Mechanical Alloying for Heat-Resistant Copper Alloys

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INTRODUCTION

Heat-resistant copper alloys that display high electrical and/or thermal conductivities are employed in a variety of applications, including resistance welding electrode contacts, electrical switches, microwave and x-ray tube components, incandescent lamp lead wires, and neutron irradiation targets. Some applications, such as welding electrodes, require elevated-temperature strength during service, while others demand resistance to softening during high-temperature manufacturing operations (e.g., brazing).

The wrought Cu-Cr and Cu-Zr alloys commonly used for elevated temperature applications are strengthened through thermomechanical treatments which cause precipitation and stabilization of a strain-hardened structure. In such alloys, recovery and recrystallization are minimized below ~450°C. Retention of mechanical properties following exposure to even higher temperatures has been demonstrated in oxide dispersion strengthened copper, and several materials in this class are now made commercially through a variation of internal oxidation.

Recently, alloy development efforts have centered on combining the strengthening mechanisms available through an inert oxide dispersion with precipitation or solute strengthening. The introduction of an oxide dispersion into a matrix having a complex composition is not feasible using traditional internal oxidation or precipitation methods. While Grant and co-workers demonstrated a powder metallurgy technique for producing such alloys by surface oxidation of fine alloyed copper flakes, which is then followed by mechanical working to distribute the oxide particles, mechanical alloying is a more versatile processing alternative, allowing independent control of both the matrix composition and oxide dispersoid.

MECHANICAL ALLOYING

Mechanical alloying is a completely solid-state process for combining disparate elemental powders or powder blends into relatively homogeneous, dense powder forms for subsequent powder processing and consolidation. The fundamental action to be performed during mechanical alloying is the repeated welding, fracturing and rewelding of a mixture of powder particles during high-energy ball milling. The greatest utility of mechanical alloying has been its ability to add stable dispersoid populations to complex matrix compositions to improve elevated-temperature performance. Oxide dispersions improve high-temperature creep strength in nickel- and iron-base alloys which have matrix compositions optimized for corrosion or oxidation resistance. Aluminum alloys have also been strengthened effectively by the addition of Al2O3 and Al4C3 dispersoids.

The mechanical alloying of nickel- and iron-base materials incorporates dry milling of the desired constituents. For aluminum, which has a lower melting point, cold welding and particle agglomeration interfere with the mechanical alloying process unless a surfactant or process control agent is used during milling.

Only limited efforts have been expended in investigating the mechanical alloying of copper-base materials for structural applications, with research generally centering on extending the amount of a metallic second phase that can be attained in a copper matrix, (e.g., in the Cu-Cr system). At the General Motors Research Laboratories, however, investigations have instead concentrated on adding an oxide dispersoid to a copper matrix that is additionally strengthened by the presence of solute or precipitates. A critical issue in this program was to determine whether a random distribution of fine oxide particles could be produced in a copper-base matrix during dry milling. Surfactants were avoided to maximize electrical and thermal conductivity in the final material by minimizing soluble impurities.

ATTRITOR MILLING OF COPPER-BASE ALLOYS

Experimental trials involved the milling of 900-g powder blends charged to a Szegvari Model 1-8 attritor mill, which incorporates a sealed cylindrical drum that possesses a vertically positioned, rotating shaft aligned along the mill central axis. During operation, five arms radiating from the shaft agitate the charge of powder and milling media (10 kg of 4.8 mm diameter steel balls).

Copper-Molybdenum

Microstructural evolution during mechanical alloying was initially studied in Cu-10% Mo by milling elemental copper and molybdenum powders. Figure 1...

In the development of heat-resistant, high-conductivity copper alloys, beneficial properties may be obtained through the application of mechanical alloying. Mechanical alloying has been applied to copper-base materials with the ultimate goal of obtaining improved elevated-temperature performance through oxide dispersion strengthening in a complex matrix that has been solute- or precipitation-strengthened. Preliminary results indicate that a random distribution of fine oxide particles can be obtained in a copper matrix through high-energy attritor milling.
Figure 3. Backscattered electron image of a Cu-10% Mo powder particle mechanically alloyed for 18 hours at 250 rpm.

Figure 4. Particle hardnesses for mechanically alloyed Cu-10% Mo. The solid circles are the average values.

Table I. Size Distribution of Original Copper Powder

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Size (d)</th>
<th>Wt.%</th>
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<tbody>
<tr>
<td>+100</td>
<td>d &gt; 150 μm</td>
<td>0.1</td>
</tr>
<tr>
<td>+140</td>
<td>106 μm &lt; d &lt; 150 μm</td>
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<tr>
<td>+200</td>
<td>75 μm &lt; d &lt; 106 μm</td>
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<tr>
<td>+325</td>
<td>45 μm &lt; d &lt; 63 μm</td>
<td>13.0</td>
</tr>
<tr>
<td>-325</td>
<td>d &lt; 45 μm</td>
<td>56.2</td>
</tr>
</tbody>
</table>

To effectively dispersion harden a complex alloy matrix, the dispersoid particles must be randomly distributed within the microstructure. The efficacy of mechanical alloying in achieving such dispersions was investigated by milling copper powder (size distribution shown in Table I) with Al₂O₃ (~50 nm particle size) and ZrO₂ (~30 nm particle size). In both cases, the initial ceramic particles existed in micrometer-sized agglomerates.

Typical structures developed in a Cu-2 vol.% Al₂O₃ alloy—following seven hours of milling—are shown in Figure 5. The resultant microstructure is characteristic of copper-oxide blends mechanically alloyed for relatively short times. At this point, oxide particles are largely restricted to interlamellar planes between adjacent copper lamellae.

Extended milling periods and higher energies (higher mill rpm levels) develop structures that are too fine to be resolved with the scanning electron microscope. Consequently, transmission electron microscopy has been used to examine a Cu-4 vol.% ZrO₂ alloy processed for 24 hours at 250 rpm. Because of difficulties in attempting to image the as-milled powder particles, the structure was investigated following 700°C hot swaging into bar form. The alloy was studied with a JEOL JEM 200C scanning transmission electron microscope operated at 200 kV.

Bright field micrographs of the consolidated Cu-ZrO₂ alloy revealed an extremely fine-grained microstructure (Figure 6). The grain size distribution was...