Microhardness of $\text{Al}_2\text{O}_3$ nanoparticles added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor prepared using auto-combustion reaction

M. S. M. Suan* and M. R. Johan

The effects of $\text{Al}_2\text{O}_3$ nanoparticles on the phase formation, microstructure and microhardness of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor prepared by citrate-nitrate auto-combustion reaction were investigated. In this study, $\text{YBa}_2\text{Cu}_2\text{O}_{7-\delta}$ precursor gels containing different compositions of Al nitrate varied from 0.02 to 0.10 mol were continuously heated at 250 °C before automatically combusted into very fine ashes. Calcination process at 900 °C for 1 h has transformed these ashes into sample powders. The XRD and EDX results revealed that $\text{Al}_2\text{O}_3$ nanoparticles were yielded as separate phase from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The nanoparticles were observed homogeneously distributed in $\leq$ 0.06 mol samples while agglomerated along $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries in other samples. The 0.06 mol sample has the highest microhardness compare with the other samples. The $\text{Al}_2\text{O}_3$ nanoparticles by $\leq$ 0.06 mol compositions were effectively acted as reinforced phase which prevent further dislocation movements of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grains. As for $\geq$0.06 compositions, agglomeration of $\text{Al}_2\text{O}_3$ nanoparticles may introduce ductility.

Keywords: $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Al}_2\text{O}_3$, Nanoparticles, Microhardness, Auto-combustion

Introduction

In present, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor has stimulated great interest among researchers because of the fact that it is currently the best suited high critical temperature $T_c$ superconductor for most bulk applications at 77 K. Continuous studies were carried out to enhance the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor properties and this includes the addition of various particles where the $\text{Al}_2\text{O}_3$ addition was highlighted to show numerous advantages. Generally, the $\text{Al}_2\text{O}_3$ nanoparticle was known as effective pinning centre material to enhance magnetic flux trapping and increase critical current density $J_c$ of superconductor. The additions of $\text{Al}_2\text{O}_3$ nanoparticles were also have a profound effect on the grain growth, density and microstructure of superconductor. It is believed that the hardness will also be affected by this microstructure alteration. However, the mechanisms of how the $\text{Al}_2\text{O}_3$ nanoparticles affect the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ microhardness were unresolved since no study was conducted about it. Thus, in this study, the $\text{Al}_2\text{O}_3$ nanoparticles were purposely added into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ using citric nitric auto-combustion reaction to achieve uniform particles distribution as suggested by the literature. The aim of this work was to determine the composition and distribution effects of $\text{Al}_2\text{O}_3$ nanoparticles towards $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor microhardness.

Methodology

Powders of $\text{Al}_2\text{O}_3$-added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were synthesised using citrate-nitrate auto-combustion reaction. The $\text{Y(NO}_3)_3$, $\text{Ba(NO}_3)_2$, $\text{Cu(NO}_3)_2$ and $\text{Al(NO}_3)_3$ stock solutions with concentration of 0.5, 0.5, 0.25 and 0.5 M were prepared by dissolving each reagents material into distilled water. The solutions were mixed with the mole ratio of $\text{Y:Ba:Cu:Al} = 1:2:3:x$, where $x$ was ranged from 0.0 to 0.10 mol. Calculated amount of citric acid was added to the mixtures to achieve the citrate/nitrate ratio, $c/n = 0.7$. This was followed by adjusting the pH to $\approx 7$ by adding ammonia solution. The mixtures were heated to 250°C on the hot plate and under the IR lamp to achieve uniform heating. This process has transformed the mixture solutions to gels before combusted to very fine and highly reactive brown ashes. The ashes were calcined in the furnace at 900°C for 1 hour to yield stable black powder. The resulting powders were pelleted to diameter of 10 mm and thickness of 2 mm by applying 12.4 MPa load. The resulting powders were sintered at 960°C for 1 hour under normal atmosphere before soaked in oxygen flow (50 mL per minute) at 500°C for 20 hours and let cooled in furnace to room temperature. The samples were labelled by refer to its Al nitrate compositions. The structural properties of sintered samples

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were characterised by X-ray diffraction (XRD) from Ni-filtered Co Kα radiation (Bruker Advanced) and the patterns were analysed by Rietveld’s refinement method. The Zeiss Auriga Ultra 40XB field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX) spectra was used to observe the microstructure and identify the elemental composition of the samples. The hardness testing was performed using Mitutoyo AVK-C2 Vickers hardness tester at room temperature. The diamond indenter with 136° of indentation angle was employed to indent the samples at five different spots by holding time of 20 s.

Results and discussions

Figure 1 shows the structural analysis of Al₂O₃-added YBa₂Cu₃O₇-δ samples. The Rietveld patterns were depicted by the red dots, whereas the actual XRD patterns and the intensity differences were, respectively, depicted by the black and blue lines as shown in Fig. 1a. The low-intensity differences between actual XRD patterns with Rietveld’s patterns confirmed that the structure and parameters achieved by this analysis are accurate. The analysis revealed that the YBa₂Cu₃O₇-δ phase was preserved even at highest Al nitrate addition as all the significant peaks diffracted accordingly to the YBa₂Cu₃O₇-δ reference positions signified with tiny green bars on the graph. The Al₂O₃ characteristic peaks, however, were unable to be distinguished from the background noise peaks because of relatively low Al₂O₃ content and highly dominant of YBa₂Cu₃O₇-δ peaks. The lattice parameters for the ≤0·06 mol samples are almost constant with the average value of \( a = 3·832 \, \text{Å}, \quad b = 3·873 \, \text{Å} \) and \( c = 11·672 \, \text{Å} \) as seen in Fig. 1b. These values are comparable with the literature of the pure YBa₂Cu₃O₇-δ. At these compositions, the YBa₂Cu₃O₇-δ lattice structure remained unchanged because the Al₂O₃ nanoparticles were yielded as the

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1 The structural analysis of Al₂O₃-added YBa₂Cu₃O₇-δ samples: a Rietveld’s analysis pattern for 0.06 mol sample, b lattice parameters of the samples and c molecular structure of YBa₂Cu₃O₇-δ.
distinct phases and well distributed in the samples. The $a$ and $c$ lattice parameters are noticed to increase as the Al$_2$O$_3$ nanoparticles content was increased in ≥0.08 mol samples. The increments are believed because O$^-$ ions try to fill in its deficiencies site and incorporation of Al$^{3+}$ ions at the Y site as shown by the YBa$_2$Cu$_3$O$_7$-$\delta$ molecular structure in Fig. 1c. These phenomena are possible since the Al$_2$O$_3$ nanoparticles yielded at higher Al nitrate compositions have a tendency to agglomerate at the YBa$_2$Cu$_3$O$_7$-$\delta$ grain boundaries and created Al$^{3+}$ and O$^-$ ion-rich regions at sintering temperature. The lattice’s changes, however, do not create any orthorhombic-to-tetragonal phase even with the presence of highest content Al$_2$O$_3$ nanoparticles.

Table 1 lists the elemental analysis of the samples using mapping and pointed EDX spectra. Although the existence of the Al$_2$O$_3$ nanoparticles phase was uncertain through XRD characterisations, it was apparent in the EDX analysis. The EDX spectra pointed to the fine particles in Al nitrate-added samples have projected Al and O elements with the atomic percentage ratio of Al/O = 2.3. This proved that the Al$_2$O$_3$ nanoparticles obtained by this reaction have successfully yielded as the distinct phase from YBa$_2$Cu$_3$O$_7$-$\delta$. The mapping of EDX analysis also evidences the incorporation of Al$^{3+}$ ions at the Y site occurred in 0.08 and 0.10 mol samples as suggested by the XRD results. The atomic percentage of Y element was decreased, whereas the

Table 1  Elemental analysis of Al$_2$O$_3$-added YBa$_2$Cu$_3$O$_7$ samples by EDX techniques

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mapping EDX of YBCO grain (at.-%)</th>
<th>Point EDX of fine particle (at.-%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y</td>
<td>Ba</td>
<td>Cu</td>
</tr>
<tr>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>8.08</td>
<td>16.18</td>
<td>23.97</td>
</tr>
<tr>
<td>0.02 mol</td>
<td>8.03</td>
<td>16.24</td>
<td>24.01</td>
</tr>
<tr>
<td>0.04 mol</td>
<td>8.05</td>
<td>17.33</td>
<td>24.15</td>
</tr>
<tr>
<td>0.06 mol</td>
<td>8.08</td>
<td>16.58</td>
<td>23.69</td>
</tr>
<tr>
<td>0.08 mol</td>
<td>7.86</td>
<td>18.17</td>
<td>24.79</td>
</tr>
<tr>
<td>0.10 mol</td>
<td>7.73</td>
<td>18.44</td>
<td>23.85</td>
</tr>
</tbody>
</table>

Table 2  Microstructures of Al$_2$O$_3$-added YBa$_2$Cu$_3$O$_7$-$\delta$ samples at different Al nitrate compositions: a 0.00, b 0.02, c 0.04, d 0.06, e 0.08 and f 0.10 mol
Al atomic percentage increased at these compositions as listed in Table 1.

The microstructure of the pure YBa$_2$Cu$_3$O$_{7-δ}$ and Al$_2$O$_3$-added YBa$_2$Cu$_3$O$_{7-δ}$ samples was shown in Fig. 2. The pure YBa$_2$Cu$_3$O$_{7-δ}$ sample has well-defined orthorhombic shape particles with the sizes ranging from 50 to 300 nm (Fig. 2a). The YBa$_2$Cu$_3$O$_{7-δ}$ microstructure remains unchanged for ≤ 0.06 mol samples that are in good agreement with the XRD results. At these compositions, the Al$_2$O$_3$ nanoparticles (∼10 nm) were observed to be well distributed as the distinct phase in the sample as shown by Fig. 2d–f. Further increase of Al$_2$O$_3$ nanoparticles content in the 0.08 and 0.10 samples results in denser and melted-like microstructure as clearly seen in Fig. 2e and f. The Al$_2$O$_3$ nanoparticles yielded at these compositions were agglomerated along YBa$_2$Cu$_3$O$_{7-δ}$ inter-grain boundaries and created the Al-rich region which diffused into the YBa$_2$Cu$_3$O$_{7-δ}$ system and act as the bridge to improve connectivity between YBa$_2$Cu$_3$O$_{7-δ}$ grains. This phenomenon can be observed in Fig. 3 where most of the Al ions in 0-10 mol sample depicted by purple dots agglomerated at certain area of micrograph while partial of it was merged into YBa$_2$Cu$_3$O$_{7-δ}$ grain.

Figure 4 shows the Vickers microhardness profile for YBa$_2$Cu$_3$O$_{7-δ}$ and Al$_2$O$_3$-added YBa$_2$Cu$_3$O$_{7-δ}$ samples as a function of the Al nitrate compositions. It can be observed that the microhardness of the YBa$_2$Cu$_3$O$_{7-δ}$ sample was drastically enhanced from 80 to 220 MPa by the 0.02 mol sample. The microhardness values keep increasing as the Al$_2$O$_3$ nanoparticles were increased and achieved the highest value of 300 MPa by the 0.06 mol sample. It is notable that these values rose with low standard deviation. The microhardness values were then decreased back to 230 MPa by further increase of Al$_2$O$_3$ nanoparticles content with larger standard deviations. The variation of microhardness can be attributed to strengthening mechanism provided by the nanoparticles reinforced phase, which has been intensely discussed by Ohji et al. This mechanism is possible since the Al$_2$O$_3$ nanoparticles were successfully yielded as the distinct phase in our YBa$_2$Cu$_3$O$_{7-δ}$ samples. The Al$_2$O$_3$ nanoparticles known as harder material will elastically interact with dislocations within the YBa$_2$Cu$_3$O$_{7-δ}$ grains and consequently, prevent the dislocation movements during indented. In addition, well distribution of Al$_2$O$_3$ nanoparticles in the samples achieved by auto-combustion reaction has resulted in the uniform microhardness value. The hardening mechanism is maximised at 0.06 mol sample as more dislocation movements are prevented by more Al$_2$O$_3$ nanoparticles. Further increase of Al nitrate composition causes the Al$_2$O$_3$ nanoparticles to agglomerate at YBa$_2$Cu$_3$O$_{7-δ}$ inter-grains and create a harder region. On the other hand, the microhardness at the intra-grains was lowered because the dislocation movements within the YBa$_2$Cu$_3$O$_{7-δ}$ grains are not prevented. In addition, Zhang et al. suggested that the decrease was due to

3 Element mapping micrograph of 0.10 mol sample

4 Vickers microhardness of the Al$_2$O$_3$-added YBa$_2$Cu$_3$O$_{7-δ}$ samples
alteration of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure by $\text{Al}^{3+}$ ions that were diffused from agglomerated $\text{Al}_2\text{O}_3$ and introduced ductility to the sample. These result in broad range of the microhardness value as depicted by longer error bars of 0.08 and 0.10 mol samples.

**Conclusion**

The microhardness of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was greatly improved by the addition of $\text{Al}_2\text{O}_3$ nanoparticles. The uniform distribution of $\text{Al}_2\text{O}_3$ nanoparticles achieved by auto-combustion reaction has effectively prevents further dislocation movements within $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grains during indented. The highest microhardness was achieved by the 0.06 mol Al nitrate sample. At higher compositions, the microhardness values were decreased because of the development of the Al-rich region along with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundary.

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**References**


