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DEVELOPMENT OF ADVANCED ALUMINUM ALLOYS WITH NANO-HETERO STRUCTURES AND THEIR MECHANICAL PROPERTIES

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Abstract

High performance aluminum alloys have been widely used for many industrial applications as light weight materials. Further development of advanced aluminum alloys mainly composed of ubiquitous elements and superior in recyclability is highly required. We have developed a novel fabrication process for the wrought and cast aluminum alloys with nano-hetero structures by combining deformation, semi-solid forming and controlled heat treatments. Iron and several microalloying elements are effectively utilized to produce fine nano-hetero structures in aluminum alloys with the combination of the spheroidized α-Al, finely distributed intermetallic compounds and nano-precipitates. The characteristics of the produced nano-hetero structures are examined and the mechanical strength and ductility are evaluated. Both of the strength and ductility are extremely improved by the controlled nano-hetero structures in the developed aluminum alloys.

Introduction

Aluminum alloys have been widely developed and applied to many industrial structure components such as the aerospace/aircraft materials, high speed transportation and automobile materials. The increased demand to improve mechanical properties, strength, ductility, toughness, is given all over the world. It is also highly required to utilize abundant resources as raw materials. In this point, aluminum materials have superior advantage. However, recycling of aluminum materials becomes also an important issue to save resources and reduce cost. During recycling one of the important problems is Fe impurities. Fe is generally avoided in the industry to be mixed because impurity Fe produces large brittle Fe containing intermetallic compounds (Fe-IMCs) with Al and Si. These Fe-IMCs are harmful to ductility and corrosion resistance property of Al alloys. Therefore, the practically acceptable amount of Fe is very limited, e.g. below 0.1 mass%. In our research group we challenge to utilize Fe as a useful material to Al alloys to extend the application fields of Al alloys and to effectively reduce cost. We proposed a new concept of producing nano-hetero structures in Al alloys containing high amount of Fe [1-3]. The process for producing the nano-hetero structures is proposed. That is the D-SSF process (Deformation-Semi-Solid Forming process). The D-SSF process can produce nano-hetero structures or multi-scale structures in the alloys. In this paper the concept of nano-hetero structures and D-SSF process is described. Then, the obtained results under the above concept will be introduced. We applied the D-SSF process to both wrought and cast Al alloys. In this paper, however, the results of wrought alloys will be mainly introduced.

Controlling nano-hetero structures in aluminum alloys
Concept of nano-hetero structures

The Fe produces coarsened and irregular shape intermetallic compounds preferentially in Al alloys and normally affects extremely reduced mechanical properties, especially ductility. The corrosion resistance also decreases by large Fe containing intermetallic compounds (Fe-IMCs). The Fe-IMCs of α-Al_8Fe_2Si and β-Al_5FeSi are typically formed when Si is contained. If Si is not contained the binary Al_3Fe compound is also produced. These Fe-IMCs are very harmful for Al alloys. Then, Fe impurities are normally required to be removed in recycling of Al materials. In the novel process proposed by our group we control the Fe-IMCs to change into less harmful or rather useful microstructure components.

The microstructure of the α-Al grains is also modified together with the Fe-IMCs to harmonize morphologies for mechanical properties. The nano-structures such as nanoclusters and nano-precipitates are also controlled. The process to produce these multi-scale structures is designated as nano-hetero structures.

The harmonized combination of Fe-IMCs and α-Al grains is fundamentally important. One of the ideal combination is that the uniform distribution of fine Fe-IMCs and finely spheroidized α-Al grains. The concept of nano-hetero structures is represented in **Figure 1**, including the uniformly distributed Fe-IMCs, spheroidized α-Al and nano-precipitates with the multi-scale. The proposed D-SSF process (Deformation-Semi-Solid-Forming process) is illustrated in **Figure 2** . The Al materials containing high Fe are first conventionally cast, then are processed through the three steps: (1) Deformation, (2) Semi-solid forming, (3) Controlled heat treatment. The evolution of Fe-IMCs and α-Al grains is schematically illustrated in **Figure 3**. The large Fe-IMCs are fragmented and distributed through the deformation process (1) and strain is simultaneously introduced into the α-Al grains. In the next stage the alloys are heated to the semi-solid temperature with the controlled heating rate (2) to produce finely recrystallized α-Al grains during heating and spheroidized α-Al grains at the semi-solid temperature. The fragmented Fe-IMCs are also well

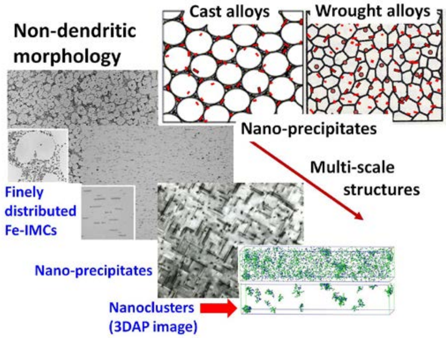

Figure 1. Nano-hetero structures with different multi-scale structures in Al alloys.

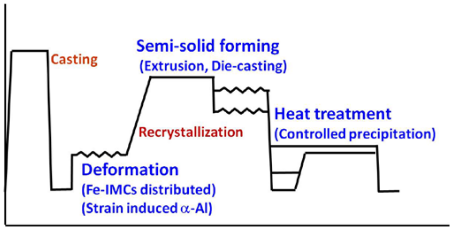

Figure 2. Schematic illustration of the D-SSF process.

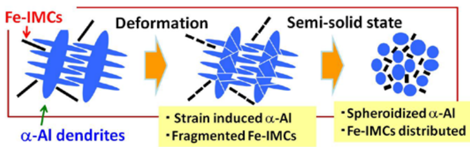

Figure 3. Evolution of Fe-IMCs and α-Al grains during D-SSF process.

distributed at the semi-solid temperature. After semi-solid forming the alloys are subjected to the controlled heat treatment (3) to produce nano-precipitates depending on the alloy types. The present paper mainly focuses on the wrought aluminum alloys of age-hardenable Al-Mg-Si and Al-Zn-Mg alloys which contain high amount of Fe compared with the impurity level of the commercials alloys

Results and Discussion

The deformation method is important to produce finely fragmented Fe-IMCs and to introduce strain into the α-Al grains effectively. Several deformation methods are applied in the present work, including cold- and hot-rolling, compression, caliber rolling and ECAP etc.. The examples of the fragmented Fe-IMCs by cold- and hot-rolling are shown in **Figure 4** for the Al-Mg-Si-1.0%Fe alloy. By the rolling deformation large Fe-IMCs (Figure 4(a)) are well fragmented and distributed as shown in Figure 4(b) and (c). The α-Al grains are elongated, indicating that strain is introduced during deformation.

The deformed alloy (Al-Mg-Si-1.0Fe alloy) is heated to the semi-solid temperature and kept for several minutes, then quenched into water at room temperature. The obtained microstructures are shown in **Figure 5**. The spheroidized α-Al grains are obtained. The Fe-IMCs are distributed among the spheroidized α-Al grains. The Fe-IMCs are found to accelerate recrystallization and also to greatly suppress grain growth in both solid and semi-solid states, resulting in the fine α-Al grains. Higher Fe concentration in Al alloys produces finer α-Al grains.

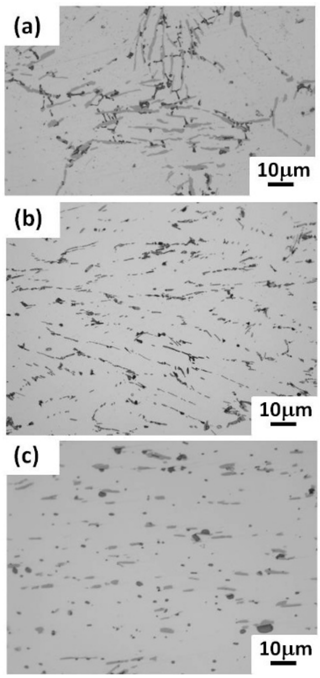

Figure 4. Fragmented Fe-IMCs by deformation in Al-Mg-Si-1.0%Fe alloy. (a) as-cast, (b) cold-rolled (40%), (c) hot-rolled(80% at 723 K)

Fabricated products and their microstructures and mechanical properties

Examples of fabricated products by the D-SSF process are shown in **Figure 6**. The wrought alloy of Al-Mg-Si-1.0%Fe is used for the semi-solid pressure casting, semi-solid forging and semi-solid extrusion in Figure 6. The optical microscope observation of these products reveals that uniformly distributed Fe-IMCs and fine α-Al grains in whole areas. Both of the alloy composition and semi-solid temperature are important factors to control the liquid fraction and formability. The mechanical properties were examined by the tensile test for the disc-shaped Al-Mg-Si-1.0%Fe alloy.

The evaluated mechanical properties of tensile strength and elongation are described in **Figure 7**. The alloys are heat treated by the T4 condition. The results of the conventionally cast alloy into an iron mold and the values for the commercial AA6082 alloy are also shown for comparison. The numbers in the figure indicate the locations of the examined specimens in the disc shaped product. It is clearly demonstrated that the D-SSF processed materials exhibit extremely improved strength and elongation even containing high Fe content of 1.0 %. Especially, elongation is 15 to 20 %, indicating that the ductility can

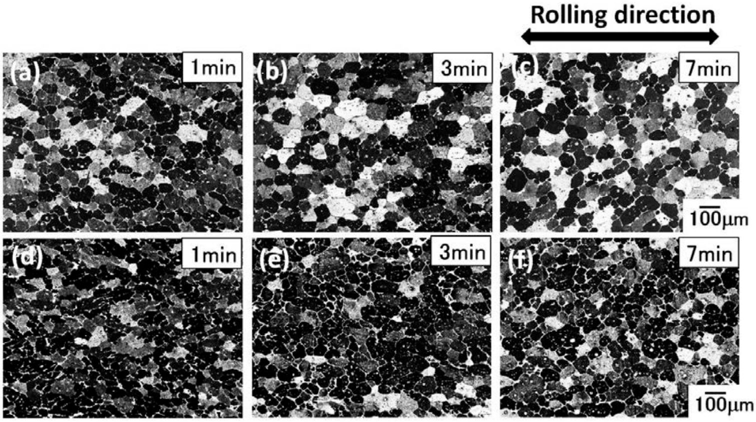

Figure 5. Evolution of microstructures during D-SSF process for Al-Mg-Si - 1.0%Fe alloy. (a), (b), (c): 873 K (d), (e), (f): 857 K

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be greatly improved in the high Fe containing alloy.

The semi-solid extrusion process for the Al alloys containing high Fe is also one of the attractive processes because the extrusion can introduce favorable metal flow for good distribution of the Fe-IMCs and can reduce forming energy. Al-Mg-Si-Fe alloys were semi-solid extruded through the D-SSF process. The obtained microstructure is shown in **Figure 8** with low and high magnifications. The Fe-IMCs are uniformly distributed with mainly very fine size. The mechanical properties of the T6 treated alloys (0.5%Fe, 1.0%Fe alloys) are shown in **Figure 9**. The D-SSF processed alloys are greatly improved in both strength and elongation compared with the 1%Fe containing as-cast alloy.

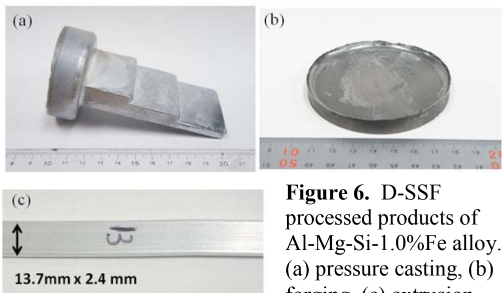

Figure 6. D-SSF processed products of Al-Mg-Si-1.0%Fe alloy. (a) pressure casting, (b) forging, (c) extrusion.

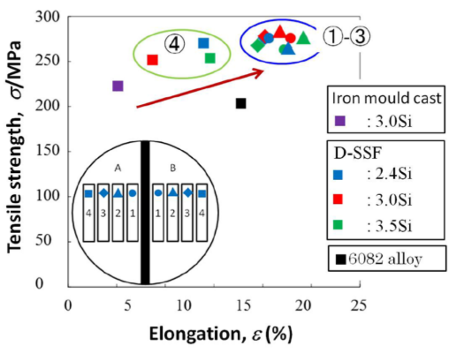

Figure 7. Mechanical properties of D-SSF processed products (Disc shaped products by forging).

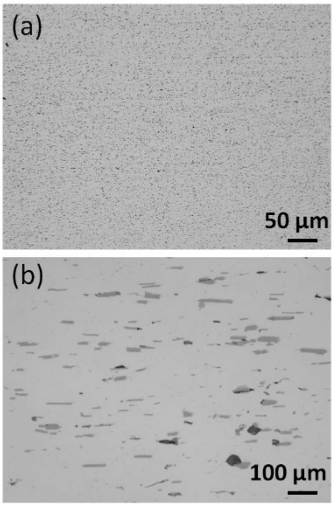

Figure 8. Microstructures of the D-SSF processed Al-Mg-Si-1.0%Fe alloy (Semi-solid extrusion).

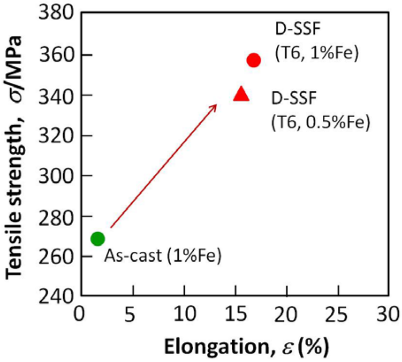

Figure 9. Mechanical properties of the semi-solid extruded Al-Mg-Si-Fe alloys.

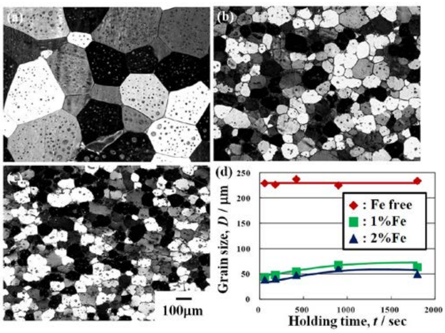

Figure 10. Microstructures of the D-SSF processed Al-Zn-Mg-Fe alloys. (a) 0%Fe, (b) 1%Fe, (c) 2%Fe

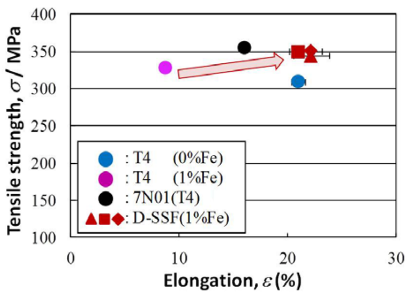

Figure 11. Mechanical properties of Al-Zn-Mg alloys with different Fe contents (D-SSF:T4 treated. ▲■◆: positions of the disc specimen, central, middle, edge).

The D-SSF process is confirmed to be effective for the Al-Zn-Mg alloy containing high amount of Fe. **Figure 10** shows D-SSF processed Al-Zn-Mg alloys containing 0%Fe, 1%Fe and 2%Fe. It is clear that the α-Al grain size becomes finer when Fe is contained, indicating that Fe effectively contributes to produce finer α-Al grains. The Fe-IMCs in the present alloy are confirmed to be Al_6Fe (metastable phase) and Al_3Fe (stable phase). All the Fe-IMCs are sufficiently fragmented and distributed uniformly. The mechanical properties of the D-SSF processed alloys are shown in **Figure 11**. All specimens were heat

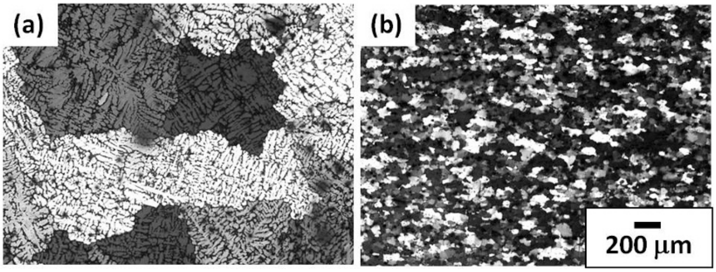

Figure 12. Microstructures of the D-SSF processed Al-Zn-Mg alloys (Semi-solid processed) (a) 0%Fe, (b) 1%Fe.

treated by the T4 condition. The properties of the several alloys are given for comparison. It is also clear that the D-SSF process is effective to increase both strength and ductility even for the 1%Fe containing alloy. The microstructures of the 1.0%Fe containing Al-Zn-Mg alloy heat treated by the T4 condition are shown in **Figure 12**. It is found that the D-SSF process can effectively produce fine α-Al grains, useful to increase strength and especially ductility.

Controlling nano-precipitates by microalloying elements and aging treatment

The Al-Zn-Mg based alloys are characteristic age-hardenable alloys which exhibit high strength and high ductility properties. These alloys are widely used for the aerospace/aircraft materials, high speed transportation and automobile materials. Recently, it becomes highly required for the Al-Zn-Mg alloys to increase both the mechanical strength and ductility. It is essential to control microstructures not only grain inside but also near grain boundaries of the alloys. To control microstructures the formation behavior of nanoclusters is extremely important because the nanoclusters greatly affect the nucleation of precipitates inside grains and in the vicinity of grain boundaries. It is characteristic of the Al-Zn-Mg alloys that the width of precipitate free zones (PFZs) is larger than that of other age-hardenable alloys. It is essentially important to control microstructures in the vicinity of grain boundaries in order to improve both of strength and ductility. The fundamental mechanism of microalloying elements and features of nanoclusters are investigated using TEM observation and 3DAP (three dimensional atom probe) technique.

The addition of microalloying elements modifies the microstructures around grain boundaries as shown in **Figure 13** [5]. Most of the precipitates inside grains are the η'-$MgZn_2$ phase. It is found that large widths of PFZ (> 350 nm) are formed in the Al-Zn-Mg ternary and Cu-added alloys, whereas a smaller width of PFZ (38 nm) is obtained in the Ag-added alloy. It is also found that the addition of Ag affects the size of grain boundary precipitates. The 3DAP technique was applies to characterize quantitatively the precipitates. Nanoclusters are found to be formed in the initial stage of aging and to transform into the η' phase with increasing aging time. Ag and Cu atoms are preferentially incorporated in both of the nanoclusters and η' precipitates.

The mechanical properties of the Al-Zn-Mg ternary and Ag-added alloys were examined and the relationship between 0.2% stress and elongation to fracture was evaluated [5]. The plots of the Ag-added alloy are located in the upper right region, indicating that both proof stress and elongation are increased compared with those of the ternary alloy. The fracture mode is also changed from the intergranular fracture to the transgranular fracture, indicating that the Ag

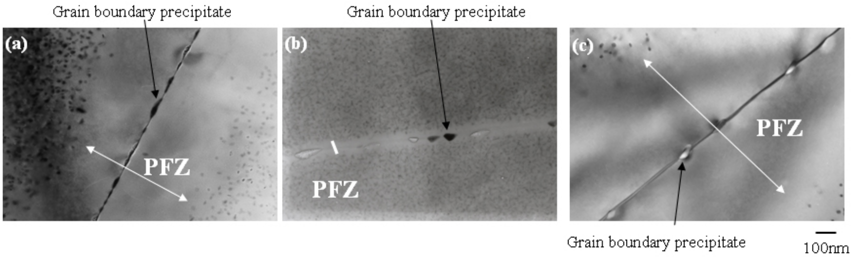

Figure 13. TEM images around grain boundaries in (a) Al-Zn-Mg ternary, (b) Ag-added and (c) Cu-added alloys aged at 433 K for 10.8 ks.

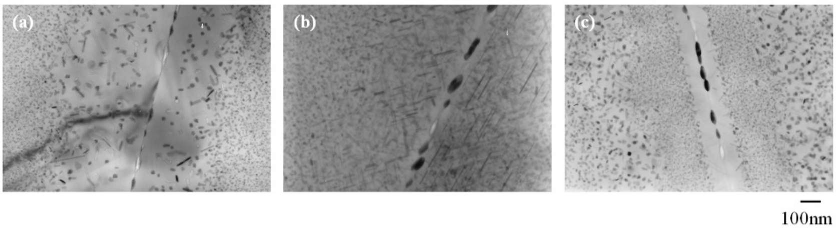

Figure 14. TEM images around grain boundaries in (a) Sn-added alloy aged at 433 K for 86.4 ks, (b) (Ag+Sn)-added alloy aged at 433 K for 86.4 ks and (c) Al-Zn-Mg ternary alloy two-step aged at 393 K for 1209.6 ks after aging at 433 K for 10.8 ks.

addition suppresses the preferential deformation in the vicinity of grain boundaries. To control the width of PFZ narrower is effective to increase strength and ductility of Al-Zn-Mg alloys.

As is described above the microalloying element of Ag is quite effective to modify the microstructure inside grains, PFZ and grain boundaries. For industrialization, however, it is necessary to find the low-cost conventional microalloying elements alternative to Ag. Then, the effects of Sn and (Ag+Sn) addition are investigated [6, 7]. **Figure 14** shows TEM images in the vicinity of grain boundaries. In the Sn-added alloy, although the PFZ is observed some precipitates exist within the PFZ. In the (Ag+Sn) combined addition with almost half amount of Ag very narrow PFZ is observed. The total amount of microalloying elements of the (Ag+Sn)-added alloy (0.05 mol%) is smaller than that of the Ag-added alloy (0.07 mol%). The precipitate morphology of the

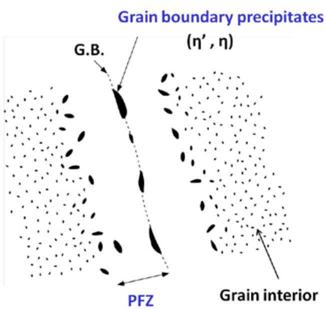

Figure 15. Schematic illustration of PFZ (Precipitate Free Zone) in Al-Zn-Mg alloy.

(Ag+Sn)-added alloy is similar to that of the Ag-added alloy. This indicates that to reduce the amount of the expensive Ag is possible by replacing with Sn. The precipitation morphology in the vicinity of a grain boundary is also dramatically changed by the two-step aging. Fine precipitates are clearly found within the initial PFZ formed after the first aging, indicating that the nucleation occurs within the initial PFZ during the two-step aging.

Schematic illustration of PFZ

The important feature of the PFZ is schematically illustrated in **Figure 15**, showing precipitates inside grains and on the grain boundaries (η': grain interiors, η: on the grain boundaries). Some coarsened precipitates are normally formed in the areas between the grain interior and PFZs. The width of PFZ is an important feature to predominate strength and ductility of Al-Zn-Mg alloys.

The relationship between 0.2 % proof stress and elongation to fracture is shown in **Figure 16** [6, 7, 8]. The plots of the Sn-added alloy are located near those of the Al-Zn-Mg ternary alloy. On the other hand, the plots of the (Ag+Sn)-added alloy are located in the upper right direction compared with those of the Al-Zn-Mg ternary alloy and near those of the Ag-added alloy. The combined addition of (Ag+Sn) is effective to improve both of proof stress and elongation.

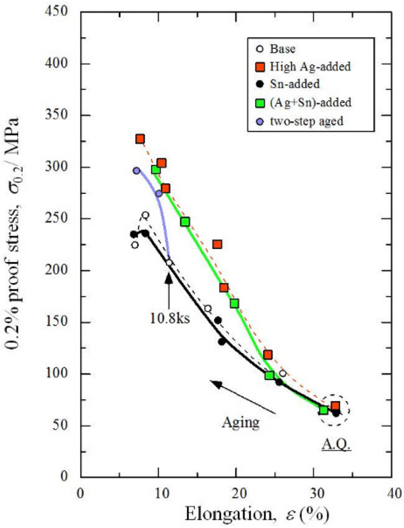

Figure 16. Relationship between 0.2% proof stress and elongation to fracture in Al-Zn-Mg alloys with microalloying elements aged at 433K.

In order to evaluate the influence of fine grains on age-hardening and ductility of the Al-Zn-Mg alloy Mn was added as a microalloying element. The combined addition of (Mn+Ag) was also examined. The obtained grain structures of the Al-Zn-Mg ternary, Mn-added, Ag-added and (Mn+Ag)-added alloys after solid solution treatment at 743 K for 3.6 ks are shown in **Figure 17**. The averaged grain sizes are approximately 180, 15, 180 and 15 μm in the ternary, Mn-added, Ag-added and (Mn+Ag)-added alloys, respectively. It is clear that the Mn addition greatly reduces the grain size of the Al-Zn-Mg alloy mainly due to the Al_6Mn dispersoid particles. The age-hardening of the Mn-added alloy with fine grains is decreased compared with that of the ternary alloy. The TEM microstructures were observed to know the age-hardening behavior and

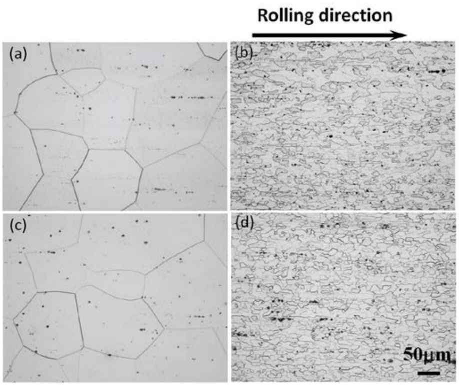

Figure 17. Optical micrographs showing grains of Al-Zn-Mg alloys. (a) ternary, (b) Mn-added, (c) Ag-added, (d) (Mn+Ag)-added alloys.

are shown in **Figure 18**. In the Mn-added alloy only small amount of precipitates are observed inside grains. Finer precipitates with high number density are observed in the Ag-added and (Mn+Ag)-added alloys. The widths of PFZ are evaluated to be 190, 40 and 30 nm in the ternary, Ag-added and (Mn+Ag)-added alloys, respectively. These results reveal that the combined addition of Mn and Ag is effective to produce finer precipitates inside grains and to narrow the width of PFZ together with small size of grains. The mechanical properties of these alloys were examined by a tensile test and are shown in **Figure 19**. It is clear that the (Mn+Ag)-added alloy exhibits the greatly increased UTS and elongation compared with other alloys. The fracture surfaces of the peak aged ternary, Ag-added and (Ag+Mn)-added alloys are shown in **Figure 20**. In the Ag containing alloys the ductile fracture surfaces are observed, indicating that the narrow PFZ is effective to increase ductility of the alloy.

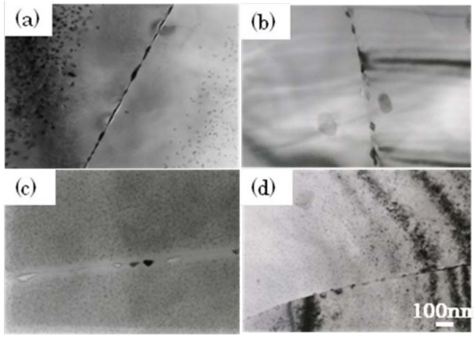

Figure 18. TEM micrographs showing precipitates and PFZ for (a) Al-Zn-Mg ternary (433 K, 86.4 ks), (b) Mn-added (433 K, 10.8 ks), (c) Ag-added (433 K, 32.4 ks) and (d) (Mn+Ag)-added (433 K, 10.8 ks) alloys.

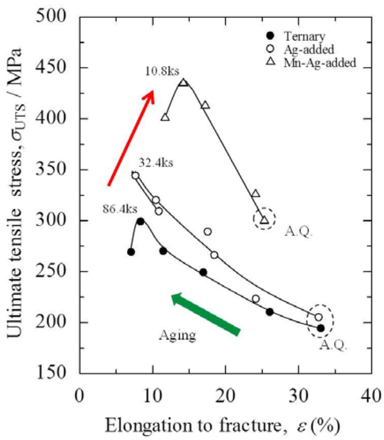

Figure 19. Relationship between tensile strength and elongation.

Controlled microalloying elements and heat treatment for the D-SSF processed alloys

As is described above, the D-SSF processed alloys exhibit both high strength and ductility even containing high Fe. The precipitate nano-structures of the age-hardenable alloys can be controlled by adding microalloying elements and optimized aging conditions. Based on the obtained results further improvement of mechanical properties of the D-SSF processed alloys are expected. The fragmented Fe-IMCs are effective to produce finer α-Al grains and to stabilize microstructures produced by the D-SSF process. Then, nano-structures can be

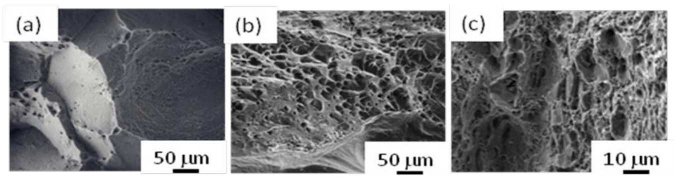

Figure 20. Fracture surfaces of the peak aged alloys. (a)ternary, (b) Ag-added and (c) (Mn+Ag) added alloys.

modified by the microalloying elements and heat treatment conditions. The whole process is expected to give new alloy systems and properties in Al alloys.

Summary

Aluminum alloys are expected to be used as promised light weight structural materials. It is required to develop advanced aluminum alloys with high strength and ductility. It is also required to utilize abundant resources as raw materials and to use recycled materials. From those points Fe is attractive materials to be controlled in Al alloys. The novel D-SSF process (Deformation-Semi-Solid Forming process) is proposed to produce nano-hetero structures in the Al alloys containing high amount of Fe. The semi-solid casting, forging and extrusion are extremely useful to develop materials in the D-SSF process. The microstructure of the uniformly distributed Fe containing intermetallic compounds (Fe-IMCs) and spheroidized α-Al grains is successfully obtained. The mechanical properties, strength and elongation, are greatly improved by the D-SSF process even containing high amount of Fe. In the Al-Zn-Mg alloy, to control PFZs (Precipitate Free Zones) is quite useful to increase both of strength and ductility. The width of PFZ is well controlled by microalloying elements such as Ag and Sn. The combined addition of Mn and Ag also greatly improve mechanical properties by producing finer grains and reduced PFZ. Aluminum alloys with nano-hetero structures produced by the D-SSF process and controlled heat treatment can be developed to extend applications of aluminum alloys.

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