Observations of a Cast Cu-Cr-Zr Alloy

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Abstract

Prior work has demonstrated that Cu-Cr-Nb alloys have considerable advantages over the copper alloys currently used in regeneratively cooled rocket engine liners. Observations indicated that Zr and Nb have similar chemical properties and form very similar compounds. Glazov and Zakharov et al. reported the presence of Cr$_2$Zr in Cu-Cr-Zr alloys with up to 3.5 wt% Cr and Zr though Zeng et al. calculated that Cr$_2$Zr could not exist in a ternary Cu-Cr-Zr alloy. A cast Cu-6.15 wt% Cr-5.25 wt% Zr alloy was examined to determine if the microstructure developed would be similar to GRCop-84 (Cu-6.65 wt% Cr-5.85 wt% Nb). It was observed that the Cu-Cr-Zr system did not form any Cr$_2$Zr even after a thermal exposure at 875 °C for 176.5 h. Instead the alloy consisted of three phases: Cu, Cu$_5$Zr, and Cr.

Introduction

High-conductivity materials with good high-temperature strength, creep resistance, and low-cycle fatigue (LCF) lives are needed for a variety of regeneratively cooled rocket engine applications especially main combustion chamber liners. Work at the NASA Glenn Research Center (refs. 1 to 3) has focused on Cu-Cr-Nb alloys such as GRCop-84, which offer great promise for these and other high-temperature heat exchanger applications.

The Cu-Cr-Nb system was selected because Cr and Nb have minimal solubility in solid copper (refs. 4 and 5) but high solubility in liquid copper. They also form a high-melting-point intermetallic compound, Cr$_2$Nb (ref. 6). Utilizing rapid solidification technology, a very fine dispersion of Cr$_2$Nb, can be formed in a nearly pure copper matrix. This dispersion gives Cu-Cr-Nb alloys such as GRCop-84 (Cu-6.65 wt% Cr-5.85 wt% Nb) an excellent combination of strength, creep resistance, fatigue life, conductivity, and thermal expansion (ref. 7).

Comparing the mechanical properties of pure copper to AMZIRC, a commercial Cu-0.15 wt% Zr alloy, revealed that the small addition of Zr greatly improved the properties of the alloy above pure copper. Of particular interest was the increase in softening temperature (refs. 8 and 9) and LCF lives (refs. 9 and 10) relative to pure copper that the small addition of Zr to Cu causes.

The Cr-Zr phase diagram (ref. 11) shows that Cr and Zr develop the intermetallic compound Cr$_2$Zr. It is assumed that, like Cr$_2$Nb, the intermetallic compound will be hard and suitable for strengthening Cu. Both Cr$_2$Zr and Cr$_2$Nb have C$_{15}$ cubic structures (refs. 12 and 13) and an Fd3m or Cu$_2$Mg space group. The lattice parameters of Cr$_2$Zr and Cr$_2$Nb are 0.721 and 0.7659 nm, respectively. These similarities in structures and unit cell sizes between the two compounds held promise for producing a microstructure with Cu and Cr$_2$Zr.

While the Cu-Zr phase diagram (ref. 14) shows that more Zr can dissolve into solid copper than Nb, the amount is still small at approximately 0.1 at.%. The potential removal of any trace oxygen from the copper matrix by the Zr could compensate for any decrease in conductivity from dissolved Zr as well.

Limited prior work on the Cr-Cu-Zr phase diagram had been conducted in the 1950s. Glazov et al. (refs. 15 and 16) and Zakharov et al. (ref. 17) determined that, in alloys with up to 3.5 wt% Cr and 3.5 wt% Zr, Cr$_2$Zr could form. They postulated a Cu-Cr$_2$Zr pseudobinary phase diagram. More recent work, in particular the papers by Zeng et al. (refs. 18 and 19), have shown that Cr$_2$Zr will not form in the Cr-Cu-Zr ternary system. An isothermal section of the Cr-Cu-Zr ternary phase diagram calculated by

NASA/TM—2006-213968 1
Zeng is shown in figure 1. Instead three phases—Cu, Cr, and Cu₅Zr—will be present up to 25 at.% Cr along the Cu-Cr₂Zr vertical section of the ternary phase diagram.

The success of the Cu-Cr-Nb alloys developed at NASA Glenn led to the desire to revisit the Cu-Cr-Zr alloys. A Cu-Cr-Zr alloy modeled after GRCop-84 with Zr directly substituting for Nb could have at least two potential advantages over the comparable Cu-Cr-Nb alloy. The Cr₂Zr should dissolve into the liquid copper at a lower temperature than Cr₂Nb. This could decrease the melt temperatures and make powder production significantly easier. If an excess of Zr is added, then the Zr in the copper matrix could act to retard the softening of the alloy at high temperatures following cold work as it does in AMZIRC. The addition of Zr should also improve LCF lives, a major necessity for rocket engine liners.

To determine if Cu-Cr-Zr alloys could form an alloy consisting of a Cu-rich matrix strengthened by Cr₂Zr precipitates, a Cu-Cr-Zr alloy was cast and analyzed for the phases present in the as-cast condition and following a high-temperature heat treatment designed to achieve equilibrium among the phases.

### Experimental Procedure

The theoretical density of Cr₂Zr was calculated based upon the crystallographic data available for the low-temperature form of the phase (ref. 13). Using this calculated density and the density of copper, a composition of Cu-6.0 wt% Cr-5.4 wt% Zr was calculated to give 14 vol% Cr₂Zr. On an atomic basis, this composition corresponds to Cu-7.4 at.% Cr-3.7 at.% Zr and gives the desired 2:1 atomic ratio of Cr to Zr needed for stochiometric Cr₂Zr. No correction to this composition was made to compensate for anticipated losses in Cr and Zr during the casting process or any solubility of Cr and Zr in the copper matrix. As shown in figure 1, this composition lies along the Cu-Cr₂Zr line.

A charge of elemental Cu, Cr, and Zr with this composition was melted using induction melting under an argon cover gas. All materials used had at least 99.9 percent purity. The molten metal was poured into a solid copper mold with a nominal cavity dimension of 25.4 by 50.8 by 76.2 mm (1 by 2 by 3 in.). Following casting samples were submitted for chemical analysis.

The casting was cut into blocks approximately 1.9 by 1.3 by 1.3 cm (0.75 by 0.5 by 0.5 in.) and examined metallographically. The samples were polished and examined in the scanning electron microscope (SEM). Backscattered electron (BSE) imaging was used to qualitatively determine the location of the elements and phases present in the casting. It was also possible to use the images to quantitatively determine the volume fraction of each phase. Energy dispersion spectroscopy (EDS) was used to semiquantitatively determine the composition of each phase observed.

![Phase Diagram](image)

Figure 1.—Calculated Cr-Cu-Zr phase diagram at 940 °C adapted from Zeng et al. (ref. 18) and alloy compositions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>Cr</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUZ-1</td>
<td>70.0</td>
<td>16.0</td>
<td>14.0</td>
</tr>
<tr>
<td>CUZ-2</td>
<td>65.8</td>
<td>21.0</td>
<td>13.2</td>
</tr>
<tr>
<td>CUZ-3</td>
<td>61.7</td>
<td>26.0</td>
<td>12.3</td>
</tr>
<tr>
<td>CU ZR-4</td>
<td>57.5</td>
<td>31.0</td>
<td>11.5</td>
</tr>
<tr>
<td>CUZ-5</td>
<td>53.3</td>
<td>36.0</td>
<td>10.7</td>
</tr>
<tr>
<td>CRZR-1</td>
<td>75.0</td>
<td>16.7</td>
<td>8.3</td>
</tr>
<tr>
<td>CRZR-2</td>
<td>67.0</td>
<td>22.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Current study

88.9 | 7.4 | 3.7 |
To determine the volume fraction of each phase present, BSE images of the alloy were analyzed using SigmaScan image analysis software. The picture was divided into three parts based upon the grayscale intensity of each pixel. This delineated the three phases well except in the fine lamella and at the boundaries of some particles. This introduces a small error judged to be much less than 5 percent of the measured values. The total pixels for each phase were counted and divided by the total pixels counted to give an area fraction for each phase. Five images were used to calculate the area fraction of each phase. The area fraction is equal to the volume fraction of each phase.

Microprobe analysis was conducted on the as-cast sample to achieve a quantitative analysis of each phase. A JEOL 8200 Superprobe with five wavelength dispersive spectrometers (WDSs) and one EDS detector allowed for simultaneous measurement of all three major elements of interest. In addition to the quantitative analysis of each phase, additional BSE images and x-ray maps were obtained. X-ray diffraction was performed on a sample using a Phillips APD3600 Automatic Powder Diffractometer to determine the crystallography of the phases present as well.

After examination of the as-cast material, a sample was cut from the casting and exposed at 875 °C (1607 °F) for 176.5 h and air cooled (AC) to determine if Cr₂Zr would form during a heat treatment through diffusion and reaction between the Cr and Zr. Samples were examined using the SEM and x-ray diffraction to determine phase and microstructural changes.

Results

The casting had detectable internal porosity, but little shrinkage or piping was noted in the central core. It is believed that the porosity is gas porosity caused by dissolved hydrogen introduced through the zirconium metal that did not have time to escape from the melt before casting into the mold.

The overall composition of the alloy is shown in table 1. In addition to the three main constituents, some trace contaminants were also detected. Their levels are low and should not affect any of the results. No additional elements beyond those listed were detectable using inductively coupled plasma spectroscopy.

Calculated volume fraction is computed from the Cr-Cu-Zr phase diagram (ref. 18) using lever rule. X-ray diffraction determined that three phases were present—elemental Cr, elemental Cu, and Cu₅Zr. No Cr₂Zr was detected.

SEM examination with both secondary electrons (SEs) and (BSEs) revealed a microstructure with three distinct and easily observed regions. Examples of both types of images are shown in figures 2 and 3. For comparison purposes, an optical micrograph of a similarly cast Cu-Cr-Nb alloy microstructure is presented in figure 3. Large Cr₂Nb precipitates are easily visible, and there is no evidence of elemental Cr in the Cu-Cr-Nb alloy.

| Table 1 — Composition of Cu-Cr-Zr Casting |
|-----------------|----------------------|
| Element | Weight percentage |
| Cu    | Bal.               |
| Cr    | 6.15                |
| Zr    | 5.25                |
| Fe    | 30 ppm              |
| N     | 6 ppm               |
| O     | 159 ppm             |
| S     | 10 ppm              |
| Y     | 150 ppm             |
Figure 2.—Overall microstructure of as-cast Cu-6.0 Cr-5.4 Zr alloy (a) BSE image (b) SE image.

Figure 3.—Detail of general microstructure (BSE image) with EDS spectra. Same area as in figure 2.

Using EDS and the information from the x-ray diffraction results, the observed regions were identified as elemental Cr dendrites, elemental Cu dendrites, and Cu-Cu₅Zr in the interdendritic spaces. The measured volume fractions for each phase are listed in table 2. The Cu-Zr phase revealed a very fine lamellar structure as seen in figure 4. The Cr and Cu have a larger, dendritic structure. Based upon this structure and the various melting points, it is surmised that the Cr solidified first followed by the Cu. The remaining Zr-rich liquid solidified last.
TABLE 2.—VOLUME FRACTION OF EACH PHASE

<table>
<thead>
<tr>
<th>Phase</th>
<th>Measured volume fraction</th>
<th>Calculated volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>10.1%</td>
<td>8.1%</td>
</tr>
<tr>
<td>Cu</td>
<td>62.0%</td>
<td>67.6%</td>
</tr>
<tr>
<td>Cu₅Zr</td>
<td>27.9%</td>
<td>24.3%</td>
</tr>
</tbody>
</table>

Calculated volume fraction is computed from the Cr-Cu-Zr phase diagram (ref. 18) using lever rule.

Figure 4.—Fine Cu-Cu₅Zr lamellar structure.

Figure 5.—BSE images showing features analyzed by microprobe.

Quantitative microprobe analysis was performed on each phase. Representative images of the areas analyzed are shown in figure 5. The quantitative results are shown in table 3. For the lamellae, the microprobe’s resolution enabled the analysis of the two different phases individually in regions where the lamellae were somewhat coarser than average or had an above-average spacing. These results were judged to be representative of the finer lamellae as well.
TABLE 3.—MICROPROBE QUANTITATIVE CHEMICAL ANALYSIS RESULTS

<table>
<thead>
<tr>
<th>Microstructural feature</th>
<th>Cu (wt%/at.%)</th>
<th>Cr (wt%/at.%)</th>
<th>Zr (wt%/at.%)</th>
<th>Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall lamellae (phase A)</td>
<td>88.4/90.6</td>
<td>0.5/0.6</td>
<td>12.0/8.6</td>
<td>Cu + Cu₅Zr</td>
</tr>
<tr>
<td>Light lamella (phase A₁)</td>
<td>76.9/82.1</td>
<td>0.7/1.0</td>
<td>22.7/16.9</td>
<td>Cu₅Zr</td>
</tr>
<tr>
<td>Dark lamella (phase A₂)</td>
<td>99.1/99.0</td>
<td>0.6/0.8</td>
<td>0.3/0.2</td>
<td>Cu</td>
</tr>
<tr>
<td>Cr dendrites (phase B)</td>
<td>2.4/2.0</td>
<td>97.4/98.0</td>
<td>0.0/0.0</td>
<td>Cr</td>
</tr>
<tr>
<td>Cu dendrites (phase C)</td>
<td>99.3/99.4</td>
<td>0.1/0.1</td>
<td>0.4/0.6</td>
<td>Cu</td>
</tr>
</tbody>
</table>

All results are the average of analysis of five different features.

The microstructure of the Cu-Cr-Zr alloy after a 176.5-h heat treatment at 875 °C is shown in figures 6 and 7. The elemental Cr dendrites appear to be unaffected by the high-temperature exposure. The solid solubility of Cr in pure Cu is only 0.1 wt% at 875 °C, so it was not expected that the Cr dendrites would dissolve. However, it was hoped that the rapid diffusion of Cr in Cu would lead to transport of Cr to Zr and the reaction of the two elements to form Cr₂Zr. No Cr₂Zr was detected in the specimen even in regions where Cr- and Zr-rich phases were in intimate contact. The Cu-Cu₅Zr lamellar structure has been replaced with what appears to be a uniform phase even at ×10,000. In all probability the areas contain very fine Cu₅Zr uniformly dispersed within a copper matrix.

Figure 6.—Overall microstructure of Cu-6.0 Cr-5.4 Zr alloy following 875 °C (1607 °F)/176.5 h/AC thermal exposure (BSE).

Figure 7.—Detail of area with Cr and Cu₅Zr in intimate contact following thermal exposure illustrating lack of observable reaction and disappearance of lamellae (BSE).
Discussion

Unfortunately, both the EDS and x-ray diffraction results confirm that there was no detectable amount of Cr₂Zr formed in the casting process. While Zr, element 40, and Nb, element 41, share many similarities, the small differences such as electronegativity (1.33 versus 1.6 on Pauling scale (ref. 20)) appear to be sufficiently great to prevent the ready formation of Cr₂Zr in the presence of copper during a conventional casting process.

Exposure of the cast alloy to 875 °C or 0.96 Tm based upon the Cu-Cr₉Zr₂ eutectic temperature of 927 °C (ref. 14) did not promote the formation for Cr₂Zr. The only detectable microstructural change observed was the Cu and Cu₅Zr lamellae disappearing and the formation of a uniform Cu₅Zr phase with no resolvable details at ×10 000 magnification. This applied even when the Cr and Cu₅Zr phases were in intimate contact.

The presence of the Cu₅Zr phase is at odds with the refereed Cu-Zr phase diagram of Arias and Abriata (ref. 14), which is based on thermodynamic and experimental data. They show the phase that should be present is Cu₅Zr₂. Cu₅Zr (ref. 21), Cu₆Zr₂ (refs. 22 and 23), and Cu₅Zr (refs. 24 to 26) have been reported by various researchers and which composition is correct continues to be a point of some contention. In this study the composition of the phase on an atomic basis had an average Cu to Zr ratio of 4.86. The presence of a Cu matrix should tend to bias the Cu to Zr ratio from the microprobe results lower due to the excitation volume of the probe beam including the adjacent Cu-rich phase. The x-ray diffraction analysis peaks correspond accurately with the published values for Cu₅Zr (ref. 27) indicating it had the proper lattice structure and lattice parameters for this phase as well.

It needs to be noted that the presence of the third element, Cr, will affect the activity of both the Cu and Zr. It is known that both Cr and Zr have limited solid solubility in Cu. At 875 °C, the solid solubility is approximately 0.1 at.% for both Cr and Zr (refs. 11, 14, 18, and 19). That would result in a lowering of the activity of Cu to 0.998 if Raoultian behavior is assumed for simplicity. Interactions between the Cr and Zr may introduce nonideal behavior, which would require determination of the activity coefficients for the three elements, but the small magnitude of both concentrations in copper would probably not result in any significant change from the Raoultian value.

Zeng et al. (ref. 18) calculated the complete Cr-Cu-Zr phase diagram including the Zr-rich corner. Their results indicate that several atomic percent of Cr and Zr can dissolve into Zr. At 875 °C, the approximate amount of Cr and Cu that can be dissolved into Zr are 3.5 and 4 at.% respectively. Assuming Raoultian behavior, the activity of the Zr would be reduced to 0.925. The solid solution is also sufficiently concentrated that nonideal behavior is likely, which could change the Zr activity further. This change in activity and corresponding shifts in the free energies of formation may account for the observed presence of Cu₅Zr instead of Cu₅Zr₂.

The compositional and phase results of this study are consistent with those obtained by Zeng et al. (ref. 19). Their reported values for the composition of the Cr and Cu₅Zr phases for four of their alloys obtained using a Noran Voyager II EDS system with a PROZA-correction system are almost identical to the microprobe compositions obtained in this study.

The volume fraction of each phase was calculated from the Cr-Cu-Zr phase diagram (ref. 18) using the lever rule and compared to the image analysis results in table 2. There are differences in the two sets of values that can be as much as a 24.7 percent difference for the volume fraction of Cr. The error in the image analysis results is likely 5 percent or less, so there is an indication that a further refinement of the calculated Cr-Cu-Zr phase diagram may be required.

While the addition of a fourth element may dramatically change the interactions between Cu, Cr, and Nb, one implication of this work is that adding Zr to the Cu-Cr-Nb system may form a Cu-Zr matrix and Cr₃Nb precipitates. If the amount of Zr is limited to approximately 0.1 at.% Zr and the Zr does not dissolve into the Cr₃Nb or react with it, the composition of the matrix will approximate the commercial alloy AMZIRC. This addition may serve to improve the LCF and creep properties of Cu-Cr-Nb alloys such as GRCop-84 with only a small decrease in thermal conductivity (ref. 28) based upon the differences observed between pure Cu and AMZIRC.
Conversely, the addition of a small amount of Nb to the Cu-Cr-Zr alloy may change the activities and free energies of formation sufficiently so that Cr$_2$Zr will form. The work by Glazov et al. (refs. 15 and 16) and Zakharov et al. (ref. 17) where Cr$_2$Zr was found and a Cu-Cr$_2$Zr pseudobinary phase diagram was postulated may have been influenced by impurities. Nb will react strongly with Cr to form Cr$_2$Nb in the liquid phase for Cu-Cr-Nb alloys (refs. 1 and 29). These precipitates may act as favorable nucleation sites for Cr$_2$Zr given the similarities in crystallography and lattice spacings.

**Summary and Conclusion**

A cast Cu-6.15 wt% Cr-5.25 wt% Zr (Cu-7.5 at.% Cr-3.7 at.% Zr) alloy was examined in the as-cast condition and after an extended heat treatment at 875 °C. In both cases three phases were identified—Cu, Cr, and Cu$_5$Zr. In neither case was the desired Cr$_2$Zr phase observed. These results are consistent with the most recent experimental and computational work by Zeng et al. (refs. 18 and 19) on the Cr-Cu-Zr phase diagram.

While Zr and Nb are chemically similar in many respects and form crystallographically analogous intermetallic compounds with Cr with the same atomic ratio, it was concluded that there are sufficient differences that prevent the formation of the desired phases and microstructure in Cu-Cr-Zr alloys. This appears to make them unsuitable candidates for additional development as a potential supplement or replacement to GRCop-84 in rocket engine applications.

**References**

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