Morphology evolution of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase in Al-4Ni-2Mn alloy during heat treatment at 350 °C

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Abstract: The morphology evolution of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase in Al-4Ni-2Mn alloy at 350 °C was examined. Two kinds of morphology evolution trends of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase were observed by using scanning electron microscopy and transmission electron microscopy. The ribbon-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase taking up a small portion of the eutectic structures gradually changes from ribbon-like morphology to rod-like during the heat treatment. The rod-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectics, primary eutectic structure in the alloy, become unstable at the transverse sub-boundaries of the eutectic rod when the samples are heat treated at 350 °C, and then split up into short rods with the extension of heat treatment time. Also, the Vickers microhardness test was used to characterize the change of local mechanical properties. The hardness test results indicate that local morphology evolution of eutectic phase has no obvious effect on the local mechanical properties of the alloy. The microhardness of the eutectic area increases slightly when the heat treatment time is extended to 192 h or 360 h.

Key words: Al-Ni-Mn alloys; morphology evolution; eutectic microstructure; transmission electron microscopy

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Al-Ni-Mn based alloys (containing 0.5wt.%–6wt.% Ni and 1wt.%–3wt.% Mn) can be cast by high pressure die-casting, squeeze casting, permanent mold casting, sand casting and semisolid die casting methods^[1]. As ternary eutectic alloys, Al-Ni-Mn based alloys have been widely used in automotive and aerospace industries requiring high corrosion resistance and mechanical properties at high temperatures^[1]. As is well known, the mechanical properties of the eutectic alloys are closely related to the morphology of the eutectic phases embedded in the matrix. In the Al-Ni-Mn alloys, fine Al- Al_3Ni eutectic forms during the solidification^[2, 3]. The elevated temperature stability of Al- Al_3Ni eutectic had been studied by many researchers^[4–8]. The results showed that the structure of the Al- Al_3Ni eutectic is intrinsically stable at elevated temperature. However, the morphology of rod-like Al_3Ni eutectic became unstable during heat treatment at high temperature.

It was found that the eutectic solidification microstructure is Al- $\text{Al}_9(\text{Mn}, \text{Ni})_2$ in the as-cast Al-

4Ni-2Mn alloy, rather than the Al- Al_3Ni eutectic as reported^[9]. The $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic grows on the primary Al with a rod-like morphology during the solidification. In this case, the mechanical properties at elevated temperature depend on the morphological stability of the dispersed eutectics. However, it should be noted that $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic is an unstable phase. Whether the $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic can sustain high temperature is still uncertain.

Considering that there has been a tendency of substituting aluminum alloys for steels and irons, especially in automotive industry, the work pieces are probably subject to heating up to 300–350 °C^[10]. Whether the Al-4Ni-2Mn alloy can withstand the limited operating temperature is a subject worth to study. So, the heat treatment temperature of 350 °C was selected to investigate the stability of the $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase, and the influence of morphology evolution on the local mechanical properties were also discussed.

1 Experimental procedure

High purity aluminum (99.99wt.% purity), Al-10wt.%Ni master alloy and Al-10wt.%Mn master alloy were used to prepare the Al-4Ni-2Mn (wt.% hereinafter) alloy. The raw materials were placed into a silicon carbide crucible (pure aluminum at the bottom, Al-Ni master alloy in the

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middle and Al-Mn master alloy at the top) and melted at 780 °C in an electric resistance furnace. After the alloys were fully melted, the melt was stirred slightly for 30 s to make sure the alloying elements were dispersed uniformly into the melt. Then the aluminum alloy liquid was refined by nonpoisonous refining agent (HGJ-1A) at 780 °C and held for 10 min. When the temperature of the melt decreased to 750 °C, slag was removed from the surface of the molten metal and the melt was poured into a steel mold preheated to about 250 °C. The dimensions of the casting are shown in Fig. 1.

Fig. 1: Dimensions of casting (mm)

The composition of the experimental alloy was measured to be Al-3.67Ni-2.31Mn by using inductively coupled plasma optical emission spectrometry (ICP-OES). To perform the heat treatment testing, five specimens with the dimensions of $\Phi 12$ mm $\times$ 10 mm were cut from the casting. These as-cast samples were heat treated at 350 °C for different times (3, 74, 122, 192 and 360 h, respectively) in a muffle furnace with air circulation, and then quenched into water. The morphology evolution of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic was investigated by means of ZEISS SUPRATM 55 scanning electron microscopy (SEM) and TecnaiTM G2 F30 (FEI company) transmission electron microscopy (TEM) operated at 300 kV. The element distribution and diffusion behavior in the eutectic phase were carefully examined by a combination of the high angle annular dark field (HAADF) imaging in scanning transmission electron microscopy (STEM) and scanning transmission electron microscopy-energy dispersive X-ray analysis (STEM-EDX). Samples for SEM investigation were prepared using standard metallographic techniques. Thin foils for TEM investigation were prepared by the ion-milling technique. The eutectic phase was identified using selected area diffraction pattern (SAED).

Since the mechanical properties of the eutectic alloys are closely related to the morphology of eutectic phase, the mechanical properties of the eutectic area were monitored by hardness testing, which is one of the easiest and most straightforward techniques. The microhardness of the samples was measured on a Vickers microhardness test device (HXP-1000TM), and the measurements were performed at ambient temperature on metallographically polished surfaces under a load of 25 gf with a dwell time of 15 s. A minimum of 20 hardness measurements were recorded for each sample.

2 Results and discussion

2.1 Morphology evolution of ribbon-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ phase

Figure 2 shows the bright-field TEM images of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase in the Al-4Ni-2Mn alloy sample, which was heat

treated at 350 °C for 122 h. As can be seen from Fig. 2(a), some “particles” having a quasi-quadrangle shape were observed inside the eutectic phase after heat treatment. However, the SAED pattern obtained from the position marked by the dotted circle, as shown in Fig. 2(e), indicates that only the diffraction spots of Al matrix and $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase can be observed in the electron diffraction pattern, there are no diffraction spots of the new phase in the pattern. This result confirms that the “particle” formed during the heat treatment is actually not a new phase produced by the phase transformation, but caused by a change in the image contrast, which is believed to result from the local variations in diffraction conditions.

In addition, an uncompleted morphology evolution process was observed in Fig. 2(b). As can be seen, the interface movement has high anisotropic characteristics. The two interfaces at the neck (denoted by the yellow solid arrow) tends to meet each other with the extension of the heat treatment time. In other words, this $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase will be separated into two parts after long-time heat treatment. However, it should be noted that the morphology evolution described here cannot be seen on the surface of the eutectic phase in some eutectic areas, such as the eutectic phase shown in Figs. 2(c) and (d), where no phenomenon of morphology evolution can be observed on the transverse section and longitudinal section of the rod-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase. Thus, it can be concluded that this kind of morphology evolution only occurs in some special eutectic area, where the transverse section of the eutectic phase always presents strip-like morphology [Figs. 2(a) and (b)], instead of elliptical section [Fig. 2(c)]. Besides, corresponding morphology evolution has not been found on the longitudinal section of the eutectic phase. This experimental result also indicates that some $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectics probably have a ribbon-like morphology in the Al-4Ni-2Mn alloy.

As can be seen from the SEM images shown in Fig. 3, some $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phases in the eutectic cell display ribbon-like morphology. The ribbon-like eutectics observed in the deep-etched sample are believed to be formed by consolidation of the adjacent eutectic rods or coarsening of a single eutectic rod along a certain direction during the solidification. This should be the reason why the ribbon-like eutectics always show an inverted U-shape characteristic, as denoted by the yellow solid arrows in Fig. 3. Therefore, it can be confirmed that the morphology evolution previously observed is actually a local morphology transformation from ribbon-like to rod-like.

To elaborate the process of morphology evolution of partial ribbon-like eutectic phase, another eutectic area has been investigated by using STEM-EDX. As shown in Fig. 4(a), the characteristic of image contrast is the same as the result in Figs. 2(a) and (b). The HAADF image obtained from the rectangular area marked in Fig. 4(a) is shown in Fig. 4(b). As we know, the HAADF detector is very sensitive to the atomic number (Z). Therefore, from the variation of brightness on the eutectic transverse section, it can be easily found that the morphology evolution observed in the bright-field image is actually caused by the difference of element composition.

Fig. 2: Bright-field TEM images of $\text{Al}_9(\text{Mn, Ni})_2$ eutectic phase in Al-4Ni-2Mn alloy after heat treatment at 350 °C for 122 h: (a, b) transverse section of ribbon-like eutectic; (c) transverse section of rod-like eutectic; (d) longitudinal section of rod-like eutectic; (e) SAED pattern obtained from region marked by dotted circle in (a)

Fig. 3: Deep-etched sample showing rod-like $\text{Al}_9(\text{Mn, Ni})_2$ eutectic phase at different positions. Ribbon-like parts of eutectic phase are indicated by yellow solid arrows

This conclusion has also been verified by the element distribution maps shown in Figs. 4(c)–(e), which are obtained by STEM-EDX method. A major advantage of elemental mapping is that the spatial distribution of phase components can be obtained. As can be seen clearly from the element mapping, the process of morphology evolution is actually a diffusion process.

The diffusion originally occurs at the interface between Al matrix and ribbon-like $\text{Al}_9(\text{Mn, Ni})_2$ eutectic phase, then proceeds slowly toward the inner region of the eutectic phase. During the diffusion, Al atoms diffuse into the host lattice of $\text{Al}_9(\text{Mn, Ni})_2$ eutectic phase, and some of the Ni and Mn atoms are replaced by Al atoms. Such variation of element also can be seen from the

Fig. 4: (a) Bright-field image of eutectic, (b) HAADF image obtained from rectangle area marked in (a), (c)–(e) STEM-EDX mappings of rectangle area marked in (b): Al in red, Ni in yellow-green and Mn in brown

line scanning result, as shown in Fig. 5. The elements along the red line in Fig. 4(b) show a distinct change. When the content of Al abruptly increases, the content of Ni or Mn decreases correspondingly, indicating that Ni or Mn atoms have been substituted by Al atoms during the morphology evolution.

In summary, the morphology evolution from ribbon-like to rod-like is essentially the process of diffusion of Al atoms from the matrix to the inner side of eutectic phase, and a distinct anisotropy in the diffusion rates can be seen from Fig. 4, where the undisturbed region tends to be bounded by two nonparallel planes. What is more, as can be seen from the SAED pattern

Fig. 5: Line scanning result obtained from eutectic phase along a red line indicated in Fig. 4(b)

shown in Fig. 2(e), the orientation relationship between the eutectic and matrix is that the [001] axis of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase parallels the [110] axis of Al matrix.

2.2 Morphology evolution of rod-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ phase

The eutectic phase with a ribbon-like morphology is only a small part of the eutectic microstructure. As far as the elevated temperature performance of the alloy is concerned, we are more interested in the stability of the rod-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase, which has been considered as the main reinforcing phase in the Al-4Ni-2Mn alloy.

As shown in Fig. 6(a), a bamboo-like morphology has been observed in the sample heat treated at 350 °C for 74 h. It means that $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase becomes unstable at the internal sub-boundary perpendicular to the axis of eutectic rod. Furthermore, the enlarged details shown in Figs. 6(b) and (c) clearly show that microscopic grooves have developed at the sub-boundary, and the morphology characteristics of the two internal sub-boundaries indicate that they should be in different stages of the morphology evolution. The upper boundary [Fig. 6(b)] is in the early stage of the morphology change process, and then the shape change will proceed if the heat treatment time is prolonged. This morphology evolution process can be described by the thermal groove model^[11–13]. If there are internal grain boundaries in a rod-like microstructure, the thermal grooves will develop

Fig. 6: TEM results of sample heat treated at 350 °C for 74 h: (a) eutectic rod with a bamboo-like morphology; (b) and (c) are enlarged details of corresponding part indicated by dotted square in (a)

along the line of intersection during the heat treatment. With the extending of heat treatment time, the grooves gradually deepen as the triple points move toward each other along the sub-boundary. Eventually, the eutectic rod breaks up at the sub-boundary. This conclusion has been confirmed by the result shown in Fig. 7(b). As can be seen, after heat treatment at 350 °C for 360 h, the thermal grooving of transverse boundaries has caused the eutectic rods to split up into short rods, and the two end faces always present a flat plane, which is definitely different from the termination produced by necking down and pinching off^[14].

In addition, it should be noted that sometimes the rate of the groove growth varies greatly in different orientation during the process of groove deepening. For instance, the boundary shown in Fig. 6(c) presents a slit-like geometry. This kind of morphology evolution is similar to grain boundary grooving by surface diffusion with a constant grain boundary flux I (in the case of $I < 0$)^[15]. The groove becomes ever steeper until a highly localized slit-like geometry develops. Actually, the groove's gradual deepening means that the constituent elements of the $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic are drained out of the sub-boundary, and Al atoms of the matrix enter into the slits and divide the eutectic rod into a series of short rods.

Besides, as can be seen from Figs. 7(a) and (b), different stages of morphology evolution can be found in different parts of the same sample due to the difference of eutectic distribution and the overlap of the diffusion fields. In fact, there are also some eutectic rods whose morphologies do not change even though the sample has been heat treated at 350 °C for 360 h, as shown in Fig. 7(c). No thermal groove can be observed in the eutectic region. It can be concluded that the breakup of the rod-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase is mainly caused by the sub-boundary splitting when the sample is heat treated at 350 °C. If there is no internal sub-boundary in the rod-like eutectic phase, the morphology will be quite stable at this temperature.

2.3 Microhardness of eutectic region

The mechanical properties of the eutectic alloys are closely linked with the morphology evolution of the eutectic phase. Micro-Vickers Hardness test has been carried out to characterize the local mechanical properties change for each heat-treated sample. Since the morphology evolution of the eutectic phase is our concern, the Vickers microhardness survey is deliberately performed on the eutectic area. As shown in Fig. 8(a), the indentations are indicated by the yellow solid arrows. The

Fig. 7: Bright-field TEM images of sample heat treated at 350 °C for 360 h: (a) thermal groove denoted by yellow solid arrow; (b) short eutectic rods caused by boundary splitting; (c) eutectic region with no morphology evolution

Fig. 8: Results of microhardness test: micrograph showing micro-indentation traces (a) and hardness measured as a function of heat treatment times at 350 °C (b)

microhardness values, as shown in Fig. 8(b), indicate that the morphology evolution of $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic has no obvious effect on the mechanical properties of the eutectic area. Although some of the long rod-like eutectics break up into short rods in the sample heat-treated at 350 °C for 360 h, the microhardness of the eutectic area does not decrease, but slightly increases after long-time heat treatment. The reason is probably that although some of the eutectic rods break up during the heat treatment, the interface between matrix and eutectic is undestroyed. What is more, the sub-boundary of eutectic rods splits so that the $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase breaks up and dissolves into the Al matrix during the heat treatment, resulting in a solid solution hardening. Consequently, the microhardness of the eutectic area increases slightly when heat treatment time is extended to 192 h or 360 h.

3 Conclusions

In the Al-4Ni-2Mn eutectic alloy, the ribbon-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectics taking up a small portion of eutectic structures gradually change into rod-like morphology during the heat treatment at 350 °C. This morphology evolution is accompanied by two-dimensional anisotropic diffusion of Al atoms inside the $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectic phase. Correspondingly, some rod-like $\text{Al}_9(\text{Mn}, \text{Ni})_2$ eutectics, as the dominant eutectic morphology, become unstable in the eutectic region after extended heat treatment at 350 °C. The results show that the observed instability is sub-boundary splitting via the thermal grooving of internal boundaries, which eventually splits the eutectic rods up into short rods. What is more, the hardness test results indicate that local morphology evolution of eutectic phase has no obvious effect on the local mechanical properties of the alloy. The microhardness of the eutectic area increases slightly when the heat treatment time is extended to 192 h or 360 h.

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