocomposites. The thermal decomposition process of the material is reduced in the presence of 10 wt.% of Al$_2$O$_3$ content. This result for the matrix decomposition can be explained by a decrease in the diffusion of oxygen and volatile degradation products throughout the composite material due to the incorporation of Al and Al$_2$O$_3$. The Al$_2$O$_3$ powder enhances the overall thermal stability of the system. All samples exhibited significant pile-up of the materials after nanoindentation testing. Increasing the wt.% of Al$_2$O$_3$ content was found to increase the creep deformation of the samples as well as the hardness and elastic modulus values.

Key words: Nanocomposite, Functionally graded material, Nanoindentation

1. Introduction

Copper base nanocomposites are usually reinforced with ceramic nanoparticles in order to improve their physical properties. One of the most important reinforcements is Al$_2$O$_3$ because the presence of fine Al$_2$O$_3$ particles, controlled size, distribution and amount, in copper matrix provides improvement in the hardness as well as decrease in the grain growth rate at temperatures even close to the melting point of the copper matrix.

The reinforcement of Cu metal matrix composites with Al$_2$O$_3$ nanoparticles results in the combination of copper high electrical conductivity together with the high strength of the Al$_2$O$_3$ phase. The achievement of high fracture toughness as well as low processing cost requires small size of particle and particulate Al$_2$O$_3$ phase. In the literature [1–8] several synthetic procedures are used for the production particulate-reinforced Cu-Al$_2$O$_3$ metal matrix composites that mainly include the addition of Al$_2$O$_3$ into the Cu melt followed by casting and internal oxidation of Cu-Al alloy nanoparticles.

For the casting process and in order for effective mixing to be performed (without clustering), several limitations are reported (related either to the Al$_2$O$_3$ size or to the additional amount of reinforcement). Composites with low volume fraction of Al$_2$O$_3$ particles could be produced via internal oxidation process, resulting in a non-homogeneous distribution of oxide particles.

According to the literature [6], blending together with solid-state mechanical alloying processes were used for fabrication of copper composites containing 0–3 wt.% Al$_2$O$_3$. The powders of Cu-Al$_2$O$_3$ composites were sintered in hydrogen at temperatures of 800°C and 900°C. Two different approaches of mixing Cu and Al$_2$O$_3$ were used; either blending together or mechanically milled in an attritor using WC balls. Both the types of powders were sintered in hydrogen atmosphere at 1073–1173 K. An increase in compaction pressure was observed resulting in an increment of both sintered density and hardness of the compacts. Moreover, it was stated that an increase in Al$_2$O$_3$ content in general increased the hardness, however, the electrical conductivity had decreased. Ying and Zhang [7] studied the synthesis of a Cu-20 vol.%
Al$_2$O$_3$ nanocomposite via mechanical milling of the Cu-Al powder together with CuO powder. It was observed that mechanical alloying of Cu and Al powders with Cu/Al atomic ratio of six leads to formation of a Cu(Al) solid solution.

Copper nanocrystalline materials including dispersed Al$_2$O$_3$ (Cu-4 vol.% Al$_2$O$_3$) were fabricated by Hahn and Hwang [9] using a simple cryo-milling at 210 K with a mixture of Cu$_2$O, Al, and Cu ingredient powders, followed by hot pressing at 1123 K. The results revealed that the hot pressed material was comprised of a mixture of Cu matrix with a homogeneous size distribution of the Al$_2$O$_3$. High-energy milling was used for production of Cu-Al$_2$O$_3$ composites by Rajkovic et al. [3] using inert gas-atomized prealloyed copper powder containing 2 wt.% Al and mixture of different sized electrolytic copper powders with 4 wt.% commercial Al$_2$O$_3$ powders. The results revealed that there was a decrease of Cu-2 wt.%Al lattice parameter with milling time due to the oxidation of aluminum which precipitated from prealloyed copper forming a fine dispersion of Al$_2$O$_3$ particles. Moreover, the starting copper particles size and size of Al$_2$O$_3$ particle affects the morphology, size and microstructure of composite powders formed during milling.

The hardness and wear behaviour of Cu-Al$_2$O$_3$ nanocomposites containing 5, 10, and 15 wt.% Al$_2$O$_3$ were prepared by Shehata et al. [4, 10] using mechano-chemical method with two different routes. According to route A, Cu was added to aqueous solution of aluminum nitrate, and in terms of route B, addition of Cu to aqueous solution of aluminum nitrate and ammonium hydroxide was accomplished. The average particle size of Cu was 209 nm in the first route and 141 nm in the second. The Al$_2$O$_3$ particle sizes were 50 and 30 nm, respectively. The relative density of the compacts decreased with increasing amount of Al$_2$O$_3$. The abrasive wear rate of the compacts increased with increasing load and decreased with increasing amount of Al$_2$O$_3$ for both routes.

Mechanical alloying of soft and low melting point metals such as Cu [1], Zn and Al [11] has been proved to result in the formation of large balls of material (instead of powder), but still retaining nanometer-sized grains. Based on these properties, Zhang et al. [8] synthesized consolidated Cu-2.5 vol.% Al$_2$O$_3$ powder. It was proved that the formation of lumps results in the incorporation of Al$_2$O$_3$ fine particles into the Cu matrix forming a composite structure. Furthermore, the maximum grain size was about 100 nm.

The preparation of Al$_2$O$_3$-dispersion-strengthened copper composites, combining mechanical alloying and heat-treatment was accomplished by Takahashi et al. [5]. The obtained Al$_2$O$_3$-copper powders had tendency to sweat pure Cu at the powder particle surface by heat-treatment. The occurrence of sweating resulted in a marked decrease in the hardness values of Al$_2$O$_3$-dispersion-strengthened alloys. Wang et al. [12] investigated the effect of Al$_2$O$_3$ particle size on the arc erosion behaviour of the ceramic-reinforced Al$_2$O$_3$/Cu composite, synthesized by mechanical alloying. It was proved that a decrease in the size of Al$_2$O$_3$ particles results in an increase of the erosion area and the appearance of the shallower erosion pits. The vacuum breakdown occurred preferentially in the area between Al$_2$O$_3$ particle and the copper matrix.

The aim of the present study is to investigate the effect of temperature variation to the weight change of Cu-Al$_2$O$_3$ composites for FGM applications. For this purpose compositions of 2, 5 and 10 wt.% of nanosized Al$_2$O$_3$ powder in Cu matrix were fabricated and subjected to high pressure sintering. The produced composites were evaluated in terms of their morphology, structural analysis, thermal behavior, nanomechanical properties and their extent of creep deformation, after assessing the creep response of 26% (as measuring protocols).

2. Materials and methods

2.1. Reagents

Aluminium nitrate [Al(NO$_3$)$_3$·9H$_2$O, Alfa Aesar, 99.5%], ammonium hydroxide (NH$_4$OH, Alfa Aesar, 25 wt.%) and copper (Sigma Aldrich, powder 99.999% trace metals basis) were used without any further purification.

2.2. Preparation of composites

The preparation of nano-alumina (Al$_2$O$_3$) reinforcement particles was accomplished via the sol-gel method that includes hydrolysis of Al(NO$_3$)$_3$·9H$_2$O, used as inorganic precursor, and poly-condensation reaction with addition of NH$_4$OH serving as catalyst. Gelation was observed immediately after the addition of ammonia solution. The reaction took place under vigorous stirring at 80 °C and ambient pressure. The as produced alumina gels were aged for 14 h at 100 °C and then calcined at 600 °C for 2 h.

High energy ball milling was applied in order to obtain the composite powders with different alumina content. The selected conditions for the production composite powders that had homogeneous distribution of alumina nanopowder into copper matrix were: run of 1 min at 900 rpm and 60 min at low rotation speed, 300 rpm; zirconia grinding media of diameter 1.5 mm and a weight ratio of composite powder to grinding media of 5/1. The compositions of the final produced samples were 2, 5 and 10 wt.% of nanosized Al$_2$O$_3$ powder in Cu matrix.

2.3. Characterization

The morphology as well as the elemental composition of the synthesized particles as well as composites were studied via Ultra-High Resolution Scanning Electron Microscopy (UHR-SEM) using Nova NanoSEM 230 (FEI Company) equipped with an Energy Dispersive X-Ray Spectrophotometer (EDS) EDAX Genesis (AMETEX Process & Analytical Instruments) and via Transmission Electron Microscopy using JEM 1200EX electron microscope. The crystallinity evaluation of the produced materials was performed via Powder X-Ray Diffraction using the Bruker D8 Advance Twin-Twin with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å, power of 40 kV × 40 mA). The XRD patterns were obtained within the range 2θ = 8–80° with a step of 0.02°/min. Thermo-gravimetric analysis (TGA) was performed in order to obtain the
thermal decomposition of each nanocomposite using a STA 409 EP-NETZSCH instrument with a heating rate of 10 K min\(^{-1}\). The samples were heated from room temperature up to 740 \(^\circ\)C and left for 8 h at 740 \(^\circ\)C. The synthetic air atmosphere was a mixture out of 80% nitrogen and 20% oxygen with a flux rate: 35 mL min\(^{-1}\).

Nanoindentation technique has been performed in order to investigate the nanomechanical properties (correlation with microindentation) of the nanocomposites. Creep investigation has also been performed, in order to determine the extent of viscoelasticity in hardness and modulus results. Nanoindentation testing was performed with Hysitron TriboLab\textsuperscript{\textregistered} Nanomechanical Test Instrument, which allows the application of loads from 1 to 30 000 \(\mu\)N and records the displacement as a function of applied loads with a high load resolution (1 nN) and a high displacement resolution. The TriboLab\textsuperscript{\textregistered} employed in this study is equipped with a Scanning Probe Microscope (SPM), in which a sharp probe tip moves in a raster scan pattern across a sample surface using a three-axis piezo positioner. In all depth-sensing tests a total of 10 indents are averaged to determine the mean hardness (H) and elastic modulus (E) values for statistical purposes, with an adequate spacing, in a clean area environment with 45% humidity and 23 \(^\circ\)C ambient temperature. In order to operate under closed loop load or displacement control, feedback control option was used. All nanoindentation measurements have been performed with the standard three-sided pyramidal Berkovich probe, with an average radius of curvature of about 100 nm [13], with 40 s loading and unloading segment time separately and 3 s of holding time, and 5 s loading and unloading segment time separately and 100 s of holding time to avoid residual viscoelasticity [14]. Prior to indentation, the area function of the indenter tip was measured in a fused silica, a standard material for this purpose [15]. The surface of the composites was characterized by SPM.

3. Results and discussion

3.1. Morphology and composition

Taking into consideration the synthesis of nano-alumina (\(\text{Al}_2\text{O}_3\)) reinforcement particles, it may be remarked that as indicated by XRD analysis, the sol-gel method yields \(\gamma\)-alumina phase, as revealed by the peaks corresponding to the characteristic lattice planes of \(\gamma\)-\(\text{Al}_2\text{O}_3\) (Figure 1). Low intensity and broadening of the peaks are indicative of a nanostructure nature. This was further confirmed by TEM micrographs demonstrating alumina particles of rod-like shape and diameter around 7 nm (Figure 2). Accordingly, SEM images displayed a highly homogeneous microstructure of aggregated nano-particles (Figure 3). Figure 4 illustrates the SEM microscopy and elemental mapping of the composite powders with composition Cu-10 wt.% Al\(_2\)O\(_3\). Regarding these characterizations, it is
clearly denoted that the ball milling, at the aforementioned conditions, yielded a composite powder of round shaped particles, excellent alumina dispersion and a mean particle size around 15 \( \mu \)m.

### 3.2. Choosing the protocol - the case of 26% Cu/Al\(_2\)O\(_3\)

Many materials such as metals and plastics exhibit creep under steady load conditions. In an indentation test, creep often manifests itself as a bowing out or “nose” in the unloading portion of the load-displacement curve. This makes it impossible to obtain a measurement of hardness and modulus of the material since the slope of the unloading response, which is ultimately used to determine the contact area, is affected by creep in the material. The most common method of measuring creep is to apply a constant load to the indenter and measure the change in depth of the indenter as a function of time. The resulting “creep curve” can then be analyzed using conventional spring and dashpot mechanical models.

With no hold segment, a “nose” in the load-displacement data in the unloading segment appears. The nose is a result of increasing displacement during unloading. During unloading, even though the load is decreasing, the material is still continuously being stressed at a decreasing rate. The instantaneous viscoplasticity rate at any particular unloading load competes with the elastic recovery due to decrease in load.

In the “nose segment,” viscoplasticity dominates and results in the nose formation. In essence, the displacement lags results in an extended nose. This behaviour is most predominant in the pure Al film.

The Poisson’s ratio is assumed to be constant or follow the rule of mixtures \( v = V_1v_1 + V_2v_2 \).

Given that: Al\(_2\)O\(_3\) Poisson’s ratio: \( v = 0.21 \), \( V = 0.74 \) and Cu Poisson’s ratio: \( v = 0.355 \), \( V = 0.26 \), then:

\[
 v_{\text{composite}} = (0.74 \times 0.21) + (0.26 \times 0.355) = 0.2477.
\]

The reported values of Young’s modulus (\( E \)) and hardness (\( H \)) of Al\(_2\)O\(_3\) and Cu are given in Table 1.

### 3.3. No creep protocol

In Figure 5, hardness and elastic modulus of sample as a function of the maximum displacement are depicted (bulk values~15 GPa and 1 GPa, respectively).

### 3.4. Creep protocol

According to the literature, the recommended hold time for alumina is 51 s [22]. However, the experiments were conducted with a hold time of 100 s. Figure 7 depicts the loading-unloading curves for composite sample (obtained with instrumentation denoted above), which exhibit interesting local discontinuities measured in the load-controlled test of this work; these are characteristic of energy-absorbing or
Table 1. Reported values of Young’s modulus ($E$) and hardness ($H$) of $\text{Al}_2\text{O}_3$ and Cu.

<table>
<thead>
<tr>
<th>Material</th>
<th>$H$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>8</td>
<td>150–155</td>
<td>[16]</td>
</tr>
<tr>
<td>Cu</td>
<td>8.8</td>
<td>169–19</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>150</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>177</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$/Cu</td>
<td>1.29</td>
<td>125</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td>136</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>1.71</td>
<td>131</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>1.80</td>
<td>150</td>
<td>[2]</td>
</tr>
</tbody>
</table>

Figure 5. Hardness and elastic modulus of sample as a function of the maximum displacement, for 26% Cu/$\text{Al}_2\text{O}_3$ sample.

Figure 6. Comparison of the load-displacement curves obtained from the nanoindentation experiments (the nose effect is noted with circle), for 26% Cu/$\text{Al}_2\text{O}_3$ sample.

Figure 7. Comparison of the load-displacement curves obtained from the nanoindentation experiments (pop-ins and elbow phenomenon are noted with circle), for 26% Cu/$\text{Al}_2\text{O}_3$ sample.
energy-releasing events occurring beneath the indenter tip. The transition from purely elastic to elastic/plastic deformation i.e. gradual slope change (yield-type “pop-in”) occurs in the load-displacement curves, at approximately 23 nm (Figure 8). In addition, the sample exhibited the “elbow” phenomenon indicated in Figure 9. Three different physical phenomena usually occur in nanoindentation testing of metals of various states of bonding and structural order; dislocation activity during a shallow indentation, shear localization into “shear bands”, and phase transformation with a significant volume increase during unloading of indentation [23, 24].

In Figure 9, hardness and elastic modulus of sample as a function of the maximum displacement are depicted (bulk values ~17 GPa and 1 GPa, respectively).

During the peak load holding, the indenter continues to penetrate into the sample with time. The penetration of the indenter tip into the sample surface (i.e. creep displacement) during the peak load holding against the holding time is presented. The creep displacement increases but at a decreasing rate, and it becomes almost linear with regard to the holding time (an initial sharp rise in creep displacement in the early part of the creep segment, followed by a region showing a smaller rate of increase in creep displacement). The general profile of these curves is similar to the strain versus time plot obtained for the uniaxial tensile creep testing of bulk materials that exhibit power-law creep behaviour. The initial stage in the following figure corresponds to transient creep (noted in circle), and after this initial displacement, the descent of the indenter continues but the rate of descent decreases to attain a steady state value. It should also be noted that decreasing the loading time, leads to an increase of the creep deformation; moreover, the trend for the curves for
higher loading rates is rather different from those of the lower loading rates. This may be attributed to (i) the strain rate, at the lowest loading rate, which also is lowest and a longer time is needed to reach the holding load, so creep deformation may also occur during the loading time [25], and then the subsequent creep during the holding time will decrease and (ii) the dislocation substructure formed beneath the indenter due to the indentation stress may be different at different loading strain rates, and this substructure will certainly affect the subsequent creep behaviour [26].

The contact area is influenced by the formation of pile-ups and sink-ins during the indentation process. To accurately measure the indentation contact area, pile-ups/sinks-ins should be appropriately accounted for. The presence of creep during nanoindentation has an effect on pile-up, which results in incorrect measurement of the material properties. Fischer-Cripps et al. observed this behaviour in aluminium where the measured elastic modulus was much less than expected [27]. Rar et al. found out that the same material when allowed to creep for a long duration produced a higher value of pile-up/sink-in indicating a switch from an initial elastic sink-in to a plastic pile-up [28].

In Figure 12, the pile-up/sink-in height $h_c/h_m$ at the end of creep is plotted versus the normalized hardness $H/E^*$ for 26% Cu/Al$_2$O$_3$ sample. It is reported that materials with high $H/E^*$, i.e. hard materials, undergo sink-in whereas materials pile-up for low $H/E^*$, i.e. soft materials. In general it is also observed that in the case when $H/E^*$ is high (hard materials), materials undergo sink-ins regardless of work hardening and strain rate sensitivity and all materials collapse to a single

Figure 12. Normalised pile-up/sink-in height for 26% Cu/Al$_2$O$_3$ sample.

Figure 13. Schematic trapezoidal of load-time function.

Figure 14. Optical microscope images for wt.% of alumina content: (a) 2, (b) 5 and (c) 10.
In addition, for materials with low $H/E^*$, soft materials, pile-up depends on the degree of work hardening [29]. Softer materials, i.e., low $H/E^*$, possess a plastic zone, which is hemispherical in shape and meet the surface well outside the radius of the circle of contact and pile-up is expected in these materials. On the other hand, for materials with high values of $H/E^*$, i.e. harder materials, the plastic zone is contained within the boundary of the circle of contact and the elastic deformations that accommodate the volume of indentation are spread at a greater distance from the indenter.

Table 2. Bulk moduli and hardness values for 2, 5 and 10 wt.% of alumina content.

<table>
<thead>
<tr>
<th>$\text{Al}_2\text{O}_3$ wt.%</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
<th>Microhardness (HV$_{0.3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>1.5</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td>5%</td>
<td>2.4</td>
<td>100</td>
<td>93.6</td>
</tr>
<tr>
<td>10%</td>
<td>2.5</td>
<td>100</td>
<td>112.4</td>
</tr>
</tbody>
</table>

Figure 15. Hardness, modulus and SPM images ($50 \times 50 \mu m^2$) for 2 wt.% of alumina content.

Figure 16. Hardness, modulus and SPM images ($50 \times 50 \mu m^2$) for 5 wt.% of alumina content.

Figure 17. Hardness, modulus and SPM images ($50 \times 50 \mu m^2$) for 10 wt.% of alumina content.
Figure 18. (a) Hardness and (b) modulus for 2 wt.% of alumina content, for both creep and no creep protocol.

Figure 19. (a) Hardness and (b) modulus for 5 wt.% of alumina content, for both creep and no creep protocol.

Figure 20. Hardness and modulus for 10 wt.% of alumina content, for both creep and no creep protocol.
Higher stresses are expected in high \( H/E^* \), hard materials, and high stress concentrations develop towards the indenter tip, whereas in case of low \( H/E^* \), soft materials, the stresses are lower and are distributed more evenly across the cross-section of the material [27]. Rate sensitive materials experience less pile-up compared to rate insensitive materials due strain hardening. Cheng and Cheng reported a 22% pile-up for a work hardening exponent [30]. This is consistent with the fact that when \( h_c/h \) approaches 1 for small \( H/E^* \), deformation is intimately dominated by pile-up [31, 32]. On the other hand when \( h_c/h \) approaches 0 for large \( H/E^* \) it corresponds to purely elastic deformation and is apparently dominated by sink-in in a manner prescribed by Hertzian contact mechanics.

3.5. Investigating the % w/w: 2, 5 and 10% Cu/Al\(_2\)O\(_3\) and creep/no creep comparison

The relation (input functions) of displacement time is plotted in Figure 13 (schematic trapezoidal load-time \( P = P(t) \)
input function). In Figure 14, optical microscope images for 2, 5 and 10% of alumina content respectively, are illustrated.

Figures 15–17 demonstrate the hardness, modulus and SPM images (50 × 50 μm²) for 2, 5 and 10 wt.% of alumina content, obtained through nanoindentation depth profile. Bulk moduli and hardness values are summarized in Table 2. Considering the results, it may be remarked that the nanomechanical properties (H, E) range from 1 to 5 GPa for the H and from 20 to 55 GPa for the E.

Figures 18–20 depict the variation of nanomechanical properties of copper alumina composite according to creep and no creep protocol. Creep deformation clearly affects the values of H and E, however this is identifiable and quantified.

3.6. Thermogravimetric analysis

Thermogravimetric analysis was performed in order the resistance to oxidation of the synthesized materials to be investigated. TGA plots for each Al₂O₃-Cu composites and mass gain (surface) calculations were obtained.

The oxidation area was calculated according to the following equation:

\[ A = 2\pi rh + 2(\pi r^2) = 2\pi r(h + r) = 1.3823 \text{ cm}^2. \]  

(1)

The parameters used in equation (1) are schematically represented in Figure 21.
The several exothermic peaks observed at almost high temperatures (corresponding to phase transformations of Al$_2$O$_3$) are recorded. The samples are oxidized at various times providing resistance to oxidation. In literature, oxidized samples are likely to follow the parabolic rate law:

$$Y^2 = k_p \times t,$$

(2)  

Table 3. Tabulated values of oxidation behaviour of Al$_2$O$_3$-Cu composites via TGA.

<table>
<thead>
<tr>
<th>Al$_2$O$_3$ wt.%</th>
<th>Initial mass (mg)</th>
<th>Mass gain (mg)</th>
<th>Mass gain (%)</th>
<th>Surface mass gain (mg/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>752.60</td>
<td>10.86</td>
<td>1.44</td>
<td>7.85</td>
</tr>
<tr>
<td>5</td>
<td>936.60</td>
<td>9.32</td>
<td>0.99</td>
<td>6.74</td>
</tr>
<tr>
<td>10</td>
<td>906.02</td>
<td>7.52</td>
<td>0.83</td>
<td>5.44</td>
</tr>
</tbody>
</table>

The several exothermic peaks observed at almost high temperatures (corresponding to phase transformations of Al$_2$O$_3$) are recorded. The samples are oxidized at various times providing resistance to oxidation. In literature, oxidized samples are likely to follow the parabolic rate law:

$$Y^2 = k_p \times t,$$

(2)  

Figure 24. Thermogravimetric analysis curves obtained for 10 wt.% Al$_2$O$_3$-Cu composite.

Figure 25. Surface mass gain results.
where \( Y \) is the mass gain per unit area (mg cm\(^{-2}\)), \( k_p \) is the parabolic rate constant (mg\(^2\) cm\(^{-2}\) h\(^{-1}\)), and \( t \) is the time (h).

According to Figures 22–24, the estimated tabulated values of Al\(_2\)O\(_3\)-Cu composites oxidation behaviour are tabulated in Table 3 and schematically represented in Figure 25. Taking into consideration the obtained TGA results, it may be remarked that increased surface mass gain with decreasing alumina content was found for the Al\(_2\)O\(_3\)-Cu composites, while no such difference of % mass gain in 5 and 10 wt.% of alumina content in Cu revealed.

4. Conclusion

Increased surface mass gain with decreasing alumina content was found for all the Al\(_2\)O\(_3\)-Cu composites. However, no such difference of % mass gain in 5 and 10 wt.% of alumina content in Cu was revealed. The increase of Al\(_2\)O\(_3\) wt.% content results in thermal stability enhancement of the nanocomposites indicating less prone to oxidation process. This result can be explained by a decrease in the diffusion of oxygen and volatile degradation products throughout the composite material due to the incorporation of Al and Al\(_2\)O\(_3\). The Al\(_2\)O\(_3\) powder enhances the overall thermal stability of the system. All samples exhibited significant pile-up of the materials after nanoindentation testing. Increasing the wt.% of Al\(_2\)O\(_3\) content was found to increase the creep deformation of the samples as well as the hardness and elastic modulus values. Variation of nanomechanical properties of copper alumina composite according to creep and no creep protocol was evidenced; creep deformation clearly affects the values of \( H \) and \( E \), however this is identifiable and quantified.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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