CHAPTER 6

Determination on the effect of Sn content on microstructure, aging temperatures, aging time and hardness of spinodal (Cu-Ni-Sn) alloys cast in metal mould.

6.1 Introduction

In the previous chapter 4, the Ni content was varied from 3 wt-% to 14 wt-% to determine the optimum aging temperature and aging time for Cu-Ni-Sn spinodal alloys cast in metal mould. The Sn was kept constant at 6 wt-%. The influence of Ni on hardness was also investigated in the previous chapter 4. In this chapter the Sn content will be varied from 4 wt-% to 12 wt-% keeping Ni content constant at 9 wt-%. The Sn content will be varied to determine the a) effect of Sn content on the microstructure and the hardness; b) optimum aging temperature for Cu-Ni-Sn spinodal alloy cast in metal mould; c) optimum aging time for the spinodal alloys cast in metal mould; d) peak aging time of Cu-Ni-Sn spinodal alloys for the varying wt-% Sn.

6.2 Results and discussions

6.2.1 Microstructure evaluation

The as-cast dendritic microstructure of a typical alloy of composition Cu-12Sn-9Ni spinodal alloy cast in metal mould is shown in Figure 6.1. Figure 6.2 shows the solutionised microstructure of the Cu-12Sn-9Ni spinodal alloy. It can be observed from the Figure 6.2 that the dendritic structure has been completely eliminated by solution treatment. Figure 6.3 shows the microstructural image of Cu-12Sn-9Ni spinodal alloy, aged at 350°C for 3 hours. An absence of the second phase is observed from this figure. Similar microstructure was observed for all the varying wt-% Sn alloys in the present investigation.
During the time of spinodal decomposition, besides clustering reaction an ordering reaction are found to take place to give a meta stable phase as reported by Schwartz et al. (1974), Ilango and Sellamuthu (2012, 2013) in sand cast alloys, Zhao and Notis (1998) and Baburaj et al. (1979). Zhang et al. (2008, 2010) reported that the ordered and the modulated microstructure cannot be resolved by using a metallurgical optical microscope or Scanning Electron Microscope (SEM). The microstructural image of Cu-12Sn-9Ni aged at 350°C for 5 hours is shown in Figure 6.4. It is visible from the Figure 6.4 that the precipitates are formed along the grain boundaries of the spinodal alloy. Baburaj et al. (1979), Zhang et al. (2008, 2010) and Schwartz et al. (1974) reported from their investigation that α and γ are the equilibrium constituents of the grain boundary precipitates. Zhang et al. (2008, 2010) reported that the grain boundary precipitates increases and completely fills the structure as aging time increases. Further aging of the spinodal bronze alloy results in the increase of the grain
boundary precipitates an observation reported by Kratochvil et al. (1984) and Zhang et al. (2008,2010) in wrought spinodal alloys.

Figure 6.3: Microstructure of Cu-12Sn-9Ni spinodal alloy aged at 350°C for 3 hr

Figure 6.4: Microstructure of Cu-12Sn-9Ni spinodal alloy aged at 350°C for 5 hr

6.2.2 Effect of aging treatment on hardness

Figure 6.5, 6.6, 6.7, 6.8 and 6.9 shows the hardness variation of the alloys with aging time at different aging temperatures for 4, 6,8,10 and 12 wt% Sn keeping Ni content constant at 9 wt-%. It is found that the hardness value increases, reaches a peak value and then decreases with aging time. A similar response was observed for all the other varying Sn wt% alloys and for other aging temperatures. The hardness values varied in each sample were within ±10 HV
Figure 6.5: Hardness vs aging time for Cu-9Ni-4Sn spinodal alloy

Figure 6.6: Hardness vs aging time for Cu-9Ni-6Sn spinodal alloy

Figure 6.7: Hardness vs aging time for Cu-9Ni-8Sn spinodal alloy
The increase in hardness of the spinodal bronze alloys is due to the initial formation of spinodal or modulated structure. The decrease in hardness values for the spinodal alloys is mainly due to the formation of grain boundary precipitates or discontinuous precipitates upon over-aging. The result in this investigation was found to be consistent with that of the previous works of Baburaj et al. (1979), Zhang et al. (2008,2010) in wrought spinodal alloys, Findik and Flower (1992) in wrought spinodal alloys, Deyong et al. (1990), in melt spun alloys, Virtanen and Tiainen. (1997), in wrought spinodal alloys.
6.2.3 Effect of Sn content on aging temperature

The peak hardness values of varying wt-% Sn alloys at various aging temperatures are reported in Table 6.1. Figure 6.10 shows the variation of peak hardness values (refer Table 6.1) versus aging temperatures for varying Sn wt-% alloys. It is observed from the Figure 6.10 that for all the alloys, the hardness increases, reaches a peak value and then decreases. The peak hardness value for all the varying wt-% Sn alloys was obtained at an aging temperature of 350°C. Hence, this can be reported as the optimum aging temperature for varying wt-% Sn (Cu-Sn-Ni) spinodal alloys cast in metal mould, an important observation not reported anywhere in the above literature.

<table>
<thead>
<tr>
<th>Aging Temperature (°C)</th>
<th>Average values of peak hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu-9Ni-4Sn</td>
</tr>
<tr>
<td>250</td>
<td>160</td>
</tr>
<tr>
<td>300</td>
<td>176</td>
</tr>
<tr>
<td><strong>350</strong></td>
<td><strong>187</strong></td>
</tr>
<tr>
<td>400</td>
<td>171</td>
</tr>
<tr>
<td>450</td>
<td>165</td>
</tr>
</tbody>
</table>

Table 6.1: Peak hardness values for varying wt-% Sn spinodal alloys.

Figure 6.10: Peak hardness versus aging temperature for Cu-Ni-Sn alloys
6.2.4 Effect of Sn content on peak aging time

The peak aging time for the varying wt-% Sn alloys cast in metal mould are reported in Table 6.2. Figure 6.11 shows the variation of peak aging time (refer Table 6.2) with varying wt-% Sn in Cu-Ni-Sn spinodal alloys cast in metal mould. It can be seen from the graph that the peak aging time remains a constant value of 3hr with an increase in wt-% Sn.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Peak aging time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-9Ni-4Sn</td>
<td>3</td>
</tr>
<tr>
<td>Cu-9Ni-6Sn</td>
<td>3</td>
</tr>
<tr>
<td>Cu-9Ni-8Sn</td>
<td>3</td>
</tr>
<tr>
<td>Cu-9Ni-10Sn</td>
<td>3</td>
</tr>
<tr>
<td>Cu-9Ni-12Sn</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 6.2: Peak aging time for varying wt-% Sn alloys

![Graph showing peak aging time versus wt% Sn alloys](image)

Figure 6.11: Peak aging time versus wt-% Sn alloys.
6.2.5 Effect of Sn content on hardness

The peak hardness values of the spinodal alloys of the present study, Ilangovan’s study and Deyong’s study are reported in Table 6.3, Table 6.4 and Table 6.5. Figure 6.12 shows the values (refer Table 6.3) of peak hardness with an increase in wt%-Sn. The data’s of Deyong et al. (1990) and Ilangovan and Sellamuthu (2013) are also included in the Figure 6.12. The results of Deyong et al are taken pertaining to (i) rapid solidification by melt spinning (data- 1) and (ii) conventional ingot casting (data-2) for aging the alloys at 400°C. The alloys used in the Deyong et al. studies are 6,8,10 and 12 wt-% Sn with the Ni content fixed at 10 wt-%. The experimental results of Ilangovan and Sellamuthu (2013) are also included in the plot. The authors had carried an investigation on sand cast Cu-Ni-Sn spinodal alloys aged at 350°C. The alloys used in the study were 4, 6 and 8wt-% Sn with the Ni content fixed at 6 wt-%. It is observed from the plot that in all the studies the peak hardness values increases with an increase in wt-% Sn. The behaviour in this study was found to be in agreement with that of Deyong et al. (1990) and Ilangovan and Sellamuthu (2013). It can also be observed from the plot that the magnitude of the peak hardness values was found to be different from each study. The difference is due to the variation in the Ni content. Therefore, it can be concluded from the above results that an increase in wt-% Sn increases the peak hardness of the alloys.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Peak hardness values (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-9Ni-4Sn</td>
<td>187</td>
</tr>
<tr>
<td>Cu-9Ni-6Sn</td>
<td>350</td>
</tr>
<tr>
<td>Cu-9Ni-8Sn</td>
<td>426</td>
</tr>
<tr>
<td>Cu-9Ni-10Sn</td>
<td>441</td>
</tr>
<tr>
<td>Cu-9Ni-12Sn</td>
<td>464</td>
</tr>
</tbody>
</table>

Table 6.3: Peak hardness values of the alloy (Present study)
<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Peak hardness (HV) Data-1</th>
<th>Peak hardness (HV) Data-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-10Ni-6Sn</td>
<td>365</td>
<td>370</td>
</tr>
<tr>
<td>Cu-10Ni-8Sn</td>
<td>385</td>
<td>400</td>
</tr>
<tr>
<td>Cu-10Ni-10Sn</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Cu-10Ni-12Sn</td>
<td>415</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.4: Peak hardness values of alloy (Deyong’s data)

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Peak hardness values (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-6Ni-4Sn</td>
<td>239</td>
</tr>
<tr>
<td>Cu-6Ni-6Sn</td>
<td>266</td>
</tr>
<tr>
<td>Cu-6Ni-8Sn</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 6.5: Peak hardness values of alloy (Ilangoavan’s data)

Figure 6.12: Variation of peak hardness values with wt-% Sn
6.2.5.1 Hardness in solutionised and aged condition

The average peak hardness values for varying wt-% Sn alloys in solutionised and aged condition are reported in Table 6.6. In order to understand the effect of Sn content on the strengthening mechanisms, it is important to look at the two different aspects of the strengthening mechanism (i) solid solution strengthening due to dissolved Sn solutes in the matrix. (ii) spinodal hardening due to formation of modulated structure along with ordering reaction. In order to understand the contribution of these two mechanisms, we have plotted the peak hardness values against Sn content in solutionised and aged condition as shown in Figure 6.13.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Hardness at solutionised condition (HV)</th>
<th>Hardness at Peak aged condition (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-9Ni-4Sn</td>
<td>116</td>
<td>187</td>
</tr>
<tr>
<td>Cu-9Ni-6Sn</td>
<td>175</td>
<td>350</td>
</tr>
<tr>
<td>Cu-9Ni-8Sn</td>
<td>252</td>
<td>426</td>
</tr>
<tr>
<td>Cu-9Ni-10Sn</td>
<td>265</td>
<td>441</td>
</tr>
<tr>
<td>Cu-9Ni-12Sn</td>
<td>285</td>
<td>464</td>
</tr>
</tbody>
</table>

Table 6.6: Peak value of hardness in solutionised and aged condition (present study)
It can be observed from the Figure 6.13 that the hardness values in solutionised condition increase with an increase in Sn content. The increase in hardness in solutionised condition illustrates that Sn contributes to solid solution strengthening mechanism. In aged condition, it can be seen that the hardness value increases with an increase in Sn content, but an important observation that can be noted from the Figure 6.13 is that the trend line for both the conditions are almost parallel and therefore it can be inferred that there is no incremental contribution due to spinodal hardening by increasing the Sn content from 4 wt-% to 12 wt-%.

The hardness values in the solutionised and aged condition of Deyong et al. (1990), Ilangovan and Sellamuthu (2013) are reported in Table 6.7 and 6.8. Figure 6.14 and Figure 6.15 shows the hardness values in the solutionised and aged condition of rapidly solidified ribbons of Cu-Ni-Sn alloys and sand cast Cu-Ni-Sn spinodal alloys. From the Figure 6.14 and Figure 6.15 it can be observed that these lines are also parallel to each other. Based on the results of previous studies of Deyong et al. (1990), Ilangovan and Sellamuthu (2013) and present study, it can be concluded that (i) Sn induces spinodal decomposition when it is around 8wt-%. (ii) A marginal increase is only observed after 8 wt-%. (iii) It is not beneficial for adding Sn more than 8 wt-% in increasing the hardness due to spinodal/ordering reaction. (iv) An increase in hardness in solutionised condition implies that Sn contributes significantly to solid solution strengthening mechanism.
<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Hardness at solutionised condition (HV)</th>
<th>Hardness at Peak aged condition (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-10Ni-6Sn</td>
<td>210</td>
<td>355</td>
</tr>
<tr>
<td>Cu-10Ni-8Sn</td>
<td>255</td>
<td>380</td>
</tr>
<tr>
<td>Cu-10Ni-10Sn</td>
<td>275</td>
<td>400</td>
</tr>
<tr>
<td>Cu-10Ni-12Sn</td>
<td>280</td>
<td>415</td>
</tr>
</tbody>
</table>

Table 6.7: Peak hardness values of solutionised and aged alloys (Deyong et al. (1990))

Figure 6.14: hardness values in solutionised and aged alloys (Deyong et al. (1990))
<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Hardness at solutionised condition (HV)</th>
<th>Hardness at Peak aged condition (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-6Ni-4Sn</td>
<td>125</td>
<td>239</td>
</tr>
<tr>
<td>Cu-6Ni-6Sn</td>
<td>154</td>
<td>266</td>
</tr>
<tr>
<td>Cu-6Ni-8Sn</td>
<td>182</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 6.8: Peak hardness of solutionised and aged alloys (Ilangovan and Sellamuthu (2013))

Figure 6.15: Hardness variation in solutionised and aged condition. (Ilangovan and Sellamuthu 2013)

6.2.6 Comparison on the hardness values of spinodal alloys (varying wt-% Sn) in the present study with the regular bronze alloy (Cu-6Sn).

The peak value of hardness of varying wt-% Sn alloys aged at 350°C with regular bronze (Cu-6Sn) are reported in Table 6.9. The bar graph comparing the peak hardness values (refer Table 6.9) of varying wt-% Sn alloys aged at 350°C versus regular bronze alloy (Cu-6Sn) is shown in Figure 6.16. It is inferred from the chart that the peak hardness value increases from the base alloy to the aged condition. The spinodal alloys possess superior hardness compared to the regular bronze alloy. Therefore, it can be concluded that the spinodal alloys cast in metal mould can be used as a substitute alloy for regular bronze (Cu-6Sn) alloy in many applications.
<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Peak hardness value (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-6Sn</td>
<td>100</td>
</tr>
<tr>
<td>Cu-9Ni-4Sn</td>
<td>187</td>
</tr>
<tr>
<td>Cu-9Ni-6Sn</td>
<td>350</td>
</tr>
<tr>
<td>Cu-9Ni-8Sn</td>
<td>426</td>
</tr>
<tr>
<td>Cu-9Ni-10Sn</td>
<td>441</td>
</tr>
<tr>
<td>Cu-9Ni-12Sn</td>
<td>464</td>
</tr>
</tbody>
</table>

Table 6.9: Peak hardness values of various alloys

![Diagram showing peak hardness values of various alloys compared to base and aged conditions at 350°C.](image)

Figure 6.16: Peak hardness of regular bronze versus wt% Sn alloys
6.2.7 Comparison on the hardness values of copper based spinodal alloys in the present study with the previous studies.

The peak hardness values of various spinodal alloys in different manufacturing process with the present study are reported in Table 6.10. The bar chart comparing the hardness values (refer Table 6.10) of various spinodal alloys of previous works with the present work is shown in Figure 6.17. It can be inferred from the chart that the spinodal alloy cast in metal mould possess superior hardness compare to the other manufacturing process but only marginal variation than sand cast alloys. The higher hardness for the spinodal alloy cast in metal mould is due to the effect of cooling rate. Grain refinement takes place in the spinodal alloys cast in metal mould since the rate of cooling is much faster in this process compared to other manufacturing processes. Further, it can be noted that the spinodal alloy with Sn content shows a higher hardness than that of the alloy with Cr, therefore it can be concluded that Sn is more effective in increasing the hardness when compared to Cr.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Authors</th>
<th>Manufacturing processes</th>
<th>Peak hardness value (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-15Ni-8Sn</td>
<td>Zhang et al.</td>
<td>Investment casting</td>
<td>300</td>
</tr>
<tr>
<td>Cu-45Ni-10Cr</td>
<td>Findik et al.</td>
<td>Wrought alloy</td>
<td>250</td>
</tr>
<tr>
<td>Cu-30Ni-2.5Cr</td>
<td>Findik et al.</td>
<td>Wrought alloy</td>
<td>180</td>
</tr>
<tr>
<td>Cu-15Ni-8Sn</td>
<td>Ilangovan and Sellamuthu</td>
<td>Sand cast alloy</td>
<td>450</td>
</tr>
<tr>
<td>Cu-9Ni-12Sn</td>
<td>Present study</td>
<td>Permanent mould casting [present study]</td>
<td>464</td>
</tr>
</tbody>
</table>

Table 6.10: Peak hardness values of various spinodal alloys
6.2.8 Comparison on the hardness values of spinodal alloys (varying wt-% Sn) in the present study with the other traditional bronze (Cu-Be, Ni bronze, Mn bronze) alloys.

The comparison on the hardness values of traditional alloys with the alloys used in the present investigation are reported in the Table 6.11. Figure 6.18 shows the bar chart comparing the hardness values (refer Table 6.11) of the traditional bronze alloys with the varying wt-% Sn spinodal alloys used in the present investigation. It is observed from the chart that the spinodal alloys cast in metal mould possesses high hardness compared to the traditional alloys. Therefore, it can be concluded that the traditional bronze alloys can be replaced by spinodal alloys in many applications.
<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Reference</th>
<th>Peak hardness value (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-0.5Be</td>
<td>[2]</td>
<td>118</td>
</tr>
<tr>
<td>Cu-39Zn-1Fe-1Al-Mn (Manganese bronze)</td>
<td>[2]</td>
<td>138</td>
</tr>
<tr>
<td>Cu-3Fe-9Al (Aluminium bronze)</td>
<td>[2]</td>
<td>128</td>
</tr>
<tr>
<td>Cu-9Ni-4Sn</td>
<td>Present study</td>
<td>187</td>
</tr>
<tr>
<td>Cu-9Ni-6Sn</td>
<td>Present study</td>
<td>350</td>
</tr>
<tr>
<td>Cu-9Ni-8Sn</td>
<td>Present study</td>
<td>426</td>
</tr>
<tr>
<td>Cu-9Ni-10Sn</td>
<td>Present study</td>
<td>441</td>
</tr>
<tr>
<td>Cu-9Ni-12Sn</td>
<td>Present study</td>
<td>464</td>
</tr>
</tbody>
</table>

Table 6.11: Peak hardness values of traditional bronze alloys versus spinodal alloys

Figure 6.18: Peak hardness values of traditional bronze alloys versus spinodal alloys
6.3 Conclusions

The Cu-Sn-Ni spinodal bronze alloys were cast in metal mould and the following conclusions were made on the basis of the above investigation.

i. The grain boundary precipitates form upon over-aging.

ii. There is an optimum aging temperature for the Cu-9Ni-xSn spinodal alloys cast in metal mould which is 350°C.

iii. There is an optimum aging time for the Cu-9Ni-xSn spinodal alloys cast in metal mould which is 3 hr.

iv. The Sn content does not have any effect on the aging temperature and aging time. Since spinodal decomposition involves short range clustering and ordering reaction, the Sn content may not be effective in changing the peak aging temperature and time.

v. The hardness of the Cu-9Ni-xSn spinodal alloys were found to be high than that of regular bronze (Cu-6Sn) alloy.

vi. The hardness values were found to increase from 100 HV for the base alloy to 285 HV for the solutionised alloy.

vii. The hardness values in the solutionised condition were found to increase with an increase in Sn content which implies that Sn contributes to solid solution strengthening mechanism.

viii. The hardness values were found to increase from 100 HV for the base alloy to 464 HV for the aged spinodal alloy.

ix. The hardness of the spinodal alloy under aged condition were found to increase as the Sn content increases and therefore, it implies that Sn contributes to spinodal decomposition process.

x. The spinodal alloys (varying wt-% Sn) cast in metal mould were found to possess high hardness compared to other manufacturing processes and other Cu-based spinodal alloys.

xi. The spinodal alloys cast in metal mould were found to possess superior hardness compared to the other traditional bronze alloys.