Magnetic Study on Phase-Decomposition in a Ni-9.6 at %Ti Alloy*

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The saturation magnetization at 77 K and the magnetization over a temperature range 77–273 K, were measured for a Ni-9.6 at %Ti alloy aged at 723–888 K. Details of the magnetization-temperature curves were interpreted on the basis of the conception of magnetic mass balance. The configurations of composition variation and their changes with aging were analysed.

Aging behaviour of the alloy below 793 K was quite different from that above 813 K. On aging below 793 K, composition fluctuations which have already existed in the quenched specimens grow in amplitude without any delay. Above 813 K, on the other hand, some nuclei are formed after an incubation period and the matrix becomes uniform during the incubation period. Thereafter, a three-phase structure is produced and the Ti-poor regions grow by encroaching the homogeneous matrix, finally resulting in a two-phase structure. It is concluded that the Ni-Ti alloy decomposes by the spinodal mechanism below 793 K and by the nucleation-growth mechanism above 813 K.

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I. Introduction

Supersaturated solid solutions transform to more stable phases either by nucleation-growth or by spinodal decomposition. In order to determine the mechanisms of the phase-separation, it is most desirable to clarify profiles of composition variations evolved during aging. Although several techniques are available for inspection of weak composition variations formed in alloys, they require refined performance of high levels. The magnetic properties are sensitive to a composition change in an alloy, and hence they are considered to be applicable for identifying weak composition variations. Recently precipitation processes in alloys of Ni-Ti⁽¹⁾⁽²⁾ and Ni-Al⁽³⁾⁽⁴⁾ have been studied by means of magnetic measurement.

In this report relations between magnetic properties and composition variations in solid solutions are discussed on the basis of the concept of magnetic mass balance⁽⁵⁾ in an attempt to establish an appropriate method for the magnetic analysis of composition variations. The newly devised method is utilized for the identification of composition variations

in a Ni-9.6 at %Ti alloy, which is known to form a modulated structure. The analysis shows that on aging below 723 K the amplitude of "concentration fluctuation" included in quenched specimens grows without any delay, while above 813 K formation of nuclei and disappearance of "concentration fluctuation" progress concomitantly, and then Ti-poor zones appear in a homogeneous matrix.

II. Experimental Procedure

The fabrication of the alloy used for this investigation was described in our previous paper⁽⁶⁾. Cubes 2 mm in side were cut off from an alloy plate. The cube specimens were solution treated for 600 s at 1453 K in a quartz tube evacuated at pressure of about 1.4×10^{-3} Pa and drop-quenched into iced brine of 263 K. On aging for less than 480 s, the specimens were heated in a nitrate-salts bath. For a longer aging time they were encapsuled in an evacuated quartz tube, heated in a salt bath, and then quenched into water by crushing the tube. After quenching or aging the specimen surface was polished using emery paper.

The magnetization, M , as a function of temperature was measured using a vibrating sample magnetometer. The temperature was measured with a copper-constantan thermocouple. The thermocouple and the specimen were wrapped in cotton soaked with grease.

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After cooling the specimen to 77 K, the magnetization was recorded at an interval of 1.5 K.

Magnetization-temperature curves were mainly measured at magnetic fields of 24 kA/m and 1.2 kA/m. The former magnetization-temperature curves are designated as 300 Oe curves and the latter as 15 Oe curves in the following description. For the 300 Oe curve a tangential line of a maximum slope was drawn. The Curie temperature, θ_c , was taken as an intercept of the tangential line with the abscissa of $M=0$. The slope of the tangential line is denoted as $(-dM/dT)$. The magnetization of all the specimens was saturated at 77 K when a magnetic field of 200 kA/m was applied. The values of the saturation magnetization measured at 77 K were designated as M_{s77} .

III. Experimental Results

The values of θ_c and $(-dM/dT)$ of the specimens are shown in Fig. 1. The mean and the minimum values of θ_c are 206 K and 202 K, respectively, and θ_c of most specimens were 205 ± 0.5 K. Figures 2 and 3 show changes of θ_c , $(-dM/dT)$ and M_{s77} with aging time at 723–888 K. Each aging curve in Fig. 2 was obtained by repeating the measurement and the aging treatment for one specimen, while one solution-treated and aged specimen was used for each measurement in Fig. 3.

Fig. 1 Relation between the Curie temperatures, θ_c , and slopes of linear portion of magnetization vs temperature curves, $-dM/dT$, in solution treated Ni-9.6 at%Ti alloy.

Figure 2 shows that the values of θ_c always increase by aging for 20 s. On subsequent aging above 813 K, the values of θ_c do not change for a long period, and then rise. The increases of θ_c at the incipient aging are larger for lower aging temperature. The values of $(-dM/dT)$ at the incipient aging are larger than that of the quenched specimen and they decrease gradually with the rise of θ_c . On the other hand, on aging at 773 K and 793 K θ_c increases continuously without any incubation. The values of $(-dM/dT)$ are extremely small at the initial stage of aging and increase with the rise

Fig. 2 Change of $-dM/dT$ and θ_c of Ni-9.6 at%Ti alloy with aging.

Fig. 3 Change of $-dM/dT$, θ_c and M_{s77} with aging.

Fig. 4 Magnetization at a field of 1.2 kA/m normalized by magnetization at 77 K. (a) 823 K and (b) 723 K aging.

of θ_c . The values of $(-dM/dT)$ do not exceed that of the quenched specimen.

The aging behaviour of θ_c and $(-dM/dT)$ at 773 K and 793 K in Fig. 2 is similar to that at 723 K in Fig. 3, and at 823 K and 888 K in Fig. 3 it is similar to that at 813 K in Fig. 2. Meanwhile, the increasing process of M_{s77}

with aging at 723–888 K is the same as that of θ_c . That is, M_{s77} remains constant during the initial stage of aging at 823 K or at 888 K, while it increases without any incubation at 723 K.

Changes in the 15 Oe curves with aging are shown in Fig. 4. On aging at 888 K the 15 Oe

curves change similarly to those on aging at 823 K.

IV. Discussion

1. Composition dependence of the Curie temperature and the saturation magnetization

An empirical relation between the Curie temperature θ_c (K) and the titanium content C in Ni-rich Ni-Ti alloys is given by Ardell⁽²⁾ as

$$C(\text{wt}\%) = (673 - \theta_c)/59.23, \quad (1)$$

where the values of θ_c were those estimated by the same method as in the present experiment.

It is well accepted that the saturation magnetization, M_s , in Ni-rich alloys such as Ni-Al or Ni-Si decreases linearly with an increase of solute-concentration⁽⁷⁾. Thus, the saturation magnetization at 0 K, M_{s0} , in a Ni-rich solid solution can be expressed from eq. (1) and the value of $M_{s0} = 0.6556 \text{ wb/m}^2$ ⁽⁸⁾ for pure nickel as

$$M_{s0}(\text{wb/m}^2) = 0.6556 - 0.0482C(\text{at}\%). \quad (2)$$

Equation (2) indicates that solid solutions containing titanium more than 13.6 at% are non-ferromagnetic and that M_{s0} of a solid solution will rise if non-ferromagnetic solute-rich zones are formed in the solid solution.

2. Magnetization-temperature curves of inhomogeneous Ni-Ti solid solutions

We assume that the spontaneous magnetization of a solid solution with composition variations is given by a superposition of the spontaneous magnetization for small regions of different solute-contents. As will be shown later, the formation of solute-poor zones has an effect mainly on the low magnetization parts of superimposed spontaneous magnetization curves. In general, a measured magnetization deviates from the spontaneous magnetization curves, because of the presence of an induced magnetization as shown in Fig. 5⁽⁹⁾. The induced magnetization is large when the measurement is done at a higher magnetic field. Therefore, the measurement at a low field is required for detecting solute-poor zones.

Fig. 5 Spontaneous magnetization for a solid solution (bold line) and magnetization curves measured at various applied field, H_a (fine lines). H_c : Saturation magnetic field at 0 K.

Fig. 6 Various types of concentration profiles. (a) two-phase structure. (b) three-phase model of G-P zone. (c) Nucleation model. (d) Sinusoidal concentration fluctuation.

We shall now derive the relation between the superimposed spontaneous magnetization and the composition variation shown in Fig. 6, and also the magnetic field dependence of magnetization-temperature curves.

We denote M_s , θ_c and a volume fraction V for each of the two composition regions shown in Fig. 6(a) by M_{s1} , θ_{c1} , V_1 , and M_{s2} , θ_{c2} , V_2 ,

Fig. 7 Spontaneous magnetization of each region in two-phase alloy (dotted lines), and the total spontaneous magnetization composed of them (bold lines). Magnetization curves obtained at a high or a low magnetic field are observed as each fine line.

respectively. The superimposed spontaneous magnetization curves for the composition variation of Fig. 6(a) are represented by the bold lines in Fig. 7, and the magnetization-temperature curves estimated at two levels of the applied field are represented by the fine solid lines. The shape of magnetization-temperature curves changes depending on the composition and the volume ratio of the two regions and also on the strength of measuring field. Figures 7(1) and (4) show the cases where $M_{s1} \cdot V_1 / M_{s2} \cdot V_2 \approx 1$ at 0 K. In (1) where $d\theta_c (= \theta_{c1} - \theta_{c2})$ is large, decrease in the magnetization takes place in two steps on the measurement under high field, $Hh^\dagger$ ⁽¹⁰⁾. In (4) where $d\theta_c$ is small, the magnetization measured at Hh field decreases in a single step. On the other hand, the magnetization decreases sharply

on the measurement at low field, $Hl^\dagger$, for both the cases of (1) and (4), and the magnetization-temperature curves do not differ from that of the homogeneous solid solution.

The above mentioned analysis for inhomogeneous solid solution of Fig. 6(a) type leads to the following conclusions: (i) The magnetization-temperature curves measured at high field is similar to those of homogeneous solid solution when either of the two regions is large. When the size of each region is equal or so, they become irregular with an increase in $d\theta_c$, as seen from comparison between (1) and (4). (ii) The measurement at low field gives abnormal magnetization-temperature curves when a small region of solute-poor zone is formed. This means that the measurement at low field gives an information about solute-poor zones.

† In this experiment $Hh = 24$ kA/m.

†† In this experiment $Hl = 1.2$ kA/m.

Figure 6(d) shows a wavy type of composition variation, i.e., so called "concentration fluctuation". As the concentration changes continuously, this composition variation may be approximated by the dotted linear line in (d). The superimposed spontaneous magnetization is shown by the bold line in Fig. 8(I). In this case the measured magnetization decreases more gradually than that for the homogeneous solid solution regardless of the strength of the applied field.

In Figs. 6(b) and (c) the Ti-content of solute-rich zones or nuclei is considered to be larger than 13.6 at%. Hence, the solute-rich zone is non-ferromagnetic at all temperatures. The composition profile of (b) is regarded to be the same as type (a), being modified slightly by addition of a small non-ferromagnetic region. Thus, the above mentioned conclusions of (i)

and (ii) about (a) can be applied to the composition profile of (b). The composition profile of (c) is considered to be a homogeneous solid solution with a small non-ferromagnetic region and a "concentration fluctuation". The superimposed spontaneous magnetization curve is shown by the solid line in Fig. 8(II). In this case the magnetization measured at a low field decreases gradually. The magnetization measured at a high field decreases smoothly only when a homogeneous solid solution exists over a wide range.

In actual solid solutions, several kinds of composition variation as shown in Fig. 6 can coexist. Hence, the relation between the magnetization-temperature curves and the composition variation summarized in (i) and (ii), and the feature pointed out in the case of "concentration fluctuation" can be applied additively to the actual solid solution according to the construction of the composition variations.

3. Composition variation in the quenched specimen

By substituting the minimum and the mean value of θ_c shown in Fig. 1 into eq. (1), the titanium contents of the solid solution are estimated to be $C_{\max}=9.58$ at% and $C_{\text{mean}}=9.50$ at%, respectively. If the quenched specimens are homogeneous, then the estimated values should be equal to the value of chemical analysis, $C_0=9.63$ at%Ti. However, the measured values are always smaller than C_0 . This means that some composition variations exist in the quenched specimens. On the other hand, Fig. 1 shows that a linear relationship holds between the values of θ_c and $(-dM/dT)$, and that θ_c increases linearly with decrease of $(-dM/dT)$. This relation can be only explained by assuming the solid solution with a "concentration fluctuation".

The 15 Oe curve for the quenched specimen whose θ_c is 205.5 K is shown in Fig. 4(a) as the S.T. line. Although the magnetization in the S.T. curve decreases relatively sharply, it decreases still less steeply than the curve for the specimen aged at 823 K for 1800 ks in which the matrix is homogeneous. The greater part of magnetization in the S.T. curve decreases

Fig. 8 Calculated spontaneous magnetization curves of solid solution containing composition variations as shown in Fig. 6(c), (d). Solid curve in (I) or (II) corresponds to the case of (d) or (c), respectively. Dotted lines correspond to the spontaneous magnetization of a homogeneous solid solution.

in the vicinity of 200 K, then by substituting 200 K into eq. (1), the Ti-content of a solute-poor region in the quenched specimen is estimated to be near C_0 . Hence, the amplitude of the "concentration fluctuation" formed in the quenched specimen is considered to be small.

4. Composition variation in specimens aged at 823 K

By aging for 30 s at 823 K, θ_c and $(-dM/dT)$ increase, and the 15 Oe curve shifts to the high temperature side by 10 K. These facts mean that the solute-distribution in the matrix becomes homogeneous and the titanium content of the matrix decreases. It is noted that decrease in the magnetization in the 15 Oe curve is still gradual compared with that for the specimen aged for 1800 ks at 823 K. This means that the "concentration fluctuation" still remain, though they are diminished in degree by aging for 30 s. On the other hand, M_{s77} increases. This indicates that decrease in the Ti-content in the matrix is caused by the precipitation of non-ferromagnetic zones.

During aging for 30 s–240 s, θ_c and M_{s77} remain constant and the value of $(-dM/dT)$ increases slightly. The decrease of the magnetization in the 15 Oe curves become sharper with the aging time, though the position of the curves does not change as a whole. Therefore, it can be considered that the composition variation grows into a rectangular type and the small "concentration fluctuation" disappears.

During aging for 480 s–14.4 ks, θ_c and M_{s77} increase and $(-dM/dT)$ decreases remarkably. The increase of M_{s77} corresponds to the increment of the amount of precipitates. The aging behaviour of the 15 Oe curves is characteristic. That is, while the temperature at which the magnetization begins to drop is fixed during the aging, the part of low magnetization shifts rapidly to the high temperature side with the aging time. The former fact means that the Ti-content of the matrix does not change. The latter fact corresponds to that the Ti-poor zones are formed and their volume increased with the aging time. Therefore, the remarkable decrease of $(-dM/dT)$ and the increase of θ_c during the aging can be understood in terms of superimposed spontaneous magnetization curve

for a solid solution containing a homogeneous matrix and some Ti-poor zones.

During aging for 14.4 ks–54 ks, θ_c and M_{s77} increase continuously, while $(-dM/dT)$ is kept at a very small value. The temperature at which the magnetization begins to drop in the 15 Oe curve rises and the part of high magnetization decreases considerably gradual. These facts indicate that the volume or the Ti-content of the matrix decreases with the aging time. Furthermore, the part of the gradual decrease of the magnetization in the 15 Oe curves disappears, and the slope of the curve becomes steeper with the aging time. This corresponds to the fact that the volume of Ti-poor zones increases substantially.

After aging for 108 ks, the rises of θ_c and M_{s77} become gradual and tend to saturate. The value of $(-dM/dT)$ exceeds that of the quenched specimen. The 15 Oe curves show a single sharp drop of the magnetization. These results mean that the homogeneous region increases again. On the other hand, the value of θ_c for the specimen aged for 1800 ks is 261 K, which corresponds to the Ti-content of 8.3 at%. After 1800 ks θ_c and M_{s77} are saturated, and it can be considered that the matrix and the non-ferromagnetic precipitates are in an equilibrium state. The Ti-content of 8.3 at% is in good agreement with the solubility limit of γ' precipitates at 823 K which was determined experimentally by Ardell⁽²⁾.

5. Composition variation in the specimen aged at 723 K

The values of M_{s77} increase continuously during aging for 20 s–10⁵ s. This means that the Ti-content or the volume of the non-ferromagnetic region increases continuously. The values of $(-dM/dT)$ are always smaller than that of the quenched specimen. This fact indicates that any region homogeneous in the solute-distribution do not exist in a significant amount in the aged specimens.

During aging for 20 s–10⁴ s, the 15 Oe curves show the magnetization drops in two steps, that is, a gradual drop at the high magnetization level and a sharp drop at the lower level. The latter indicates existence of the solute-poor region whose solute-distribution is roughly

homogeneous. On the progress of aging, the latter portion shifts to the higher temperature side without changing its form (height and slope). This fact means that the volume of the Ti-poor region formed by aging for 20 s remains constant and the Ti-content in the region decreases with the aging time.

A remarkable feature is observed in the 15 Oe curves of the specimen aged for 5×10^4 s or for 10^5 s. Apart from the rise of temperature at which the magnetization begins to decrease, the magnetization decreases gradually over a very wide range of temperature. This fact means that the volume of the Ti-poor region increases and the Ti-content in the region is changing continuously over a wide range of composition.

6. On the decomposition process

The decomposition process at 723 K is quite different from that at 823 K. While the values of θ_c and M_{s77} remain constant for 30 s–240 s at 823 K, the values rise continuously after the aging of 20 s at 723 K. While the values of $(-dM/dT)$ rise at 823 K after the aging of 20 s or 30 s, they decrease at 723 K. On the initial aging at 823 K, the 15 Oe curves show a single and sharp transition from ferromagnetic to non-ferromagnetic, but at 723 K the curves indicate plural and gradual transitions. As a decrease of $(-dM/dT)$ corresponds to a reduction of the homogeneous region in a solid solution, the decrement of $(-dM/dT)$ occurring on an incipient aging at 723 K is considered to be amplification of the “concentration fluctuation” by up-hill diffusion inherited from the quenching process. This interpretation is supported by the fact that the amount of precipitates detected as M_{s77} increases continuously without incubation. Therefore, it is concluded that the alloy decomposes spinodally at 723 K.

The values of θ_c and M_{s77} did not change during 20 s–240 s on aging at 823 K, which can be explained as an incubation period for nucleation. Some of embryos slightly smaller than the critical size are supposed to be changed gradually to nuclei with some distinct surface by an aid of thermal fluctuation during the incubation period. Composition variations

fairly smaller than the critical size dissolve, which makes the solute-distribution in the matrix homogeneous. Furthermore, the increases in $(-dM/dT)$ and the slope in the 15 Oe curves during the incubation period can be interpreted as a process where the “concentration fluctuation” with a lower amplitude than the critical composition for growth is dissolved by down-hill diffusion. Therefore, it should be concluded that the temperature above 823 K is outside the spinodal region and the decomposition at 823 K proceeds by the nucleation-growth process.

From the shape of the 15 Oe curve for the specimen aged at 823 K for 240 s, shown in Fig. 4(a), we can infer that only the two phases of nuclei and matrix exists in the specimen and solute-poor zones around the nuclei do not yet appear. This reason may be attributed to a large number of excess vacancies existing in the incipient aging. After dissipation of excess vacancies, the diffusion rate of solute-atoms decreases, and then the filling up of the solute-poor zones by flow of solute atoms from the matrix becomes difficult. Thus after the aging for 480 s, the solute-poor zones appear and grow with the aging time encroaching the matrix until most of the matrix is consumed at 108 ks. Therefore, it can be considered that a three-phase structure of the precipitates, the solute-poor zones and the matrix is constructed for 480 s–108 ks.

As shown in Figs. 2 and 3, the values of θ_c and $(-dM/dT)$ for the specimen aged above 813 K change similarly to those for the specimen aged at 823 K. Hence, the decomposition process at 813–888 K can be considered to be controlled by the nucleation-growth process. Meanwhile, as shown in Fig. 2, the aging behaviour of θ_c and $(-dM/dT)$ at 773 K and 793 K is similar to that at 723 K where the spinodal decomposition proceeds. It is apparent that the decomposition processes below 793 K and above 813 K are different from each other, and the spinodal temperature of this alloy can be estimated to be about 803 K.

V. Conclusion

A method of the magnetic analysis for a

composition variation formed in a solid solution was discussed by assuming that the spontaneous magnetization of a solid solution with a composition variation was given by a superposition of the spontaneous magnetizations for small regions of different solute-contents. The result suggests that formation of solute-poor regions in the matrix deforms strongly "tails" of the superimposed spontaneous magnetization curve. The method was applied to clarify the decomposition process in the supersaturated solid solution of the Ni-9.6 at%Ti alloy.

Results obtained are as follows:

- (1) "Concentration fluctuations" exist in the quenched specimen.
- (2) The "concentration fluctuation" inherited from the quenching process grow in the amplitude during aging at 723 K, and both of nuclei and the homogenized matrix appear simultaneously during the incipient aging at 823 K.
- (3) On aging at 823 K, after the formation of the two phase structure, i.e., nuclei and the matrix, solute-poor zones are formed and then they encroach on the matrix.
- (4) During aging at 723 K, inhomogeneities of the solid solution increase and the titanium-

content of solute-poor regions decrease with the aging time.

- (5) The spinodal temperature of this alloy is estimated to be about 803 K.

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