Quantitative comparison of three Ni-containing phases to the elevated-temperature properties of Al–Si piston alloys

Yunguo Li\textsuperscript{a}, Yang Yang\textsuperscript{a}, Yuying Wu\textsuperscript{a}, Liyan Wang\textsuperscript{b}, Xiangfa Liu\textsuperscript{a,∗}

\textsuperscript{a} Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, PR China
\textsuperscript{b} Shandong Binzhou Bohai Piston Co., Ltd., Binzhou 256602, Shandong, PR China

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The different contributions of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_2\)Cu\(_4\)Ni phases to the elevated-temperature strength of Al–Si piston alloys were investigated in this paper. Four kinds of Al–Si alloy containing different Ni-containing phases were prepared and their UTS values were obtained. The volume fractions and morphology characteristics of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_2\)Cu\(_4\)Ni phases were calculated by the analysis of multicomponent phase diagrams and ImageJ software. The different contributions of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_2\)Cu\(_4\)Ni phases to the elevated-temperature properties were analyzed. The \(\delta\)-Al\(_3\)CuNi phase was found to have the most effective volume utilization and possess the most efficient contribution to the elevated-temperature strength among the examined three Ni-containing phases, and the strip-like morphology was proved to be the most favorable morphology in the improvement of elevated-temperature strength.

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1. Introduction

Multicomponent Al–Si based casting alloys are widely used in piston production and other automotive applications, due to good castability, high strength, light weight, good wear resistance and low thermal expansion [1–3]. In recent years, many countries have promulgated increasingly demanding legislation about exhaust emissions, leading to the constantly rising of automotive engines efficiency, which has placed greater demands on the performance of piston materials [4,5]. In order for such alloys to continue to operate at increasingly higher temperatures, alloying elements modifications are continually made to further enhance the elevated-temperature properties [5–7]. The mechanical and physical properties of Al–Si piston alloys strongly depend upon the types, morphologies and distributions of the second phases. The microstructures are a function of alloy composition and other processing parameters [4,8].

The addition of alloying elements into the Al–Si alloys allows many complex intermetallic phases to form, including \(\theta\)-Al\(_2\)Cu, \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi, \(\gamma\)-Al\(_2\)Cu\(_4\)Ni, T-Al\(_3\)FeNi, \(\pi\)-Al\(_3\)FeMg\(_3\)Si\(_5\), \(\beta\)-Al\(_5\)FeSi, \(\alpha\)-Al(Mn,Fe)-Si, \(Q\)-Al\(_2\)Cu\(_3\)Mg\(_8\)Si\(_6\) and \(M\)-Mg\(_2\)Si phases. The \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_2\)Cu\(_4\)Ni phases have much bigger contributions to the elevated-temperature properties of Al–Si piston alloys, owing to their better thermal stability, mechanical properties, morphologies and distributions. Ni is recognized as the most effective element in improving the elevated-temperature properties of Al–Si piston alloys [4,10]. However, T-Al\(_3\)FeNi phase is not very effective to improve the elevated-temperature properties because of its bad morphology and distribution. In the past decades, many excellent studies of Al–Si piston alloys have been done centering on the evolution of these intermetallic phases, especially Ni-containing phases. Belov performed the evaluation of phase equilibria in quinary systems that constitute the commercially important Al–Cu–Fe–Mg–Ni–Si alloying system in the compositional range of casting alloys [2]. M.M. Haque investigated the effect of process variables on structure and properties of aluminium–silicon piston alloy [8]. Chen and Thomson used a combination of electron backscatter diffraction (EBSD) and energy dispersive X-ray analysis (EDX) for the identification of the various phases [11]. Many physical and mechanical parameters of Ni-containing phases have been obtained [12–14]. Some brilliant Al–Si alloys were also developed. However, the different contributions of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_2\)Cu\(_4\)Ni phases to the elevated-temperature properties have not been investigated. The investigation of this problem will give very important information and have directive meaning to the design of Al–Si piston alloys in composition and casting technology.

The aim of the work is to investigate the different contributions of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_2\)Cu\(_4\)Ni phases to the elevated-temperature properties. Four kinds of Al–Si alloy were prepared and their elevated-temperature ultimate tensile strength (UTS) values were obtained. The volume fractions (\(Q_V\)) and morphology
Table 1
Chemical compositions and UTS of alloys.

<table>
<thead>
<tr>
<th>Alloy grades</th>
<th>Elements (wt.%)</th>
<th>UTS 350 °C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>Mg</td>
</tr>
<tr>
<td>A1</td>
<td>13.1</td>
<td>1.10</td>
</tr>
<tr>
<td>A2</td>
<td>13.1</td>
<td>1.03</td>
</tr>
<tr>
<td>A3</td>
<td>13.0</td>
<td>1.05</td>
</tr>
<tr>
<td>A4</td>
<td>12.8</td>
<td>1.01</td>
</tr>
</tbody>
</table>

characteristics of ε-Al₃Ni, δ-Al₃CuNi and γ-Al₇Cu₄Ni phases were calculated. The different contributions of ε-Al₃Ni, δ-Al₃CuNi and γ-Al₇Cu₄Ni phases to the elevated-temperature properties were analyzed.

2. Experimental

An important start is to choose the appropriate chemical compositions of alloys. Each of the designed alloys mainly has one kind of Ni-containing phases. Four kinds of Al–Si piston alloys designated as A1, A2, A3 and A4, were prepared in a clay-bonded graphite crucible heated by 25 kW medium frequency induction furnace, using 99.85% commercial purity Al, 98.5% commercial purity crystalline Si and 99.9% purity Cu, Ni and Mg. The melts were poured into one mold to gain ingots. The real compositions of the four kinds of alloys were listed in Table 1.

Then the four kinds of alloy ingots were superheated to a temperature of 750 °C in an electric resistance furnace, respectively. The temperature was measured using a digital chromel–alumel thermocouple. 1 wt.% of Al-3.5P master alloy (Provided by Shandong Al&Mg Melt Technology Co., Ltd) was added to modify primary silicon. Then the melts were carried out using 0.5 wt.% C₂Cl₆ at 750 °C for slag-removing and degassing. 30 min after addition of the Al-P master alloy, the melts were finally poured into a pre-heated (200 °C) mold at 720 °C to gain tensile test bars and specimens for microstructural analysis.

Fig. 1. Pattern dimensions for ‘dog-bone’ type specimen.

Fig. 2. XRD patterns of examined alloys: (a) alloy A1, (b) alloy A2, (c) alloy A3, (d) alloy A4.
Test bars were then heat-treated in the process: solution treated at \(490^\circ\text{C}\) for \(3\) h; water quenched; aging treated at \(200^\circ\text{C}\) for \(8\) h and cooled in air. The test bars were machined to ‘dog-bone’ type specimens (shown in Fig. 1), and then tested by electronic all-purpose test machine at \(350^\circ\text{C}\). The tensile strength data of each alloy reported below is an average of four tensile specimens.

Specimens for metallographic microstructure observation were cut from tensile bars after heat-treatment. Metallographic speci-

Table 2
Volume fractions calculated values for phases of examined alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phases</th>
<th>Al</th>
<th>Si</th>
<th>Mg2Si</th>
<th>Al1FeMg1Si5</th>
<th>Al1Ni</th>
<th>Al1CuNi</th>
<th>Al1Cu4Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td></td>
<td>2.70</td>
<td>2.33</td>
<td>1.88</td>
<td>2.82</td>
<td>3.95</td>
<td>3.46</td>
<td>5.48</td>
</tr>
<tr>
<td>Alloy A1</td>
<td>Qm, wt.%</td>
<td>84.54</td>
<td>12.19</td>
<td>0.96</td>
<td>2.67</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Qv, %</td>
<td>82.40</td>
<td>13.77</td>
<td>1.34</td>
<td>2.49</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alloy A2</td>
<td>Qm, wt.%</td>
<td>82.06</td>
<td>11.79</td>
<td>1.01</td>
<td>2.76</td>
<td>2.38</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Qv, %</td>
<td>80.89</td>
<td>13.47</td>
<td>1.43</td>
<td>2.61</td>
<td>1.60</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alloy A3</td>
<td>Qm, wt.%</td>
<td>81.04</td>
<td>11.71</td>
<td>1.03</td>
<td>2.76</td>
<td>–</td>
<td>3.46</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Qv, %</td>
<td>80.48</td>
<td>13.48</td>
<td>1.47</td>
<td>2.62</td>
<td>–</td>
<td>1.95</td>
<td>–</td>
</tr>
<tr>
<td>Alloy A4</td>
<td>Qm, wt.%</td>
<td>75.80</td>
<td>11.86</td>
<td>0.94</td>
<td>2.85</td>
<td>–</td>
<td>–</td>
<td>8.55</td>
</tr>
<tr>
<td></td>
<td>Qv, %</td>
<td>77.48</td>
<td>14.05</td>
<td>1.38</td>
<td>2.79</td>
<td>–</td>
<td>–</td>
<td>4.31</td>
</tr>
</tbody>
</table>
mens were polished in the usual manner and final polishing was carried out with fine magnesia powder by hand. The microstructure analyses were performed using a JSM-6380LA scanning electron microscope and X-ray diffraction (XRD, Rigaku D/max-rB).

The volume fractions ($Q_V$) and morphology characteristics of $\epsilon$-$\text{Al}_3\text{Ni}$, $\delta$-$\text{Al}_3\text{CuNi}$ and $\gamma$-$\text{Al}_7\text{Cu}_4\text{Ni}$ phases were calculated using two methods. The first is the well-known method of the analysis of multicomponent phase diagrams: calculate the mass fractions ($Q_M$) of phases using the data of component concentration in phases, and then determine the volume fraction using the phase density. The second is the phase extraction technology that is performed by widely used ImageJ software to extract Ni-containing phases from eutectic colonies. The characteristics of intermetallic phases were extracted and calculated by the ImageJ software from well prepared back-scattering images based on the different electron diffraction intensities.

3. Results

3.1. Tensile testing

Results of the tensile testing at 350°C are shown in Table 1. As can be seen, the UTS of alloy A1 is low. While the UTS of alloy A2 is increased to 49.51 MPa with 1 wt.% Ni addition. That is 15.8% higher than alloy A1. The UTS of alloy A3 is 44.2% higher than alloy A1 when 1 wt.% Ni and 1.08 wt.% Cu were added. However, the UTS of alloy A4 is almost the same with alloy A3 when alloy A4 has 2.15 wt.% Cu more than alloy A3.

3.2. Microstructure analysis and phase identification

Fig. 2 shows XRD patterns taken from Alloy A1, A2, A3 and A4. As can be seen, alloy A1 only contains Mg$_2$Si and Al$_8$FeMg$_3$Si$_6$ phases, apart from $\alpha$-$\text{Al}$ and Si. Each of the other three alloys also contains one kind of Ni-containing phases. They are $\epsilon$-$\text{Al}_3\text{Ni}$, $\delta$-$\text{Al}_3\text{CuNi}$ and $\gamma$-$\text{Al}_7\text{Cu}_4\text{Ni}$ for A2, A3 and A4, respectively. Fig. 3a–c show the microstructures of A2, A3 and A4, respectively. In SEM photos (Fig. 3), Mg$_2$Si is black, Al$_8$FeMg$_3$Si$_6$ phase is gray, and Ni-containing phase is most brilliant. The eutectic colonies distribute in grain boundaries and Mg$_2$Si phase is not easy to find in low magnified photo as it is so close to Ni-containing phases.

The sequence of solidification reactions in alloy A1 quaternary system is as follows: $L \rightarrow (\text{Si}); L \rightarrow (\text{Al}) + (\text{Si}); L \rightarrow (\text{Al}) + (\text{Si}) + M + \pi$. When 1 wt.% Ni is added to the system, the occurrence of “primary” phase $\epsilon$-$\text{Al}_3\text{Ni}$ phase will be seen in A2. The sequence of solidification reactions is as follows: $L \rightarrow (\text{Si}); L \rightarrow (\text{Al}) + (\text{Si}) + e; L \rightarrow (\text{Al}) + (\text{Si}) + e + M + \pi$. The “primary” Ni-containing phases are $\delta$-$\text{Al}_3\text{CuNi}$ and $\gamma$-$\text{Al}_7\text{Cu}_4\text{Ni}$ for A3 and A4, respectively, when Cu is added.

3.3. Volume fraction calculations and morphology characterizations

Firstly the well-known method of the analysis of multicomponent phase diagrams was used to calculate the volume fractions ($Q_V$) of phases in the four alloys. The calculated values are listed in Table 2.

The method of multicomponent phase diagrams analysis is a strict theoretic method and used widely. It is an exact and credible method to analyze alloys quantificationally. As can be seen from Table 2, the $Q_V$ of $\epsilon$-$\text{Al}_3\text{Ni}$ in alloy A2 is 1.60%. The $Q_V$ of $\delta$-$\text{Al}_3\text{CuNi}$ in alloy A3 is 1.95%, which is 21.9% more than $\epsilon$-$\text{Al}_3\text{Ni}$ in alloy A2. The $Q_V$ of $\gamma$-$\text{Al}_7\text{Cu}_4\text{Ni}$ has a dramatic increase in alloy A4, which is 4.31% and 169% more than $\epsilon$-$\text{Al}_3\text{Ni}$ in alloy A2. However, the $Q_V$ values might have some deviations from the practical values since the chemical stoichiometries of Ni-containing phases are within a certain range.

Then morphology characterizations were performed by widely used ImageJ software. The most brilliant Ni-containing phases were extracted from back-scattering images by ImageJ software. Six randomly selected zones for each alloy were calculated to get average characteristic values for intermetallics. The extracted Ni-containing phases can be seen in Fig. 4. The calculated results are listed in Table 3, including counted phase numbers, average sizes and circularities.
4. Discussion

The strength of Al–Si materials for piston application decreases sharply with temperature increasing, especially when the temperature is beyond 300°C. It is generally considered that the eutectic grain boundaries are the weakest areas in alloys at elevated temperature [15,16]. The intermetallic phases are the main elevated-temperature strengthening phases in Al–Si piston alloys. At elevated temperature, the thermally stable intermetallics like Ni-containing phases could impose drag on boundaries and help to increase the elevated-temperature strength. The distribution and morphology of intermetallic phases have great influence on the elevated-temperature strength of Al–Si piston alloys [6,9].

However, it is still not clear which Ni-containing phase has the most efficiency in strengthening Al–Si piston alloys. Because Al–Si piston alloy is a complex multicomponent system and several Ni-containing phases appear together in one alloy. The X-ray diffraction results reflect that only one kind of Ni-containing phases formed in A2, A3 and A4 alloys, respectively. It is very important to the quantification of the contributions of Ni-containing phases to the elevated-temperature strength.

As can be seen from the results of UTS of alloys and $Q_V$ of Ni-containing phases, 1.6% $\varepsilon$-Al$_3$Ni phase contributed 6.77MPa to alloy A2 based on A1, 1.95% $\delta$-Al$_3$CuNi phase contributed 18.89MPa, and 4.31% $\gamma$-Al$_7$Cu$_4$Ni phase contributed 18.97MPa. Apparently, the $\delta$-Al$_3$CuNi phase possesses the most efficient contribution to the elevated-temperature strength; $\gamma$-Al$_7$Cu$_4$Ni phase takes the second place, and followed by $\varepsilon$-Al$_3$Ni phase.

The morphology characterizations for examined alloys performed by ImageJ software revealed the reason why $\delta$-Al$_3$CuNi phase possesses the most efficient contribution to the elevated-temperature strength. The $\varepsilon$-Al$_3$Ni phase in A2 alloy has the most regular morphology among the Ni-containing phases, as can be seen from the circularity column in Table 3. Compared with $\varepsilon$-Al$_3$Ni phase in A2 alloy, the Ni-containing phase $\delta$-Al$_3$CuNi in A3 alloy decreased in counted number but increased in $Q_V$ and average size. The Ni-containing phase expands in one dimension in A3 alloy as can be seen from the compare between Fig. 4a and b. The Ni-containing phase continue to expand from A3 to A4 alloy, however, it expands in two dimensions. The $\gamma$-Al$_7$Cu$_4$Ni phase is larger than $\varepsilon$-Al$_3$Ni phase in both width and length and exhibits skeleton-like morphology as can be seen in Fig. 4. So the $\delta$-Al$_3$CuNi has the most effective volume utilization and possesses the most efficient contribution to the elevated-temperature strength.

![Fig. 5. The morphologies of Ni-containing phases in Al–Si piston alloys: (a) $\varepsilon$-Al$_3$Ni, (b) $\delta$-Al$_3$CuNi, (c) $\gamma$-Al$_7$Cu$_4$Ni.](image-url)
Actually, the \(\varepsilon\)-Al\(_3\)Ni phase is prone to exhibit block-like morphology in Al–Si piston alloys, and the \(\delta\)-Al\(_3\)CuNi phase is inclined to exhibit strip-like morphology, while the \(\gamma\)-Al\(_7\)Cu\(_4\)Ni phase trends to exhibit skeleton-like morphology. It can be seen from Fig. 5. So it is better to increase the amount of \(\delta\)-Al\(_3\)CuNi phase in Al–Si piston alloy composition designs so as to meet higher property requirements.

5. Conclusion

The investigation of the different contributions of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_7\)Cu\(_4\)Ni phases to elevated-temperature properties was conducted. Four kinds of Al–Si alloys were prepared and their UTS values were obtained. The volume fractions and morphology characteristics of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_7\)Cu\(_4\)Ni phases were calculated. The different contributions of \(\varepsilon\)-Al\(_3\)Ni, \(\delta\)-Al\(_3\)CuNi and \(\gamma\)-Al\(_7\)Cu\(_4\)Ni phases to the elevated-temperature properties were analyzed and following conclusions can be drawn:

(a) The \(\varepsilon\)-Al\(_3\)Ni phase is prone to exhibit block-like morphology in Al–Si piston alloys, and the \(\delta\)-Al\(_3\)CuNi phase is prone to exhibit strip-like morphology, while the \(\gamma\)-Al\(_7\)Cu\(_4\)Ni phase tends to exhibit skeleton-like morphology.

(b) The \(\delta\)-Al\(_3\)CuNi phase has the most effective volume utilization and possesses the most efficient contribution to the elevated-temperature strength among the examined three Ni-containing phases.

(c) The strip-like intermetallic phase distributed in \(\alpha\)-Al grain boundaries is best to increase the elevated-temperature strength of Al–Si piston alloys, followed by skeleton-like morphology and block-like morphology phases in sequence.

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