Effect of Sulfur on the Ductility of Copper Shaped-Charge Jets

D. H. Lassila, E. L. Baker, D. K. Chan,
W. E. King, A. J. Schwartz

This paper was prepared for submittal to the
16th International Symposium on BALLISTICS
San Francisco, CA
September 23-28, 1996

July 1996

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
EFFECT OF SULFUR ON THE DUCTILITY OF COPPER SHAPED-CHARGE JETS

David H. Lassila, Ernie L. Baker*, David K. Chan, Wayne E. King, and Adam J. Schwartz
Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551
*U. S. Army, ARDEC, Picatinny, NJ 07806

We have observed that a change in the bulk sulfur content imposed by doping has a marked effect on the ductility of copper shaped-charge jets as measured by the breakup times and length-to-diameter ratios of the particulated jet. The base-line material in this work was Oxygen-Free-Electronic (ofe) copper with a sulfur concentration of 3 - 4 ppm. Several liners were doped using a copper sulfide powder pack method to increase the sulfur level up to 9 ppm while keeping other impurities concentrations and the microstructure (grain size and texture) unchanged. Using flash x-ray radiographs to record the formation of the jets, both the length-to-diameter ratios of the jet particles and the breakup times were measured. Increasing the bulk sulfur content of the ofe Cu to 9 ppm, the breakup times decreased from 186 µs to 147 µs, while the length-to-diameter ratios observed at 260 µs decreased from 8:1 to 5:1. Since the solubility of sulfur in copper at the processing temperatures is extremely low, we conclude that the bulk rise in sulfur content is due to sulfur segregating to the grain boundaries. Thus, the decrease in ductility of liners doped with sulfur appears directly related to the sulfur content at the grain boundaries.

INTRODUCTION

The microstructural and chemical parameters which control the breakup behavior of copper jets formed from the explosive deformation of shaped-charge liners are not well understood. It has been reported [1-3] that the grain size, texture, and impurity levels are important factors which affect the performance of liners due to their influence on the breakup behavior of copper jets undergoing high strain rate (10^3 s^-1) and high temperature (400-1000°C) deformation. It is generally accepted that copper liners with small grain sizes and low impurity concentrations exhibit good performance with long breakup times. Corresponding to this, the jets are observed to undergo ductile rupture. Conversely, liners with large grain sizes and high impurity contents tend toward poorer performance, shorter breakup times and jets which exhibit more brittle breakup behavior. Duffy and Golaski [2] have examined the penetration of copper jets as a function of grain size and found nearly a two-fold increase in penetration when the grain size was reduced from 120 µm to 10 µm. In addition, they observed jet instabilities with starting grain sizes between 30 and 50 µm. Lassila [3] examined shaped-charges with two different types of electrodeposited copper and found the liners produced fragmented and particulated jets of poor quality. Using tensile testing and chemical analysis of the fracture surfaces, Lassila showed that segregated impurities caused grain boundary embrittlement under tensile loading. It was observed that a good correlation existed between the fracture behavior and the chemical analysis of the fracture surfaces of the materials and the degree of jet fracture and particulation. Gurevitch et al. [4] have characterized the recovered jet particles from copper and tantalum shaped-charges
and observed a reduction in grain size in the recovered particles. The authors conclude the reduction in grain size is due to dynamic recrystallization during jet formation and stretching. Although many investigators have examined the effects of various microstructural features on the performance of copper shaped-charge jets, there have not been any systematic studies of the effect of individual impurities on the ductility of the jets, keeping other microstructural parameters constant.

In this investigation, ofe copper (99.99% Cu) was thermomechanically processed into shaped-charge liners, microstructurally and chemically analyzed, then doped in a copper sulfide powder pack to increase the sulfur content. The objective was to start with a consistent grain size, change only the impurity (sulfur) content, then to observe the effect on the jet ductility by measurements of breakup time and length-to-diameter ratios of the particulated jets.

EXPERIMENTAL PROCEDURES

The copper shaped-charge liners were produced from ofe 99.99% Cu, Hitachi Cl0100 bar stock with the measured impurity concentration obtained by chemical analysis listed in Table 1 [5]. The liners were back extruded using a standard cold-forge process into the shape of hollow cones (base inner diameter = 81 mm, apex angle = 42° at Northwest Industries, Albany, OR [6]. After forging, the liners were annealed at 315 °C or one hour and 400 °C or 10 minutes and 100 hours in order to stabilize the microstructure. Standard optical metallographic techniques as well as conventional and high resolution transmission electron microscopy were used to characterize the microstructure.

Table 1. The measured impurity concentrations in ofe copper, Hitachi C10100 stock. All other elements had concentrations of < 0.1 ppm.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration (ppm)</th>
<th>Impurity</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.9</td>
<td>Ni</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>5.0</td>
<td>As</td>
<td>0.4</td>
</tr>
<tr>
<td>N</td>
<td>&lt;0.1</td>
<td>Se</td>
<td>0.3</td>
</tr>
<tr>
<td>O</td>
<td>6.0</td>
<td>Ag</td>
<td>6.4</td>
</tr>
<tr>
<td>Si</td>
<td>0.2</td>
<td>Sb</td>
<td>0.3</td>
</tr>
<tr>
<td>P</td>
<td>0.4</td>
<td>Pb</td>
<td>0.2</td>
</tr>
<tr>
<td>S</td>
<td>4.0</td>
<td>Bi</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After the recrystallization anneal, several of the liner cones were doped with sulfur using a Cu$_2$S powder pack method as shown schematically in Figure 1. This method consisted of placing the copper liners in an evacuated (<10^-5 Torr) Pyrex container containing Cu$_2$S powder. The interior of the Pyrex container was lined with graphite to getter any residual oxygen. The liners were heated at 250°C for six hours or 310°C for 48 hours. Under these annealing conditions, no grain growth was observed. The partial pressure of sulfur that was obtained in the closed environment was equal to the partial pressure required to maintain equilibrium between Cu$_2$S with copper and sulfur [7] according to equation 1.
After annealing, the surfaces of the liners had a slight tarnish which was easily removed by etching in a dilute nitric acid solution. The sulfur concentration of the doped liners was measured using standard titration methods.

Fig. 1 A schematic diagram of Cu$_2$S powder pack system used to dope the copper liners.

A relatively standard shaped-charge design was used for this study which consisted of a precision BRL 81 mm liner loaded with Octol 70/30 into an aluminum constant diameter cylindrical body. The shaped-charge liner is a 42 degree, 1.9 mm constant wall thickness cone with a spherical apex cap. Flash x-ray radiographs were obtained at 140 µs, 180 µs and 260 µs after detonation and used to calculated the jet breakup time, and the length-to-diameter ratios of the jet particles. The jet breakup time, $t_b$ is an indication of the ductility of the jet and the amount of ductile rupture that occurs. Longer breakup times indicate a greater amount of ductile rupture. The length-to-diameter ratios measured at 260 µs also reveal important characteristics of the breakup behavior. Long, thin particles with smooth, rounded tips indicate a ductile jet breakup, while shorter, wider particles which often have “ragged” ends indicate a less ductile jet.

RESULTS AND DISCUSSION

Glow discharge mass spectrometry and LECO chemical analysis of the sulfur doped liners showed that the sulfur concentration increased from the baseline of 3 - 4 ppm up to 7 - 9 ppm, while the remaining impurity concentrations remained unchanged. The grain size of the liners remained unchanged at 15-25 µm and 30-50 µm after heating at 310 and 400°C, respectively. Optical micrographs of the undoped copper liner shown in Fig. 2a revealed

\[
\text{Cu}_2\text{S} \xleftrightarrow{T} 2\text{Cu} + \text{S} \tag{1}
\]
no second phases, inclusions, or porosity. Similar features including the lack of inclusions, porosity or second phases were observed in the sulfur doped liners (Fig. 2b-d), indicating that no change in grain size had occurred during the sulfidation process. This result was corroborated by conventional transmission electron microscope results, in which no additional features in the sulfur doped liners were observed as compared with the original liners.

Fig. 2   Optical micrographs showing the grain structure of the copper liners with different sulfur concentrations, \(c_S\). (a) \(c_S = 4\) ppm; (b) \(c_S = 7\) ppm; (c) \(c_S = 8\) ppm; and (d) \(c_S = 9\) ppm.

X-ray radiographs of the short time (140 \(\mu\)s after detonation) shaped-charge jets containing 3 ppm and 9 ppm sulfur are shown in Fig. 3. It is obvious from the radiograph in Fig. 3b that the higher sulfur content liner exhibited an earlier onset of necking compared to the undoped ofe Cu liner in Fig. 3a. Radiographs of the shaped-charge jets taken at 260 \(\mu\)s are used to characterize the breakup behavior. The starting ofe Cu with 3 ppm sulfur, shown in Fig. 4a, had jet particles with axisymmetric, uniform breakup with length-to-diameter ratios of greater than 8:1. The calculated breakup time was 186 \(\mu\)s. This breakup behavior was typical of jets formed from liners with similar purities, that is, low sulfur contents. A
dramatic difference in breakup behavior was observed in the sulfur doped liners as compared to the undoped liners. X-ray radiographs of the shaped-charge jets formed from higher sulfur concentration liners, shown in Fig. 4b-d, reveal jet particles with irregular particulation (non-axisymmetric), fragmentation, and off-axis tumbling. The length-to-diameter ratios decreased to approximately 5:1, and the breakup times decreased by approximately 35 μs to about 150 μs. These results are summarized in Fig. 5 of breakup time as a function of sulfur concentration. The breakup times measured by Lichtenberger [1] for copper bearing 13 ppm and 20 ppm of sulfur were included in this plot to demonstrate the negative relationship between sulfur concentration in the liner and jet breakup time.

Fig. 3 X-ray radiographs (at 140 μs) showing the early onset of necking of the copper shaped-charge jet with 9 ppm sulfur. The dark contrast is the copper jet, and the vertical lines are fiducials for timing. (a) \( c_S = 3 \) ppm; (b) \( c_S = 9 \) ppm.

Fig. 4 X-ray radiographs (at 260 μs) showing the breakup behavior of the copper shaped-charge jets. (a) \( c_S = 3 \) ppm, \( t_b = 186 \) μs, length-to-diameter ratio (L/D) = 8:1; (b) \( c_S = 7 \) ppm, \( t_b = 148 \) μs, L/D = 5:1; (c) \( c_S = 8 \) ppm, \( t_b = 148 \) μs, L/D = 5:1; and (d) \( c_S = 9 \) ppm, \( t_b = 152 \) μs, L/D = 5:1.
An increase in the sulfur grain boundary concentration during the doping procedure is believed to be the underlying cause for the change in breakup behavior. The pack-powder doping established a sulfur concentration in the copper liner such that the activity of sulfur at the surface was equal to the activity of sulfur in the grain boundary and in the bulk. However, the establishment of an equilibrium distribution in the copper was diffusion limited. The root mean square diffusion distances of sulfur in bulk copper at 250°C for six hours and 310°C for 48 hours are 4.8 x 10^{-7} cm and 7.4 x 10^{-6} cm [8], respectively, while the respective grain boundary diffusion distances are 0.1 cm and 0.7 cm [9]. Therefore, most of the sulfur was dissolved into the grain boundaries, and very little sulfur was dissolved into the bulk. We infer from the sulfur kinetics that the measured bulk increase in the sulfur concentration was due to an increase only in the grain boundary sulfur concentration. This increase was calculated as approximately 6 wt. % sulfur if we assume that the grains are cubes with a 3 x 10^{-3} cm width and an estimated grain boundary width of 1 x 10^{-7} cm. 

To test this assumption that the sulfur is segregating to the grain boundaries, two 99.9999% copper single crystals were bonded to form a 100/553 [110] bicrystal. The 553 planes are approximately 4° off the 221 planes, and therefore the grain boundary is off Σ=3 by 4°. The bonding conditions were 850°C for 2 hours. These high purity bonded bicrystals were then used to characterize the sulfur doping. Two specimens were analyzed using a focused ion beam (FIB) secondary ion mass spectrometry (SIMS) using an FEI FIB 200 workstation with SIMS capabilities at Riga Analytical Labs, Santa Clara, CA. The two samples that were analyzed: 100/553 [110] — one as made, another doped with sulfur. Secondary electron images (SEI), which are similar to SEM SEI images are used to locate the grain boundary and elemental sulfur maps were obtained. We observed that there was an enhancement of sulfur at the doped grain boundary, but no additional sulfur was observed at the undoped grain boundary as shown in Figure 6.
CONCLUSIONS

The change in sulfur concentration in copper, from 3 - 4 ppm to 7 - 9 ppm, resulted in a change in jet breakup behavior: the measured breakup times of the jets decreased over 20%, from 186 µs to 147 µs. We infer from the sulfur kinetics in copper and the FIB SIMS elemental map that the sulfur increase in copper is localized to the grain boundaries, resulting in a calculated increase of 6 wt.% at the grain boundaries. Although the total concentration of 9 ppm is under the ClO1000 limit of 15 ppm sulfur [10], the 6 ppm increase in sulfur had a profound effect on the shaped-charge jet ductility.

ACKNOWLEDGMENTS

This work performed under the auspices of the U.S. Department of Energy, the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48, and the U. S. Army ARDEC Technology Base Target Defeat Program.

REFERENCES

[5] Interstitial impurities were measured by Luvak Inc., and metallic impurities were measured by Northern Analytical Laboratory Inc. using glow discharge mass spectrometry.

