Quality assessment of aluminum-based grain refining master alloys

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Abstract: Based on some theoretical and practical approaches, the main stages of the quality assessment of aluminum-based grain refining master alloys have been revealed. Methods for the quality improvement of Al-Ti and Al-Ti-B grain refiners have been described.

Keywords: aluminum master alloys; quality; hereditary influence

CLC number:TG243

1. Introduction

The improvement of the properties of aluminum products is still a real problem in the theory and practice of foundry. It can be solved by different methods including grain refinement, which is considered to be one of the most effective, simple and reliable methods. A grain refiner is known to contain numerous high-melting particles, which are released after the aluminum matrix dissolves in a melt and subsequently act as heterogeneous nuclei on cooling. It provides a fine equiaxed grain structure, which ensures improved castability and mechanical properties, reduces hot tearing and micro-porosity, as well as improving machinability in castings [1-3].

Grain refiners used in common aluminum foundry practice are usually Al-Ti, Al-Ti-B, and others based on these systems. In spite of their wide application, there is not a common standard for their quality. Foundry practice shows that the assessment of the grain refiner quality cannot be done fruitfully unless the whole sequence of events during the grain refinement process is seen in one context. Much of the research work has been focused on the grain refinement mechanism, which is undoubtedly of great importance, whereas less attention has been paid to the grain refiner structure and the nature of the liquid state. This paper analyses some theoretical and practical approaches to the problem of the quality of aluminum-based grain refining master alloys, and reveals the most important quality criteria used, and describes some methods for the improvement in grain refiner quality.

2. Fundamentals for quality assessment of grain refiners

Some investigations and developments in the foundry of aluminum alloys have shown that the structure of a grain refiner exerts a hereditary influence on the structure and properties of cast products [⁹]. That was also confirmed and explained by physical studies of melts [⁵-⁷]. This idea is based on the micro-inhomogeneous nature of the melt, which results from the initial heterogeneity of the melt, inherited from its prehistory (e.g. melting a heterogeneous ingot with eutectic or primary crystals, master alloys with inter-metallic crystals). According to this concept, the structure of binary and multi-component molten alloys can be considered as a mixture of clusters of different atoms, which are immersed into a predominant liquid component. The clusters enriched with different components do not have distinct interfaces with the surrounding melt. Their local composition and structure change gradually with the distance from the center. In addition to the clusters, large domains enriched with one of the components are present in multi-component melts. These domains are separated from the surrounding melt by sharp interfaces. They are classified as disperse phases, which make the system heterogeneous on the nano-metric scale, or micro-inhomogeneous. Investigations of the temperature properties and short-range order of the melts have shown that their micro-inhomogeneous state is meta-stable or non-equilibrium. Thus, the melt, forming after melting the grain refiner, relaxes to the thermodynamically stable state of the true solution. During its evolution, the fragments inherited from the furnace charge, including inter-metallic particles added with a master alloy, gradually disperse until they reach a size between 1 and 200 nm. This relaxation can be completed by the

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[Received date] 2004-11 -14; [Accepted date] 2005-03-02
establishment of meta-stable equilibrium between the dispersed particles, enriched with one of the components, and the surrounding melt, enriched with another component. When the melt solidifies, the dispersed particles act as nuclei, and their concentration, size, and composition affect the structure of the cast product. It means that the structure of the furnace charge exerts a hereditary influence on the cast alloy through the melt.

Based on this principle, the main components of the grain refiner quality assessment have been revealed as chemical composition assessment, phase composition assessment, macrostructure assessment, and microstructure assessment.

3. Chemical composition assessment

The analysis of the chemical composition of a grain refiner is the first stage of its quality assessment. The content of the main components must correspond to the set composition and vary only insignificantly within the grain refiner ingot or rod. The ingot thickness was found to affect the Ti content variation in Al-Ti master alloy. The increase in the ingot thickness from 10 to 60 mm resulted in the increase of Ti content variation from the center to the edge of the ingot by a factor of three. Sometimes, the higher Ti content can be in the central zones of the ingot and is connected with a slow solidification rate and development of shrinkage defects. It can be explained by the long pouring duration under industrial conditions, when moulds are overheated and cooling rate reduces by the end of the pouring. The chemical inhomogeneity is accompanied by the structural inhomogeneity. More homogeneous composition and structure can be obtained at a higher cooling rate and mechanical working.

The content of impurities is also of great importance for the grain refiner quality, since some of them have a poisoning effect on the nuclei. Such impurities as Fe, Si, and Cu if incorporated into the lattice of primary inter-metallic particles, change it, reducing the lattice matching between the particles and the aluminum matrix and thereby impairing the grain refiner effectiveness. Zr was found to be the most unwanted impurity in B-containing master alloys. It was found that Cu, Si and Zn in aluminum poison the effectiveness of TiAl3 as a nucleant, but promote the role of (Al,Ti)B2. Zr in aluminum seemingly does the opposite - it poisons the action of borides. The evidence of the poisoning effect of Si, Zr and Cr and the neutralizing effect of Mg in Al-Ti-B master alloy are shown in Murty et al.’s study.

Chemical composition, by itself, cannot guarantee excellent grain refining performance of the master alloys, since this also depends on the phase composition, which must be controlled and tested in grain refiners.

4. Phase composition assessment

The phase composition of the grain refiners is one of the most important parameters, influencing their effectiveness and depends on the method of their production. The commercial grain refiner Al-Ti in ingot form is known to contain the TiAl3 phase with a tetragonal lattice of the DO23 type, which shows good matching with the aluminum lattice. However, at higher cooling rates (over 3 × 103 °C/s) of Al-Ti and Al-Ti-B master alloys a meta-stable compound TiAlx was formed. The crystal structure was reported to be an ordered cubic phase of the L12 type. It was shown to have lower lattice disregistry with aluminum than the tetragonal one and provide better grain refinement, but it is difficult to make economically on a commercial scale.

The typical phases in Al-Ti-B master alloys are known to be TiAl3 and TiB2. But, depending on its chemical composition and production method, (Al,Ti)B2 can also be formed. Much work has been done to study the role of these phases in the nucleation, which is an indication of the importance of the grain refiner phase composition, but the problem has not yet been solved. According to some results, TiAl3 acts as a nucleant according to others TiB2 is doing the nucleation. The (Al,Ti)B2 phase was found to be inefficient for the nucleation of pure aluminum, but becomes effective in the presence of some Ti. The required phases in the master alloy also depend on the parent-metal composition. For example, (Al,Ti)B2 phase was shown to be very effective for hypoeutectic Al-Si alloys.

These examples show that the effect of the phase composition of master alloys is still not fully understood, but must be taken into account when the master alloy quality is estimated.

5. Macrostructure assessment

The macrostructure assessment is the fast test of the grain refiner quality and is carried out visually by its fracture. The fracture must be uncontaminated (free from non-metallic inclusions and oxides), quite dense (low gas content) and homogeneous (free from conglomerations of high-melting particles). It was found that boron-containing particles could be accumulated on large oxide inclusions and form boride-oxide "rings", which were not dissolved during melting, could not be easily extracted by the next filtration, and then were found in the casting. This
assessment is simple, evident and is widely used in the foundry practice.

6. Microstructure assessment

The microstructure assessment is the most complicated stage. Generally, such parameters as quantity, sizes, and morphology of high-melting particles in the master alloy are used. The requirements to them are quite indistinct when the grain refiner quality is assessed, a value for the stage. Generally, such parameters as quantity, sizes, and morphology of high-melting particles is seldom given. It can be connected with some difficulty, to the calculation of the quantity of crystallization centers, \( N \), in a unit volume \( A^{-1/\sqrt{N}} \) indicates the importance of \( N \). However, when the grain refiner quality is assessed, a value for the quantity of high-melting particles is seldom given. It can be connected with some difficulty, to the calculation of the quantity of particles in a unit volume. The minimum size and more globular morphology \( [9] \).

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The Al-Ti-B master alloy with such small particles was activated in several minutes \( [26] \). Such master alloys can be used successfully only in the continuous casting or in-mould grain refinement.

The regulation of the intermetallic sizes in master alloys is also connected with their sedimentation due to the difference in the density between crystals and melts. After the dissolution of the aluminum matrix of a master alloy in a melt, high-melting particles start to settle down at the bottom that causes non-uniform grain refinement in the lower and upper parts of the casting \( [34] \). According to Stock's law, a doubling of the inter-metallic particle size results in an increase in its settling rate in the melt by a factor of four \( [8] \). Smaller particles can provide a lower rate of sedimentation.

The statistical study plays an important role in the assessment of an average size of high-melting particles in grain refiners, since it gives some information about the uniformity of particle distribution by sizes \( [18] \). As a criterion for uniformity of the distribution of particles by sizes, a variation coefficient can be used. It is also useful to indicate the confidence interval and the maximum size of high-melting particles, which, as was mentioned above, may exert a negative influence on the alloy's properties.

The studies of the effect of high-melting particle morphology on the grain refiner efficiency are quite contradictory. It was shown that the titanium aluminide phase in Al-Ti and Al-Ti-B master alloys, solidifying with normal cooling rates, has two main morphologies - blocky (or globular) and acicular (or plate-like) depending on the temperature history of the master alloy production \( [8, 9] \). According to these works, the crystals start growing as blocky structures. With the increase in the melt holding time, the preferred growth of one of the crystal planes begins that result in the formation of acicular or plate-like aluminides with impurities accumulated on the surface of...
this plane. It was noticed that the ability of these particles to act as nuclei decreases. The crystals of both morphologies have the tetragonal lattice with the same parameters, but the blocky crystals have several planes isomorphic to aluminum, whereas in acicular crystals there is only one isomorphic plane. A greater undercooling of the melt after the addition of the grain refiner with acicular crystals was observed, which meant a worse grain refining ability, than that with blocky crystals [3]. The third morphology of aluminide crystals in Al-Ti-B master - petal-like - was observed after the overheating and fast cooling of the master alloy melt [10,16]. It was found that the grain refining response of the master alloy depends on the morphology of titanium aluminides. Blocky crystals act fast, but their effect fades quickly. Petal and plate-like structures act more slowly, but their grain refining efficiency improves with time and lasts longer [36]. The blocky structure is more important for the continuous casting or for grain refinement in the ladle or mould. When furnace additions are made, the longer-lasting plate-like structure is preferred [10]. The results of some studies showed that the morphology of the TiAl3 phase has almost no effect on the grain refining ability of Al-Ti and Al-Ti-B master alloy [18,20,37] others take it as a key factor in controlling the grain refining performance [21,38]. It should be noted that blocky particles usually have smaller sizes than needle- or plate-like ones, and this does not permit easy separation of the effects of morphologies and sizes.

The effect of the microstructure of Al-Ti master alloys on their grain refining response was studied by the authors [27]. Master alloys with coarse, needle-like TiAl3 particles (A); with fine blocky particles (C); and with mixed structures (B) were added to aluminum. Differences in the grain refining ability of the different structures of master alloys were observed only with an increase in their contact time with the melt. The dissolution processes of inter-metallic particles then played a more important role and even higher Ti content in Al could not nullify the influence of the structure (Fig.1). The grain refining effect was shown to fade away markedly for the master alloy with large needle-like Al,Ti crystals and to show a further small improvement at a longer holding time. For the master alloy containing both needle-like and blocky aluminide crystals with middle sizes the fading effect was less significant, and more noticeable improvement in the grain refining was found after a shorter holding time. For the master alloy with finer blocky particles, the grain refining effect did not fade away during the whole period of the melt holding time.

The importance of the effect of master alloy microstructure is evident, though it is difficult to separate the effects of different structural parameters of master alloys on their effectiveness; and sometimes the results are even inconsistent, which shows the complexity of the grain refinement nature.

7. Ways to improve the quality of aluminum master alloys

Ways for the improvement of the quality of grain refiners are readily apparent from this paper, and mainly concern the refinement of their structure. One of the most efficient methods, mentioned above, is the rapid solidification. It can be realized either by casting thinner ingots into water-cooled moulds, by spun casting, or even by making granules [4,29,30]. In some cases the effective way to affect the master alloys' structure is their thermo-mechanical treatment and heat treatment [31,32-35].

The quite new method of self-propagating high-temperature synthesis (SHS) in aluminum melt also provides some advantages for making Al-Ti and Al-Ti-B grain refiners. The microstructures of the master alloys can be controlled through SHS parameters, which are affected by initial melt temperature, powder particle size, stoichiometric ratio of powders and flux addition [27,39,40]. Fig.2 shows the variety of microstructures of Al-Ti master alloys produced by different methods: by the reduction of potassium fluorotitanate and casting in the form of thicker (a) and thinner ingots (b), by the addition of titanium sponge and rapid solidification (c) by SHS technology (d). Multi-component master alloys, such as Al-2 %wtTi-2%wt Zr and Al-2% wt Ti-1%wt V, used for the grain refinement of alloys containing two or three high-melting compounds, were found to have finer inter-metallic particles than the corresponding binary master alloys. The addition of metallic Na or sodium compounds to the melt during the preparation of Al-Ti-B master alloy prevents the growth of high-melting particles and promotes their uniform distribution [33]. This direction can be also used for improvement in the quality of master alloys.
An effective way to refine the structure of master alloys is casting from the liquid-solid state. The mixing of master alloy melt containing up to 35% of high-melting component with liquid aluminum at 700–750 °C enables the production of a quality master alloy with low hydrogen content and fine inter-metallic particles. The volume ratio of the two melts is selected so that the mixture temperature can be lower than its melting point. In this case, during the mixing, a great number of primary inter-metallics are formed because of the high cooling rate. Depending on the mixing time of “hot” and “cold” melts, the cooling rate can reach several hundred degrees per second since, during the mixing, the heat transmission is caused only by the mass transfer. Two aluminum melts - one with titanium and another with boron - can also be mixed or added to the molten aluminum to provide the formation of fine high-melting particles [9].

The continuous intensive agitation of the Al-Ti melt allows it to be cooled to 700 °C while holding the fluidity sufficient for casting. Al-Ti-B master alloys can be produced at high temperatures, then cooled and poured at 680–720 °C, in fact from liquid-solid state. The master alloys prepared by this technology have fine structure, high density, and chemical homogeneity.

Another way to improve the quality of master alloys is to add components to molten aluminum in the dispersed form that causes their high dissolution rate and produces a great number of inter-metallic crystals through the direct reaction of the molten aluminum with a solid particle. The peculiarity of this process is the quite low temperature of the aluminum melt during the addition, 750–900 °C for Al-Ti master alloy depending on the quantity of Ti. The higher temperatures result in the intensive growth of particles [1].

The improvement in conventional methods of master alloy production and development of new ones should evidently take into consideration the quality parameters of master alloys. Their selection is affected by the current state of theories about melting, melt structure, and solidification. The quality of master alloys should also be assessed based on the alloy nature and the technology of the master alloy application that determines the flexibility of the requirements for their quality. However, as a basis for the quality assessment of master alloys, we recommend the use of the combination of all the stages described in this paper. They provide for a more comprehensive assessment of the grain refiner quality.
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