The influence of post-processing on creep and microstructure of rolled Cu–8Cr–4Nb

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A B S T R A C T

Previous work has shown that rolling of an extruded Cu–8Cr–4Nb (GRCop–84) alloy results in higher steady-state creep rates over a range of stresses, leading to concern that other post-processing methods could have substantial deleterious effects on creep properties. To explore that possibility, constant-stress creep tests were conducted at 773 K on rolled GRCop–84 after it was subjected to either friction stir welding (FSW) or a 24 h 1073 K simulated-life heat treatment. The FSW had no measurable effect on the creep rate of the rolled material, but did have detrimental effects on the creep ductility caused by softening, and thus strain localization, in the heat-affected zone of the weld. The simulated-life heat treatment decreased the steady-state creep rate by approximately 45% as compared to the rolled material, leading to longer creep life at a particular applied stress. Electron backscatter diffraction methods were used to compare the microstructural features of extruded, rolled and annealed material forms. It was determined that the rolling procedure decreased the grain size, and decreased the intensity of the texture as compared to the extruded form. The simulated-life heat treatment allowed for the substantial development of twins along with minor grain growth, and a substantial decrease in texturing.

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1. Introduction

Creep resistant copper alloys are of interest for moderate to high-temperature applications where the design limiting properties are the strength and thermal conductivity of the material at the service temperature. In particular, actively cooled structural components in rocket nozzles and combustion chamber walls require a material with high strength to weight ratio, good creep resistance, and high thermal conductivity. Dispersion strengthened copper alloys are a natural choice for these applications because of their inherently excellent thermal conductivity and high creep strengths in oxygen and hydrogen rich environments. Copper alloys are also relatively easy to machine, form, and weld into desired components [1]. A dispersed, high melting temperature, second phase increases room temperature strength and creep resistance by pinning grain boundaries to limit recrystallization and grain growth and by also interfering with dislocation motion [2]. One such dispersion strengthened copper alloy is the NASA Glenn Research Center developed GRCop–84, in which copper is alloyed with 8 at% Cr and 4 at% Nb, resulting in the formation of 14 vol% Cr2Nb precipitates dispersed in the copper matrix [3]. One proposed application of this alloy, regeneratively cooled rocket engine combustion chamber liners, requires good creep resistance at temperatures ranging from 773 to 1073 K for 100 launch cycles. For this application, depending upon the specifics of engine design, GRCop–84 could be used in extruded or rolled conditions, with or without friction stir welding needed for joining. Recent work has shown that there is an order of magnitude difference in creep rates between extruded and rolled material conditions [4]. Due to the substantial differences in creep rate with respect to material processing conditions, it is important to further understand this material’s mechanical properties as a function of processing methods. The goal of the present study was to compare creep properties of extruded and rolled GRCop–84 with rolled GRCop–84 subjected to subsequent processing: a heat treatment simulating the service life cycle and a friction stir welding (FSW) step [5,6]. An additional goal was to explain changes in the creep properties in relation to the microstructural changes caused by the different post-processing methods.

2. Materials and methods

All forms were produced from conventionally argon gas atomized ~140 mesh (<106 μm) Cu–8Cr–4Nb powders that were consolidated via extrusion at 1133 K (extruded form) as described in earlier work [4]. Some of the extruded material was subsequently warm rolled to 1 mm thick sheets (rolled form). Each rolling pass consisted of a 15% reduction at temperatures between 473 and
673 K. Once rolled, the sheet was given a 15 min anneal at 773 K followed by air-cooling. This rolled material has been characterized in detail by Vettraino et al. [7]. The FSW samples were produced by friction stir butt-welding the rolled sheets. The 1 mm sheets were butt-welded together using proprietary methods on a high-speed FSW tool, with pin diameter of approximately 3.2 mm, at the NASA Marshall Space Flight Center (MSFC). The FSW process was followed by a residual stress relief heat treatment at 873 K for 15 min [8].

Creep and tensile test specimens from the extruded and rolled forms were electro-discharge machined and the FSW specimens were mechanically milled. The sample gage length was 38.1 mm, the sheet was 1 mm thick and the gage width was 2.5 mm. Following machining, some rolled form samples were given a simulated-life heat treatment at 1073 K for 24 h in vacuum ($< 7 \times 10^{-10}$ MPa); this condition is described throughout the rest of the paper as the annealed form. The annealing temperature and duration are based upon the maximum expected temperature of the combustion chamber liner for the duration of 100 missions. Two samples of each processing type were tested under tension at room temperature using an Instron 4204 machine with computer control at a constant displacement rate of 0.0423 mm/s. All creep tests were conducted in tension at 773 K under vacuum ($<3 \times 10^{-9}$ MPa) with stresses ranging from 75 to 200 MPa using a custom built constant-stress creep machine, as described by Decker [4,9]. Only one creep test at each stress was conducted for both the annealed and FSW forms. Several tests at each stress level were conducted on the rolled and extruded forms of the material as a method of validating data trends. The 773 K test temperature was selected for comparison because previous annealing experiments showed that the rolled material completely recovers after 15 min at 873 K, and that the recovery process is temperature dependent but not strongly time dependent [10]. Therefore, at temperatures above 873 K it would be expected that the rolled and annealed conditions would have similar creep behaviors, but at 773 K the creep behaviors should differ.

Micro-hardness measurements were taken across the friction stir weld transverse cross-section with a Buehler MicroMet microindentation hardness tester using 500-g force and a Vickers indenter. Samples were prepared for testing by gently polishing with 600-grit SiC paper to remove surface oxides. Two measurements were taken at each location across the weld, and each pair was spaced 380 μm apart along the transverse direction. Micro-hardness measurements were then grouped based on location with respect to the nugget, heat-affected zone (HAZ), and parent metal. The HAZ data, for example, consisted of all data points in the HAZ on both sides of each weld joint, resulting in 14 data points. Reference measurements were taken far away from the weld and were averaged to obtain parent material information. A one-way ANOVA on ranks statistical analysis was conducted to determine if any variations in hardness as a function zone location were statistically relevant within a 95% confidence level.

Microstructural analysis of polished sample surfaces near the fracture surface after creep testing was conducted using a Phillips FEI XL30 field emission gun, scanning electron microscope (FEG-SEM) nominally operated at 20 kV. Samples for electron backscatter diffraction (EBSD) and orientation image mapping (OIM) were epoxy mounted and mechanically polished through a final polishing step using 0.05 μm colloidal silica on Struers MD Nap, followed by an electro-polish in 50 vol% phosphoric acid and 50 vol% water solution at room temperature [7]. The electro-polishing parameters were 12Vdc in an agitated solution using a stainless steel cathode for approximately 20 s. EBSD acquisition was conducted at the Los Alamos National Laboratory (LANL) on a Phillips FEI XL30 FEG-SEM, operating at 25 kV, using the EDAX TSL-OIM software package. The EDAX TSL-OIM software allows simultaneous acquisition of grain orientation, texture, and grain size distribution. Several 6 μm by 9 μm areas were scanned, with a step size of 60 nm. The analysis of the Kikuchi orientation lines of the copper matrix was conducted using standard Hough pattern recognition. These data were compared with data collected using the same method for the extruded and rolled material forms [7]. For all three material types, the constraints used for distribution analysis were that a grain must consist of at least five data points with no more than 5° of misorientation between adjacent points. Also, the EDAX OIM software consistently recognizes twin boundaries as special high angle grain boundaries in FCC materials with adjacent grains having a misorientation of 60 ± 2° off the [1 1 1] axis. The dark areas in the images produced by the OIM method are the locations of the Cr2Nb particles; they appear black because the EDAX software does not index these regions as copper.

### 3. Results and discussion

#### 3.1. Mechanical properties

Results from the room temperature tensile tests conducted on the rolled, annealed and FSW samples were averaged and are listed in Table 1. The variation between the two averaged tests for each processing condition was less than ±5 MPa for strength and ±2% for elongation measurements. The results show that the annealed condition, as expected, is softer and more ductile than the rolled condition. The FSW condition exhibits a tensile strength between those for the rolled and annealed conditions with no appreciable difference in elongation to failure as compared with the rolled form. Fractography indicated that FSW samples failed in the HAZ. Softening in the HAZ is also hypothesized to cause the reduction in tensile strength in the FSW form. Since the tensile properties of the FSW specimens are a combination of properties of the weld zone, HAZ and the parent metal loaded in series, a decrease in total elongation in a tensile test may or may not accompany the decrease in strength due to the combination of properties of the different zones.

| Table 1
<p>| Average tensile data from the processing forms tested. Variations in average stresses are within ±5 MPa, and within ±2% for total elongation. |</p>
<table>
<thead>
<tr>
<th>Rolling</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Total elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolled</td>
<td>492</td>
<td>500</td>
</tr>
<tr>
<td>Annealed</td>
<td>264</td>
<td>377</td>
</tr>
<tr>
<td>FSW</td>
<td>361</td>
<td>418</td>
</tr>
</tbody>
</table>

Statistical analysis of the 48 microhardness measurements in the parent metal of the friction stir welded material indicates that GRCop-84 has a median Vickers hardness of 146HV, with 50% of the data falling between 141.3 and 152.1HV. The median hardness of the HAZ was 140.8HV, with 50% of the 14 data points falling between 138.9 and 142.5HV. The softening in the HAZ begins approximately ±1.8 mm from the center of the weld joint, and extends away from the center about 1 mm. The location of the softer HAZ is consistent with a 3.2 mm diameter pin tool. The weld nugget had a median hardness of 146HV with 50% of the 20 data points falling between 145 and 148.9HV. The amount of scatter in all regions and softening in the HAZ are consistent with findings by the NASA MSFC welding group on other GRCop-84 sheet butt welds [8]. The one-way ANOVA on ranks statistical analysis conclusively indicates, with a 95% confidence interval, that the HAZ is softer than...
Fig. 1. Micro-hardness measurements across the weld traverse. The vertical lines are the approximate boundaries of the HAZ, and the horizontal dashed line represents the median hardness of the parent metal.

Fig. 2. Example of creep curves for friction stir welded rolled material at 773 K.

Fig. 3. Changes in strain to failure as a function of creep stress and post-processing method.

Fig. 4. Summary of creep properties for Cu–8Cr–4Nb at 773 K. The power law fit for the extruded material excludes the highest two stress tests because they represent creep rates in the power law breakdown region. The data for the extruded material are taken from the work of Decker et al. [4] and rolled material data are from work of Vettraino [13].
and power law breakdown not seen in the rolled or post-processed forms [9].

Fig. 5 shows that the life of the FSW material is significantly shorter than that of the rolled condition. This shortened creep life is due to the decrease in creep ductility of the FSW form, Fig. 3. In contrast, the decrease in the strain rate exhibited by the annealed material results in a slightly longer life at a given applied stress, as compared to the rolled condition, but generally not as long as the creep life of the extruded material (except for stresses at which the latter exhibits power law breakdown).

3.2. Fractography

SEM images of the polished gage section of post-creep test specimens are presented in Fig. 6. Each specimen was tested at the same true stress independent of processing condition (rolled, annealed, and FSW). A qualitative comparison of the overall creep damage is accomplished by comparing the distance from the fracture surface to the last visible surface crack at a particular magnification. The rolled sample has cracks that extend 1300 μm away from the fracture surface. The annealed sample exhibits visible cracks 1000 μm away from the fracture surface, similar to the rolled material. The FSW sample has very little secondary cracking, with cracks extending only 400 μm away from the fracture surface. It was also observed that the FSW specimens fractured outside of the weld nugget, in the heat-affected zone. The micro-hardness data indicates that FSW process causes a drop in hardness in the heat-affected zone leading to strain localization and a decrease in macroscopic creep ductility. The observation of the polished faces away from the fracture surface indicates that the strain is localized in the heat-affected zone, which is consistent with the conclusions drawn from the micro-hardness measurements. Based upon these observations it was possible to conclude that the decrease in creep ductility is caused by localization of the deformation and damage to a small volume of the heat-affected zone. The microstructural causes for softening in the HAZ were not explored.

3.3. Microstructure

For this study, the grain morphology and texture of the annealed material were compared to those of the extruded and rolled materials which were described in detail by Vettraino et al. [7]. The FSW sample was not analyzed via OIM because the subsequent microstructure apparently does not affect creep rate and the loss of creep ductility can be attributed to strain localization in the softer heat-affected zone. Also, the substantial amount of microstructural inhomogeneity present in friction stir welds makes characterizing the resulting microstructure by OIM very difficult.

The OIM inverse pole figure images (Fig. 7) confirm that there are distinct differences between the annealed, extruded and rolled forms. The dark areas in the images are the locations of large Cr2Nb particles; they appear black because the EDAX software does not index these regions as copper. There are more dark regions in the
Fig. 7. Representative OIM images showing (a) the extruded material, with the extrusion direction along the x-axis, (b) the rolled material and (c) the annealed material. The rolling direction in (b) and (c) is along the y-axis and the sheet normal is out of the page.

rolled images because the software has a difficult time indexing points with high residual strains, which would be expected in rolled microstructures. The major difference in grain morphology of the annealed material is the development of recrystallization twins, Fig. 7c that are not present in the other two forms of the material. The large number of grains containing twins in the annealed material is apparent from Fig. 7c. It was quantitatively determined by the OIM software that 40–45% of the grains in the annealed material contain twins, as compared to 1–4% in the rolled and extruded materials. It is also apparent that the extruded material has a substantially different crystallographic texture.

The grain size analysis of the annealed material included adjacent grains along a twin boundary as belonging to the same grain. The small number of twin boundaries observed for the other two material types did not warrant adding this constraint to the analysis. Table 2 lists the grain size averages of the different processing types as determined by the OIM software over surface areas containing 2000 or more grains. Although the sizes for the extruded and rolled materials are slightly larger than those reported by Vettraino et al. [7] the same trends are still observed. The disparity between data presented is caused in part by difficulties of accurately distinguishing subgrain boundaries from true grain boundaries in the visual inspection methods used by Vettraino et al. [7]. In Fig. 7a subtle changes in color indicate that the largest grains of the extruded material indeed contain several subgrains. The OIM approach does not rely on visual inspection for grain boundary delineation but on crystallographic orientation of particular points to discern differences between subgrain boundaries (misorientation less than 10°) and true grain boundaries.

The rolled material has the smallest grain size, just slightly smaller than that of the extruded material. The annealed material underwent grain growth when compared to both the extruded and rolled material. A visual observation of the annealed microstructure leads to the conclusion that a majority of the larger grains contain twins, which is consistent with an annealed copper microstructure. It also appears that the Cr2Nb particles effectively reduce grain boundary mobility, leading to limited grain growth during the 24 h heat treatment. This is consistent with work by Garg that recovery time is temperature but not time dependent [10].

Since the annealed material has a larger average grain size as compared to the extruded material, it could have been hypothesized that the former should have lower creep rates than the extruded material if grain size was the only microstructural feature that influenced creep rate at the temperatures and stresses of interest. Since this is not the case, it can be concluded that the creep rate is also related to other features such as texture as well as Cr2Nb particle size and distributions.

The OIM software also allows for the comparison of the bulk texture of the three material types. Stereographic pole figures (PF) of the extruded form, with the extrusion direction normal to the page, are presented in Fig. 8 and show a duplex fiber texture in the

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Avg. grain size (μm)</th>
<th>Grains with twins (%)</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruded</td>
<td>1.65</td>
<td>3.5</td>
<td>1.63</td>
</tr>
<tr>
<td>Rolled</td>
<td>1.50</td>
<td>3</td>
<td>1.75</td>
</tr>
<tr>
<td>Annealed</td>
<td>2.43</td>
<td>45</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Fig. 8. Stereographic pole figures of the extruded material showing ⟨1 1 1⟩ and ⟨0 0 1⟩ duplex fiber textures and a rotated recrystallization cube texture.
Fig. 9. Stereographic pole figures of the rolled material. The \(\langle 1\,1\,1\rangle\) PF shows a rolling texture with missing brass and gross components and the other PFs show a strong cube texture.

\(\langle 1\,1\,1\rangle\) and \(\langle 0\,0\,1\rangle\) directions consistent with an FCC extrusion texture [15]. For the extruded material there is no distinction between the rolling direction (RD) and transverse direction (TD) presented along the x and y-axes of the PF.

The rolled material exhibits a combination of a rolling texture missing brass and gross components, seen in the \(\langle 1\,1\,1\rangle\) PF of Fig. 9 as well as a recrystallization cube texture as seen in the \(\langle 1\,0\,1\rangle\) and \(\langle 0\,0\,1\rangle\) PFs. The overall intensity of the texture in the rolled material is not as pronounced as the texture of the extruded material. The \(\langle 1\,0\,1\rangle\) cube texture is not normally associated with a rolling process but associated with recrystallization after extrusion or stress relief anneal after rolling [16]. Without conducting a texture analysis on the rolled sheet before stress relief anneal it is not possible to determine the exact cause of the cube texture.

Analysis of the annealed material’s PFs shows a substantial decrease in the intensity of the texture, Fig. 10. The rolling texture seen in \(\langle 1\,1\,1\rangle\) is now missing copper and Dillamore components but instead includes brass and gross components [16]. Since the dominant rolling texture is still prevalent it is not possible to pick out a twinning texture from these PFs even though 40–45% of the grains contain twin boundaries. The major effect that grain growth and twinning have had on texture development is the elimination of the recrystallization cube texture seen in the rolled material and overall weakening of the texture intensity.

4. Conclusions

The post-processing steps had varying effects on the properties of rolled Cu–8 at% Cr–4 at% Nb alloy tested at 773 K. As expected, the simulated-life heat treatment of annealing for 24 h at 1073 K reduced the tensile strength and increased ductility at room temperature. The simulated-life heat treatment anneal also decreased the steady-state creep rate as compared to the rolled form at a particular stress and thus increased the creep life of the material. This is a favorable outcome for applications of the rolled form at this temperature. The main difference between the rolled and annealed microstructures is the grain growth and development of recrystallization twins during annealing. This leads to a reduction in the strength of the texture still present in the rolled material. The removal of the cube texture could be the cause of decreased steady-state creep rate at this particular temperature.

Friction stir welding resulted in a small decrease in strength with no loss of tensile ductility at room temperature. The friction stir welding process had no effect on the steady-state creep rate exhibited by the rolled material, but it did significantly decrease the creep ductility from 10–13% to 2–4%, resulting in a substantial decrease in creep life. Hardness profiles across the weld and post-fracture observations of specimen faces confirm that softening in the heat-affected zone causes strain localization resulting in a decrease in the creep ductility.

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