EXPERIMENTAL RESEARCH ON SUPERLATTICES IN IRON-CHROMIUM SYSTEM*

Shuzo TAKEDA and Naoki NAGAI

Department of Metallurgy

(Received on 16 May, 1956)

Synopsis

By means of microscopic observation, thermo-magnetic, dilatometric and X-ray analyses, as well as measurements of specific heat and electric resistance at elevated temperatures, hardness, electric resistance and intensity of magnetization at room temperature, etc., the formations of superlattices as well as of compound in Fe-Cr system were systematically investigated. And it was discovered that there are formed three metastable ferromagnetic superlattices, Fe_3Cr (α'_{3-1}), FeCr (α'_{1-1}) and $FeCr_3$ (α'_{1-3}), and also two meta-compounds, Fe_2Cr (τ-phase) and $FeCr_2$ (ω-phase), besides the well-known stable nonmagnetic compound, σ-phase. σ-phase is formed from disordered α solid solution at higher temperatures near 800°. Whlie, superlattice α'_{1-1} can be formed for once from the supercooled α-phase at lower temperatures near 500° by prolonged annealing, but finally transforms into σ-phase by further annealing. From these results, it was concluded that the superlattice FeCr (α'_{1-1}) is a metastable and intermediate phase between the disordered solid solution α and the stable compound σ.

I. Introduction

Many investigations[1]−[4] on the equilibrium diagram of iron-chromium system have been carried out hitherto, but none has referred to the existence of superlattices in this system. It was discussed formerly whether the σ-phase (FeCr), formed from the α-phase in the narrow composition range centered at $50_{at.}\%$ Cr, was an intermetallic compound or a superlattice; Dehlinger[5] and Monypenny[6] regarded the σ-phase as a nonmagnetic superlattice. It is now, however, doubtless that this phase is a nonmagnetic intermetallic compound, and some reseaches on its crystal structure also have recently been reported. The superlattices dealt with in the present paper are, of course, not this stable nonmagnetic compound σ-phase, but other metastable ferromagnetic superlattices, which are formed from the supercooled α-phase by prolonged annealing at about 500°, preventing the formation of the σ-phase.

The so-called 475°C (885°F)-embrittlement in high chromium stainless steels has long been in question in every country.[7]−[13]   Also, soon after the Second World War, the embrittlement and the decrease in electric resistance in Fe-Cr-Al electric resistance alloys by prolonged annealing at about 500° were discussed in this country.[14][15]   The cause of these phenomena, however, has not yet been elucidated till now, for which merely the precipitation of either σ-phase, chromium carbide or oxide has been proposed.

On the other hand, Adcock[16] reported in 1931 that magnetic transformation points of Fe-Cr binary alloys containing 30 to 70% Cr were changeable according to the modes of heat-treatment.   From this result the present authors intuited that any superlattice might be formed in Fe-Cr system and it might be the chief cause of these phenomena above mentioned.

So, with the object of realising this intuition, the authors carried out a systematic research on superlattices in Fe-Cr system, and found, as was expected, that besides the σ-phase there are formed in this system three ferromagnetic superlattices, named α'_{3-1} (Fe$_3$Cr, 23.6% Cr), α'_{1-1} (FeCr, 48.8% Cr) and α'_{1-3} (FeCr$_3$, 73.7% Cr), respectively, by the present authors, as well as two meta-compounds, named τ-phase (Fe$_2$Cr, 31.7% Cr) and ω-phase (FeCr$_2$, 65.1% Cr), respectively, also by them. This paper is concerned with the summarized results of the experimental research on these superlattices, which were read in eight reports[17] at the lecture-meetings of the Japan Institute of Metals in 1949~1952.

II. Formations of Compound σ-Phase as well as of Superlattice α'

Before detailing the experimental deta, the main results of this research will be described ahead.

II-1. $\alpha \rightleftarrows \sigma$ Transformation Points

As $\alpha \rightarrow \sigma$ transformation points in Fe-Cr system are markedly affected by minute impurities, those reported are diverse with investigators.   So, the present authors reexamined the formation of σ-phase in this system by means of microscopic observation of quenched specimens and dilatometric analysis, etc., through which the equilibrium diagram as shown in Fig. 1 was obtained.

σ-phase is an intermediate solid solution of nonmagnetic compound FeCr ranging from about 40 to 60% Cr, formed by $\alpha \rightarrow \sigma$ allotropic transformation or precipitation change, whose transformation points show a maximum at 900° at the equiatomic composition FeCr, falling in alloys with either higher or lower chromium contents.

II-2. Velocity of $\alpha \rightarrow \sigma$ Transformation

Fig. 2 illustrates the intensity of magnetization at room temperature versus annealing time in practically pure Fe–Cr binary alloys with 45 to 50% Cr as well as those with 45% Cr containing impurities of 0.5% Si and 0.5% Al, respectively, annealed at 850° (except at 750° in the case of Al-containing specimen) immediately below the $\alpha \rightarrow \sigma$ transformation points.   As seen from the decrease in intensity of magnetization which denotes the formation of nonmagnetic compound σ-phase, the velocity of $\alpha \rightarrow \sigma$ transformation is so sluggish that the σ-phase is formed little by little on prolonged annealing at higher temperatures just below the transfor-
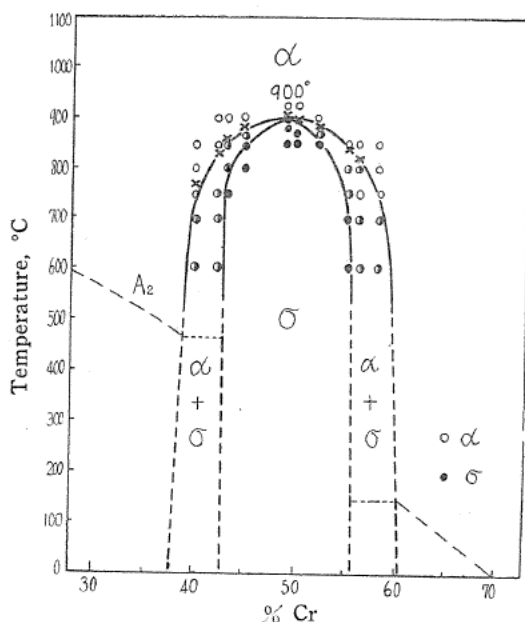
FIG. 1. Stable equilibrium diagram of
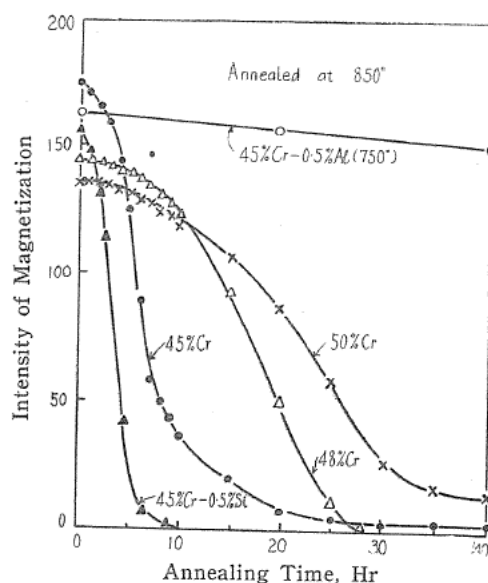Fe-Cr alloys.

FIG. 2. Behaviour of $\alpha \to \sigma$ transfor-
mation by annealing.

mation points, and hence it is hardly formed at lower temperatures.   Here, Si ex-
isting as minor impurities in Fe-Cr alloys hastens the formation of σ-phase, but Al
retards it markedly.

*II-3. Behaviour of Formation of Superlattices, Fe₃Cr (α'_{3-1}), FeCr (α'_{1-1}) and
FeCr₃ (α'_{1-3}), as well as Meta-Compounds, Fe₂Cr (τ) and FeCr₂ (ω)*

As above mentioned, $\alpha \to \sigma$ transformation takes place so slowly that quenching
from temperatures above 900° allows α-phase to be supercooled entirely to room
temperature.   As will be discussed later, however, on annealing this supercooled
α-phase at lower temperatures near 500° for about 100 hr, there are formed, in-
stead of σ-phase, three ferromagnetic superlattices, Fe₃Cr (α'_{3-1}), FeCr (α'_{1-1}) and
FeCr₃ (α'_{1-3}), according to the composition of alloys.   All these ordered phases are
partly formed even on furnace-cooling, though they may be imperfectly ordered.
Moreover, they again come back to the disordered solid solution α-phase on heat-
ing them to temperatures above 650°; these phenomena prove that there occurs a
reversible change, α (disorder) $\rightleftarrows \alpha'$ (order), at lower temperatures near about 600°.

After all, it is a rare and noticeable example that there occur in an alloy of
the same composition near FeCr, two transformations, $\alpha \rightleftarrows \sigma$ at higher temperatures,
while $\alpha \rightleftarrows \alpha'_{1-1}$ at lower temperatures; in this case, it was concluded that σ is a
stable phase while superlattice α'_{1-1} a metastable one, considering from remarkable
discrepancy in their transformation or decomposition temperatures.

Besides the superlattices, α'_{2-1}, α'_{1-1} and α'_{1-3}, there are also formed two meta-
compounds, Fe₂Cr (τ-phase) and FeCr₂ (ω-phase), that is, the intermediate phases

between compound and superlattice phase, in alloys of the respective neighbouring stoichiometric compositions, on annealing the supercooled α at about 500°.

II-4. $\alpha \rightleftarrows \alpha'$ Transformation Points (T_c)

Fig. 3 illustrates α (disorder) $\rightleftarrows \alpha'$ (order) transformation points (T_c), that is, the formation or decomposition temperatures of the respective superlattices, Fe_3Cr (α'_{3-1}), $FeCr$ (α'_{1-1}), $FeCr_3$ (α'_{1-3}) and metacompounds, Fe_2Cr (τ), $FeCr_2$ (ω), obtained by measurements of specific heat and electrical resistance at elevated temperatures as well as dilatometric and magnetic analyses, etc., which corresponds to the metastable equilibrium diagram of this system, so far as concerning $FeCr$ (α'_{1-1}). The stable equilibrium diagram, in which σ-phase is formed, is added in dotted lines.
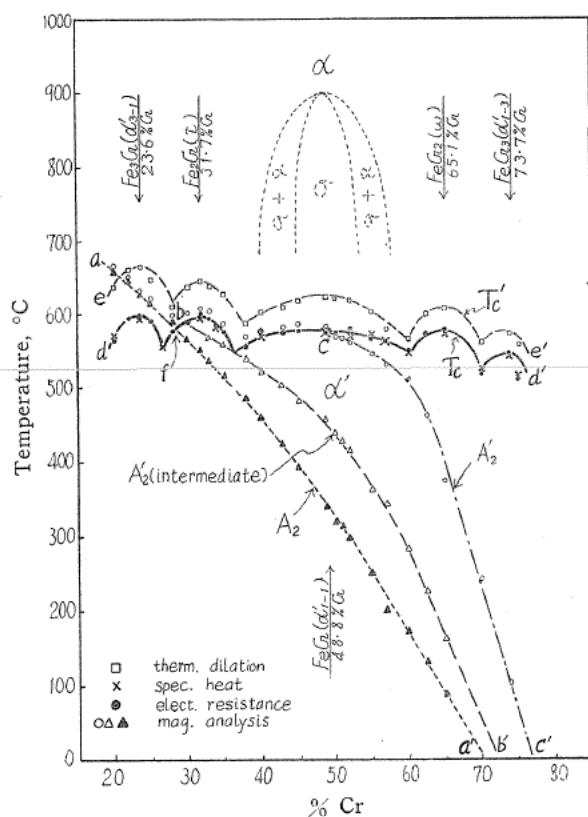

FIG. 3. Metastable equilibrium diagram of Fe-Cr alloys.

Curve *dfbcd'* (full-lined) denotes T_c points, that is, the temperatures of transformations, α (disordered solid solution) $\rightleftarrows \alpha'_{3-1}$, α'_{1-1} or α'_{1-3} (superlattice of long range order) and $\alpha \rightleftarrows \tau$ or ω (meta-compound), while curve *ee'* (broken-lined) those of transformation $\alpha \rightleftarrows \alpha'$ (superlattice of short range order), named T_c' points by the present authors. These T_c points show five peaks at the respective stoichiometric compositions corresponding to Fe_3Cr (α'_{3-1}), Fe_2Cr (τ), $FeCr$ (α'_{1-1}), $FeCr_2$

(ω) and FeCr$_3$ (α'_{1-3}), slightly declining in both sides with higher and lower Cr contents.

Curve afa' (partly chain- and the rest dot-lined) denotes the Curie magnetic critical points (A$_2$) of α solid solution disordered obtained by water-quenching, while curve cc' (chain-lined) those of superlattices of perfect long range order, α'_{1-1} and α'_{1-3}, obtained by extraordinarily slow cooling, which were named A$'_2$ points by the present authors. Here, curve fbc, a part of T$_c$ curve $dfbcd'$, denotes also the magnetic critical points of superlattice α'_{1-1}, though they are not pure Curie points A$'_2$, caused by the appearing or disappering of ferromagnetism accompanied by the transformation, disordered α (paramagnetic) $\rightleftarrows$ ordered α'_{1-1} (ferromagnetic).

Moreover, curve bb' (broken-lined) represents the A$''_2$ (intermediate) points, that is, the magnetic critical points of superlattice of intermediate ordering, α' (intermediate), obtained by furnace-cooling.

III. Preparation of Specimens

The materials used in this research were electrolytic iron, metallic chromium and a mother alloy containing 57.42% Cr, vacuum-melted in high frequency induction furnace. The alloys were melted in a high alumina tube in Tammann furnace and then cast in a cylindrical form (5 mm in dia. and 210 mm in length) by the aid of an iron mould. They were annealed in vacuum for 1 hr at 1200° to remove the dendritic structures. The compositions of specimens thus prepared were at intervals of about 2% Cr within the range from 20 to 75% Cr, besides the respective stoichiometric compositions, Fe$_3$Cr, FeCr and FeCr$_2$. Their carbon content may be assumed to be less than 0.05%. In addition, specimens of other appropriate forms were prepared for X-ray analysis, measurements of specific heat at elevated temperatures and magnetization curves, etc., respectively.

IV. Measurement of Magnetic Properties

IV-1. Thermo-Magnetic Analysis

In 1931, F. Adcock[16] discovered that the magnetic transformation points of Fe-Cr binary alloys were changeable according to the modes of heat-treatment, as shown on two curves in Fig. 4; he found that alloys containing 30 to 70% Cr quenched from the temperatures ranging from 550 to 650°, which he called "lowering range," showed magnetic transformation points (the lower curve) lower than those (the upper one) of alloys cooled slowly, the differences between them amounting to about 100°. He considered that the upper magnetic transformation points were the normal ones of α-phase, though he did not refer to the reason of their lowering by quenching. There have been no studies on this phenomenon till now.
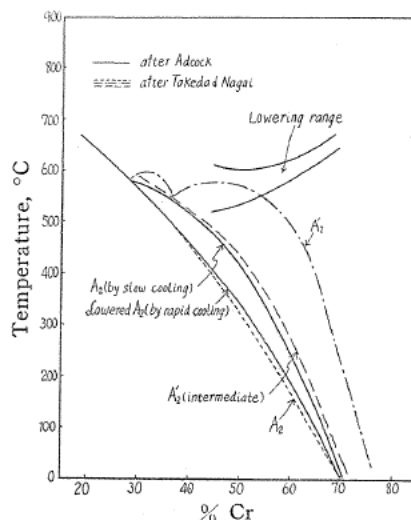

FIG. 4. Magnetic transformation points of Fe-Cr alloys after adcock.[16]

Such an anomaly let the authors suspect the existence of superlattice. Because, if any ferromagnetic superlattice is formed even imperfectly during slow cooling, the rise of magnetic transformation point may be naturally expected. At the first place, therefore, an alloy with 48.86% Cr (nearly stoichiometric composition of superlattice FeCr, α'_{1-1}) was quenched into water after heating for 1 hr at 1000°, so as to prevent the formations of σ-phase as well as superlattice, and then the magnetic analysis was carried out till 600°. Just as was expected, the result showed the anomaly that the magnetic transformation point on cooling from 600° was higher by 60° than that on heating, as shown in Fig. 5-(a), whereas no microstructural change was observable before and after heating. Such an anomaly was recongnized over the composition range from 30 to 70% Cr.
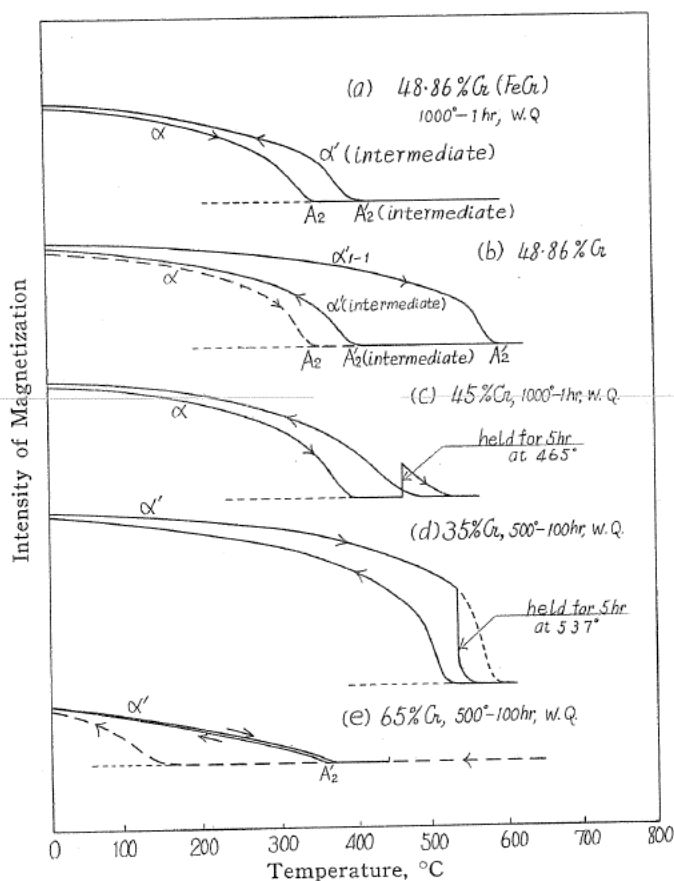

FIG. 5. Thermo-magnetic curves.

So, contrary to F. Adcock's interpretation, the authors regarded the lower magnetic transformation point as that of disordered α-phase (A₂ point) and the upper one as that raised by a ferromagnetic superlattice, which was formed at about 500° and named α'-phase by the present authors. That is to say, a disordered α-phase stable at higher temperatures transforms into a ferromagnetic superlattice α' at lower temperatures, and the magnetic transformation point of the latter phase,

which was called A_2' point by the present authors in order to distinguish from A_2 point, is higher than that of the former (A_2 point).

Thus, a drastic quenching is necessary to maintain the disordered α-phase, whereas heating at $800{\sim}900°$ may cause to form the stable nonmagnetic compound σ-phase. Consequently, such a heat-treatment as water-quenching after heating for 1 hr at $1000°$, was adopted to obtain a perfectly disordered α-phase. It was confirmed with X-ray analysis and others that by such a treatment, α-phase could be supercooled down to room temperature avoiding both changes, $\alpha \rightarrow \sigma$ and $\alpha \rightarrow \alpha'$. The A_2 points of specimens consisting of disordered α-phase obtained by such a treatment were remeasured (with heating rate of $5°/min$), which are shown on curve afa' in Fig. 3, nearly coinciding with the lower one of Adcock's Curie curves, as compared in Fig. 4.

On the other hand, the magnetic transformation points of alloys cooled in furnace from $1200°$ are shown on curve bb' in Fig. 3, also agreeing nearly with the upper one of Adcock's curves, as compared in Fig. 4. That is to say, during slow cooling in furnace, ordering takes place to some extent, leading to the rise of magnetic transformation point, which is proved by many experimental facts described later. However, as such an ordering is imperfect, curve bb' indicates only the magnetic transformation points of alloys ordered imperfectly or intermediately, that is, A_2' (intermediate).

It is, therefore, necessary for perfect ordering to anneal for much prolonged time at about $500°$, or to cool extremely slowly through this temperature range. Thus, the A_2' points, i.e., the magnetic transformation points of ferromagnetic superlattice, α'-phase, were measured in alloys cooled very slowly from $650°$ to room temperature taking a week in order to complete an ordering, which are shown on curve $fbcc'$ in Fig. 3. As seen on curves afa', bb' and $fbcc'$, the magnetic transformation points are raised markedly by complete ordering within the composition range from 30 to 75% Cr.

That no rise of magnetic transformation points is observable over the composition range from 20 to 30% Cr near Fe_3Cr (α'_{3-1}), is ascribed to the fact that $\alpha' \rightarrow \alpha$ transformation points or so-called T_c points of these alloys lie at so lower temperatures than the A_2 points or magnetic transformation points (curve af) of disordered α-phase that true A_2' points can not be detected. Also, in alloys of the composition range from τ-phase to α'_{1-1}, the true A_2' points are not detectable, but, in these cases, the magnetic critical points of superlattice α' of some intermediate ordering are observable at temperatures corresponding to the T_c points, which are shown on curve fbc in Fig. 3. Because, at these T_c points, there occurs, during heating, a superposition of the two changes, a disintegration of superlattice and a disappearance of ferromagnetism, which is recongnizable from the reaction, ordered α' (ferromagnetic) $\rightleftarrows$ disordered α (paramagnetic). Such a phenomenon is just like the magnetic transformation at the A_{3-2} points of steels containing 0.4 to 0.9% C.

Consequently, the true A_2' points of α' perfectly ordered are observable only in alloys containing more than about 48% Cr, which are shown on curve cc' in Fig. 3, being below their T_c points (curve cd' in Fig. 3).

On an alloy, for an example, with 48.86% Cr corresponding to FeCr, magnetization-temperature curve of disordered α (heating curve in dotted line) is compared with that of perfectly ordered α'_{1-1} (heating curve in full line), as shown in Fig. 5-(b), in which about $200{\sim}250°$ rise of magnetic transformation point, as well as

an increase in intensity of magnetization at room temperature, accompanied by ordering, become clear at a glance.

Furthermore, an interesting behaviour on an alloy with 45% Cr is shown in Fig. 5-(c). As this magnetic analysis began with disordered α obtained by heating for 1 hr at 1000° and subsequent water-quenching, it becomes for once paramagnetic at 390°, its A_2 point; during further heating, however, on holding for 5 hr at 465°, which is the suitable temperature for ordering, it becomes again ferromagnetic in consequence of forming α'_{1-1} to some extent. Again, on further heating, the magnetic transformation point corresponding to the ordering formed in this condition appears at 525°, though the T_c-A'_2 point of this alloy perfectly ordered is 570~580°. Moreover, as it is heated to 570°, the superlattice is decomposed mostly but not perfectly, and so the magnetic transformation point on cooling is lower than that on heating, but considerably higher than its A_2 point.

Another example on an alloy with 35% Cr, opposite to that above mentioned, is shown in Fig. 5-(d). As it is heated from perfectly ordered α' obtained by annealing for 100 hr at 500°, but held for 5 hr at 537° during heating, its ferromagnetism disappears mostly, as shown on full line, owing to most decomposition of superlattice, which has taken place by heating to the temperature near its T_c point (580°). In addition, on continuous heating at the rate of 10°/3 min, it behaves as shown on dotted line; in this case, the magnetic critical point coincides with its Tc and A'_2 point.

Fig. 5-(e) shows other beaviours of magnetization-temperature curves of perfectly ordered state on an alloy with 65% Cr annealed for 100 hr at 500°; the cooling curve on full line and that on dotted line have different maximum heating temperatures with each other, 450 and 650°, respectively, that is, below and above the T_c point of this alloy. In the former case, the cooling curve is nearly equal and reversible to the heating one, owing to no decomposition of superlattice. On the other hand, in the latter case, the superlattice α' is decomposed perfectly on heating, but it is again formed reversibly on cooling only to some intermediate ordering according to the quickness of cooling rate, and hence the magnetic Curie point appears at 140°, being lower than its A'_2 point, 380°.

From the phenomena above mentioned, in particular, the rise of magnetic transformation point by furnace-cooling, and also from various experimental facts, which will be described later, it is proved that the superlattice may be formed easily to some extent (probably to short range order), but it is necessary for perfect ordering to anneal at least for 50 hr at about 500° in any case of α'_{3-1}, α'_{1-1} and α'_{1-3}.

IV-2. Magnetic Transformation Points and Other Properties of Superlattice Phases vary with their Ordering Degree

From the experimental results above mentioned, it may be inferred that magnetic transformation points of alloys containing 30 to 70% Cr vary with modes of heat-treatment, that is, not only cooling rate, but also heating temperature as well as time. For an example, in Fig. 6 there are compared the heating curves in theromo-magnetic analysis on an alloy with 45% Cr, annealed for 50 hr at various temperatures, i.e., 420° (curve a), 465° (curve b), 480° (curve c), 500° (curve d), 515° (curve e), 530° (curve f), 550° (curve g), 575° (curve h), 600° (curve i) and 630°, 650°, 1000° (curve j), below and above its T_c point (570°) and subsequently water-quenched after previous heating for 1 hr at 1000° with subsequent water-
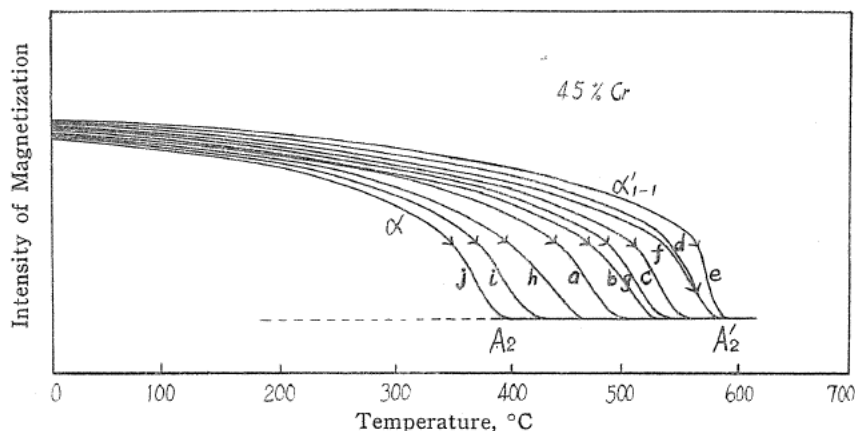
FIG. 6. Thermo-magnetic curves.

quenching. It is seen that magnetic transformation points vary nearly continuously within temperature range between A_2 point (390°) of disordered phase (α) and A_2' point (585°) of superlattice phase of long range order (α_{1-1}').

This aspect is shown in another expression on curve *aejl* in Fig. 7-(a), where observed magnetic transformation temperature and estimated ordering degree are plotted versus annealing temperature. It is seen that magnetic transformation temperature A_2' of ferromagnetic superlattice α' varies in proportion to its ordering degree. In this case, the alloy annealed at 515° (*e*) has a maximum A_2' point due to a maximum ordering degree, while alloys annealed at lower and higher temperatures than that show lower A_2' points due to retardation and decomposition of ordering, respectively; and it shows the normal A_2 point of α-phase only on heating above its T_c' point, which was proposed by the present authors to be the transformation point at which locally ordered superlattice changes completely into disordered phase, as will be described later.
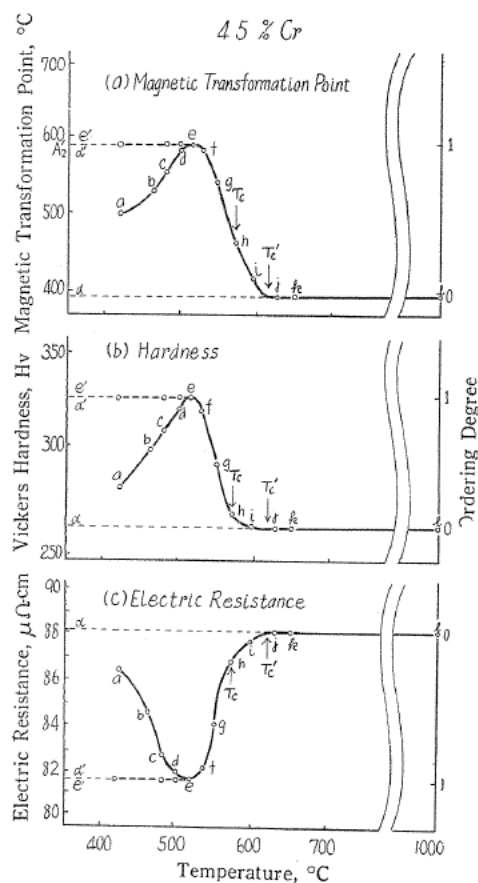

FIG. 7. Change of properties with annealing temperature.

In addition, the dotted line shows a magnetic transformation points of alloys annealed down accumulatively for 50 hr at the respective temperatures below 515° (*e*); in this case, the magnetic transformation point rises as the ordering degree increases gradually with lowering of annealing temperature, as shown on curve *jee'* in Fig. 7·(*a*).

Simultaneously, the analogous changes were observed also in hardness and electric resistance, which are shown in Fig. 7·(*b*) and -(*c*), respectively; there occur gradual increase in hardness and decrease in electric resistance as the ordering proceeds.

Thus, it is shown that magnetic transformation point and other properties of superlattice phase are not constant but vary gradually with its ordering, that is, the steps of transformation—disorder → short range order → long range order. This fact proves that the order-disorder transformation bears a close resemblance to magnetic transformation of ferromagnetic substance in regard to the gradual change with temperature and also no changes in crystal lattice and concentration; and hence, it should be clearly distinguished from ordinary allotropic change as well as solubility change in solid solution, which are accompanied by changes in crystal lattice and concentration.

Moreover, because A_2' point is considerably higher than A_2 point as stated previously, the intensity of magnetization at room temperature may be expected to increase by ordering. Fig. 8 shows the intensity of magnetization of disordered α versus composition (upper curve) and its increase by ordering (lower curve). It has three peaks on increase in intensity of magnetization at the respective compositions of α'_{2-1}, α'_{1-1} and α'_{1-3}; this supplies the first proof for the existence of these three superlattices in this system. On the contrary, it has a sharp decrease in intensity of magnetization at the composition of Fe_2Cr (τ-phase), while its increase at the composition of $FeCr_2$ (ω-phase) is markedly smaller than those at other compositions, although no decrease is observable.
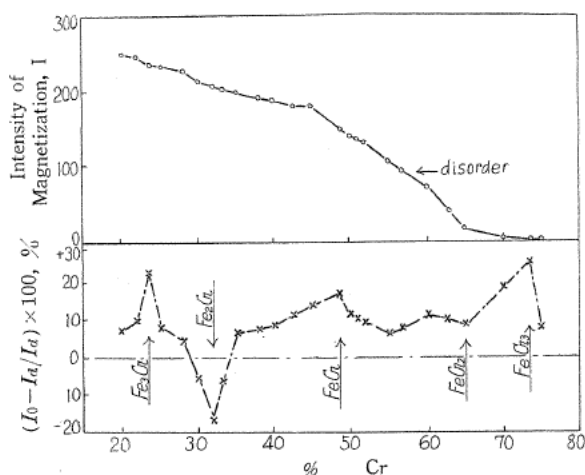

FIG. 8. Intensity of magnetization of Fe-Cr alloys and its change by ordering.

IV-3. Magnetization Curve

For an example, on an alloy with 48.86% Cr corresponding to FeCr, changes of magnetization curve with formation of superlattice are shown in Fig. 9; curve (*a*) corresponds to α-phase obtained by annealing for 1 hr at 1000°, followed by air-cooling, and curve (*b*) to α'_{1-1}-phase obtained by annealing for 50 hr at 500°, followed by furnace-cooling. As was expected, earlier magnetization is disturbed considerably owing to the internal stress sprung up by ordering, just like the case of superlattice FeCo. Owing to insufficiency of magnetic field strength, maximum induction was unable to be measured, but residual magnetism and coercive force measured in field of 70 Oersted, increased to 2.2 and 4.5 times by ordering, respectively.
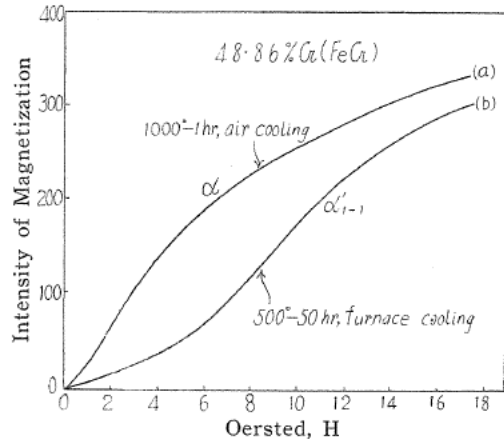

FIG. 9. Magnetization-curves of ordered and disordered states.

V. Thermo-dilatometric Analysis

In order to examine the volume change accompanying $\alpha' \rightleftarrows \alpha$ transformation, and also compare it with that accompaying $\sigma \rightleftarrows \alpha$ transformation, the differential thermal dilation of some alloys was measured, using as neutral body, a 80 Fe-20 Co alloy in the former and a 80 Ni-20 Cr alloy in the latter, respectively.
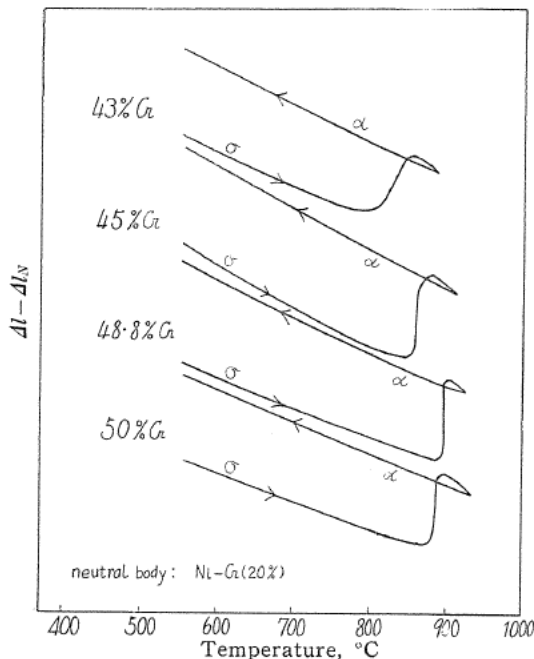
In Fig. 10, some dilation curves for $\sigma \rightarrow \alpha$ transformation are shown on alloys with 43 to 50% Cr, almost σ-nized by previous prolonged annealing at about 800°. On each heating curve (with heating rate of 1°/min), an anomalous expansion due to $\sigma \rightarrow \alpha$ transformation is observable, the ending point of which is plotted as cross in Fig. 1. On cooling curves (with cooling rate of 3°/min), however, no contraction due to $\alpha \rightarrow \sigma$ transformation is observable at all. From these results, it is found that the velocity of $\alpha \rightarrow \sigma$ transformation is so sluggish that no σ-phase is formed on ordinary

FIG. 10. Differential thermal dilation curves.

slow cooling, and hence α-phase is easily and perfectly supercooled to room temperature on such a rapid cooling as water-quenching.

In Fig. 11, some typical dilation curves for $\alpha' \rightleftarrows \alpha$ transformation are shown on alloys containing 20% Cr, 23.6% Cr (Fe₃Cr), 48.8% Cr (FeCr) and 73.7% Cr (FeCr₃), corresponding to the three superlattice phases, α'_{3-1} (curve (a) and (b)), α'_{1-1} (curve (c)) and α'_{1-3} (curve (d)), respectively, obtained by extremely slow cooling from 600°, and also to a disordered phase α (curve (c')), obtained by water-quenching from 1000°.
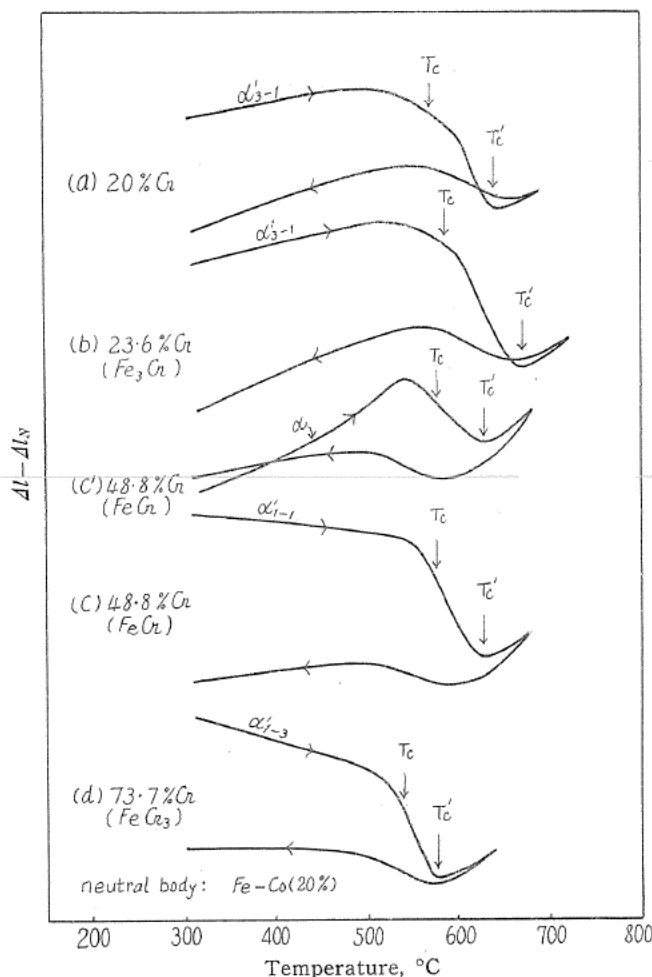

FIG. 11. Differential thermal dilation curves.

On heating curves (a), (b), (c) and (d), there occurs in each case a large anomalous contraction at about 550 to 670°, which is mostly due to the gradual decomposition of the respective superlattice phases, α'_{2-1}, α'_{1-1} or α'_{1-3}, and partially to the decrease in ferromagnetism. On their cooling curves, however, a small expansion is observable, which is probably due to the local or short range ordering,

corresponding to a slight rise of magnetic transformation point on furnace-cooled specimens as mentioned previously.

From these results it is found that the formation of the superlattices in this system is accompanied by a volume expansion, being contrary to a contraction in the case of formation of σ-phase in this system (cf. Fig. 9) or well-known superlattice Fe_3Al. Therefore, as regards the specific volume of these three phases, α, α' and σ, there exists the following relation:—

$$V_{\alpha'} > V_\alpha > V_\sigma$$

This fact has also been confirmed by X-ray analysis and measurement of density.

On curve (c') begun with the disordered state (α), an anomalous expansion caused by ordering (i.e., $\alpha \to \alpha'_{1-1}$) is clearly observable at about 420 to 550°; but its ordering is imperfect owing to the quickness of heating rate (i.e., 2°/min), and hence it is natural that contraction taking place subsequently at higher temperatures than about 550° is smaller in magnitude than that on curve (c) begun with the perfect ordered state (α'_{1-1}). Moreover, comparing the slopes of heating curves (c) and (c'), and also those before and after $\alpha \rightleftarrows \alpha'$ transformation with each other, it is inferred that the expansion coefficient of α'-phase is smaller than that of α-phase.

Now, the T_c points, that is, the temperatures at which the decomposition of superlattice occurs most strikingly, obtained by the measurement of specific heat at elevated temperatures, which will be described later, are inserted on these dilatic heating curves; it is, however, practically hard to point out where the T_c point is on each dilation curve, as such a T_c point is merely situated during the process of anomalous contraction but signifies no characteristic point.

On the other hand, the beginning point of anomalous contraction on each dilatic heating curve regarded as the beginning of decomposition of superlattice does not coincide with the corresponding point on specific heat- or electric resistance-temperature curve, whereas its ending point is not only recognized sharply as the beginning point of the reversible expansion on the cooling curve, but also agrees with the corresponding point on specific heat-temperature curve. Therfore, the present authors named this ending temperature of contraction the T'_c point to distinguish from T_c point, regarding it as the critical temperature at which local (or short range) order $\rightleftarrows$ disorder transformation may occur, which has been inferred also from the results of hardness- and electric resistance-measurements besides those of magnetic and dilatic analyses above mentioned. Curve ee' in Fig. 3 denotes these T'_c points, which are higher about 50° than T_c point at every composition.

Furthermore, the T'_c point and the magnitude of expansion accompanying $\alpha' \to \alpha$ transformation are highest at the respective compositions, Fe_3Cr, $FeCr$ and $FeCr_3$, compared with their neighbouring ones; this fact supplies the second proof for the existence of three superlattices, α'_{3-1}, α'_{1-1} and α'_{1-3}.

VI. Measurement of Specific Heat at Elevated Temperatures

On specimens of a cylindrical form of 18 mm $d \times 30$ mm l, each weighed about 55 g, and perfectly ordered by extremely slow cooling from 700° to room temperature taking 10 days, specific heat (C_p) at elevated temperatures have been measured

with heating rate of 1°/min, by means of Smith's method, but somewhat improved in accuracy by one of the authors and Y. Iwama.[15]

The typical results obtained are shown in Fig. 12. Curve (g) for an alloy with 48.86% Cr, corresponding to superlattice α'_{1-1}, shows a large anomalous heat-absorption of λ shape owing to the order $(\alpha'_{1-1}) \to$ disorder (α) transformation. The nature of a smaller peak close to the maximum peak on specific heat curve, observable also on some other curves, has been left unexplained. The anomaly owing to the $\alpha'_{1-1} \to \alpha$ transformation, begins at about 450° and then reaches a maximum peak at 575°, which was taken for T_c point, and subsequently ends at 630°, coinciding fairly with the ending temperature of contraction on the dilatation curve. Curve $dfbcd'$ in Fig. 3 denotes such T_c points at every composition. The anomalous change in specific heat, in this case, contains indeed two superposed co-operative phenomena, that is, a decomposition of superlattice and a disapperance of ferromagnetism, as shown in a reaction, α' (ferromagnetic) $\to \alpha$ (nonmagnetic).
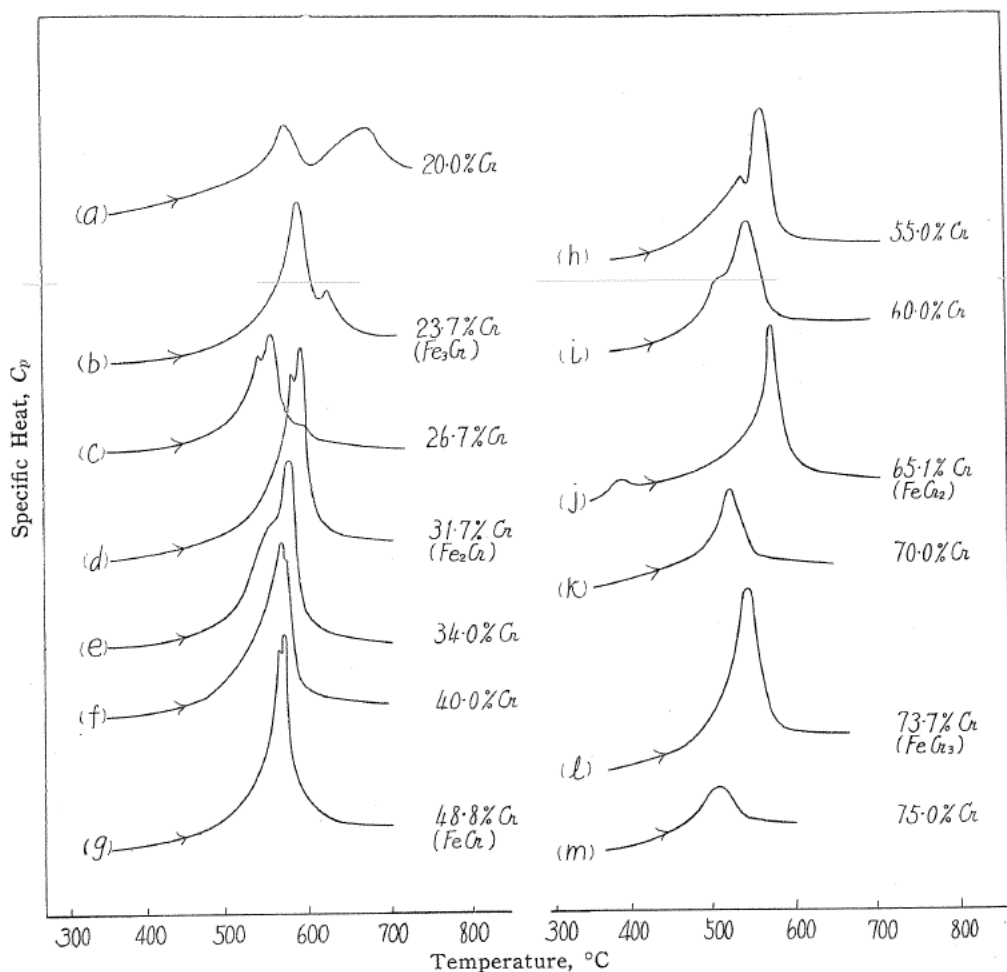

FIG. 12. Specific heat curves.

Curve (f) for an alloy with 40% Cr shows the similar change, but ΔC_p, that is, magnitude of the anomalous specific heat change, becomes somewhat smaller. A bump behind the maximum peak observable on C_p curve is considered to be probably due to the disapperance of ferromagnetism retarded above its T_c point even with the heating rate of $1°/\text{min}$.

Curve (e) for an alloy with 34% Cr shows another anomaly at 558° in addition to the similar maximum peak; it is supposed to be concerning the decomposition of Fe_2Cr (τ-phase) (cf. curve (e) in Fig. 14). On curve (d) for an alloy with 31.7% Cr, stoichiometric composition of Fe_2Cr (τ-phase), there are detectable a large anomalous heat absorption with very steep C_p increase, high value of ΔC_p and also high T_c point, due to the decomposition of this meta-compound. This phenomenon resembles to that in the case of an intermetallic compound, and it suggests the existence of meta-compound Fe_2Cr (τ-phase). On curve (c) for an alloy with 26.7% Cr, both this anomaly and T_c point are brought down remarkably.

Curve (b) for an alloy with 23.7% Cr, corresponding to the stoichiometric composition of Fe_3Cr (α'_{3-1}), shows also a large C_p peak and a high T_c point. On this curve, two peaks at 590 and 630° are clearly recongnized (as well as curves (a) and (c)); these two peaks are considered to be produced by separation of two co-operative phenomena, in other words, the lower peak corresponds to decomposition of superlattice, α' (ferromagnetic) $\to \alpha$ (ferromagnetic) at T_c point, and the higher one to disappearance of ferromagnetism at A_2 point of disordered α-phase, as summarized in Fig. 3. On curve (a) for an alloy with 20% Cr, its T_c point is lowered remarkably to 568°, while A_2 point of disordered α-phase is raised to 670°, and thus these two co-operative phenomena are separated completely. Moreover, it is noticeable that the further the composition apart from Fe_3Cr, the smaller becomes the heat absorption for order $\to$ disorder transformation, while that for disapperance of ferromagnetism grows larger at lower Cr-content.

In alloys containing higher Cr than equiatomic composition, curve (h) for an alloy with 55% Cr shows two separated peaks like curve (b) for that with 23.7% Cr; in this case, however, contrariwise to the cases of lower Cr-content, the small peak at lower temperature corresponds to A'_2 point (i.e., Curie point of the ordered α'-phase), while the large one at higher temperature corresponds to T_c point, where there takes place the order-disorder change such as α' (nonmagnetic) $\to \alpha$ (nonmagnetic). Curve (i) for an alloy with 60% Cr shows comparatively smaller peaks.

However, on curve (j) for an alloy with 65.1% Cr, corresponding to the stoichiometric composition of $FeCr_2$, a large and steep C_p peak as in the case of τ-phase is detectable, while a small peak for A'_2 point comes to lower temperature and becomes considerably smaller in magnitude; from this fact the existence of meta-compound $FeCr_2$ (ω-phase) is inferred. On curves (k) and (m) for alloys with 70 and 75% Cr, respectively, C_p peaks are very small and T_c points are low, but on curve (l) for an alloy with 73.7% Cr, corresponding to the stoichiometric composition of $FeCr_3$, C_p peak becomes so larger and T_c point is also raised so higher that the existence of superlattice $FeCr_3$ (α'_{1-3}) is provable. Moreover, in alloys with more than 65% Cr, A'_2 point is so low that overlapping of the two co-operative phenomena disappers, C_p peak at T_c point representing merely the order-disorder transformation in nonmagnetic state, as above mentioned.

Summarizing the above results, anomalous specific heat change ΔC_p transformation energy ΔE as well as T_c point are plotted versus composition as shown in

Fig. 13, in which five peaks are recognized at the respective stoichiometric compositions on every curve; this fact supplies the third proof for the existence of three superlattices, Fe_3Cr (α'_{3-1}), $FeCr$ (α'_{1-1}) and $FeCr_3$ (α'_{1-3}), and besides, suggests that of meta-compounds, Fe_2Cr (τ-phase) and $FeCr_2$ (ω-phase).
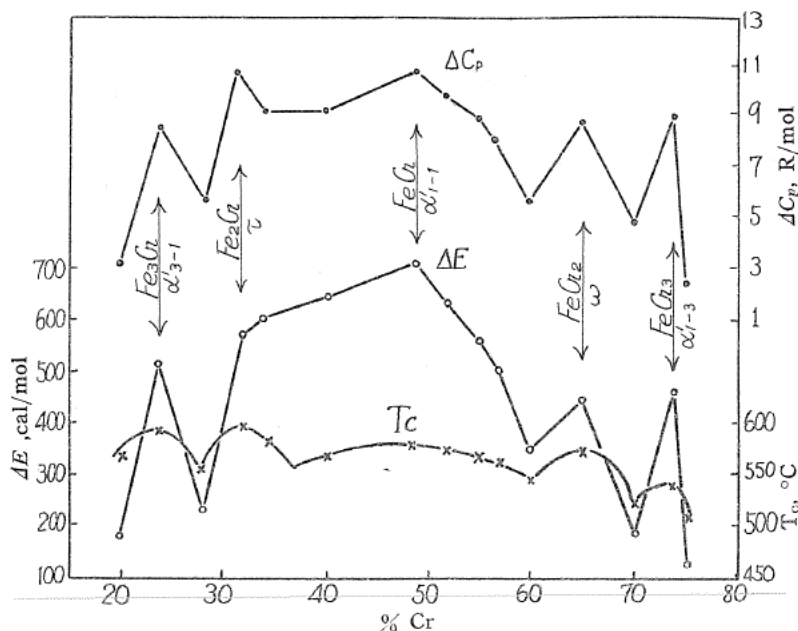

FIG. 13. Anomalous specific heat change (ΔC_p), transformation energy (ΔE) and transformation temperature (T_c) of Fe-Cr alloys.

VII. Measurement of Electric Resistance

VII-1. Electric Resistance at Elevated Temperatures

Fig. 14 represents some typical results of measurement of electric resistance at elevated temperatures on alloys of various compositions (curves (a)–(l)) which were perfectly ordered by well annealing. Besides, only on an alloy with 48.86% Cr (α'_{1-1}), its measurement began also with disordered state as shown on curve (m). In Fig. 14, it is readily recongnized that there occurs an anomalous increase in electric resistance due to the decomposition of superlattice on every heating curve beginning at about 500°. These beginning temperatures of order-disorder transformation on electric resistance-temperature curves are generally higher by about 50° than those on specific heat-temperature curves (cf. Fig. 12). But, the ending points in the former cases are in agreement with their respective T_c points, that is, maximum peaks on λ-curves, in the latter ones; therefore, they are lower by about 50° than the T'_c points defined from the dilatation-temperature curves (cf. Fig. 11).

From these results, it becomes known that decomposition of long range order gives rise to a conspicuous change in electric resistance, while change of short range order has little influence upon electric resistance, because dimension of order-
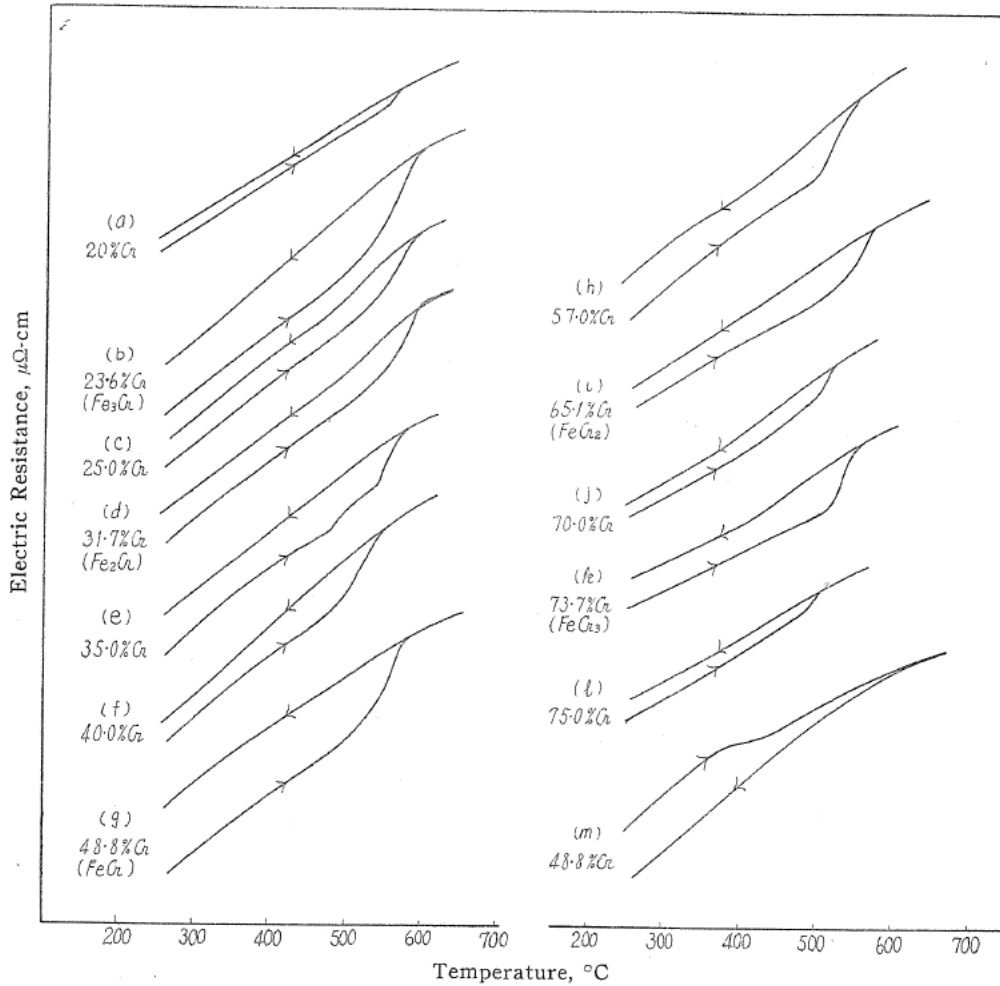
FIG. 14. Electric resistance-temperature curves.

ing in short range order may be smaller than mean free path of conduction electrons. Also from this point of view, T_c' point is inferred to be order (short range) $\rightleftarrows$ disorder transformation point.

The T_c points thus observed are also plotted on curve $dfbcd'$ in Fig. 3, where the temperature and the magnitude of anomalous changes in electric resistance at these T_c points are higher at the respective stoichiometric compositions, Fe_3Cr, $FeCr$ and $FeCr_3$, than other ones about them; these facts coinciding well with various results previously mentioned, supply the fourth proof for the existence of three superlattices, α_{3-1}', α_{1-1}' and α_{1-3}'.

The slight decrease in electric resistance observable on all cooling curves implies that the partial formation of superlattice may occur on cooling. Furthermore, from the facts that the decrease in electric resistance is observable from about 400° on heating curve for a disordered alloy with 48.86% Cr and also its cooling curve lies under the heating one as shown on curve (m), it is understood that the

partial formation of these superlattices occurs relatively rapidly. Another small knick observable on curve (e) for an alloy with 35% Cr, like the specific heat-temperature curve (cf. curve (e) in Fig. 12), is supposed to correspond to the decomposition of τ-phase as above mentioned.

VII-2. Electric Resistance at Room Temperature

As seen in Figs. 7 and 14, formations of superlattices, α'_{3-1}, α'_{1-1} and α'_{1-3}, are all accompanied by the decrease in electric resistance. Fig. 15 shows the relative decrease in electric resistance by ordering versus composition of alloys, namely $(\rho_0 - \rho_d)/\rho_d \times 100$, where ρ_0 and ρ_d denote specific resistance of ordered and disordered phases, respectively. There exist three minima at the stoichiometric compositions, Fe_3Cr, $FeCr$ and $FeCr_3$, respectively; this fact supplies the fifth proof for the existence of three superlattices, α'_{3-1}, α'_{1-1} and α'_{1-3}. Moreover, little changes are observable at the compositions corresponding to Fe_2Cr (τ-phase) and $FeCr_2$ (ω-phase), reason of which, however, will be described later.
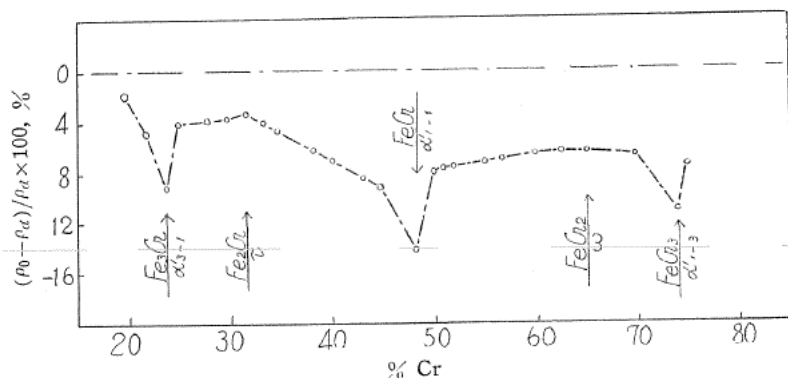

FIG. 15. Change in electric resistance of Fe-Cr alloys by ordering.

In Table 1, electric resistance as well as Vickers hardness at room temperature in α, α'_{1-1} and σ states, respectively, measured on some alloys are compared with each other. Thus, the decrease in electric resistance following the formation of α'_{1-1} from α is quite contrary to its marked increase in the case of σ formation (about three times as high as that of α-phase); and hence, as regards the specific electric resistance of the phases accounted, there exists the following relation :—

$$R_\sigma > R_\alpha > R_{\alpha'}.$$

TABLE 1

% Cr ↓ \ Structures →	Electric resistance, $\mu\Omega$·cm			Vickers hardness, Hv		
	α	σ	α'	α	σ	α'
43	86.5	235.2	80.6	248	832	308
45	88.3	271.1	81.8	265	818	327
48.8	91.0	278.3	78.0	282	861	408
50	92.8	278.4	85.4	289	852	360

VIII. Measurement of Hardness and on the 475°C (885°F)-Embrittlement in Ferritic High Chromium Stainless Steels

Because hardness increase accompanies the formation of superlattice as shown in Fig. 7, Vickers hardness of both disordered and perfectly ordered phases in this system was measured. In Fig. 16, curve (a) indicates Vickers hardness of α disordered, curve (b) that of α' ordered, and curve (c) the relative hardness increase by ordering versus composition of alloys, namely $(H_0 - H_d)/H_d \times 100\%$, where H_d and H_0 express Vickers hardness of disordered and ordered phases, respectively. There exist five maxima on curves (b) as well as (c) at the stoichiometric compositions, Fe_3Cr, Fe_2Cr, $FeCr$, $FeCr_2$ and $FeCr_3$, respectively; among these, the relative hardness increase is strikingly largest (70%) at Fe_2Cr composition. These facts supply the sixth proof for the existence of three superlattices, α'_{2-1}, α'_{1-1} and α'_{1-3}, and also suggest that of two meta-compounds, τ- and ω-phases.
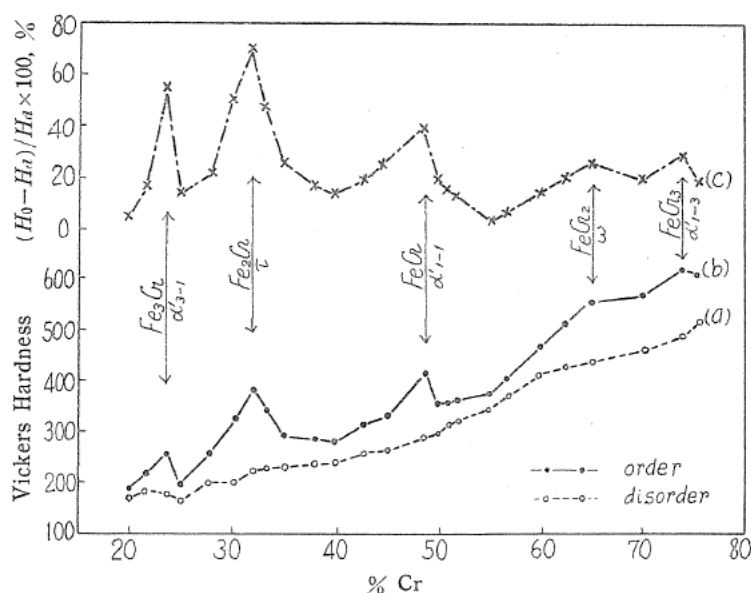

FIG. 16. Hardness of Fe-Cr alloys and its change by ordering.

Furthermore, formation of σ-phase is also accompanied by hardness increase as shown in Table 1, whose hardness values are, however, far larger than those of α'_{1-1}, although the formers have not attained to their true values (about Hv 900), owing to co-existing small amounts of α-phase unchanged to be protected from embrittling destruction of specimens.

Thus, Fe-Cr binary alloys containing more than about 15% Cr are hardened remarkably by the formation of superlattices or meta-compounds. Hence, it is self-evidently concluded that the so-called 475°C-embrittlement in high chromium ferritic stainless steels (12.5~75% Cr) as well as in Fe-Cr-Al electric resistance alloys, which has long been discussed in many countries but whose true cause has not yet been elucidated, is undoubtedly attributed to the formation of either of these three su-

perlattices, α'_{3-1}, α'_{1-1} and α'_{1-3}, according to the composition of alloys, without actual proof of impact test, as was proved by the present authors in another paper.[19]

IX. X-Ray Diffraction Analysis

IX-1. Ordered Structure of Superlattice Fe₃Cr (α'_{3-1})

A fine cylindrical specimen (0.35 mm in dia.) containing $25_{at.}\%$ Cr was prepared by sucking up the melt into a narrow porcelain tube. It was perfectly ordered by cooling extremely slowly from 600° to room temperature taking one week. The powder patterns were taken with a Debye-Scherrer camera (114.6 mm in dia.) using a target of manganese (exposed for 10 hr at 40 kv, 5 mA), for the purpose of utilizing its anomalous atom-scattering phenomenon at the absorption edge, on account of Fe and Cr atoms being close to each other in atomic number.

Though the disordered specimen quenched from 1000° showed only diffraction lines of body-centered cubic lattice, such as (200), (400), (422) etc., the perfectly ordered one showed obviously new superlattice lines such as (200), (311), (222) etc., in addition to those basal lines. Comparing the diffraction angles and the relative intensities of these superlattice lines with their calcurated structure factors, it was concluded that the ordered structure of the superlattice Fe₃Cr (α'_{3-1}) is the same as that of superlattice Fe₃Al, as shown in Fig. 17, having twice as large lattice as the disordered one and following atomic arrangement:—
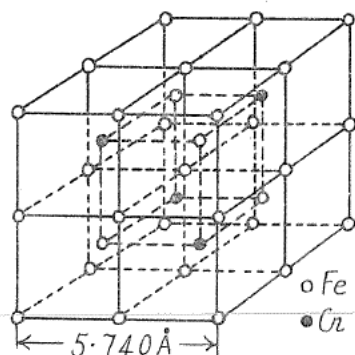

FIG. 17. Ordered structure of α'_{3-1} (Fe₃Cr).

Fe-atom : (0   0   0)(1/2 1/2 1/2)(1/2 1/2 0)(1/2 0 1/2)(0 1/2 1/2)
(1/2 0   0)(0 1/2 0)(0   0 1/2)(3/4 1/4 1/4)(1/4 3/4 1/4)
(1/4 1/4 3/4)(3/4 3/4 3/4)

Cr-atom : (1/4 1/4 1/4)(3/4 3/4 1/4)(3/4 1/4 3/4)(1/4 3/4 3/4)

Their lattice parameters obtained are 5.740 Å for the ordered phase, Fe₃Cr (α'_{3-1}), and 2.866 Å for the disordered one, respectively, which indicate that this ordering is accompanied by a volume increase, agreeing well with the results of measurements of density and thermal dilatation mentioned previously.

The structure of superlattice FeCr₃ (α'_{1-3}) seems probably to be similar to that of superlattice Fe₃Cr (α'_{3-1}) above mentioned, merely Fe and Cr atoms taking another's place in lattice, but its determination has not yet been carried out.

IX-2. Ordered Structure of Superlattice FeCr (α'_{1-1})

The similar analysis as for Fe₃Cr was carried out for the specimen containing $50_{at.}\%$ Cr. The disordered specimen quenched from 1100° gave wellknown diffraction lines of body-centered cubic lattice, while the ordered one extremely slowly cooled from 600° did new superlattice lines such as (111), (311), (331), (333), (511)

etc., besides its basal lines. From these diffraction lines and their intensities it was concluded that the ordered structure of superlattice FeCr (α'_{1-1}) is not CsCl-typed but has twice as large lattice as the disordered one, as shown in Fig. 18, having following atomic arrangement :—

Fe-atom: (1/2 0   0)(0 1/2 0)(0   0 1/2)(1/2 1/2 1/2)
         (1/4 1/4 1/4)(3/4 3/4 1/4)(3/4 1/4 3/4)(1/4 3/4 3/4)
Cr-atom: (0   0   0)(0 1/2 0)(0   0 1/2)(1/2 1/2 1/2)
         (3/4 1/4 1/4)(1/4 3/4 1/4)(1/4 1/4 3/4)(3/4 3/4 3/4)

The lattice parameters obtained are 5.745 Å for the ordered phase, α'_{1-1}, and 2.868 Å for the disordered one, respectively, which indicate that a volume increase accompanies also the formation of superlattice α'_{1-1}, coinciding well with the results of measurements of density as well as thermal dilatation mentioned previously.

Finally, this ordered structure is characterized by its large unit cell, and based upon this conception one of the authors and Y. Iwama have gave out a theory on the formation of superlattice FeCr (α'_{1-1}) in their 7th Report,[17] which will be, however, published in the next issue.
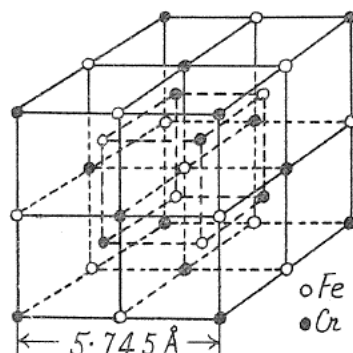

FIG. 18. Ordered structure of α'_{1-1} (FeCr)

IX-3. Crystal Structure of Compound σ-Phase

Although a number of researches[20-22] on the crystal structure of compound σ-phase have been reported till now, their results are very diverse and its structure is not yet fully established at present. For examples, only as for lattice type, various ones such as tetragonal, hexagonal or orthorhombic lattice, in details, β-Uranium or α-Manganese type are proposed, and its size and number of atoms per unit cell (N) are also different.

The present authors also have been investigating on its crystal structure and have not yet attained an well-defined conclusion. From the results obtained till now, however, it is presumably concluded that its crystal structure is a tetragonal lattice having $a = 8.83$ Å, $c = 4.60$ Å, $c/a = 0.52$, $N = 30$ and $\rho_{cal.} = 7.62$, nearly as shown in Fig. 19.

Here, $N = 32$ in the ideal crystal structure of σ-phase shown in Fig. 19, having 2 atoms more than $N = 30$ obtained actually by the present work. It is now under re-examination, from the points of view of structure factor and symmetry of crystal structure, whether $N = 32$ is correct, owing to a little error in measured value of density which caused to determine $N = 30$, or actual unit cell becomes to have 30 atoms by displacement of any 2 atoms from the ideal lattice during its lattice formation. It has now been treated as $N = 30$.
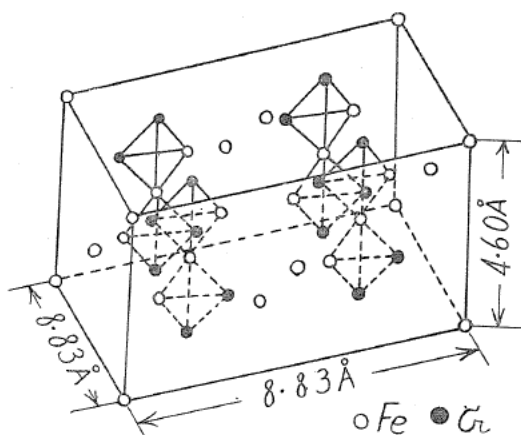
FIG. 19. Crystal structure of σ (FeCr).

X. Transformation of Superlattice FeCr (α'_{1-1})
into Compound σ-Phase

X-1. Process of Transformations, $\alpha \to \alpha'_{1-1} \to \sigma$, by Prolonged Annealing at low Temperature

As previously described, α solid solution disordered is easily obtained at room temperature by water-quenching from temperatures above 900°, and nonmagnetic compound σ-phase is formed in alloys containing 40~60% Cr, by annealing the supercooled α-phase at about 850° slightly below the $\alpha \to \sigma$ transformation point, whereas ferromagnetic superlattice α'_{1-1} is formed instead of σ-phase, in alloys with compositions near FeCr by prolonged annealing the supercooled α-phase at about 500° below the $\alpha \to \alpha'$ transformafion point (T_c point).

Thus, there is clear difference in forming condition between σ and α'_{1-1}. But, because a superlattice phase is generally said to be an intermediate phase between a disordered solid solution and an intermetallic compound, it is suspectable that there may exist, in this case, such a co-relation as stable-metastable, between σ and α'_{1-1}, of which, of course, the former is presumed to be a stable phase and the latter a metastable one, judging from the marked discrepancy in their transformation or decomposition temperatures; thereby, if α'_{1-1} be a metastable phase, it should probably transform finally into stable phase σ.

Hence, in order to confirm whether the $\alpha'_{1-1} \to \sigma$ transformation above mentioned may occur, an alloy with 48.86% Cr corresponding to FeCr, that is, stoichiometric composition of σ and α'_{1-1} phases, and consisting of homogeneous disordered α-phase, obtained by water-quenching from 1000°, was annealed accumulatively for 500 hr at 650° above its T'_c point (625°) and at 500° below its T_c point (575°), respectively. During this process, the formation of α'_{1-1}- and σ-phases was inquired by measuring the changes in magnetic intensity, Vickers hardness and electric resistance at room temperature with progress of annealing time.

The results obtained are shown in Fig. 20-(a), (b) and (c). Curves (1) are the case annealed at 500°, which is the most suitable temperature for α'_{1-1} formation, in which changes taking place can be devided into three stages according to form

of curves. The first stage is characterized by gradual increase in magnetic intensity (a) and hardness (b), and, in return, decrease in electric resistance (c), occurring before 100 hr-annealing, showing the formation of α'_{1-1}-phase by $\alpha \rightarrow \alpha'_{1-1}$ transformation. Because, this is inferred from the following relations: $I_\alpha < I_{\alpha'}$, $H_\alpha < H_{\alpha'}$, and $\rho_\alpha > \rho_{\alpha'}$ as above described. Thus, the formation of α'_{1-1}-phase is finished by annealing for about 100 hr at 500°.

The second stage is a period between about 100 and 300 hr, in which no change is observable at all, but really corresponding to an incubation period of the next third stage change. Therefore, superlattice α'_{1-1} is left as it is during this second stage.

On further annealing, however, from a little before 300 hr onward, there occur increase in hardness (b) and electric resistance (c), and, in return, decrease in magnetic intensity (a), the latter two changes being contrariwise to those in the first

FIG. 20. Change of properties with annealing time.

stage and both values becoming equal to those before annealing for once on the way. Finally, after annealing for 500 hr, it becomes much lower in magnetic intensity (a) and much higher in hardness (b) and electric resistance (c) than those before annealing. These changes appearing after annealing for about 300 hr correspond to the third stage which shows the formation of σ-phase by $\alpha'_{1-1} \rightarrow \sigma$ transformation. Because, this is inferred from the following relations: $I_{\alpha'} > I_\sigma$ (nonmagnetic), $H_{\alpha'} < H_\sigma$ and $\rho_{\alpha'} < \rho_\sigma$ as above mentioned. At this final annealing stage, σ-phase has appeared obviously in microstructure.

Curves (2) are the case annealed at 650° just above the T'_c point (625°). In this case, in spite of annealing at higher temperature than in the case of curves (1) (500°), there is no change in magnetic intensity, hardness and electric resistance, during annealing for 500 hr; this fact indicates that there occurs no σ-formation directly from α-phase ($\alpha \rightarrow \sigma$), which has also been confirmed in microstructure.

Thus, when the supercooled α-phase is prolongedly annealed at lower temperature than its T_c point, the superlattice FeCr (α'_{1-1}) is formed from α at first, but afterward this α'_{1-1} transforms into compound σ-phase by further annealing, as was expected. In other words, on low temperature annealing, there occur the two staged changes, $\alpha \rightarrow \alpha'_{1-1} \rightarrow \sigma$; that is, α-phase transforms finally into σ-phase, but it passes through the state of superlattice α'_{1-1} on the way. Moreover, it is noticeable that σ-phase can be formed more easily through the state of α'_{1-1}-phase ($\alpha \rightarrow \alpha'_{1-1} \rightarrow \sigma$)
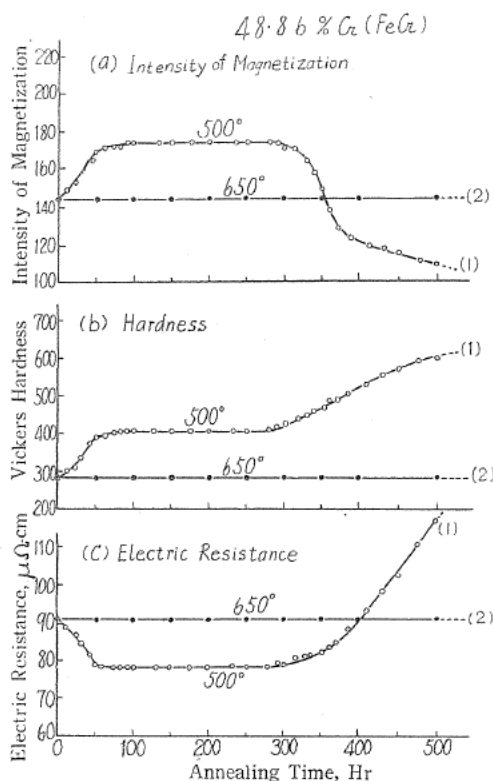
than in the case of direct formation of σ-phase from α-phase $(\alpha \rightarrow \sigma)$.

X-2. Crystallographical Consideration of the Transformation, $\alpha'_{1-1} \rightarrow \sigma$

As previously mentioned, from the results obtained by prolonged annealing at lower temperatures, it was shown experimentally that $\alpha'_{1-1} \rightarrow \sigma$ transformation occurs more easily than $\alpha \rightarrow \sigma$ transformation. So, it was tried to consider crystallographically a mechanism of $\alpha'_{1-1} \rightarrow \sigma$ transformation, as one of its theoretical supports. In this case, the crystal structures of α'_{1-1}- and σ-phases are already illustrated in Figs. 18 and 19, respectively.

In the unit cell of superlattice FeCr(α'_{1-1}), a sublattice noted by thick lines as shown in Fig. 21-(a), should be noticed. This sublattice is reproduced comprehensibly in Fig. 21-(b), being regarded as a complex tetragonal lattice having the lattice constants, $a = 4.063$ Å, $c = 5.745$ Å, $c/a = 1.413$ and $N = 8$. In this sublattice, when six atoms noted by numerals from 1 to 6 are displaced a little, it may be considered that a tetrahedron $(a = x)$ having atomic arrangement as shown in Fig. 21-(c), would be easily formed in it. In this case, one Cr atom having larger atomic radius than Fe atom is displaced from c-axis, and so it causes a contraction in the direction of c-axis as well as a relative expansion in the direction of a-axis, which results in a formation of the sublattice as shown in Fig. 21-(c), having the lattice constants, $a = 4.415$ Å, $c = 4.60$ Å and $c/a = 1.04$. Subsequently, four of these sublattices assemble, on which two Fe atoms in the center of each axis are displaced to face-center, then it results in a formation of the crystal structure as shown in Fig. 19, which is entirely identical with that of σ-phase proposed by the present authors.
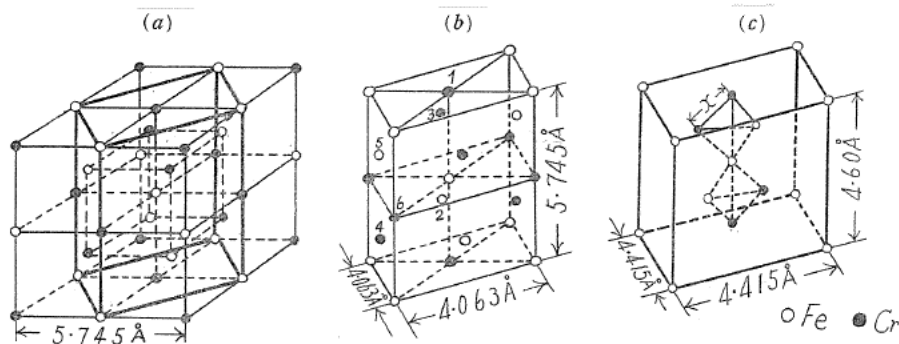

FIG. 21. Process of changes of crystal structure accompanying $\alpha'_{1-1} \rightarrow \sigma$ transformation, suggested by Takeda and Nagai.

During this process of changes of crystal structure, since only 8 atoms are displaced and also their paths are very small, it may be expected that such a change can take place easily even at lower temperatures about 500°. On the other hand, it seems difficult that such a complex crystal structure as σ-phase is formed directly from a simple body-centered cubic lattice of disordered α-phase. Accordingly, it may be said that such a complex change can proceed only at higher temperatures at which migration of atoms become violent.

Thus, also from crystallographical consideration, it is inferred that at lower temperatures the transformation, $\alpha'_{1-1} \rightarrow \sigma$, can take place more easily than that, $\alpha \rightarrow \sigma$.

XI. The Relation between Superlattice FeCr (α'_{1-1}) and Compound σ-Phase

A superlattice is generally said to be an intermediate phase between a disordered solid solution and an intermetallic compound; in other words, a superlattice may be regarded as a solid solution having properties like a compound. In spite of that, there has been published neither theoretical nor experimental study upon this conception till now, probably due either to the fact that there have been no example in which both superlattice and compound are formed simultaneously in an alloy of the same composition, or to the fact that intermediate phase, superlattice could not be caught, owing to its rapid change into compound, even if they might coexist for a moment.

The experimental results above mentioned, however, afford such a rare and peculiar example that both superlattice α'_{1-1} and compound σ are formed from the same disordered solid solution α with compositions near FeCr. In addition, there can be rather formed superlattice α'_{1-1} instead of compound σ, according to the conditions of heat-treatment, owing to the slow formation velocity of compound σ at lower temperatures. Accordingly, from the study of relation between them, not only this case but also a general problem upon the difference between a superlattice and a compound may be fairly solved.

As above described, the three phases, disordered solid solution α, superlattice α'_{1-1} and compound σ are easily distinguishable from one another, because they are different in many properties, e.g., microstructure (except an indistinguishableness between α and α'), magnetic property, specific volume, hardness, electric resistance and crystal structure, etc. Moreover, the formation temperatures of these two phases, σ and α'_{1-1}, are generally distinguishable from each other; that is, the former is formed at higher temperatures about 800°. while the latter does at low temperatures about 500°, but this α'_{1-1} transforms finally into σ by prolonged annealing at 500°. These facts prove that superlattice α'_{1-1} is really a metastable phase while compound σ is a stable one, and also that superlattice α'_{1-1} is an intermediate phase between disordered solid solution α and compound σ.

After all, merely from a crystallographical point of view, without consideration from electron theory, both superlattice and compound are analogous at such point that constitutional atoms are arranged regularly in each lattice. However, they are different in the mode of regular arrangement, that is, in lattice type; this difference is attributed to the difference in type of combination of concerned atoms, and accordingly results in the difference in stability between these two phases. Thus, it can be concluded that a superlattice has atoms more strongly combined in it than in the case of a disordered solid solution; however, it is rather near a solid solution, whereas a compound has atoms combined most strongly and is accordingly stabilized.

In addition, as above mentioned, the order $\rightleftarrows$ disorder transformation is not accompanied by changes in lattice type and concentration, and proceeds gradually with temperature, as in the case of magnetic transformation of a ferromagnetic substance. On these points, this transformation quite differs from an allotropic transformation and a solubility change in solid solution, which are accompanied by changes in lattice type and concentration. It is, therefor, emphasized that not only a superlattice phase must be metallographically clearly distinguished from a dis-

ordered solid solution as well as an intermetallic compound, but also order $\rightleftarrows$ disorder transformation point, that is, T_c point should be treated in phase diagram similarly as Curie magnetic transformation point.

XII. Meta-Compounds, Fe$_2$Cr (τ-Phase) and FeCr$_2$ (ω-Phase)

When alloys containing 30 to 33% Cr and 63 to 67% Cr are annealed for more than 30 hr at 450°, after heating for 1 hr at 1000° and subsequent water-quenching to prevent the formation of σ-phase, they exhibit a characteristic Widmannstätten microstructure as shown in Photo. No. 1. Photo. No. 2 shows its electron-microscopic photograph at a magnification of $\times 2,800$. It develops more rapidly, if they are coldworked before annealing. The needle-like precipitates in Photo. No. 1 are the meta-compound Fe$_2$Cr (τ-phase), which will be described later, and the matrix is probably the superlattice α'_{1-1}.

Photographs

No. 1 $\times 150$
(Etched electrolytically
with 10% H$_2$SO$_4$)
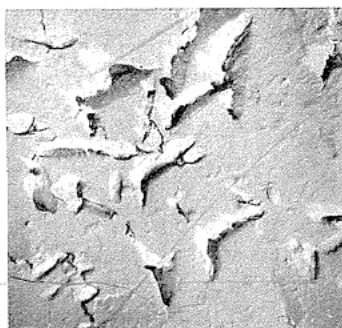
No. 2 $\times 2,800$
Ditto, shadow casting

Microscopic (No. 1) and electron-microscopic (No. 2) structures of τ-phase (33.0% Cr, annealed for 100 hr at 450°).

The alloys in these composition ranges show various characteristic properties as previously mentioned; above all, their increase in hardness (cf. Fig. 16) and decrease in magnetic intensity (cf. Fig. 8) are quite conspicuous. Their change in electric resistance (cf. Fig. 15), however, is somewhat obscure, probably by the reasons that the annealing temperature 500°, adopted in this case, has been a little too high to form meta-compound τ- or ω-phase, and also there has been formed, besides the meta-compound, the superlattice α'_{1-1} which has an influence opposite to the meta-compound upon electric resistance. Now, from the various characteristic properties above described, particularly from their apperance in microstructure, it is unreasonable to regard these needle-like precipitates as superlattice phase. On the other hand, they never show characteristic properties of intermetallic compound.

Therefore, the present authors have called them "meta-compound"; their stoichiometric compositions are Fe$_2$Cr (31.7% Cr) and FeCr$_2$ (65.1% Cr) and they have been named τ- and ω-phases, respectively (although G. Bandel[9] considered Fe$_2$Cr

as an intermetallic compound). Moreover, this nomenclature has come from the consideration that meta-compound means an intermediate phase between superlattice and intermetallic compound, and is rather close to the latter. Now that the difference between superlattice and compound depends, as proposed by U. Dehlinger,[23] upon the difference in affinity between the concerned atoms, it should be expected that such a meta-compound probably exists as an intermediate phase between superlattice and compound.

Furthermore, the X-ray analysis showed the new diffraction patterns different from those of σ-phase, chromium-nitride and -carbide, the determination of their crystal structures, however, has not yet been achieved.

XIII. Summary

The results of the present research may be summarized as follows:—

(1) By means of microscopic observation, thermo-magnetic, dilatometric and X-ray analyses, as well as measurements of specific heat and electric resistance at elevated temperatures, hardness, electric resistance and intensity of magnetization at room temperature, etc., the formations of superlattices as well as compound in Fe-Cr system were systematically investigated.

(2) It was discovered that there are formed three metastable ferromagnetic superlattices, Fe_3Cr (α'_{3-1}), $FeCr$ (α'_{1-1}) and $FeCr_3$ (α'_{1-3}), and also two meta-compounds, Fe_2Cr (τ-phase) and $FeCr_2$ (ω-phase), besides the well-known stable nonmagnetic compound, σ-phase, and the characteristic properties of these phases were described in detail.

(3) In connection with these results, it was proposed that the so-called 475°C (885°F)-embrittlement in high chromium ferritic stainless steels (12.5~75% Cr) as well as in Fe-Cr-Al electric resistance alloys is attributed to the formation of either of the three ferromagnetic superlattices in Fe-Cr system, Fe_3Cr (α'_{3-1}), $FeCr$ (α'_{1-1}) and $FeCr_3$ (α'_{1-3}), according to the composition of alloys.

(4) In order to clarify the relation between the ferromagnetic superlattice $FeCr$ (α'_{1-1}) and the nonmagnetic compound σ-phase, differences in various properties and forming conditions between them were throughly studied; σ-phase is formed from disordered α solid solution at higher temperatures near 800°, while superlattice α'_{1-1} is formed for once from the supercooled α-phase at lower temperatures near 500° by prolonged annealing. The latter, however, transforms finally into the former by further annealing.

(5) From these results, it was concluded that the superlattice $FeCr$ (α'_{1-1}) is a metastable and intermediate phase between the disordered solid solution α and the stable compound σ.

(6) It was emphasized that order-disorder transformation should be treated in phase diagram similarly as magnetic transformation of ferromagnetic substance, because they both proceed gradually with temperature without changes in crystal lattice and concentration.

Acknowledgements

References

1) E. C. Bain and W. F. Griffiths, Trans. A.I.M.E., **75** (1927), 166.

2) P. Oberhoffer and H. Esser, Stahl und Eisen, **47** (1927), 2001.

3) F. Wever and W. Jellinghaus, Mitt. K-W-I Eisenforsch., **13** (1931), 107.

4) A. B. Kinzel and W. Craft, Alloys of Iron and Chromium, **1** (1937), 43.

5) U. Dehlinger, Chemische Physik der Metalle und Legierungen, (1938), 85.

6) J. H. G. Monypeny, Metallurgia, **33** (1940), 134.

7) A. Fry, Techn. Mitt. Krupp, **2** (1934), 9.

8) G. Riedrich and F. Loib, Arch. Eisenhütt., **15** (1941), 175.

9) G. Bandel and W. Tofaute, Arch. Eisenhütt., **15** (1942), 307.

10) J. T. Heger, Metal Progress, **48** (1945), 321; **61** (1951), 55; A.S.T.M. Spec. Tech. Publ., No. 110 (1950), 75.

11) H. S. Link and P. W. Marshall, A.S.M., **41** (1952), 549.

12) R. M. Fischer, E. J. Dulis and K. G. Carroll, Jour. Metals, **5** (1953), 690.

13) A. J. Lena and N. F. Hawkes, Jour. Metals, **6** (1954), 607.

14) K. Shinji, Reports of Research Committee of Japan Institute of Metals, **IV-A** (1952), 99.

15) T. Murakami, M. Mizuno, T. Suzuki and T. Shoji, *Ditto*, (1952), 118.

16) F. Adcock, Jour. Ir. St. Inst., **124** (1931), 99.

17) S. Takeda and N. Nagai, Abstracts of Papers read at the Lecture-meetings of Japan Institute of Metals, Rept. I (1949-Apr.); Rept. II (1949-Nov.); Repts. III and IV (1951-Apr.); Repts. V~VII (1951-Oct.); Rept. VIII (1952-Apr.).

18) S. Takeda and Y. Iwama, Research Reports of Faculty of Engineering, Nagoya University, **IV-1** (1951), 16.

19) N. Nagai and A. Higuchi, Jour. Japan Inst. Metals, **19** (1955), 77.

20) A. J. Bradley and H. J. Goldschmidt, Jour. Ir. St. Inst., **145** (1941), 273.

21) P. Pietrokowsky and P. Duwez, Jour. Metals, **188** (1950), 1283.

22) G. J. Dickins, M. B. Douglas and W. H. Taylor, Jour. Ir. St. Inst., **167** (1951), 27.

23) U. Dehlinger, Chemische Physik der Metalle und Legierungen, (1938), 133.