Cellular Precipitation in Ni-Sn Alloys*

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The characteristics of the cellular precipitation in Ni-8 mass%Sn and Ni-15 mass%Sn alloys on aging at 823 K after quenching from 1273 K were investigated by quantitative metallographic methods and X-ray analysis.

The cellular precipitation in these alloys proceeded in three stages. Before the first cells with fine lamellae engulfed entirely all the matrix, the second cells with coarse lamellae began to grow into the first cells. After the second cells engulfed almost all the first cells, the third cells with coarser lamellae began to grow into the second cell. The lattice parameter of α phase in the cells decreased gradually until the finish of the second cellular precipitation. The precipitates in the first cells were the equilibrium phase (Ni_3Sn) with DO_{19} type structure. Precipitate free zones were observed near by the grain boundaries before the growth of the first cells.

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I. Introduction

Cellular precipitation has conventionally been defined as the precipitation which cells with the lamellar mixture of α and precipitate phases of equilibrium compositions nucleate in grain boundaries and grow into the matrix⁽¹⁾. However, many reports have recently been published on different types of cellular precipitation, e.g. such the type that α and precipitate phases in cells do not have equilibrium compositions at the early stage of cell growth⁽²⁾. Thus, there still remain many problems to be clarified for the cellular precipitation.

A few papers have been published on the cellular precipitation in Ni-Sn alloys⁽³⁾⁻⁽⁶⁾. Frebel *et al.*⁽⁴⁾⁽⁵⁾ reported that the cellular precipitation in a Ni-Sn alloy proceeded in three stages. They studied on the growth rate and the interlamellar spacing of the first cell, but did not study on those of the second and third cells. Therefore, entire processes of the precipitation in this alloy are still obscure.

In the present work, growth behavior and the microstructural changes of the first, second and third cells in Ni-8 mass%Sn and Ni-15 mass%

Sn alloys were investigated in detail. In a later paper, we will describe about the effect of additions to B and P on the cellular precipitation in these alloys.

II. Experimental Procedure

Table 1 shows chemical compositions of alloys used in this work. Each alloy was prepared by melting Ni(99.95%) and Sn(99.9%) in a high purity alumina crucible in an Ar atmosphere. The ingot was homogenized at 1273 K and then cut out into plates. After cold rolling, each plate was shaped into a specimen suitable for individual measurements. The specimens were quenched from 1273 K, aged isothermally at 823 K, and then examined by hardness measurement, optical and scanning electron microscopic observations, and X-ray diffraction. The interlamellar spacing, the area fraction and the mean width of cells were measured on optical and electron micrographs. The area fraction of cells was measured by the point counting method. Area fractions of the first and

Table 1 Chemical compositions of alloys (mass %).

Nominal	Ni	Sn	Fe	Co, Mn, Pb
Ni-15Sn	bal.	14.97	0.004	<i>t</i> *
Ni-8Sn	bal.	8.07	0.005	<i>t</i>

* $t < 0.003\%$.

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second cells were measured on optical micrographs of 150 times and scanning electron micrographs of 2000 times, respectively. The hardness measurement was done with a micro-Vickers hardness tester with the load of 2.94 N.

III. Results

1. Microscopic observation

Figure 1 shows the change in microstructure of cells in the 15%Ni alloy during aging at 823 K. Figure (a) shows that the first cells (C1) are growing into the matrix (M) at the early stage of aging. It can be seen that the second cells (C2) initiate to grow into the first cells already in this time. Figure (b) shows the structure after the first cells engulfed all the matrix. The second cells with coarser lamellae grow considerably into the first cells. With further aging, the second cells engulf the first cells and the third cells (C3) with more coarser lamellae appear (Fig. 1(c)).

Figure 2 shows the microstructure of an another region of the same specimen as in Fig. 1(a), where the growth of the first cells is retarded compared with the region in Fig. 1(a). In this figure, coarse precipitates in the matrix and precipitate free zones (PFZ) in the vicinity of grain boundaries can be seen. It must be noted that the cells are growing passing through the PFZ. It has been confirmed by EPMA analysis that the concentrations of Sn are nearly the same in the matrix and PFZ. It seems, therefore, that this PFZ is caused by the lack of vacancies in the vicinity of grain boundaries.

Figure 3 shows the change in area fraction of the first (solid lines) and the second (dashed lines) cells during aging. It can be seen that the growth of the second cells is slower than that of the first cells, while the initiation times for the first and second cells are nearly the same.

The precipitation kinetics may well be analyzed by applying Johnson-Mehl's equation⁽⁷⁾,

$$X = 1 - \exp(-bt^n), \quad (1)$$

where X is the fraction of precipitation, t is the aging time, and b and n are constants. Modify-

Fig. 1 Scanning electron micrographs of the cells in the Ni-15%Sn alloy aged at 823 K for 5.4×10^3 s (a), 7.8×10^4 s (b) and 1.2×10^6 s (c). Mark M, C1, C2 and C3 show the matrix, the first, second and third cell, respectively.

ing the eq. (1), we get the next equation,

$$\log \cdot \log \{1 - (1 - X)\} = n \log t + \log (b/2.303) \quad (2)$$

By substituting the values in Fig. 3 into X and t , linear relations between $\log \cdot \log \{1 - (1 - X)\}$ and $\log t$ are obtained for the first and second cells, as shown in Fig. 4. The values of n deter-

mined from the relations are 1.0–1.2 and 0.6–0.7, respectively.

Figure 5 shows the change in cell width during

Fig. 2 Scanning electron micrograph showing the precipitate free zone (PFZ) and the first cell in the Ni-15%Sn alloy aged at 823 K for 5.4×10^3 s.

aging. The relations between the cell width and the aging time are linear in the early stage of aging, and the growth rate of the second cell is $1/20$ – $1/30$ of the first cell.

Figure 6 shows the change in interlamellar spacing in the first and second cells during aging. The interlamellar spacing increases in the latter stage of aging in both cases of the first and second cells. The interlamellar spacing in the second cells is 2–3 times larger than that in the first cells.

2. Hardness measurement

Figure 7 shows the change in hardness of the matrix and the cells during aging. The matrix is only slightly hardened, while the hardening in cells is considerable at the early stage of cell growth. The hardness in cells decreases in two stages with progress of aging. The first and

Fig. 3 Change in area fraction of cell in the Ni-15%Sn and Ni-8%Sn alloys on aging at 823 K.

Fig. 4 Relation between $\log \log \{1/(1-X)\}$ and aging time for the cells of the Ni-15%Sn and Ni-8%Sn alloys aged at 823 K.

Fig. 5 Growth rate of the cells in the Ni-15%Sn and Ni-8%Sn alloys on aging at 823 K.

Fig. 6 Change in interlamellar spacing in the cells of the Ni-15%Sn and Ni-8%Sn alloys on aging at 823 K.

Fig. 7 Hardness change in the matrix and the cell of the Ni-15%Sn and Ni-8%Sn alloys on aging at 823 K.

second stage decrease in hardness of cells seems to be correspond with the increase in area fraction of the second and third cells, respectively. Therefore, such decrease in hardness of cells may be explained by the difference in interlamellar spacing among the first, second and third cells, because the hardness in cells decreases with increase in interlamellar spacing⁽⁸⁾.

3. X-ray diffraction

Figure 8 shows the change in X-ray diffraction patterns in low diffraction angles. In the early stage of aging (6×10^3 s), where the first cell growth occurred slightly, many new diffraction lines appeared besides the lines from the matrix α phase. When the first cells engulfed all the matrix (8.4×10^4 s), some of these lines disappeared. On further aging, the diffraction

Fig. 8 Change in X-ray diffraction pattern of the Ni-15%Sn alloy on aging at 823 K.

angles of the residual lines did not change, but their intensities increased. It is considered from these results that the new diffraction lines appeared after 6×10^3 s aging are those from the precipitates in the matrix and the cell. The lines remained after the full development of cells may be those from precipitates in cells. By analyzing these lines, the precipitate phase in cells was identified as the θ phase (Ni_3Sn)⁽⁹⁾. The precipitate phase in the matrix should be metastable, because its diffraction pattern is different from that of the equilibrium precipi-

tate phase (θ) in cells. The crystal structure of the metastable phase (θ') was not yet clarified in this work.

Figure 9 shows the change in X-ray diffraction pattern in high angles. With increase in area fraction of the first cells, new diffraction lines from the α phase in the first cells appeared besides the lines from the α phase in the matrix. The new lines increased in intensity and shifted to high angles with progress of aging. After aging for 8.4×10^4 s, when the first cells engulfed all the matrix, the lines from the

Fig. 9 Change in X-ray diffraction pattern of the Ni-15%Sn alloy on aging at 823 K.

Fig. 10 Change in lattice parameter of the Ni-15%Sn alloy on aging at 823 K.

α phase in the matrix completely disappeared, and new lines from the θ phase in cells appeared. The intensity of lines from the θ phase increased with progress of aging, but the diffraction angles of these lines were hardly changed. Therefore, it seems that the θ phase had nearly the equilibrium composition at the beginning of the cell growth and the volume fraction of the θ phase increased during aging.

Figure 10 shows the change in lattice parameter of the α phases in the matrix and the cell during aging at 823 K. The lattice parameter of the α phase in the matrix decreased slightly with the precipitation of the θ' phase, while the lattice parameter of the α phase in the cells decreased markedly from 0.3595 nm to 0.3536 nm. The lattice parameter of the α phase in the cells continued to decrease even after the full development of the first cells and attained to a constant value when the second cells fully developed. Therefore, it seems that the concentration of Sn in the α phase in cells attained to its equilibrium value, not when the first cells engulfed all the matrix, but when the second cells engulfed all the first cells. The lattice parameters of α phases in the first and second cells were not separately measured in this work. However, it may be assumed that the reduction in lattice parameter occurring up to times around the full development of the first cells is mainly responsible for the first cells and that

at around the full development of the second cells for second cells.

IV. Discussion

As shown in the results, the cellular precipitation in the Ni-Sn alloys proceeded in three stages. Here we discuss about the driving force for the cell growth in each stage.

As shown in Fig. 10, the lattice parameter of the α phase in the matrix hardly decreased by the precipitation of the θ' phase, but the lattice

Fig. 11 Lattice parameter of Ni-Sn solid solution⁽¹⁰⁾.

parameter of the α phase in the cells decreased markedly during the periods from the formation of the first cells to the completion of the second cells. Figure 11 shows the relation between the lattice parameter and Sn content in Ni-Sn solid solution⁽¹⁰⁾. From Figs. 10–11, it can be seen that the Sn concentration in the α phase in cells after water quenching, after aging for 2×10^3 s (the first cell: 15% in area fraction), 6×10^4 s (the first cell: 100% in area fraction) and 5×10^6 s (the second cell: 100% in area fraction) can be estimated to 15.1, 9.0, 6.0 and 2.6%, respectively. The value of 2.6% is in good agreement with the Sn concentration⁽¹¹⁾ in the solubility limit of the Ni-Sn alloy at 823 K. Therefore, if we take the supersaturation of Sn in as-quenched α phase to 100%, there are supersaturations of 90% or more, and 50% in α phases in the matrix and the first cells, respectively, when the first cell engulfs 15% of the matrix. Therefore, the growth of the first cells should be due to the chemical driving force resulting from the difference in Sn concentrations between the α phases of matrix and first cells. The growth of the second cells may be due to both the chemical driving force resulting from the difference in Sn concentrations between the α phases of the first and second cells, and the driving force resulting from the difference in the interfacial energies of α - θ phase boundaries between the first and second cells. Thus, the growth of the second cells can be explained by the discontinuous coarsening mechanism proposed for a Fe-Ni-Ti alloy by Fournelle⁽¹²⁾.

For the third cell growth, only the difference in interfacial energies of α - θ phase boundaries in the second and third cells should be responsible, the chemical driving force being not concerned, since the α phase in the second cells already attains to its equilibrium composition when the second cells engulf completely the first cells. Thus, the third reaction is consistent in its mechanism with discontinuous coarsening reaction proposed for a eutectic alloy by Livingston and Cahn⁽¹³⁾.

The secondary cellular reaction has been reported to take place in several alloys such as Ag-Cu⁽¹⁴⁾, Cu-Ag⁽¹⁵⁾, Fe-Zn⁽¹⁶⁾ and Al-Zn⁽¹⁷⁾. It has been shown that the secondary

cellular reactions in these alloys are caused by the residual supersaturation in α phase in the first cells in consistent with the mechanism proposed by Fournelle. Whereas, the entire cellular reactions in the Ni-Sn alloys include both the mechanisms by Fournelle and by Livingston and Cahn.

As shown in Fig. 6, the interlamellar spacings in the first and second cells increase at the later stage of aging. For this phenomenon, two reasons may be considered; (1) the progressive reduction in Sn concentrations in α phases of both matrix and first cells⁽¹⁸⁾, and (2) the coagulation of precipitates in cells by a discontinuous coagulation reaction⁽¹⁹⁾. However, we could not clarify in this work which mechanism dominate this phenomenon.

V. Summary

The characteristics of the cellular precipitation in Ni-8%Sn and Ni-15%Sn alloys on aging at 823 K after quenching from 1273 K were investigated by means of quantitative metallographic methods and X-ray analysis. Results are as follows:

(1) The cellular precipitation in these alloys proceeded in three stages. Before the first cells with fine lamellae fully developed, the second cells with coarse lamellae began to grow into the first cells. After the second cells engulfed almost all the first cells, the third cells with coarser lamellae began to grow into the second cells.

(2) The lattice parameter of the α phase in cells decreased gradually until the finish of the second cellular precipitation. The precipitates in cells were the equilibrium phase (Ni_3Sn) with DO_{19} type structure.

(3) The growth rate of the second cells was 1/20–1/30 times as large as that of the first cells. The interlamellar spacing of the second cells was 2–3 times as large as that of the first cells.

(4) The area fraction of the cell, X , could be represented by Johnson-Mehl's equation; $X = 1 - \exp(-bt^n)$, and 1.0–1.2 and 0.6–0.7 were obtained as the values of n for the first and second cells respectively.

(5) Precipitate free zones were observed near by the grain boundaries before the growth

of the first cells.

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