

Available online at www.sciencedirect.com



Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 28(2018) 1913–1919

Phase transformation behavior of Al₉(Mn,Ni)₂ eutectic phase during heat treatment at 600 °C in Al–4Ni–2Mn alloy

Wen-tao YU, Qi-tang HAO, Qian WANG

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

Received 23 September 2017; accepted 8 March 2018

Abstract: The morphology evolution and phase transformation of $Al_9(Mn,Ni)_2$ eutectic phase in an Al-4Ni-2Mn alloy during heat treatment at 600 °C were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Results show that nearly all of the eutectic fibers change into prolate ellipsoid and spherical particles in the process of heat treatment, and Ostwald ripening phenomenon occurs in the eutectic region with the increase of the heat treatment time. Besides, a phase transformation from $Al_9(Mn,Ni)_2$ to *O*-phase is confirmed. The morphologies of the transformed particles indicate that the *O*-phase preferentially nucleates on the specific crystal plane of the $Al_9(Mn,Ni)_2$ eutectic phase and grows in a certain direction. During the phase transformation, the (010)[001] slip system in *O*-phase is activated, and the resultant slip traces appear on the surface of some *O*-phase particles.

Key words: Al-Ni-Mn alloys; phase transformation; quasicrystal approximant; slip phenomenon

1 Introduction

During the last two decades, Al-based alloy systems including transition metals (TMs) have attracted increasing attention due to a multitude of binary and ternary intermetallics they often contain. Such as Al-Ni-Mn alloy system, studies have shown that several kinds of intermetallics can be formed in this alloy system when the material produced by different casting processes. Besides the binary intermetallics Al₆Mn, Al₄Mn, and Al₃Ni, at least six ternary phases have been reported up to now [1-4], including three ternary thermodynamically stable intermetallics, the φ -phase (Al₅Co₂-type, hP26, P6₃/mmc; a=0.76632(16) nm, c=0.78296(15) nm), the κ -phase (κ -Al_{14.4}Cr_{3.4}Ni_{1.1}-type, *hP*227, *P*6₃/*m*; *a*=1.7625(10) nm, *c*=1.2516(10) nm), and the O-phase (O-Al₇₇Cr₁₄Pd₉-type, Pmmn, oP650; a=2.3316(16) nm, b=1.2424(15) nm, c=3.2648(14) nm), as well as three ternary metastable phases, the decagonal D_3 -phase with periodicity about 1.25 nm, the Al₉(Mn,Ni)₂-phase (Al₉Co₂-type, $P112_1/a$, mP22; a=0.8585(16) nm, b=0.6269(9) nm, c=0.6205(11) nm, $\beta = 95.34(10)^{\circ}$ and the O_1 -phase (base-centered orthorhombic, $a \approx 2.38$ nm, $b \approx 1.24$ nm, $c \approx 3.22$ nm).

Although several intermetallics in Al-Ni-Mn alloy have been reported in recent years, little research has been conducted on the phase transformation of the known metastable phase. Taking Al₉(Mn,Ni)₂ phase as an example, this ternary compound has been firstly reported by BALANETSKYY et al [2]. However, the phase transformation of the Al₉(Mn,Ni)₂ phase is not clear. Recently, we observed that the Al₉(Mn,Ni)₂ eutectic phase can transform into a ternary hexagonal κ -phase after heat treatment at 350-550 °C for a long time [5]. However, it should be noted that a new phase transformation appears in the Al-4Ni-2Mn alloy when the heat treatment temperature rises to 600 °C. It is important to reveal this phase transformation process, because the research can not only enrich the understanding of Al₉(Mn,Ni)₂ phase but also lay a foundation for the further study of Al-4Ni-2Mn alloy. In this work, we will mainly discuss the phase transformation of Al₉(Mn,Ni)₂ based on SEM and TEM observation.

2 Experimental

Al-4Ni-2Mn (mass fraction, %, used throughout the paper unless noted) alloys were melted in a silicon

Corresponding author: Qi-tang HAO; Tel: +86-29-88494276; E-mail: haoqitang@nwpu.edu.cn DOI: 10.1016/S1003-6326(18)64836-8

carbide crucible in an electric resistance furnace by using high purity aluminum (99.99%), Al-10Ni and Al-10Mn master alloys. After refining with sodium-free refining agent, the melt was poured at 750 °C into a steel mold preheated up to about 250 °C. The composition was measured to be Al-3.67Ni-2.31Mn by using inductively coupled plasma optical emission spectrometry (ICP-OES). The heat treatment was performed in an electric resistance furnace with a temperature accuracy of ± 2 °C. The as-cast samples were heat treated at 600 °C for 75, 312, and 432 h, respectively, and then quenched into water. The microstructures of eutectic phase were observed by ZEISS SUPRATM 55 scanning electron microscope. Phase transformation was identified using the selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX) in TecnaiTM G2 F30 transmission electron microscopy operated at 300 kV. Samples for SEM observation were prepared using standard metallographic techniques. Thin foils for TEM investigation were ground to a thickness of about 100 µm and then punched into discs with a diameter of 3 mm. Finally, the discs were thinned using dimpling and ion milling.

3 Results and discussion

3.1 Morphological change during heat treatment

Figure 1 shows the eutectic microstructures in the specimen heat-treated at 600 °C for 75, 312, and 432 h, respectively. In contrast to the morphology of the

eutectic solidification microstructure in the as-cast Al–4Ni–2Mn alloy [6], an obvious change in the morphology of the Al₉(Mn,Ni)₂ eutectic phase can be observed during the heat treatment at 600 °C. As can be seen, nearly all of the eutectic fibers have changed into prolate ellipsoid and spherical particles. With the increase of the heat treatment time, Ostwald ripening of the eutectic particles appears in the eutectic region. This coarsening phenomenon is particularly evident in the sample after heat treatment at 600 °C for 432 h (Fig. 1(e)).

However, the detailed morphology evolution mechanism of the Al₉(Mn,Ni)₂ eutectic phase is beyond of the scope of the present investigation. In this study, we focus our attention on the structural phase transition during heat treatment at 600 °C. Observations under higher magnification, i.e., the backscattered electron images shown in Figs. 1(b), (d) and (f), demonstrate that a phase transformation occurred during heat treatment at 600 °C. As can be seen, the untransformed parts of the particles have a white contrast, while the transformation products have a darker contrast. Furthermore, the morphology characteristics of the transformed particles indicate that partly the new-phase particles are likely to nucleate at the interface between the Al matrix and Al₉(Mn,Ni)₂ eutectic phase, and then grow into the Al₉(Mn,Ni)₂ particles. During the growth of new-phase particles, a distinct phase boundary can be found on the partly transformed particles.



Fig. 1 Backscattered electron images of samples heat treated at 600 °C for different time: (a, b) 75 h; (c, d) 312 h; (e, f) 432 h

3.2 Determination of phase transformation behavior

The phase transformation of Al₉(Mn,Ni)₂ eutectic phase has also been characterized by TEM. Figure 2(a) presents the morphology of the particle after phase transformation. The EDX result shows that the phase transformation product is a ternary intermetallic with a composition of Al_{79,70}Mn_{13,51}Ni_{6,78} (mole fraction, %), which is very close to the stoichiometric composition of the Al₆₀Mn₁₁Ni₄ and C_{3.1}-Al₆₀Mn₁₁Ni₄ phases. However, it should be noted that even if the Al₆₀Mn₁₁Ni₄ and $C_{3,I}$ -Al₆₀Mn₁₁Ni₄ phases have the same nominal composition, the structure parameters of these two phases are not exactly the same. The Al₆₀Mn₁₁Ni₄ phase is an orthorhombic intermetallic compound with the structure parameters: *Bbmm*, $Al_{31}Mn_6Ni_2$ -type, *a*= 0.755 nm, b=1.25 nm and c=2.38 nm (the unit-cell parameters have been rearranged according to present systematization) [7]. The $C_{3,1}$ -Al₆₀Mn₁₁Ni₄ phase is also an orthorhombic intermetallic compound, but it has different structure parameters: Pmmm, oP650. $O-Al_{77}Cr_{14}Pd_9$ -type; a=3.27 nm, b=1.24 nm and c= 2.40 nm [1,8]. In particular, orthorhombic $Al_{60}Mn_{11}Ni_4$ and $C_{3,1}$ -Al₆₀Mn₁₁Ni₄ phases belong to the (1/0, 2/1) and (3/2, 2/1) approximants of a decagonal quasicrystal (DQC), respectively. They have almost the same parameter c and the parameter a is rough in τ^3 $(\tau = (\sqrt{5} + 1)/2)$ ratio [9]. Besides, it should be noted that the $C_{3,I}$ -Al₆₀Mn₁₁Ni₄ phase is also termed as *O*-phase in Refs. [1,2], so we use O-phase to denote the C_{31} -Al₆₀Mn₁₁Ni₄ phase in this work. In order to identify the phase transformation product, typical SAED patterns have been taken from the transformed particle. As shown in Figs. 2(b) and (c), all of the SAED patterns can be consistently indexed based upon the O-phase with an orthorhombic structure. In addition, it can be found that the diffraction patterns shown here present strong spots in a hexagonal formation, which is a significant characteristic of the O-phase, as reported in Ref. [9]. Furthermore, based on the orthorhombic structure, the lattice parameters a, b and c of the phase transformation product can be easily determined to be a=3.33 nm, b=1.25 nm and c=2.42 nm from the SAED patterns, the results obtained in this study are in good agreement with that of O-phase reported by TENDELOO et al [8].



Fig. 2 TEM image of transformed product in specimen heat treated at 600 °C for 312 h, SAED patterns and EDX result: (a) Bright-field TEM image; (b, c) SAED patterns obtained from selected area marked with dotted circle in (a); (d) EDX result of transformed particle

In order to further confirm that the phase transformation occurred in the specimen during the heat treatment at 600 °C, many partly transformed particles were examined by TEM. One of the particles is shown in Fig. 3(a), bright-field TEM image shown in Fig. 3(b) is the high-magnification morphology of this particle. As can be seen, during the phase transformation, an unambiguous phase boundary formed between the parent

phase and the phase transformation product. The two particles show different contrast even in the bright-field image. Figures 3(c) and (d) are the EDX results obtained from the two particles in Fig. 3(a) respectively, and corresponding SAED patterns are shown in Figs. 3(e) and (f). By SAED patterns together with the composition of the particles measured by EDX, the two particles have been identified to be the untransformed $Al_9(Mn,Ni)_2$



Fig. 3 TEM images of partly transformed eutectic particle in specimen heat treated at 600 °C for 312 h, SAED patterns and EDX results: (a) Bright-field TEM image; (b) High-magnification TEM image; (c, d) EDX results of two particles denoted by solid arrows in (a); (e, f) SAED patterns obtained from circled areas in (a)

1916

eutectic particle and transformation product (*O*-phase), respectively, as denoted in Fig. 3(a). These results confirm that the phase transformation from $Al_9(Mn,Ni)_2$ to *O*-phase occurred during the heat treatment at 600 °C.

From the above analysis of phase transformation, it can be seen that the composition of transformation product is different from that of the parent phase. This means that the phase transformation observed in the present study is accompanied by redistribution of Ni and Mn atoms between the Al₉(Mn,Ni)₂ and O-phase. However, it should be noted that the Al₉(Mn,Ni)₂ phase is enriched with Ni atoms and the O-phase is enriched with Mn atoms, therefore, a large number of Mn atoms are required for the phase transformation to proceed. It is believed that the Mn solute atoms and Mn-containing particles in the Al matrix can supply Mn atoms for the phase transformation. But beyond that, the dissolution of the Al₉(Mn,Ni)₂ eutectic phase is considered to be an important contributing factor. Because the morphology evolution is always accompanied by the dissolution of eutectic phase [10]. In this case, a large amount of Ni and Mn atoms dissolve into the surrounding $\alpha(AI)$, resulting in the enrichment of Ni and Mn atoms around the undissolved Al₉(Mn,Ni)₂ eutectic particles, which is beneficial for the nucleation of O-phase.

Furthermore, as can be seen from Fig. 1, it can be concluded that the nucleation of the O-phase particle most probably occurs at the boundary between the Al matrix and the Al₉(Mn,Ni)₂ eutectic particle, because nucleation at boundary zone is encouraged by several factors. First, the phase boundary has a high energy and the nucleation energy barrier can be easily overcome at the boundary. Second, the atomic diffusion is fast at the phase boundary, which can easily cause a relatively strong concentration fluctuation, and local solute concentration at boundary zone will satisfy the nucleation condition of the O-phase. In addition, the morphologies of the transformed particles shown in Fig. 1(f) also manifest that the O-phase preferentially nucleates on the specific crystal plane of the Al₉(Mn,Ni)₂ eutectic phase (i.e. the habit plane) and then grows in a certain direction in order to minimize the interface energy. As is reported in Ref. [6], Al₉(Mn,Ni)₂ has a low-symmetry monoclinic structure, which has few equivalent crystal planes. This means that the habit plane is probably a certain crystal plane of the Al₉(Mn,Ni)₂ eutectic phase. In this case, the phase transformation of Al₉(Mn,Ni)₂ during heat-treatment is likely to occur only at the specific interface between the Al₉(Mn,Ni)₂ and Al matrix. Moreover, Al₉(Mn,Ni)₂ eutectic phase in a eutectic cell has the same orientation, therefore, the transformed particles in the same eutectic cell will show similar phase transition behavior. This conclusion has been confirmed by the experimental results. As shown in Fig. 1(f), there are three transformed particles in the eutectic region. It is apparent that the phase transformation appears on the same side of the $Al_9(Mn,Ni)_2$ eutectic particles, and the interface between $Al_9(Mn,Ni)_2$ and *O*-phase nearly has the same orientation.

3.3 Slip phenomenon in new-phase particle

The slip traces were observed on the surface of the transformed particle, as shown in Fig. 2(a). In order to further investigate the slip phenomenon, high- resolution transmission electron microscopy (HRTEM) was used to characterize the O-phase particle. Figure 4(a) shows the high resolution TEM image of the selected rectangular region in Fig. 2(a). Figures 4(b) and (c) are the diffraction patterns obtained via Fast Fourier Transform (FFT) of the selected square (indicated as numbers 1 and 2) in Fig. 4(a), respectively. By comparing the two FFT patterns, it can be found that the FFT pattern obtained from the second area shows a characteristic of stacking fault displaying streak lines perpendicular to the (010) plane, which is believed to be the slip plane of O-phase. According to the classical theory of plastic deformation [11-14], different types of lattice have different slip systems (slip planes and slip directions). The dominant slip plane of orthorhombic system is (010) plane, slip direction is parallel to the [100] or [001] zone axis [15,16]. In the present study, it should be noted that



Fig. 4 High resolution TEM images taken along $[10\overline{1}]$ zone axis and FFT patterns: (a) Low-magnification HRTEM image of selected rectangular region in Fig. 2(a); (b, c) Diffraction patterns obtained via FFT of selected square (indicated as numbers 1 and 2 in (a), respectively; (d) High-magnification HRTEM image (The inset is the FFT of the HRTEM image)

the bright-field TEM image shown in Fig. 2(a) is taken along the [100] zone axis, and the corresponding SAED pattern (after calibration of magnetic declination) is shown in Fig. 2(c). According to the characteristics of slip steps and the SAED pattern, it can be concluded that the slip direction is parallel to the [001] zone axis of O-phase. Therefore, the results show that the (010)[001] slip system in O-phase was activated during the phase transformation.

However, it should be noted that the existing experimental results are unable to fully reveal the primary cause of the slip phenomenon. It is believed that the activation of this slip system may be related to the elastic strain energy induced by the phase transformation. Although the microscopic structure of the interface between the Al₉(Mn,Ni)₂ eutectic phase and the O-phase is still not clear, the morphologies of the transformed particles show that the O-phase preferentially nucleates on specific crystal plane of the parent phase. Even though the habit-plane index cannot be determined in the present study, the existence of habit plane means that there exists a definite orientation relationship between the new phase and the parent phase, implying that the two-phase interface is coherent or semi-coherent. In this case, the lattice distortion near the phase interface is inevitable owing to the difference of lattice structure between the new phase and the parent phase, resulting in high elastic strain energy at the interface. Besides, the phase transformation is always accompanied by a volume change as result of the difference of specific volume between the parent phase and the new phase. Nevertheless, it is impossible for the new phase to be free to contract and expand under the constraint of surrounding parent phase. Thus, the elastic strain energy is stored during the phase transformation. The strain energy induced by phase transformation increases with the growth of the O-phase. Eventually, microscopic deformation occurs when plastic the phase transformation stress is higher than the elastic limit of the O-phase. This is why the slip traces are often observed on the surface of the O-phase particle.

Besides, as shown in Fig. 4(d), in one b=1.25 nm period, a stacking of six layers can be observed clearly along the [010] direction. This characteristic agrees well with the layer structural model of the *O*-phase constructed in Refs. [9,17].

4 Conclusions

1) After heat treatment of the Al–4Ni–2Mn alloy at 600 °C for different time, nearly all of the Al₉(Mn,Ni)₂ eutectic fibers have changed into small particles with prolate ellipsoidal and spherical morphology. With the increase of the heat treatment time, Ostwald ripening

phenomenon of the eutectic particles can be observed.

2) A phase transformation from $Al_9(Mn,Ni)_2$ to *O*-phase has been confirmed, for the first time, in Al-4Ni-2Mn alloy during the heat treatment at 600 °C.

3) The slip traces observed on the surface of O-phase particle indicate that the (010)[001] slip system has been activated during the phase transformation.

Acknowledgments

We are grateful for the assistance from State Key Laboratory of Solidification Processing and Material Analysis and Testing Center of Shaanxi Province, China.

References

- BALANETSKYY S, MEISTERERNST G, FEUERBACHER M. The Al-rich region of the Al-Mn-Ni alloy system, Part I: Ternary phases at 750-950 °C [J]. Journal of Alloys & Compounds, 2011, 509: 3787-3794.
- [2] BALANETSKYY S, MEISTERERNST G, GRUSHKO B, FEUERBACHER M. The Al-rich region of the Al-Mn-Ni alloy system, Part II. Phase equilibria at 620-1000 °C [J]. Journal of Alloys & Compounds, 2011, 509: 3795-3805.
- [3] ZOLOTOREVSKY V S, BELOV N A, GLAZOFF M V. Casting aluminum alloys [M]. 1st ed. Oxford: Elsevier, 2007.
- [4] FAN Y, HUANG K, MAKHLOUF M M. Precipitation strengthening in Al–Ni–Mn alloys [J]. Metallurgical & Materials Transactions A, 2015, 46: 5830–5841.
- [5] YU Wen-tao, HAO Qi-tang. The phase transformation of Al₉(Mn,Ni)₂ eutectic phase in an Al-4Ni-2Mn alloy during heat treatment [J]. Materials Characterization, 2017, 129: 53–59.
- [6] YU Wen-tao, HAO Qi-tang, Fan Li, LI Jie-hua. Eutectic solidification microstructure of an Al-4Ni-2Mn alloy [J]. Journal of Alloys & Compounds, 2016, 688: 798–803.
- [7] ROBINSON K. The determination of the crystal structure of Ni₄Mn₁₁Al₆₀ [J]. Acta Crystallographica, 1954, 7: 494–497.
- [8] TENDELOO G V, LANDUYT J V, AMELINCKX S, RANGANATHAN S. Quasi-crystals and their crystalline homologues in the Al₆₀Mn₁₁Ni₄ ternary alloy [J]. Journal of Microscopy, 2011, 149: 1–19.
- [9] SUI H X, SUN K, KUOK H. A structural model of the orthorhombic C_{3,1}-Al₆₀Mn₁₁Ni₄ approximant [J]. Philosophical Magazine A, 1997, 75: 379–393.
- [10] SHI Yun-jia, PAN Qing-lin, LI Meng-jia, LIU Zhi-ming, HUANG Zhi-qi. Microstructural evolution during homogenization of DC cast 7085 aluminum alloy [J]. Transactions of Nonferrous Metals Society of China, 2015, 11: 3560–3568.
- [11] BUNGE H J, ESLING C. Texture development by plastic deformation [J]. Scripta Metallurgica, 1984, 18: 191–195.
- KUHLMANN-WILSDORF D. Theory of plastic deformation: Properties of low energy dislocation structures [J]. Materials Science & Engineering A, 1989, 113: 1–41.
- [13] RODRIGUEZ P. Grain size dependence of the activation parameters for plastic deformation: Influence of crystal structure, slip system, and rate-controlling dislocation mechanism [J]. Metallurgical & Materials Transactions A, 2004, 35: 2697–2705.
- [14] WEINBERGER C R, BOYCE B L, BATTAILE C C. Slip planes in bcc transition metals [J]. International Materials Reviews, 2013, 58: 296–314.

- [15] YANG S J, NAM S W, HAGIWARA M. Abnormal acceleration of creep deformation rate above 700 °C in the orthorhombic based Ti-22Al-27Nb alloy [J]. Journal of Alloys & Compounds, 2004, 368: 197–210.
- [16] LI Guo-zhen, TANG Jia-zhen, XU Guo-shu. The structure and

morphology of high temperature superconductive YBCO thin film [J]. Journal of Yunnan University, 1993, 15: 12–17. (in Chinese)

[17] DEMANGE V, WU J S, BRIEN V, MACHIZAUDF, DUBOIS JM. New approximant phases in Al-Cr-Fe [J]. Materials Science & Engineering A, 2000, 294-296: 79-81.

600 °C 热处理时 Al-4Ni-2Mn 合金中 Al₉(Mn,Ni)₂ 共晶相的相变行为

余文涛,郝启堂,王 倩

西北工业大学 材料学院 凝固技术国家重点实验室, 西安 710072

摘 要:采用扫描电子显微镜和透射电子显微镜研究 600 ℃ 热处理时 Al-4Ni-2Mn 合金中 Al₉(Mn,Ni)₂ 共晶相的 形貌演变及相结构转变。结果表明:在热处理过程中,纤维状的 Al₉(Mn,Ni)₂ 共晶相几乎全部转变成了椭球状和 球状颗粒。而且,随着热处理时间的延长,共晶区的 Al₉(Mn,Ni)₂颗粒发生了 Oswald 熟化现象。此外,通过研究 证实热处理过程中的确存在由 Al₉(Mn,Ni)₂ 到 *O* 相的相变过程。发生了相变的颗粒形貌表明:*O* 相优先在 Al₉(Mn,Ni)₂相的特定晶面上形核,然后沿一定方向朝母相生长。在相变过程中,由于 *O* 相的(010)[001]滑移系被 激活,因此,在一些*O* 相颗粒表面出现了滑移迹线。

关键词: Al-Ni-Mn 合金; 相变; 准晶近似相; 滑移现象

(Edited by Xiang-qun LI)