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## EFFECT OF Fe-Mn SOLID SOLUTION PRECURSOR ADDITION ON MODIFIED AA 7075

This study suggests a new way to modify the size and morphology of Al-Fe phases in modified AA 7075 by using an Fe-Mn solid solution powder as the precursor. When Fe and Mn are added in the form of a solid solution, the diffusion of Fe and Mn toward the Al is delayed, thus altering the chemical composition and morphology of the precipitates. The fine, spherical precipitates are found to provide a good balance between strength and ductility compared to the case where Fe and Mn are separately added.

*Keywords:* Al-Zn-Mg alloy, Solid solution precursor, Mechanical properties

## 1. Introduction

The Al-Zn-Mg-Cu-based AA 7xxx series is widely used in the aircraft and automotive industries for structural materials due to their high strength-to-density ratio [1-3]. Although the effects of relatively minor alloying elements such as Fe or Mn upon the microstructures and mechanical properties of these 7xxx aluminum alloys are significant, they are yet to be studied in detail.

As the content of Fe exceeds its solubility limit in Al (0.052 wt.%), a coarse plate-like Al-Fe phase is readily formed and can act as a crack source, thus significantly deteriorating the plastic deformation capacity [4,5]. Therefore, Fe is considered to be harmful and its concentration is generally recommended to be reduced in order to prevent the formation this Al-Fe phase. However, the content of Fe tends to increase in aluminum alloys during recycling because it is difficult to eliminate [6,7]. Furthermore, the Fe content of Al alloys is generally designed to be more than 0.052 wt.% to prevent the dissolution of Fe atoms from steel-based molds into the Al alloy melt, e.g. in the die soldering phenomenon [8]. In this case, when the size and morphology of Al-Fe phases are appropriately controlled, the mechanical properties can be improved by modification of the stress distribution around the Al-Fe phases [9]. For example, an increase from 0.6 to 2 wt.% Fe in Al-7Si alloys has been shown to result in increased average size, thickness, and volume fraction of the Al-Fe intermetallic phase, resulting in a 58% decrease in elongation along with a 25% decrease in strength [10].

While various methods, such as modification of the solidification conditions [11] or alloying element [12], have been used in order to eliminate the negative effects of the Al-Fe phase by reducing its size as well as changing its morphology and distribution [13,14], these methods can be difficult to be applied in industrial processes. The present study suggests a new way to alter the size and morphology of the Al-Fe phase in the modified AA 7075 alloy by using an Fe-Mn solid solution powder as the precursor.

## 2. Experimental procedure

Pure aluminum ingot (>99.9%, Hanjinmetal, Co. Ltd), Al-5Fe, Al-5Mn, Al-5Cr, Al-50Cu, Al-5Ti, and Al-38Mg (wt.%) master alloys (>99.9%, Hanjinmetal Co. Ltd), and Zn (<1 cm$^3$, 99.99%, RND Korea) were used to fabricate the modified AA 7075. The Fe-Mn solid solution was prepared in powder form via gas atomization (<45 μm, 99.95%, Changsung Co.).

The pure aluminum was melted in a crucible via high-frequency induction under an atmosphere of air. After heating the pure Al to 700°C, the master alloy was added to melt according to the chemical composition of Table 1. The molten Al alloy was cast in a 2-inch billet mold that was pre-heated to 480°C. The samples prepared by the separate addition of Fe and Mn are designated hereafter as $Fe_{0.1}Mn_{0.1}$, $Fe_{0.3}Mn_{0.3}$, and $Fe_{0.5}Mn_{0.5}$, while those prepared by the addition of the Fe-Mn

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Chemical compositions of modified AA7075 alloy

| Sample | Composition (wt.%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cr | Cu | Fe | Mn | Fe-Mn | Mg | Ti | Zn | Al |
| $Fe_{0.1}Mn_{0.1}$ | 0.2 | 0.6 | 0.1 | 0.1 | — | 2.4 | 0.2 | 5.5 | Bal. |
| $Fe_{0.3}Mn_{0.3}$ | 0.2 | 0.6 | 0.3 | 0.3 | — | 2.4 | 0.2 | 5.5 | Bal. |
| $Fe_{0.5}Mn_{0.5}$ | 0.2 | 0.6 | 0.5 | 0.5 | — | 2.4 | 0.2 | 5.5 | Bal. |
| $(Fe-Mn)_{0.2}$ | 0.2 | 0.6 | — | — | 0.2 | 2.4 | 0.2 | 5.5 | Bal. |
| $(Fe-Mn)_{0.6}$ | 0.2 | 0.6 | — | — | 0.6 | 2.4 | 0.2 | 5.5 | Bal. |
| $(Fe-Mn)_{1.0}$ | 0.2 | 0.6 | — | — | 1.0 | 2.4 | 0.2 | 5.5 | Bal. |

solid solution powders are designated as $(Fe-Mn)_{0.2}$, $(Fe-Mn)_{0.6}$, and $(Fe-Mn)_{1.0}$.

Extruder with 200 tons of hydraulic force or pressure was used to extrude the 2-inch cast billet into a 10Ø rod (extrusion ratio 25:1) at 1.2 mm/s of ram speed. The extruded specimens were subjected to the T6 heat treatment.

Thermophysical modeling was performed using the commercial software JMatPro® 9.1 to obtain the stable (or metastable) phase fraction in the given composition. The microstructures of the T6 heat-treated wrought alloy were examined via optical microscopy (OM, OLYMPUS, GX51) and field emission scanning electron microscopy (FE-SEM, FEI, Verios G4 UC). In addition, quantitative analysis was performed using energy dispersive spectroscopy (EDS, EDAX, Octane Elect EDS System) to determine the phase composition. Finally, the tensile properties of the T6 heat-treated specimens were examined according to the ASTM E8 standard using a material testing system (MTS810, MTSC) at a strain rate of 3 mm/min.

## 3. Results and discussion

The phase fraction of the modified 7075 AA alloy with various Fe and Mn contents, as predicted using the JMatPro® software, is presented in Fig. 1. A comparison of Fig. 1a-c indicates that the fraction of $Al_3Fe$ phase increases with increasing Fe and Mn content. Further, the $Al_6Mn$ phase (blue line, Fig. 1b) appears when the Mn and Fe contents are 0.3 wt.% each, and its fraction dramatically increases with further increase in the amount of Fe and Mn to 0.5 wt.% each (Fig. 1c). It is hypothesized that $Al_6Mn$ may easily formed when Mn content exceeds 0.5 wt.% while

$Al_6Mn$ is hardly formed when Mn is deficient. Interestingly, the $Al_7Cr$ phase (red line, Fig. 2a-c) is also found to increase with increasing amounts of Fe and Mn. This is possibly because the addition of Fe and Mn stimulates the formation of this phase [15]. By contrast, the formation of T-phase and Al-Ti intermetallic remains constant regardless of the amount of Fe and Mn.

The OM and SEM images in Fig. 2 represent the T6-treated alloys with Fe and Mn contents of 0.1 (a and d), 0.3 (b and e), and 0.5 (c and f) wt.%. When the Fe and Mn are added separately (Fig. 2a-c), the size of the precipitated dark phase increases with increasing amount of Fe and Mn so that the alloy containing 0.5 wt.% Fe and Mn displays large precipitates with faceted planes. However, when the Fe and Mn are added in the form of an Fe-Mn solid solution powder (Fig. 2e-g), the majority of precipitates display fine and spherical morphologies and their size does not vary significantly with varying Fe and Mn content. Comparably to the optical images, the SEM images of (d) the $Fe_{0.5}Mn_{0.5}$ and (h) the $(Fe-Mn)_{1.0}$ samples in Fig. 2 indicate that coarse and faceted precipitates are formed when Fe and Mn are added separately, whereas the majority of precipitates in the alloys prepared using the Fe-Mn solid solution powders are small and non-faceted. The chemical compositions of the areas marked by the yellow circles in the SEM images were analyzed by EDS. In the case of the $Fe_{0.5}Mn_{0.5}$, the large and faceted precipitates contain ~5 wt.% each of Cr and Mn along with a relatively small amount of Fe. By contrast, the small and non-faceted precipitates $(Fe-Mn)_{1.0}$ are found to contain a large amount of Fe and no detectable amounts of Cr. When Al and Fe are added separately, it is hypothesized that $Al_7Cr$ can be predominantly formed and that isomorphic substitution of Cr atoms by Fe atoms may occur due to the stronger interaction of the latter with Al, thus leading
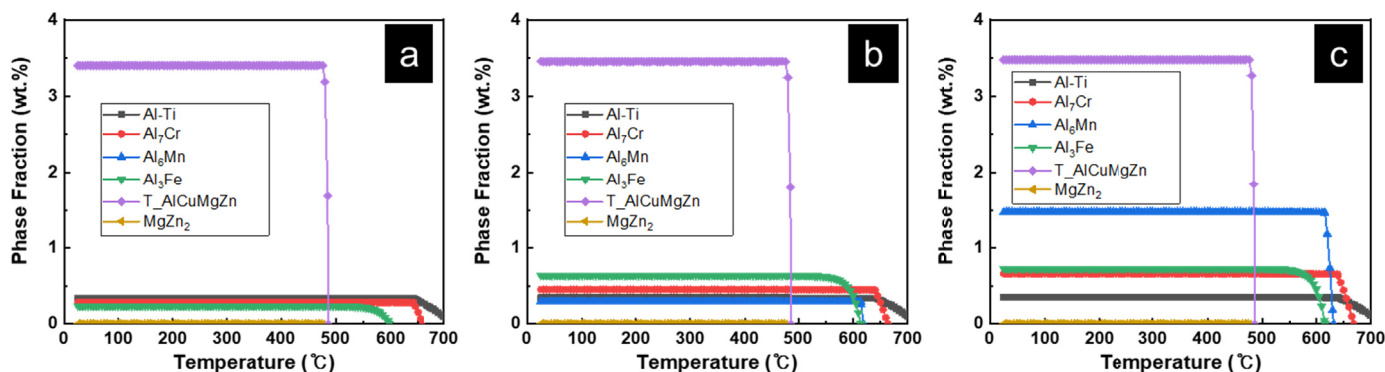


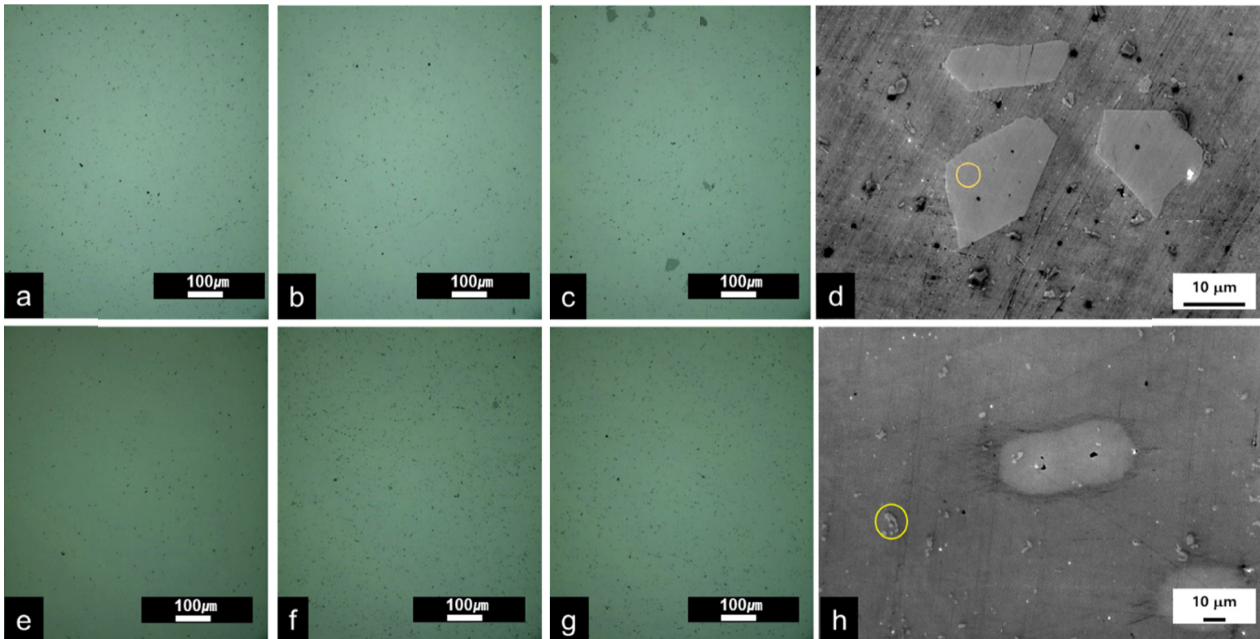Fig. 1. The phase fraction of the modified AA7075 alloy with various Fe, Mn contents using the JMatPro® software

Fig. 2. OM images of T6-treated modified AA7075 alloy with Fe, Mn contents of 0.1 (a and e), 0.3 (b and f), 0.5 (c and g) wt.% and SEM images of (d)$Fe_{0.5}Mn_{0.5}$, (h) (Fe-Mn)$_{1.0}$ samples

to a lower heat of mixing [16] and introducing the $Al_6$(Fe, Mn, Cr) phases. However, when the Fe and Mn are added in the form of a solid solution, the $Al_6$(Fe, Mn, Cr) phases are not detected and Cr is found to be preferentially located in the matrix.

The formation mechanism of the precipitation phase is shown schematically in Figure 3 for (a) the $Fe_{0.5}Mn_{0.5}$ and (b) the (Fe-Mn)$_{1.0}$ sample. When Fe and Mn are added separately, the Fe and Mn atoms may readily diffuse through the molten
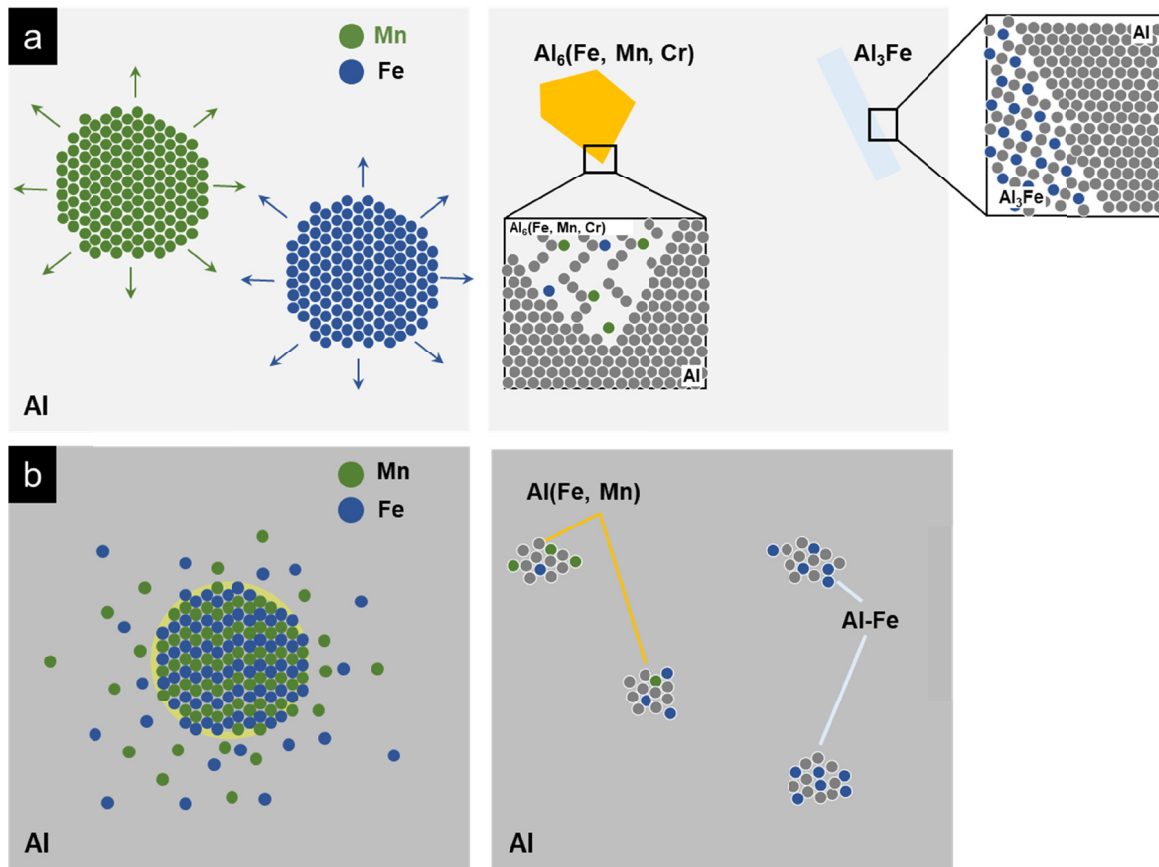


Fig. 3. Schematic images of the formation mechanism of the precipitation phase according to (a) Fe, Mn added separately, (b) Fe-Mn solid solution precursor
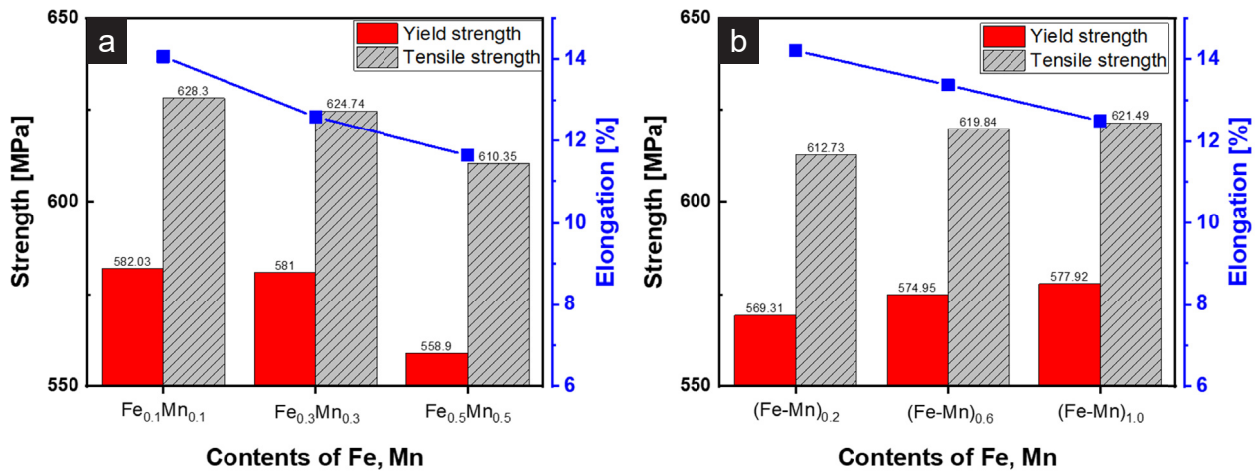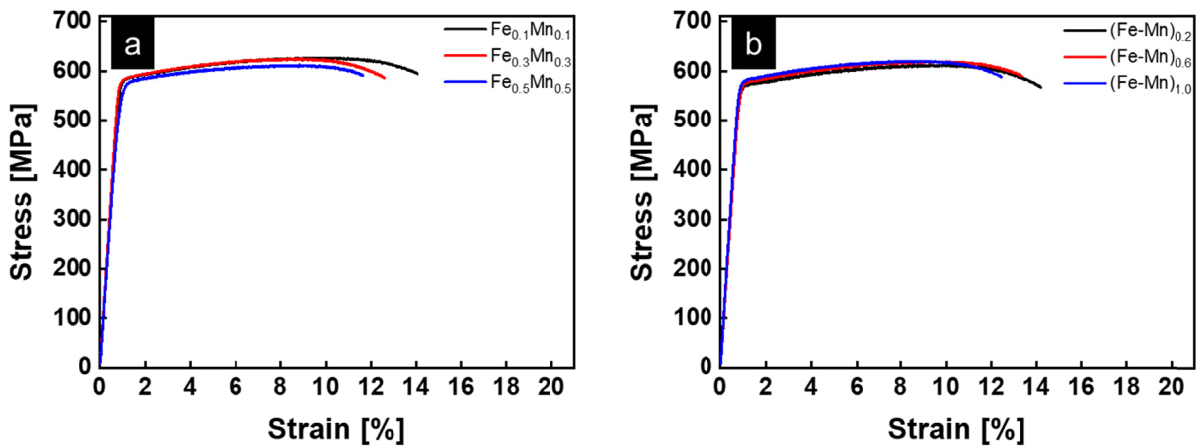
Fig. 4. Mechanical properties of modified AA7075 alloy with various Fe, Mn added form of (a) Fe and Mn separately, (b) Fe-Mn solid solution



Supplementary Fig. 1. The stress-strain curves of modified AA7075 alloy with various Fe, Mn added form of (a) Fe and Mn separately, (b) Fe-Mn solid solution

Al to form $Al_3Fe$ and $Al_6(Fe, Mn)$ during the solidification process, as predicted by JMatPro® simulation and as observed in Fig. 2. The $Al_3Fe$ and $Al_6(Fe, Mn)$ phases are each known to grow in a specific direction with a strong intrinsic tendency to form facets in order to reduce the interface mismatch energy [13,17]. These large precipitates exhibit brittle characteristics due to their flat faceted shapes [17]. However, when the alloys are cast using the Fe-Mn solid solution powder, precipitate phases of relatively small size and non-faceted shapes are observed. Since Fe and Mn are mixed at an atomic scale in the solid solution phase, each type of atom impedes the diffusion of the other. Therefore, it is difficult for Fe and Mn to react individually with Al and the Al-Fe-Mn phase is formed instead, as detected by the EDS analysis (Fig. 2). In addition, since the Fe-Mn solid solution is stable (they form solid solution throughout [18]), the rate of diffusion of Al toward the solid solution powder is slow, thus further impeding the growth of precipitates.

The yield strengths, tensile strengths, and elongations of samples are summarized in Fig. 4; raw data are given in Supplementary Figure 1. With the separate precursor additions, the yield strength, tensile strength and elongation tend to decrease with increasing amount of Fe and Mn. By contrast both the yield strength and tensile strength are increased with increasing amount of Fe-Mn solid solution, while the reduction in elongation is smaller than in the case of separate additions. As noted above, when even as little as 0.1 wt.% each of Fe and Mn are added separately, large, faceted precipitates of $Al_3Fe$ and $Al_6(Fe, Mn)$ are easily formed. Hence, the precipitate hardening effect is already maximized when $Fe_{0.1}Mn_{0.1}$ is added. With an increase in the Fe and Mn content, these precipitates play a harmful role in terms of both strength and ductility due to their brittle characteristics. However, when Fe and Mn are added in the form of a solid solution, increasing quantities of small and spherical precipitates are formed as the amount of Fe and Mn is increased. Hence, these phases may effectively strengthen the alloys. Furthermore, the change in the chemical composition of the phase leads to a delayed increase in the amount of Cr in the aluminum matrix, which may further increase the strength and work-hardening capacity and delay the onset of necking [19]. Hence, these fine and spherical precipitate morphologies help to provide a good balance of strength and ductility.

## 4. Conclusions

Two different cases were compared in which Fe and Mn were added to AA 7075 either separately or in the form of a solid solution. When Fe and Mn were added separately, the formation of large, faceted $Al_3Fe$ and $Al_6(Fe, Mn)$ precipitates led to increasing deterioration of both the strength and ductility with increasing Fe and Mn content above 0.1 wt.%. When the Fe and Mn were added in the form of a solid solution, however, the atomically mixed precursors delayed the diffusion of Fe and Mn toward the Al, thus altering the chemical composition and morphology of the precipitates. The resulting fine and spherical precipitates were found to provide a good balance of strength and ductility compared to the case when Fe and Mn were added separately.

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