Measurements of Electrical Resistivity Change due to Transitions in Quenched γ -Phase Mn-(16.5–20.5) at%Ni Alloys

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An accurate measuring system of electrical resistivity has been designed and constructed, and has been applied to determination of transition temperatures in quenched γ -phase Mn–Ni alloys containing 16.5 to 20.5 at%Ni. The Néel temperature as well as the fcc to fct ($c/a > 1$) structure transformation temperature is detectable, and a small change in electrical resistivity due to an orthorhombic distortion is also detected. The magnetic and crystallographic phase diagram for the Mn–Ni alloy system was found to be well confirmed.

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I. Introduction

The face-centred cubic (fcc) γ -phase of Mn–Ni alloys is metastable at room temperature, being retained by quenching⁽¹⁾. Quenched alloys containing Ni more than 16 at% exhibit a paramagnetic-antiferromagnetic transition and a lattice distortion to the face-centred tetragonal (fct) structure with the axial ratio $c/a > 1$ ⁽²⁾, while in Mn–Ni alloys containing Ni less than 15 at% another tetragonal distortion with the axial ratio $c/a < 1$ takes place⁽³⁾. It has been also known that an orthorhombic distortion takes place in a composition range from 13 to 17 at%Ni at room temperature^{(3)–(5)}. The magnetic and crystallographic phase diagram of Mn–Ni alloys has been reported, as shown in Fig. 1, where the Néel and structural transformation temperatures were determined with the aid of neutron⁽²⁾⁽³⁾⁽⁶⁾ and X-ray^{(2)–(6)} diffraction methods, Young's modulus^{(3)–(5)(7)}, shear modulus⁽⁵⁾, internal friction⁽⁵⁾, electrical resistivity⁽²⁾, specific heat⁽³⁾ and magnetic susceptibility⁽²⁾ measurements. It should be noted here that these transition temperatures were always determined with the aid of several supplemental methods.

It has been well known that, when a suffi-

Fig. 1 Phase diagram of γ Mn-(16.5–20.5) at%Ni alloys, previously reported by several authors. —: Honda *et al.*⁽⁵⁾, —: Uchishiba⁽³⁾, —: Endoh and Ishikawa⁽⁶⁾, —: Hicks *et al.*⁽²⁾

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cient caution is paid to the experimental procedure, the electrical resistivity is structure sensitive so that small changes in both lattice distortion and electronic structure occurring in

the materials⁽⁸⁾ may be detected. Therefore, among the above measurements an electrical resistivity measurement is considered to be one of the powerful and reliable methods for detecting both structural and magnetic transitions. In the previous experiments, however, conventional potentiometric techniques were employed, and no special attention was paid to an accurate measurement⁽²⁾.

The purpose of the present study is to establish an accurate measuring system and to determine all transition temperatures in metastable γ -phase Mn-Ni alloys with the aid of only the measurement of electrical resistivity.

II. Experimental Procedure

1. Specimen preparation

Electrolytic Mn (99.99% purity) and Ni (99.999%), weighed out in quantities sufficient to prepare about 15 g of alloys, were melted together in an evacuated quartz tube at about 1623 K, and then quenched into ice water. The resultant ingots containing 16.5 to 20.5 at%Ni, for which no appreciable change in mass (less than 0.1 at%) was detected after the melting, were subjected to the following heat treatments. The final composition was checked by chemical analysis. The γ -phase Mn-Ni alloys containing Ni less than 16 at% could not be prepared because of brittleness against cold-rolling. After prolonged homogenization just below the solidus in the γ -phase region for 6.7×10^5 s (8 d), all the ingots were quenched into ice water to retain the disordered γ -phase. Each of them was cold-rolled into a sheet 4 cm long, 0.2 cm wide and 0.01 cm thick. In addition, in order to eliminate the effect of aging, the resultant sheet was annealed again at 1223 K (γ -phase region) for 6×10^2 s in an evacuated quartz tube and quenched into ice water just before the measurement.

2. Features of designed apparatus

In order to detect a very small variation of resistivity, a new measuring system, including a current supply and a kind of operator circuit (analog computer), was designed and con-

structed. (Detailed data of circuits can be offered at one's request.) The block diagram of the present measuring system is shown in Fig. 2. This system is characterized by that both the current supply and analog computer are unified into one system organically together with test piece, dummy resistor and reference resistor. From the block diagram, we can see that the measurement is made by detecting a voltage difference between the specimen and a dummy resistor. Accordingly, this system can be a kind of differential electrical resistivity analysis. In this system, the reference resistor can play as a monitor of electric current.

The measurement of electrical resistivity is substantially based on the four-terminal potentiometric technique, and a resistivity variation is measured as a voltage signal. Accordingly, the design principle of the apparatus was laid in amplifying the voltage signal as high as possible. A current supply was constructed so as to satisfy the following conditions: (1) An output current is highly stable. (2) An electric ripple component is as small as possible, less than $2 \times 10^{-2}\%$ at the maximum output current of 1 A. (3) The stability of the output current for the environmental temperature is less than 10^{-4} K^{-1} with a low drift less than $2 \times 10^{-4} \text{ V}$ for 1 h. These specifications were obtained by using high quality electric devices such as Zener diodes (LM399) and FET (25K30A-GR),

Fig. 2 Schematic diagram of the present resistivity measuring system. The dummy resistor used, made of the same material as the test piece, plays a very important role as a part of the analog computer. The reference resistor (manganin resistant wire; 0.9005 Ω) is soaked in a bath filled with water-cooled silicon oil.

which were all guaranteed for temperature variations. Consequently, this current supply proved to be superior to an ordinary marketing one in quality.

The function of the analog computer is to eliminate noise signals effectively. Through this circuit, contact potentials and the thermoelectromotive forces between the copper lead wires and the specimen can be cancelled. This can also allow us to have a resistivity-temperature curve in an arbitrary expanded scale around a desired point. The performance of this circuit was investigated by the measurement of resistivities of highly pure copper and nickel (99.999%) sheets from room temperature to 523 K with reference to the data in the book of Landolt and Börnstein⁽⁹⁾. Preliminary experiments with currents from 0.1 to 0.5 A showed almost the same performance within experimental accuracy. The resultant performances were (1) the resolution: 10^2 n Ω for 1 mm of an X-Y recorder used (RIKADENKI, RW-11), (2) the response time: 0.1 s for 1 mm of the X-Y recorder used, and (3) the accuracy for voltage signal: within $\pm 0.1\%$ at a desired point in the recorder. These specifications were obtained by using twelve FET input OP amplifiers with high response and low drift such as LM308A (National Semiconductors) and CA3140 (RCA). This circuit allows us to measure voltage variations continuously with real time during the experiment: Voltage signals are recorded on the Y axis and the thermoelectric power of the thermocouple (CA) is amplified and recorded on the X axis on the recorder.

3. Method of measuring

The resistivity measurement was made in the following way: Four highly purified copper wires are welded on a specimen by electric spot welding so that the current distribution may be kept homogeneous over the gauge length (25 mm) with reference to the conditions proposed by van der Pauw⁽¹⁰⁾. The specimen is not fixed on a supporting plate (insulator), because the specimen may vary its length due to structural transformation during the heating and cooling processes[†]. In order to control heating and cooling rates, a furnace was made which is

composed of an electric resistance wire for heating and a copper pipe for water cooling, and the following conditions were obtained thereby: The maximum heating rate was 6.7×10^{-2} K/s and the maximum cooling rate -5×10^{-2} K/s. The temperature control was made using a PID control system. In order to avoid any disturbance of voltage signals to the specimen, a thermocouple (CA) was deliberately not attached to the specimen. Accordingly, the temperature was measured using a dummy specimen placed near the true specimen. The temperature difference between them proved to be less than 0.3 K. In the present experiment, temperature change of specimens was made mainly at a rate of $2 \sim 4 \times 10^{-2}$ K/s. When the specimen was held at a temperature higher than 550 K for more than 7.2×10^3 s, the effect of aging was observed clearly on resistivity curves. Therefore, all measurements were done so carefully as to suppress the effect of aging.

III. Results and Discussion

Figure 3 shows a resistivity-temperature curve in a normalized form on heating in (a) and the plot of the differential resistivity in (b) for a Mn-18.5 at%Ni alloy. In Fig. 3(a), one can clearly see two large slope changes on the curve, as indicated by arrows, although several small changes are also appreciated faintly. No conventional standard potentiometric technique could reveal all these slope changes clearly⁽²⁾. Accordingly, the present measuring system proved to be highly sensitive to structural changes occurring in the specimen. On the contrary, differential resistivity has been already obtained on a Mn-18.7 at%Ni alloy by Hicks *et al.*⁽²⁾, who demonstrated that the differential resistivity curve was able to exhibit appreciable slope changes both at the Néel temperature and at the structural transformation temperature. According to the phase diagram shown in Fig. 1, a Mn-18.5 at%Ni alloy exhibits

[†] The volume change $\Delta V/V$ due to phase transformations is considered to be very small ($< 10^{-3}$), and thereby the resultant resistivity change could be unmeasurable. However, secondary effects such as deformation due to fixing must be removed, because this alloy exhibits a so-called shape memory effect.

Fig. 3 (a) Temperature-resistivity curve for a quenched γ -phase Mn-18.5 at%Ni alloy on heating. (b) Corresponding differential value of resistivity-temperature curve.

an antiferromagnetic-paramagnetic transition around 450 K, and with decreasing temperature shows an fcc to fct ($c/a > 1$) phase transformation around 320–380 K. From these facts, it seems reasonable that the two kinks observed on the curve correspond to the Néel temperature, T_N , and the structural transformation temperature, T_I . A large change observed at T_N may be related to the domain wall movement, as expected from the ΔE effect⁽⁵⁾. The detailed inspection shows that the behavior of differential resistivity curve obtained is different from the result reported by Hicks *et al.*⁽²⁾, although their results must be reviewed. This is due probably to the difference in heating rate which can result in, for example, an enhanced specific heat in terms of kinetics. Further detailed studies must be done on this point.

Figure 4(a) shows a curve obtained in a Mn-16.5 at%Ni alloy, where three large slope changes are observed clearly, as indicated by arrows on the curve. An obtained differential resistivity curve also shows sharp changes at the corresponding temperatures in Fig. 4(b). The Mn-16.5 at% Ni alloy exhibits three successive transitions with decreasing temperature⁽⁵⁾: The first is a magnetic transition, the second is an fcc to fct ($c/a > 1$) structure transformation and the third an fct to face-centred orthorhombic (fco) structure transformation. A comparison between Figs. 3 and 4 shows that the first slope change appears at nearly the same temperature for both alloys, and that their differential resistivity curves show almost the same changing mode around each transformation temperature. This supports that the first change also corresponds to a magnetic transition temperature, T_N . Consequently, the other changes can correspond to the structural transformation with reference to the phase diagram already reported, although one small unexplainable peak is still seen between the two slope changes marked by T_N and T_I in Fig. 4(b).

The same analysis was made for the other alloys. The results obtained are summarized in Fig. 5, together with the data reported by Honda *et al.*⁽⁵⁾. Each point in the figure denotes the results obtained from 4 to 5 specimens. The

Fig. 4 (a) Temperature-resistivity curve for a quenched γ -phase Mn-16.5 at%Ni alloy on heating. (b) Corresponding differential value of resistivity-temperature curve.

Fig. 5 Magnetic and crystallographic phase diagram of Mn-Ni alloys determined by the present study, together with the result obtained by Honda *et al.*⁽⁵⁾

present Néel temperatures are about 15 K above those obtained by Honda *et al.*, which were determined by the elastic measurements. In their experiments, both Young's and shear modulus vs temperature curves showed a step-like change over a temperature range of about 20 K. Accordingly, the difference in temperature between both data does not seem to be substantial.

In spite of several unexplainable findings, one can see that two phase diagrams are fairly in agreement with each other. Accordingly, we can conclude that the resistivity measurement is available for determining the transition temperatures in metastable γ -phase Mn-Ni alloys.

The temperature dependence of electrical resistivity was able to be studied. However, detailed inspection is not made, because it seems unlikely that the expression of the temperature dependence of electrical resistivity

of magnetic (para- and antiferro-magnetic) metals has been well established⁽¹¹⁾.

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