High strength Cu-Ni-Cr alloys by thermomechanical treatment

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The effect of thermomechanical treatment (TMT) on the mechanical properties of a spinodal Cu-44Ni-5Cr alloy has been investigated. The alloy has been subjected to three different heat treatments: quench→age; quench→cold work→age; and quench→age→cold work→age. Hardness measurements and tensile studies show improved mechanical properties after TMT. While these are found to be stable on aging at 550°C, a rapid loss has been noticed on aging at 600°C. DSC studies show that this is due to a recovery processes at the higher aging temperature.

Spinodal decomposition refers to a continuous type of phase transformation that occurs homogeneously in which the change begins as compositional waves that are small in amplitude and large in spatial extent. These fluctuations grow in intensity as a function of time, eventually yielding the final product phases. Spinodal decomposition proceeds with a progressive decrease in free energy from the very beginning, without any need for surmounting a nucleation barrier. Spinodal decomposition is indeed an interesting transformation mechanism. Many intermetallic systems and also certain ternary systems have been found to exhibit spinodal decomposition. A number of copper based ternary alloys in which spinodal decomposition occurs have been found to be of commercial interest.

One of the prominent applications of copper alloys is their use as connectors, diaphragm members and spring material in electromechanical relays. Phosphor bronze, nickel silver and Cu-Be are some alloys which have been used for these purposes. Amongst these, Cu-Be alloys are popular, as these attain very high strength levels. Further, by suitable thermomechanical treatments, strength levels in excess of 1000 MPa can be achieved in these systems. Current efforts towards miniature relays and device assemblies have resulted in higher stresses on these components and hence a need for increased strength of the alloys. Attempts have been made to achieve required higher strength by modifying Cu-Be system. In spite of such developments, Cu-Be and related alloys continue to suffer from higher cost and pollution problem associated with their production. Therefore, extensive research is being carried out to develop low cost high strength alternatives to Cu-Be alloys. The Cu-Ni-Sn system has been investigated as a possible substitute, due to its age hardening capabilities. While they possess attractive mechanical properties and good electrical conductivity, both these are generally inferior to that of Cu-Be alloys. Furthermore, use of Cu-Ni-Sn alloy at the contact points leads to segregation of tin at the grain boundaries.

Another important copper based spinodal alloy is Cu-Ni-Cr. The nature of phase transformations and resulting mechanical properties of a wide range of alloys in this system have been investigated. Tensile strengths of 870 and 843 MPa in Cu-45Ni-10Cr and Cu-52Ni-15Cr alloys, respectively, have been reported after peak aging at 500°C. These systems show very high values of elongation, i.e., greater than 20%. These properties make them attractive as possible substitutes for Cu-Be alloys. Therefore, it is important to study the effect of thermomechanical treatment on the tensile properties of these alloys, with the hope that strength levels approaching 1000 MPa might be obtained. With this point in view, the present investigation has been taken up to study the effect of prior deformation as well as prior aging followed by deformation on the tensile properties of a Cu-44Ni-5Cr alloy.

Experimental Procedure
The alloy was prepared by melting high purity
Results

Hardness measurements—Variation of hardness with aging time during conventional aging in the temperature interval of 400-650°C is shown in Fig. 1. At the lower aging temperatures, hardness increases monotonically with aging time. At the higher temperatures of 600 and 650°C, a rapid increase in hardness is observed during early aging period, reaching a peak hardness within a short period. Thereafter, the hardness is found to remain a constant at this peak value for long peri-
ods of aging. The peak hardness decreases with increasing temperature. As peak strength on aging is observed to occur in the temperature interval of 550 and 600°C, TMT and MTMT studies were restricted to only these two temperatures.

The effect of prior deformation on the aging behaviour is shown in Fig. 2. This shows a rise in hardness during initial stages, followed by a drop and a subsequent gradual rise or drop. The exact nature of the curve depends on the specific combination of prior deformation and aging temperature. Higher prior deformation and lower aging temperature results in higher hardness.

Figs 3a and 3b show the age hardening behaviour of MTMT samples at 550 and 600°C, respectively. These show contrasting behaviour. While at 550°C hardness generally remains a constant at a high value, at 600°C, a rapid decrease is noticed. The hardness studies thus reveal that age hardening behaviour of spinodal alloys is very sensitive to prior aging and prior deformation.

Differential scanning calorimetry—The results of DSC study are presented in Figs 4 and 5. In Fig. 4a heat output during conventional aging is compared with that of TMT, with prior deformations of 65 and 80%. All the curves are very closely spaced and no difference is observed between them. However, when held at 600°C, the

![Fig. 3](image-url)  
**Fig. 3—Age hardening of MTMT samples at (a) 550°C and (b) 600°C**

![Fig. 4](image-url)  
**Fig. 4—DSC curves for samples with different prior deformation. Isothermal runs at (a) 550°C and (b) 600°C. Numbers on the curves indicate percentage prior deformation**
TMT samples show a greater heat output, and pronounced exothermic peaks can be observed. Such a peak is absent in the non deformed sample. Similarly, Figs 5a and 5b correspond to MTMT samples isothermally held at 550 and 600°C, respectively. Here again, exothermic peaks (indicated by arrow) are observed only at 600°C and not at 550°C.

Tensile studies—As hardness measurements revealed that maximum strength is obtained in the temperature interval of 550 to 600°C, tensile studies were confined to only these two temperatures. Variation of ultimate tensile strength, yield strength (measured as 0.2% proof stress) and percentage elongation are shown in Fig. 6 for the two aging temperatures. The yield and tensile strength values are found to rise quickly to a plateau. The rise is quicker at 600°C than at 550°C. The strength values are slightly higher at 550 than at 600°C. This behaviour is similar to that observed during hardness measurements. Moderately high values of ductility of about 15% is observed at both temperatures for short aging periods. This decreases gradually for longer periods.

![DSC curves for samples with different durations of preaging followed by 80% deformation. Isothermal runs at (a) 550°C and (b) 600°C. Numbers on the curves indicate preaging time in hours](image)

![Tensile properties after conventional aging](image)

![Tensile properties of TMT samples after aging at 550°C](image)
The effect of prior deformation on the mechanical properties of aged samples is shown in Figs 7 and 8 for the aging temperatures of 550 and 600°C, respectively, where a substantial increase in strength is observed. The samples aged at 550°C after a prior deformation of 80% showed tensile strengths in the range of 860 MPa as compared to 650 MPa of conventionally aged samples. Similarly, the yield strength of TMT sample was about 830 MPa as compared to a maximum of 400 MPa in CA. However, the ductility decreased drastically to about 1.5%. The samples subjected to prior deformation of 65% showed lower strength values than those deformed by 80%. They also showed a substantial decrease in strength after longer aging periods.

The results of Fig. 8 show a marked departure from those of Fig. 7. At this higher aging temperature, at both 65 and 80% prior deformation, ultimate tensile strength is found to decrease continuously with increasing aging time. At both levels of prior deformation, yield strength drops rapidly initially, and later, rises gradually during longer aging periods. The ductility is higher at 2.5% as compared to the lower aging temperature. The yield and tensile strengths are much lower than at the aging temperature of 550°C.

As the results of hardness study showed a substantial fall in hardness in MTMT samples that were aged at 600°C, tensile studies were confined to the aging temperature of 550°C. The results are presented in Fig. 9. Samples preaged by 1 h showed high tensile strength of about 925 MPa. Those preaged for 5 h showed slightly lower strength, but still greater than 900 MPa. The ones preaged for 10 h showed still lower strength, but even these were higher than those of TMT samples. After a slight decrease during initial aging period, the strength values were quite steady over long aging periods. The samples preaged by 1 h showed good ductility of 4%.

Discussion

A substantial increase in strength is observed in the samples subjected to prior deformation. Greater the deformation, greater is the strength. The aging temperature is found to have a considerable influence. The hardness or strength values are quite steady over long aging periods at 550°C. The dislocation structure generated during plastic deformation can be assumed to be quite stable. However, at 600°C, a fall in strength is observed on aging. This can be attributed to a recovery process that occurs in the cold worked material. This is supported by results of DSC study. At 600°C, greater heat output is observed in the prior deformed samples. While the sample deformed by 80% shows a rather sharp peak after only a short holding time, that deformed by 65% shows a broad peak after a relatively longer period.

Preaging the sample before plastic deformation is also found to give a substantial increase in

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![Fig. 8 — Tensile properties of TMT samples after aging at 600°C](image)

![Fig. 9 — Tensile properties of MTMT samples. Preaging times are —○—1 h, —□—5 h, — △—10 h](image)
strength. The hardness results indicate that substantial drop in strength is associated with the higher aging temperature. Similar to TMT, this can be attributed to recovery processes in the cold worked matrix. The results of DSC in Fig. 5b show pronounced peaks in the samples preaged by 5 and 10 h while a broad peak is observed in that preaged for only 1 h. No such peaks are observed at 550°C.

The strengthening in thermomechanically treated samples is a result of two opposing processes, i.e. a rise in strength due to spinodal decomposition and a drop in strength due to recovery of the cold worked structure. The exact nature of the hardness or strength curves, therefore, depends on the combined effect of these two processes. During initial stages, hardness will increase, as the former will dominate over the latter. During later stages, the loss in strength due to recovery processes will dominate over increase in strength due to spinodal decomposition. Therefore, plot of hardness against aging time will show stages as shown in Fig. 10. The three stages could be explained based on the model of loss of coherency as proposed by Livak and Thomas. During stage I, hardness rises due to spinodal decomposition. In the case of conventionally aged material, dislocation density will be very low. Coherency strain can then activate the normal dislocation sources, which will emit dislocations that move to the interface. But this occurs only after long periods of aging. Thus in this case, a continuous rise in hardness is observed till the aging time of 31 h employed here.

If the matrix dislocation density can be raised by plastic deformation, abundant dislocations are available which can easily migrate under coherency strain to the interface of the developing particle. This accounts for the early loss of coherency in the cold worked material. This is shown as stage II and is referred to as recovery stage. Higher the amount of cold work, higher will be the dislocation density, and earlier will be the loss of coherency. As the migration of dislocations is a thermally activated process, this can be very sensitive to aging temperatures. As the temperature is raised, dislocations are able to migrate faster to the interface under an increased thermal driving force. This accounts for the early loss of coherency at high temperatures. The drop in hardness is

<table>
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<tr>
<th>Alloy,</th>
<th>Prior cold work reduction in thickness, %</th>
<th>Yield strength 0.2% plastic strain, MPa</th>
<th>UTS MPa</th>
<th>Ductility %</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphor bronze (CA 510)</td>
<td>97.3</td>
<td>810</td>
<td>830</td>
<td>2-3</td>
<td>1</td>
</tr>
<tr>
<td>Nickel Silver (CA 762)</td>
<td>97.4</td>
<td>970</td>
<td>1050</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Modified cupronickel (CA 725)</td>
<td>98</td>
<td>820</td>
<td>850</td>
<td>3-4</td>
<td>1</td>
</tr>
<tr>
<td>Cu-2% Be (CA 172)</td>
<td>96.5</td>
<td>1230</td>
<td>1400</td>
<td>1-2</td>
<td>1</td>
</tr>
<tr>
<td>Cu-9Ni-6Sn</td>
<td>98.4</td>
<td>965</td>
<td>—</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>Cu-44Ni-5Cr TMT</td>
<td>80</td>
<td>830</td>
<td>880</td>
<td>1-2</td>
<td>Present investigation</td>
</tr>
<tr>
<td>Cu-44Ni-5Cr MTMT</td>
<td>80</td>
<td>888</td>
<td>908</td>
<td>3-4</td>
<td>-do-</td>
</tr>
</tbody>
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BHAT et al.: EFFECT OF TMT ON ALLOYS PROPERTIES

only of a temporary nature. As the well of dislocation sources dries up and the dislocations rearrange themselves into low energy configurations, the strain amplitude may build up again as spinodal decomposition continues. This is what is observed in stage III. Thus the exact nature of the decomposition depends on the aging temperature and extent of cold work.

It is clear from the tensile data, that substantial increase in strength can be obtained by appropriate thermomechanical treatment. This material can be considered as a potential candidate to substitute for Cu-Be alloys. Other alloys which find widespread applications in similar areas are phosphor bronze (CA-510), nickel silver (CA-762) and modified cupronickels (CA-725). These, as well as, Cu-2Be (CA-172) and Cu-9Ni-6Sn alloys have been thermomechanically processed to give yield strengths greater than 810 MPa. The data is presented in Table 1 alongside those for the present alloy after subjecting it to TMT and MTMT. It can be seen that the yield strength values of Cu-Ni-Cr alloy subjected to TMT and MTMT are comparable with most of the alloys except Cu-9Ni-6Sn and Cu-2Be alloys. It should be noted that Cu-Be alloy was subjected to a prior cold work of 96.5% reduction in thickness. Similarly, Cu-9Ni-6Sn, the other alloy with high strength was also subjected to a large reduction in thickness of 98.4% during prior cold work. In comparison, the Cu-Ni-Cr alloy of the present investigation was given a reduction of only 80% during prior deformation. Therefore, strength levels similar to that of Cu-Be alloys can be expected in this alloy too, if it would have also been given larger reductions.

The values presented here are along longitudinal direction of rolled samples. The copper based alloys are known to show higher strength along transverse direction because of the particular texture they develop. This increment may vary from 10 to 20% depending on the particular alloy.

Conclusions

The Cu-44Ni-5Cr alloy can be subjected to thermomechanical treatment to attain tensile strengths approaching 1000 MPa. The treatment involving aging before cold working is preferable as it gives not only higher strength, but also higher ductility. Aging at 600°C or higher leads to major loss of strength due to recovery processes. This alloy can be considered as a potential substitute for Cu-Be.

Acknowledgement

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References

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