A new intermetallic phase formation in Mg–Si–Ni magnesium-based in-situ formed alloys

Nima Barri, Amir Reza Salasel, Alireza Abbasi, Hamed Mirzadeh*, Massoud Emamy, Mehdi Malekan

School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran

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ABSTRACT

The effects of nickel addition on the microstructure and phase formation in the magnesium-silicon alloy were studied. Besides the primary and eutectic in-situ formed Mg2Si phase in the Mg–Si alloys, a new intermetallic phase was identified in the Ni-containing alloys. Based on energy-dispersive spectroscopy (EDS) and X-ray diffraction analyses, it was shown that this phase contains Mg, Ni, and Si elements, which contradicts the presence of the expected Mg2Ni phase. Through rigorous EDS analysis, the new in-situ formed phase was identified as (Mg,Ni)3Si or more accurately as Mg8Ni7Si5 intermetallic compound, called χ-phase, which has not been reported so far in the Mg–Si–Ni ternary space. Finally, the properties of the studied Mg–Si–Ni alloys were also briefly discussed.

1. Introduction

Owing to their favorable properties such as low density, high strength-to-weight ratio, good castability and machinability, Mg alloys are being used extensively in medical, chemical, automotive, and aerospace industries [1–5]. Unfortunately, these alloys suffer from poor ductility and insufficient strength for many applications. The ductility issue has been addressed by alloying, hot working, and grain refinement [6–10] while the composite strengthening effect has been put forward as a viable method for the enhancement of mechanical strength of Mg alloys [11,12]. Among the methods for the introduction of the second-phase in composites, the in-situ formation has unique advantages [13,14]: good bond with the matrix, uniform distribution, and cost effectiveness.

Among various in-situ reinforcements, MgSi shows favorable properties such as high melting point and elastic modulus as well as low density and easy manufacturing based on the simple Mg–Si system [15,16]. The renowned in-situ MgSi-based composites have aluminum matrices based on the Al–Mg–Si system but the interest on the lightweight Mg-based composites has been increased in recent years [11,17,18]. For improvement of mechanical properties of these composites, alloying elements such as Ba [19], Bi [20], Ca [21–23], Gd [24], La [25], Nd [26,27], Sb [18], Sr [23,28,29], Y [30], and Zn [31] have been added as the modifier of primary and eutectic Mg3Si phase.

Most of these elements, as well as some other effective ones such P [13,32] and Ni [33–35], have been also used as a modifier in Al–Mg3Si in-situ composites. However, to the best of authors’ knowledge, there is no report on the effect of nickel in the Mg–Si system. It is known that in-situ Mg3Ni intermetallic forms in the Mg–Ni system [36,37]. The Mg–Ni–Si system on the Ni-rich corner has been studied by Song and Varin [36,38]. However, the ternary Mg–Si–Ni system should be further studied on the Mg-rich corner to identify the possible intermetallic phases in this system.

The present work has been dedicated to the Mg–Si–Ni alloys with the focus on the effect of Ni addition to unravel the encountered phases.

2. Experimental materials and procedure

Mg–4Si and Mg–4Si–5Ni alloys (all expressed in wt%) were prepared in an induction furnace under a protective CO2 + 5% SF6 atmosphere by the addition of Mg–10Si and Mg–20Ni master alloys to molten Mg followed by pouring from 750°C in a metallic mold (Fig. 1a). The cooling curve during solidification was also recorded by a thermocouple and a data acquisition system to determine the final solidification temperature of the alloys (Fig. 1b), which was determined as ~ 641 and 636°C for Mg–4Si and Mg–4Si–5Ni alloys, respectively. Subsequently, extrusion at 430°C (homologous temperature of 0.77) with extrusion ratio of 12:1 (Fig. 1c) was used to produce these alloys in the wrought condition. Room-temperature tensile testing with cross-head speed of 1 mm/min based on the ASTM E8-04 standard for sample
3. Results and discussion

3.1. Microstructural analysis and elemental and phase identification

The as-cast microstructures are shown in Fig. 2. It can be seen in Fig. 2a that the as-cast Mg−4Si alloy contains (I) in-situ formed primary Mg$_2$Si (Mg$_2$Si$_p$) in the long dendritic form, (II) eutectic constituent of the form of (α-Mg + Mg$_2$Si)$_e$, and (III) α-Mg. The backscatter electron image (BSE-SEM) of Fig. 2a reveals that Mg$_2$Si$_p$ particles and Mg$_2$Si$_e$ lamellae, that have Si, are brighter than the surrounding α-Mg due to the higher atomic number of Si (14) compared with Mg (12). The EDS maps and point analysis taken from the primary particles are shown in Fig. 3, which confirm that this phase is Mg$_2$Si. The presence of Mg$_2$Si$_p$ and (α-Mg + Mg$_2$Si)$_e$ can be verified based on the equilibrium Mg−Si phase diagram shown in Fig. 2b. However, under non-equilibrium conditions, after formation of Mg$_2$Si$_p$, α-Mg forms prior to the eutectic reaction. Accordingly, the solidification path can be expressed as L→L$_1$ + Mg$_2$Si$_p$ → L$_1$ + Mg$_2$Si$_p$ + α→ α-Mg → Mg$_2$Si$_p$ + α→ α-Mg + (α-Mg + Mg$_2$Si)$_e$ [15]. It should be noted that a similar solidification path has also been observed for Al−Si−Mg alloys (Al−Mg$_3$Si$_2$ in-situ composites) [13,39]. The final solidification temperature determined based on cooling curve (641 °C, as shown in Fig. 1b) is consistent with the eutectic reaction temperature of 637.6 °C (Fig. 2b).

In the case of Mg−4Si−5Ni alloy (Fig. 2c), the microstructural features are similar to the case of Mg−4Si alloy (Fig. 2a). However, the morphology of Mg$_2$Si$_p$ (denoted as 1 in the BSE-SEM image) has changed from the long dendrites to much shorted ones. Image analysis reveals that the amount of Mg$_2$Si$_p$ in Mg−4Si and Mg−4Si−5Ni alloys is ~ 8.5 and ~ 6 vol%, respectively. Moreover, another intermetallic phase (brown particles in the optical image or bright ones in the BSE image denoted by 2) has been appeared. This phase appears highly bright in the BSE image, and based on the higher atomic number of Ni (28), it is expected that this phase contains Ni. Based on the Mg−Ni binary phase diagram (Fig. 2d), this phase is expected to be Mg$_2$Ni intermetallic.

The EDS analyses of the Mg−4Si−5Ni alloy are shown in Fig. 4. Point analysis taken from the Phase1, reveals that this phase is Mg$_2$Si$_p$, similar to the case of Fig. 3. Point analysis of Phase2, however, shows that this phase not only contains Ni and Mg, but it is also consists of high amount of Si. These observations can be verified based on the EDS maps, which reveal that both Phase1 and Phase2 contain Si. However, these maps imply that the amount of Mg in Phase2 is lower than α-Mg and Phase1. To provide another evidence for the presence of Mg in Phase2, EDS line analysis (as denoted by 3) was taken from α-Mg to Phase2 to α-Mg as shown in Fig. 4. It can be seen that Phase2 contains Mg, Si, and Ni.

It can be seen that the elemental analysis of this phase does not consistent with Mg$_2$Ni intermetallic. To support this argument, XRD analyses of studied alloys are shown in Fig. 5a with incorporation of XRD patterns of pure Mg and Mg−4Si−1Ni alloy (which were cast using the same conditions). It can bee seen that Mg−4Si alloy shows diffraction peaks of Mg$_2$Si as well as those of Mg. In the case of Mg−4Si−5Ni alloy, three unknown peaks were identified, which did not match with the diffraction peaks of Mg$_2$Ni phase (reference code of 00-001-1268) as shown in Fig. 5b. Similarly, at lower Ni content (Mg−4Si−1Ni alloy), two of these peaks can also be distinguished (Fig. 5a).

Conclusively, Phase2 (New Phase in Fig. 5a) is not Mg$_2$Ni intermetallic and contains Mg, Si, and Ni, which needs more rigorous EDS point analysis as summarized in Table 1.

Table 1 reveals that the atomic percent of Mg and Ni change from ~ 38 to ~ 42 and ~ 31 to ~ 37, respectively. However, the atomic percentage of Si is ~ 25%. The latter means that the atomic percentage of Mg + Ni is ~ 75%. Therefore, the atomic ratio of (Mg + Ni)/Si is ~ 3, and hence, Phase2 might be identified as (Mg,Ni)$_2$Si intermetallic. On the other hand, it can be seen in Table 1 that Mg/(Mg + Si + Ni) and Ni/(Mg + Si + Ni) are ~ 0.40 and 0.35, respectively. Therefore, Phase2 might be more specifically identified as Mg$_2$Ni$_2$Si$_5$ compound.

Note that (Mg,Ni)$_2$Si can be written as (Mg,Ni)$_{15}$Si$_5$ and based on Table 1, it can be expressed more accurately as (Mg$_2$Ni)$_2$Si$_5$ or simply as Mg$_2$Ni$_2$Si$_5$. While other possible phases might be inferred based on these results, the new Phase2 is certainly composed of Ni, Si, and Mg. It is noteworthy that based on Fig. 2b (Mg$_2$Si) and Fig. 2d (Mg$_2$Ni), another expected ternary phase is Mg$_3$(Si, Ni) intermetallic phase through replacement of some Si atoms with Ni atoms. However, Table 1 shows that the atomic ratio of Mg/(Si + Ni) is much lower than 2, which reveals that this phase is not an option.

Another important point is the stability of Phase2 after homogenization treatment at elevated temperatures. The final solidification temperature of the Mg−4Si−5Ni alloy was determined as 636 °C (Fig. 1b). The homologous temperature of 0.5 is equivalent to the temperature of 454.5 K (181.5 °C). Therefore, the Mg−4Si−5Ni alloy
was heated to the high temperature of 470 °C (homologous temperature of ~0.82) and held there for 4 h and then quenched in water. The obtained microstructure reveals the presence of Phase2 after homogenization (Fig. 6b) and EDS point analysis taken from one of these particles (Point 6 in Table 1) is comparable with the points taken from the as-cast alloy.

The ternary phase diagram of Ni-Mg-Si system has been partially developed by Song and Varin [36,38] on the Ni-rich corner as shown in Fig. 7. Several phases have been identified but none of them conforms to the elemental analysis of Phase2. The results of Table 1 are shown by red dots in Fig. 7. It can be seen that these points can be enveloped by an ellipse and specify a unique region in this ternary space. Accordingly, the new phase was named as χ-phase in this study to contribute to this subject by providing data for Mg alloys.

3.2. Mechanical properties

Tensile stress-strain curves of Mg-4Si and Mg-4Si-5Ni alloys in the as-cast condition are shown in Fig. 8a. It can be seen that both tensile strength and total elongation of Mg-4Si-5Ni alloy are slightly better than Mg-4Si alloy, which can be related to the morphological change of long primary Mg2Si dendrites to smaller ones with rounder edges (modification effect of Ni) and also partial replacement of primary Mg2Si with the blocky χ-phase. This is consistent with the previous reports on the hypereutectic Mg-Si alloys, in which the increase in the amount of primary Mg2Si results in the deterioration of both tensile strength and ductility [16]. The microhardness of primary Mg2Si and χ-phase was determined as 291 ± 4 HV and 271 ± 5 HV, respectively. Therefore, the hardness of χ-phase is lower than Mg2Si phase. As a result, the morphological enhancement cannot significantly improve the tensile properties of the alloy.

Tensile stress-strain curves for the extruded condition are also shown in Fig. 8a. It can be seen that the extruded alloys have much higher tensile strength and ductility compared with the as-cast counterparts. To better show the enhancement of strength-ductility balance, tensile toughness (the area under the stress-strain curve) was
determined by $Area = \sum (\varepsilon - \varepsilon_{\text{in}}) (\sigma + \sigma_{\text{in}})/2$ [40]. The value of tensile toughness for the as-cast and extruded Mg–4Si–5Ni alloy is respectively 2.14 and 14.53 MJ/m$^3$, which reveals 578% enhancement. In the case of Mg–4Si alloy, the tensile toughness for the as-cast and extruded conditions is respectively 1.61 and 11.87 MJ/m$^3$, which reveals 637% enhancement. These magnificent enhancements can be related to the improvement of microstructure by hot extrusion: The fracture of primary particles and eutectic lamellae toward round shapes along the extrusion direction as can be seen in Fig. 8b for the Mg–4Si–5Ni alloy and also reducing the effects of casting defects via hot working [41].

Fig. 4. EDS analyses of Mg–4Si–5Ni alloy.

Fig. 5. (a) XRD patterns of different alloys and (b) Comparing diffraction peaks of the New Phase with Mg$_2$Ni.
4. Conclusions

Microstructural evolutions and phase formation in the magnesium-silicon-nickel alloys were studied. The following conclusions can be drawn from this study:

(1) Besides the primary and eutectic in-situ formed Mg$_2$Si phase in the Mg–Si alloys, an intermetallic phase was identified in the Ni-containing alloys. Based on the energy-dispersive spectroscopy (EDS) and X-ray diffraction analyses, it was shown that this phase contains Mg, Ni, and Si elements, which contradicts the presence of the expected Mg$_2$Ni phase.

(2) Based on the rigorous EDS analysis, the in-situ formed phase in Mg–4Si–1Ni and Mg–4Si–5Ni alloys was identified as (Mg,Ni)$_3$Si or more accurately as Mg$_8$Ni$_7$Si$_5$ intermetallic compound. This phase was named as χ-phase, which has not been reported so far in the Mg–Si–Ni ternary space.

(3) Through the addition of Ni to the Mg–Si base alloy, the long Mg$_2$Si dendrites were replaced by much shorter particles with rounder edges. However, it was revealed that the microhardness of χ-phase is lower than Mg$_2$Si phase. As a result, the tensile properties of the Mg–4Si–5Ni alloy were comparable with those of the Mg–4Si alloy. After hot extrusion process, remarkable enhancement in mechanical properties was observed due to the microstructural refinement imposed by hot deformation.

Table 1

<table>
<thead>
<tr>
<th>Point</th>
<th>Mg</th>
<th>Si</th>
<th>Ni</th>
<th>(Mg + Ni)/Si</th>
<th>Mg/(Mg + Si + Ni)</th>
<th>Ni/(Mg + Si + Ni)</th>
<th>Mg/(Si + Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.46</td>
<td>24.72</td>
<td>33.83</td>
<td>3.04</td>
<td>0.41</td>
<td>0.34</td>
<td>0.71</td>
</tr>
<tr>
<td>2</td>
<td>41.91</td>
<td>26.55</td>
<td>31.55</td>
<td>2.77</td>
<td>0.42</td>
<td>0.31</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>39.61</td>
<td>23.10</td>
<td>37.28</td>
<td>3.32</td>
<td>0.39</td>
<td>0.37</td>
<td>0.65</td>
</tr>
<tr>
<td>4</td>
<td>38.11</td>
<td>24.82</td>
<td>37.07</td>
<td>3.03</td>
<td>0.38</td>
<td>0.37</td>
<td>0.61</td>
</tr>
<tr>
<td>5</td>
<td>38.23</td>
<td>25.68</td>
<td>36.09</td>
<td>2.89</td>
<td>0.38</td>
<td>0.36</td>
<td>0.62</td>
</tr>
<tr>
<td>6</td>
<td>40.78</td>
<td>23.19</td>
<td>36.03</td>
<td>3.31</td>
<td>0.41</td>
<td>0.36</td>
<td>0.69</td>
</tr>
<tr>
<td>Average</td>
<td>40.01</td>
<td>24.67</td>
<td>35.31</td>
<td>3.06</td>
<td>0.40</td>
<td>0.35</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Fig. 6. Microstructures of (a) as-cast alloy and (b) heat treated alloy at 470°C for 4 h followed by water quenching.

Fig. 7. Incomplete ternary phase diagram of Ni-Mg-Si [36] with incorporation of the data for the new χ-phase. EDS point analyses of Table 1 are shown as red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 8. Tensile test results as well as the microstructure of extruded Mg–4Si–5Ni alloy. ED represents the extrusion direction.
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References

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