Strategy of refining the structure of aluminum-magnesium alloys by complex microalloying with transition elements during casting and subsequent thermomechanical processing*

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The article reviews the studies on the microalloying of aluminum alloys with such transition metals as Nb, Zr, Hf and Sc for the purpose of grain refinement. It has been shown that each of these elements is intrinsically able to refine the structure during casting. Peritectic reaction explains the capability of all above elements, except Sc, to modify structure during casting. Zr and Sc belong to the best grain refiners in aluminum alloys, while Nb is close second, and Hf is also a good grain modifier. However, using these elements in combination gives higher effect on grain refinement and lower concentration required for it. Analysis of Al – Zr – Hf, Al – Sc – Hf, Al – Sc – Nb and Al – Zr – Nb ternary diagrams shows that Nb, Zr, Hf and Sc reduce each other's solid solubility in aluminum, which makes their combined use in grain refinement very effective. In addition, it has been analyzed how beneficial complex microalloying can be for grain refinement during hot deformation. It is especially evident in magnesium rich aluminum alloys. Such alloys contain large amount of the second phase coarse particles, which present potential new grains nuclei. Besides, due to small size of subgrains in such alloys, these particles specifically will be the major nucleation source during recrystallization. At the same time, the above transition elements facilitate formation of secondary fine (including nano-size) particles, retarding recrystallization, thus stimulating activation of maximum nuclei. To achieve the maximum effect, it is necessary to maintain the correct proportion of coarse intermetallic compounds capable to be potential nucleation sites and fine particles precipitated from supersaturated solid solution, which shall retard recrystallization without blocking it completely.

Key words: aluminum alloys, structure modification, grain refinement, transition metals, recrystallization, second phase intermetallic particles.

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Introduction

Magnesium rich aluminum alloys (more than 4%) are used in almost all modern scopes of activity such as the motor-car, food, transport and aerospace industries [1–5]. An acceptable corrosion resistance and ductility combined with high strength are the main advantages of these alloys [6–7]. The latter is achieved by dissolving magnesium in aluminum. It is possible to additionally improve the properties of magnesium rich aluminum alloys by their microalloying with transition and rare-earth elements. Each of such metals as Nb, Zr, Hf and Sc is intrinsically effective grain refiner during casting [8–13]. Combined microalloying with such elements as Zr, Nb and Hf seems to be especially promising. They reduce each other's solid and liquid solubility in aluminum that makes the grain refinement more effective [14–17].

Moreover, Zr and Sc as well as Hf according to some data, are able to form reinforcing Al_3Zr- and Al_3Sc-type nanoparticles coherent to aluminum matrix [18–22]. Their production is explained by the fact that formation of Zr and Sc oversaturated solid solution, i. e. hardening in fact, occurs at sufficiently fast casting rate due to their low solubility in aluminum [23–24]. The subsequent particles falling from the supersaturated solid solution can take place both during homogenization and during hot deformation and artificial aging [24].

*The article is published as a platform for discussion.

Another possibility for grain refinement is provided by large intermetallic particles of Mg_2Si and $Al_6(FeMn)$ types, which are common in similar alloys [25–26]. These particles can play the role of effective recrystallization centers [2, 27]. In combination with nanoparticles inhibiting the movement of intergranular boundaries, it is possible to achieve an effect when the maximum possible number of nucleation sites would be activated. The increase in the nuclei number is explained by the fact that the movement of grain boundaries is retarded and potential nuclei have time to become active before their absorption by the newly formed structure. Thus, with proper planning of casting modes and hot deformation technology, it is possible to achieve in these alloys a combined effect that allows one to fulfill grain refinement up to the sizes necessary for successful superplastic deformation.

The purpose of this work is to analyze and propose the most promising approaches to combined microalloying with such transition elements as Nb, Zr, Hf and Sc. The solution of this problem will allow to refine the grain structure as much as possible and to increase the strengthening and plastic properties of the metal.

Discussion

Influence of Nb, Zr, Hf *and* Sc o*n grain refinement during casting*

Let us consider the Nb, Zr, Hf and Sc influence on grain refinement during casting singly first of all and then the possible synergetic effect during complex microalloying.

Nb is commonly used for aluminum alloying in combination with B [28]. However, recent studies show that Nb by itself is a powerful grain refiner and begins to have a positive impact already at a concentration of 0.2 wt.% [8] even at a slow cooling rate of 1 C s^{-1}. This can be explained by the fact that according to [29], peritectic reaction in the Al – Nb system occurs just at the Nb concentration of 0.2 wt.%. Besides, recent studies [9] have shown that the mismatch between interatomic planes of the Al_3Nb intermetallic phase and aluminum matrix is minimal. Therefore, Al_3Nb are very efficacious as grain refiners during casting.

To achieve peritectic reaction in Al – Hf system, the Hf concentration under equilibrium conditions have to be 0.43 wt.% [30]. In [10], the ability of Hf to grain refinement during aluminum casting has been also studied. Unfortunately, this study does not contain any data on the exact cooling rates during casting; mentioned is only that the latter is conducted into a water-cooled iron mould. Therefore, one can assume that the cooling rate was sufficiently high. Hafnium concentration increase from 0.1 wt.% to 0.6% reduces the structure size from 400 to 220 μm. At lower concentrations, hafnium refines the grain at the expense of local supercooling on the border of the emerging nuclei and the liquid phase.

At Hf concentration of 0.2 wt.%, the first Al_3Hf particles begin to form under non-equilibrium crystallization conditions, which causes an increase in the grain refinement effect. The greatest effect of the refinement appears when equilibrium peritectic point is achieved at a Hf concentration of 0.43 wt.%. In [31] it is shown that grain would be refined up to 50 μm at Hf content of 1.4 wt.% and cooling rates of $2{\times}10^2 - 2{\times}10^4$ K s^{-1}. When the cooling rate reaches $10^5 - 10^6$ °/s, a strongly refined structure with a grain size of 1.6 μm will be observed in aluminum alloy Al – 0.94 at.% Hf (5.91 wt.%). Thus, Hf can also serve as a structure refiner when casting aluminum alloys, although it ranks below Nb in efficiency.

Zirconium is one of the strongest grain modifiers. For example, a study [8] showed that Zr is an even stronger grain refiner than Nb. At the same concentration and cooling rate, zirconium acts more effective than niobium does. The same work shows, that there is minimal mismatch between the interatomic planes of Al_3Zr particles and aluminum matrix like that in the case of Al_3Nb particles. That once again points to the effectiveness of Zr as an inocular.

Scandium's ability to grain refinement is well known and described in a variety of sources [12, 23]. We'll just note that without the addition of zirconium, scandium will have a significant impact on grain refinement when casting aluminum only at its concentration of 0.5.... 0.6 wt.% [12, 23].

Combined impact of transition elements on grain refinement during casting

First of all, it is worth noting that using scandium without the addition of other rare-earth elements (zirconium Zr is mainly used for this purpose) would be economically inexpedient despite the significant effect of grain refinement caused by its insertion into aluminum. For example, in [13] it is shown that the addition of 0.1 wt.% of Zr results in a shift of scandium concentration, from which it begins to effectively act as a refiner from 0.5 wt.% to 0.2 wt.%. In another domestic study [14], it is demonstrated that combined alloying of aluminum alloys with scandium (0.2 wt.%) and zirconium (0.2 wt.%) also significantly increases the effect of grain refinement [32]. Erbium also contributes to the modification of grain structure and is sometimes added to zirconium and scandium. For example, [33] describes how adding of about 0.25 wt.% Sc, 0.1 wt.% Zr and 0.38 wt.% Er to a magnesium reach aluminum alloy results in the structure refinement up to 90 μm during casting. In fact, almost all transition elements reduce their solubility in each other in aluminum matrix during joint microalloying, which explains the combined effect. This in turn leads to a decrease in their concentration required for the start of peritectic reaction.

When analyzing the literature, the authors found practically no sources, which would have discussed how grain refinement is affected by combined microalloying with Sc, Zr, Hf and Nb. However, in recent years many studies devoted to the research on the aluminum angle of ternary diagrams with transition elements have appeared. For example, the Al – Zr – Hf phase diagram aluminum angle research [17] shows that Zr and Hf significantly reduce each other's solubility in aluminum matrix. At the same time, Hf and Zr practically do not dissolve in Al_3Zr- and Al_3Hf-type particles, respectively. The Al – Zr – Nb diagram aluminum angle research has been implemented in [34] only. However, the temperature of 500 ^oC for which the diagram has been studied, is too far from the solid solution crystallization point. At the same time, this work demonstrates that Nb and Zr are well dissolved in Al_3Zr and Al_3Nb, respectively. In [15] it is revealed that the Al_3Sc and Al_3Hf phases in an Al – Sc – Hf ternary system can dissolve hafnium and scandium, respectively, i.e. these particles exist not in isolation, but in the form of triple compounds $Al_3(Sc, Hf)$. By analogy with the impact of zirconium on Al – Sc alloys, hafnium should retard the particle coagulation processes during process heating, but this fact should be verified experimentally, since there is no information in the literature about this yet. Two phases, Al_3Sc and Al_3Nb, also exist in Al – Sc – Nb system [16], but no information on the solubility of Nb in Al_3Nb and Sc in Al_3Nb was found. Thus, the study of aluminum angle in the above diagrams allows us to conclude that Sc, Zr, Hf and Nb will significantly reduce the solubility in each other and contribute to an earlier start of the peritectic reaction, thereby increasing the efficiency of grain refinement.

Grain refinement during recrystallization

Additional grain refinement can be achieved by managing the recrystallization process by controlling the size and number of intermetallic particles. It is well known that size of new grains being formed during recrystallization is largely determined by the volume to radius ratio of the second phase particles [27]. Thus, with a small number of particles and their coarse sizes, the newly recrystallized grains will have a fairly large size since the number of recrystallization centers is quite small. When increasing the number of intermetallic particles, greater number of growth centers appears allowing to obtain a fine-grain structure. Also, the structure refinement process is promoted by the fact that the number of fine particles is also growing, which allows to slow down the movement of large-angle boundaries and to increase proportion of the nuclei involved in the recrystallization process. A unique feature of aluminium alloys with additions of transition elements is the presence of an oversaturated solid solution formed upon casting (the above mentioned "effect of self-hardening"). This, in its turn, makes it possible to manage the number of fine particles by controlling their separation from the solid solution with the use of the thermal and deformation treatment temperatures.

It should be marked that magnesium reach aluminum alloys are characterized by the particle- stimulated nucleation (PSN) recrystallization mechanism (i.e., nuclei formation on the second phase particles). It was observed in a high-magnesium 5182 alloy [35], which has allowed significantly refining the grain in it. Other studies have shown that the cast structure with 500÷400 µm can be refined to 22 µm [2], or even to 12 µm [36] in the course of industrial hot rolling (including both reversible and continuous ones) in this alloy. To the point, predisposition the PSN mechanism in 5XXX alloys is explained not so much by the second phase particle coarse size as by the subgrain fine-grained size typical for these alloys [37–38]. The fine-grained size of subgrain in this group of aluminum alloys in relation to their other series is explained by the fact that magnesium significantly reduces the packing defect size, thereby increasing the dislocation density [38]. Thus, exactly coarse intermetallic particles become nuclei in most cases, since they are usually bigger than subgrains. At the same time, due to the significant accumulated non-equilibrium energy (i. e. subgrains of fine-grained size); the particle size with critical dimensions for recrystallization is quite small. It should be noted that number of particles and therefore the tendency to PSN mechanism increases as adding the alloying elements poorly soluble in aluminum matrix, especially transition metals, to Al – Mg alloys is fulfilled [25–26].

General strategy of grain refinement by microalloying of aluminum alloys with transition elements

In that way, the general strategy of microalloying of magnesium-reach aluminum alloys is to find the most effective combinations of the transition elements considered above with or without scandium. At the same time, it is necessary to achieve the most cost-effective combination that allows one to reach the peritectic point from the minimum concentration of elements. This will allows reducing the share of expensive scandium. It is also necessary to take into account that after reaching the point of maximum solubility, further increase in the content of transition elements would not lead to grain refinement [12]. Finally, too many transition elements and, as a consequence, the second phase particles, can completely block the recrystallization processes, which would make it impossible to control the grain size during hot multi-pass deformation (rolling, for example).

At the stage of thermomechanical processing, the grain refinement strategy should be to select optimal heating conditions on homogenization. These modes should promote in obtaining such a ratio of coarse and fine-graded intermetallic particles, which allows one to activate the maximum number of recrystallization centers. At the same time, on the subsequent stages of production it is possible to cause formation of a large number of fine particles by artificial ageing, in order that to fix the substructure and to increase the efficiency of processing the aluminum alloys by methods of severe plastic deformation (SPD).

Conclusion

1. Transition elements such as Nb, Zr and Hf are in themselves good modifiers during casting of aluminum alloys. Peritectic reaction is the main mechanism during grain refinement and sometimes an additional liquid phase super cooling is also used. Scandium Sc is also a very effective modifier, but with not added other transition elements it starts to act effectively only when the concentration of 0.6% wt is reached. With Zr added, the scandium concentration required for effective refinement of the cast structure becomes 0.2–0.3 wt.%. Erbium Er in combination with Zr and Sc can also be an effective modifier in casting of aluminum alloys.

2. Analysis of aluminum angle of the Al – Zr – Hf, Al – Sc – Hf, Al – Sc – Nb and Al – Zr – Nb triple diagrams shows that transition elements significantly reduce each other's solubility, which allows to reduce their concentration necessary for the start of peritectic reaction. This in its turn makes various combinations of Zr, Sc, Nb and Hf very promising for microstructure refinement during casting.

3. The structure can also be refined then in the recrystallization process by achieving an optimal ratio between the coarse particles serving as the nuclei of new grains and fine-grade particles retarding the movement of intergranular boundaries. The main objective of this strategy is to set in motion the maximum number of nuclei during recrystallization.

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