An Experimental Study on the Ordered Alloy Ni₂Cr

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The ordered alloy Ni₂Cr has been investigated by means of electron diffraction, electron microscopy, calorimetry, resistometry and tensile tests. The formation of the Pt₂Mo type superstructure is revealed by an electron diffraction study on the single crystalline specimens. The size of ordered domains is of the order of magnitude of several hundred Å even in the well annealed state. The so-called 'K-state' which is characterized by the initial increase in electrical resistivity upon isothermal annealing is attributed to the existence of very fine ordered domains. Superdislocations consisting of triple dislocations are sometimes observed in various stages of ordering, and the mechanical properties are briefly discussed in the light of electron microscopic observation. The energy and entropy of transformation are evaluated as about 1.0 kcal/g·atom and 1.2 cal/g·atom-deg on the alloy of 32.1 at% Cr annealed at 500°C for about 3000 hr.

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I. Introduction

Although numerous works have so far been carried out on the order-disorder transformation of alloys of the A₃B and AB types, a rather limited number of studies have been done on the alloys of the A₂B type. For the nickel-chromium system, Baer⁽¹⁾ and Bagariatskii and Tiapkin⁽²⁾ observed the existence of the superlattice Ni₂Cr by an X-ray diffraction technique, and Goman'kov et al.⁽³⁾ confirmed it by a neutron diffraction study. The atomic arrangement of this ordered alloy is isomorphous with the Pt₂Mo type, the space group D_{2h}²⁵-Immm (No. 71). The orthorhombic unit cell containing six atoms has the lattice parameters $a \approx a_0/\sqrt{2}$, $b \approx 3 a_0/\sqrt{2}$ and $c \approx a_0$, where a_0 is that of the original fcc cell (see Fig. 3).

Several workers^{(1)(4)~(8)} observed anomalous changes in physical and mechanical properties of this alloy long before the crystal structure of the ordered state had been

established. For instance, the temperature coefficient of electrical resistivity is negative around 600°C and the resistivity of the quenched alloy increases initially with time during isothermal annealing. The state of an alloy showing such a peculiar behavior is often called the "K-state" though little is known about its microstructure.

Recently Popov et al.⁽⁹⁾⁽¹⁰⁾ investigated the nature of dislocations and the effect of atomic order on the work-hardening in Ni₂Cr. It was suggested from the atomic arrangements on the slip planes that in eight of the twelve slip systems no anti-phase boundaries are created by a slip dislocation, while single dislocations in the remaining four systems form anti-phase boundaries, thus forming superdislocations which consist of three dislocation lines linked in a pair with strips of anti-phase boundaries. However, the triple dislocations have not yet actually been revealed by electron-microscopic observation.

A statistical theory on the order-disorder transformation of the Pt₂Mo type was presented by Shtremel⁽¹¹⁾, but no thermodynamical data on the stoichiometric alloy Ni₂Cr were available for quantitative comparison with the calculation.

A joint effort has been made by two groups of the present authors (Tohoku Univ. and Osaka Univ.) to investigate the nature of the ordered alloy Ni₂Cr by a comprehensive method of electron microscopy, electron diffraction, calorimetry, resistometry and mechanical tests. Experimental works were independently carried out by the two groups, but the observed results were consistent with each other as described in the later sections. The present paper will mostly deal with changes in thermodynamical quantities due to the order-disorder transition, and microscopic configurations of ordered domains and of superdislocations. The observed

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results of electron microscopy will be discussed in relation to the changes in the physical and mechanical properties.

II. Experimental Procedures

Four specimens containing 32.1, 32.9, 33.3 and 35.2 at% Cr were prepared by vacuum-melting of the required amounts of the constituent metals. Chromium contents of the specimens were determined by chemical analysis. In this comprehensive study, the work of Saburi et al. was concentrated on an alloy of 35.2 at% Cr, while the effort of Hirabayashi et al. was made for the other three alloys.

Calorimetric measurements were made in vacuum by an adiabatic calorimeter using cylindrical specimens of about 50 g in weight. Measurements of the electrical resistivity were made at liquid-nitrogen temperature by a usual potentiometric method using specimens in the form of either a thin plate or wire. The wire specimens were also used for tensile tests at a strain rate of $5 \times 10^{-2} \text{ min}^{-1}$. Microhardness was measured under a load of 500 g using plate samples. Thin foils for observations by electron diffraction and electron microscopy were prepared by electropolishing sheet specimens 0.1 or 0.2 mm thick. Lattice constants were determined by means of X-ray powder diffraction using $\text{Cu } K\alpha$ radiation.

III. Experimental Results

1. Calorimetry

Anomalous thermal effects of the alloys near in composition to Ni_3Cr have previously been observed by some workers⁽⁵⁾⁽⁷⁾⁽¹²⁾, but no quantitative data have been available yet for the composition Ni_2Cr . In the present study, therefore, calorimetric measurements were performed up to about 700°C under vacuum on an alloy, 32.1 at% Cr, after various heat treatments. The specific heat vs. temperature curves are given in Fig. 1. In this figure, a dotted curve *a* was obtained after water-quenching of the specimen from 1000°C . A small amount of heat evolution is observed around 530°C . Since this was interpreted as the occurrence of atomic ordering during the heating measurement, the specimen was subsequently annealed to attain the ordered state at 500°C for 96 hr after quenching again from 1000°C . Then the second-run measurement was done as shown by the curve *b*. The third- and fourth-run measurements were successively made on the specimen annealed for 480 and 2900 hr at 500°C , respectively. The results are drawn by the curves *c* and *d*. An appreciable amount of heat absorption is observed on both the curves, indicating a fairly high degree of order obtained by the pre-treatment. The critical temperature of the order-disorder transformation is estimated to be about 590°C from the location of the peak in the curves *c* and *d*.

The heat absorption (E) evaluated from these measurements is plotted against annealing time in Fig. 2. The energy tends to reach a saturated value of about $1000 \text{ cal/g}\cdot\text{atom}$ after annealing as long as 2900 hr,

which is thought to be the heat of transformation (E_0) of Ni_2Cr . The ordering at 500°C seems to be a first-order reaction from a linear relation between $\ln\{(E_0 - E)/E_0\}$ and the annealing time, as depicted in this figure.

Fig. 1 Specific heat curves of 32.1% Cr alloy. The alloy was initially quenched from 1000°C (a), then annealed at 500°C for 96 hr (b), 480 hr (c) and 2900 hr (d)

Fig. 2 Heat absorption against time of isothermal annealing at 500°C

The entropy of transformation is evaluated as $1.2 \text{ cal/g}\cdot\text{atom-deg}$ from the calorimetric measurement of the alloy annealed for 2900 hr. The change in configurational entropy $\Delta\Phi$ from the perfect order to the random distribution of the A_2B superlattice is theoretically given as

$$\begin{aligned} \Delta\Phi &= R \left(\ln 3 - \frac{2}{3} \ln 2 \right) \\ &= 1.26 \text{ cal/g}\cdot\text{atom-deg}, \end{aligned} \quad (1)$$

where R is the gas constant. Consequently, there is an excellent agreement between the experimental value and calculation.

2. Ordered structure of Ni_2Cr

Electron diffraction studies and electron microscopic

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observations of fully annealed specimens were carried out in order to investigate the crystal structure and the ordered domains. The diffraction patterns of Photos. 1 (a), (b) and (c) (33.3 at% Cu) show many superlattice reflections in the three reciprocal planes (001)_c, (110)_c and (112)_c of the original *fcc* lattice, respectively. These patterns can be interpreted in terms of the superstructure of the Pt₂Mo type illustrated in Fig. 3. Figs. 3 (a) and (b) show the atomic arrangement and the reciprocal

only a single variant. In the (112)_c reciprocal plane (Photo. 1 (c)), there are three variants.

Microscopic configurations of the ordered domains were examined by means of the dark-field image technique. A dark-field micrograph of the (110)_c orientation shown in Photo. 2 (b) (33.3 at% Cr) was formed by a superlattice spot (1/3 1/3 1). A number of small bright regions are the ordered domains with the same orientation. Since the ordered domains have six equivalent

Photo. 1 Electron diffraction patterns of 33.3% Cr alloy annealed at 500°C for 1600 hr. (a), (b) and (c) correspond to (001)_c, (110)_c and (112)_c orientations, respectively. Schematic illustration is given in Fig. 4

Fig. 3 (a) Ordered structure of Ni₂Cr. Broken lines indicate the original *fcc* cell

lattice of the ordered alloy Ni₂Cr, respectively. The crystallographic relationships of the orientation between the ordered orthorhombic lattice and the disordered cubic lattice are given as follows :

$$\begin{aligned} \{100\}_r // \{110\}_c \\ \{010\}_r // \{1\bar{1}0\}_c \end{aligned} \quad (2)$$

and

$$\{001\}_r // \{001\}_c,$$

where suffixes *r* and *c* refer to the orthorhombic and cubic lattices, respectively. This relationship consists with the results obtained from the X-ray study of Bagariatskii and Tiapkin⁽²⁾. It is interesting to note that there are six possible orientations equivalent with the above relation. As illustrated in Fig. 4, therefore, the superlattice spots observed in the (001)_c reciprocal plane (Photo. 1(a)) consist of those from two different variants, whereas those in the (110)_c reciprocal plane (Photo. 1(b)) come from

Fig. 3 (b) Reciprocal lattice of Ni₂Cr, showing a single orientation of superlattice by thin lines. Full and shaded circles are the fundamental and superlattice spots, respectively

orientations, the bright regions in this picture correspond merely to one sixth of the existing domains, but the domains with other five orientations are not excited. The ordered regions with two different orientations can actually be recognized in the dark-field images formed by superlattice spots in the (112)_c reciprocal plane. Photos. 3 (b) and (c) were the dark-field micrographs formed by the superlattice spots of (1/3 1/3 1)_c and (2/3 2/3 0)_c,

Fig. 4 (a), (b) and (c) are the reciprocal lattice planes of $(001)_c$, $(110)_c$ and $(112)_c$, respectively. Open circles, shaded circles, triangles and squares are the superlattice spots with different orientations. Full circles are the fundamental spots

Photo. 2 Electron micrographs of 33.3% Cr alloy with $(110)_c$ orientation, annealed at 460°C for 1600 hr after quenching from 1000°C
(a) : Bright-field image
(b) : Dark-field image formed by $(\frac{1}{3} \frac{1}{3} 1)_c$ spot

respectively. Different regions are excited in these photographs, since the two reflections arise from the ordered regions with different orientations as illustrated in Fig. 4(c). It is noticed in the electron micrographs of Photos. 2 and 3 that the ordered domains are as small as about $500 \text{ \AA}$, even after a prolonged ordering treatment, and the boundaries do not seem to be restricted to any particular crystallographic planes. These domains give rise to irregular diffraction contrasts in bright-field images as seen in Photos. 2(a) and 3(a). The findings

Photo. 3 Electron micrographs of 33.3% Cr alloy with $(112)_c$ orientation. Heat-treatment is the same as in Photo. 2. (a) : Bright-field image, (b) and (c) : Dark-field images formed by $(\frac{1}{3} \frac{1}{3} 1)_c$ and $(\frac{2}{3} \frac{2}{3} 0)_c$ spots, respectively

just described are also obtained on the other specimens with 32.9 and 35.2 at% Cr.

The lattice constants of the alloys with 33.3 and 35.2 at% Cr were measured by an X-ray diffraction technique for both the ordered and disordered states as listed in Table 1. The lattice contraction due to ordering is noted

here. Since neither rhombic splitting nor broadening of the diffraction lines could be detected in the fully annealed state, the lattice parameter of the ordered alloy is given in terms of the original cubic coordinate.

Table 1 Lattice constants of the cubic cell (Å)

Composition (at% Cr)	Disordered state		Ordered state	
33.3	3.566	Quenched from 1000°C	3.562	Annealed at 460°C for 3200 hr
35.2	3.569		3.560	485°C for 670 hr

Photo. 4 Electron-diffraction pattern (a) and bright-field image (b) of 33.3%Cr alloy annealed at 500°C for 48 hr after quenching from 1000°C. Arrows in (a) indicate diffuse scatterings

3. Isothermal ordering around 500°C

Referring to the resistivity change measured at liquid-nitrogen temperature, various stages of isothermal ordering near 500°C were studied by means of electron microscopy and electron diffraction. As shown in Fig. 5 (a), the electrical resistivity first increases slightly (the *K*-state) and then decreases with increasing annealing time in agreement with the previous works⁽¹⁾⁽⁶⁾. Superlattice spots were hardly observed up to an annealed state corresponding to the end of the plateau of resistivity curves. In the *K*-state, however, the fundamental spots are accompanied by weak diffuse scattering parallel to $\langle 110 \rangle$ directions, and irregular tweed contrasts appear in the bright-field image, as shown in Photos. 4 (a) and (b), respectively. These phenomena may be a manifestation of lattice modulation or distortion due to the initiation of ordering from the disordered state, as in the case of CuAu⁽¹³⁾. In comparison with the latter system, however, no superlattice reflections could be observed in Ni₂Cr, probably because of the close scattering factors of the constituent elements.

Changes in hardness and yield strength of the alloy of 35.2 at% Cr are plotted against annealing time at 485°C in Fig. 5 (b). The alloy becomes hardened considerably after keeping for more than about 100 hr, but only a small increase in strength occurs in the *K*-state. It was observed that the stress-strain curves for the disordered and ordered states are almost parallel after yielding, indicating that the hardening rate is scarcely affected by the atomic ordering. These results are consistent with

those of previous workers⁽¹⁾⁽⁶⁾⁽¹⁰⁾.

4. Superdislocations

Electron microscopy revealed the existence of triple superdislocations, though not so frequent, in various stages of ordering. The electron micrographs of Photos. 5 (a) and (b) exhibit triple superdislocations observed in the alloy, 32.1 at% Cr, annealed for 48 hr and in the alloy, 33.3 at% Cr, annealed for 2400 hr at 500°C, respectively. It is noticed in Photo. 5 (a) that the separation between the first and second dislocations (r_1) is larger than that between the second and third ones (r_2).

Fig. 5 (a) Changes in electrical resistivity at -196°C during isothermal annealing after quenching from 1000°C . Curves (a) and (b) correspond to the alloys of 32.1 and 35.2% Cr annealed at 500°C and 485°C , respectively

The values of r_1 and r_2 in this electron micrograph are estimated to be about 1000 and 400 Å, respectively. In Photo. 5 (b), the separations seem to be nearly equal in each group, ranging between 200 and 700 Å. Triple dislocations were also observed in the 35.2 at% Cr alloy annealed for more than 710 hr. In this case, the spacings are of an order of magnitude of a few hundred Å, which seems relatively large in comparison with the stoichiometric alloy. However, the occurrence of triple

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Fig. 5 (b) Changes in hardness and yield strength of 35.2% Cr alloy with annealing time at 485°C after quenching from 980°C

Photo. 5 Superdislocations in Ni_2Cr , annealed at 500°C for 48hr (32.1% Cr) (a), and for 2400 hr (33.3% Cr) (b)

dislocations is rather seldom, and most of the observed dislocations in the ordered state were single dislocations.

IV. Discussion

The theory of Shtremel⁽¹¹⁾ based upon the Bragg-Williams approximation gives the following relations among the ordering energy $v (=v_{AA} + v_{BB} - 2v_{AB})$, the transition temperature T_c , and the heat of transformation E_0 for the stoichiometric alloy A_2B , i.e.

$$\left. \begin{aligned} k T_c &= 0.68 v \\ E_0 &= \frac{v}{3} \end{aligned} \right\} \quad (3)$$

where k is the Boltzmann constant. Consequently if we take $T_c = 863^\circ\text{K}$ from the experiment, the heat of transformation E_0 will be 840 cal/g·atom, which is somewhat smaller than the observed value (~ 1000 cal/g·atom). The ordering energy v is evaluated roughly as 2.5~3.0 kcal/g·atom.

According to the theory, the transformation of the stoichiometric A_2B alloy is of a first order accompanied by a latent heat $\Delta S^2 E_0$ at the critical point, where ΔS (≈ 0.3) is the decrement in the degree of long-range order at this temperature. Thus, in this case, the latent heat of the order of 80 cal/g·atom would appear. It may practically be impossible, however, to detect such a minor quantity of the latent heat by means of the heating calorimeter because of the extremely slow reaction of this transformation.

Next specific features of the ordered domain structure

and of the superdislocation will be discussed. As mentioned before, the orthorhombic phase with six different orientations will be formed from the original cubic solid solution during the ordering process. Further there should be three kinds of ordered domains for each of these orientations, because the superlattice of Ni_2Cr can be resolved into three sublattices of the body-centered orthorhombic cell. Therefore, eighteen kinds of ordered domains are formed, thus creating numerous types of anti-phase boundaries at the interfaces of these domains. As shown in Photos. 2 and 3, the size of domains does not exceed 1000 Å even in the fully annealed state, which is slightly smaller than the estimate (~ 1200 Å) from the line width of neutron diffraction patterns by Goman'kov

et al.⁽³⁾

The spacings of triple dislocations have been calculated by Popov and Kozlov⁽⁹⁾ as a function of energy γ of anti-phase boundaries left behind after the movement of the dislocations, i.e.

$$\left. \begin{aligned} r_1 &= \frac{\sqrt{3} G b^2}{2 \pi x \gamma} \\ r_2 &= \frac{\sqrt{3} G b^2}{2(1 + \sqrt{3}) \pi x \gamma} \end{aligned} \right\} \quad (4)$$

where G is the rigidity modulus, b is the Burgers vector and x is equal to $(1 - \nu)$ for pure edge dislocation and 1 for pure screw dislocation (ν is the Poisson's ratio). In the case of a perfect order, the boundary energy is given as,

$$\gamma = \frac{1}{9} N' Z' v \quad (5)$$

where N' is the number of atoms per unit area in the slip plane, Z' is the number of nearest neighbors at an atom in a neighboring plane. Taking the ordering energy as $v = 2.5$ kcal/g·atom and putting in all the necessary values, γ is obtained as about 110 ergs/cm². Substituting this value in eq. (4), we will obtain 120 and 50 Å for the spacings r_1 and r_2 for screw dislocations, respectively. These values are smaller than the observation of Photo. 5. The fact that the spacings in an early stage of ordering (Photo. 5 (a)) or in the off-stoichiometric alloy are considerably larger than the calculation is qualitatively explained as follows. The boundary energy is reduced if the atomic order is imperfect. Furthermore, as

suggested by Popov et al.⁽⁹⁾, it may be reasonable to replace γ by $\gamma/3$ in eq. (4) if the domain size is considerably small in comparison with the spacings of dislocations, since merely one third of the anti-phase domains are responsible for the interaction with dislocations. Therefore, the spacings of superdislocations are increased in the imperfectly ordered state.

As mentioned before, no rhombic distortion other than the lattice contraction appears upon ordering, so that the lattice strain induced at the domain boundaries seems to contribute to the strengthening to relatively minor extent. The fact that the work-hardening rate of Ni_2Cr is not appreciably affected by the ordering is consistent with the electron-microscopic observation that most dislocations move separately even in the ordered state. Therefore the major part of the large increment in strength of the ordered alloy Ni_2Cr may be attributed to the formation of anti-phase boundaries left behind after the moving of single dislocations⁽⁹⁾.

V. Summary

The observed results on the nature of the ordered alloy Ni_2Cr will be summarized as follows :

(1) The formation of the superstructure of the Pt_2Mo type was revealed by electron diffraction, but the anti-phase domains existing even in the fully annealed state were as small as less than 1000 Å.

(2) The heat of transformation was evaluated as about 1.0 kcal/g·atom. The entropy change obtained was 1.2 cal/g·atom-deg, in good agreement with the calculated configurational entropy.

(3) Triple superdislocations were observed in various stages of ordering, and the separations between dislocation lines were generally larger than the values evaluated from the ordering energy which was obtained from the calorimetric measurement.

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Note added in proof : Recently Vintaikin and Vlasova (Sov. Phys.-Doklady, **13** (1969), 1066) observed diffuse scattering along the $\langle 110 \rangle$ directions around the fundamental reflections in X-ray patterns of a single crystal of 34.5 at% Cr.