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UNDER HIGH PRESSURE

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THE  $\alpha \rightarrow \gamma$  CONVERSION IN IRON-NICKEL ALLOYS UNDER HIGH PRESSURE

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11608

Abstract:  $\gamma$ - $\alpha$  conversion of iron alloys containing 30-35% nickel by cooling to low temperatures. Determination of the amounts of the  $\gamma$  phase re-formed by heating through measurement of electrical resistance and magnetic property. Experiments were carried out under normal pressure and pressures of 5,000-10,000 kg/cm<sup>2</sup>. Short-interval experiments were carried out by heating to 250, 300, 350, or 400° C without any essential change in concentration. Experiments at 430° C were performed under normal pressure and also under higher pressures and for prolonged intervals. The authors demonstrated changes of concentration.

By using high pressure, the temperatures of the phase equilibria can be displaced. In phase conversion from unbalanced states, pressure may also influence the rate and completeness of the conversion, especially if the conversion is accompanied by changes of volume.

*Author*

During the isothermal decomposition of the deep-cooled austenite, i.e., of a cubic face-centered mixed crystal of iron and carbon, a slight increase of volume occurs. W. Jellinghaus and H. Friedewold (1) found a considerable reduction of the rate of conversion at temperatures between 250 and 350° C and pressures of 4,000 and 5,000 kg/cm<sup>2</sup> as compared with the behavior under customary pressure. As a consequence of the increase of pressure, they found an increase of the rate, in the elimination of carbide from austenitic manganese steel, where this process results in a reduction of volume. However, this example was not very convincing as proof for the favoring or accelerating action of high pressures in the case of reduction of volume because the amount of the carbide created during elimination represents only a small fraction

(1) Arch. Eisenhüttenwes. 31 (1960 P. 309/17 (Mitt. Max-Planck-Inst. Eisenforsch., Treatise 848, and Werkstoffaussch. 1228).

of the total mass whereas, in the decomposition of austenite, the conversion affects either the total mass or an appreciable part of the latter. For the inhibiting action of pressure in the decomposition of austenite linked with an increase of volume, data have also been adduced by E. Schmidtman, W. Biermann and H. Schenek (2). Further experiments on the influence of pressure seemed desirable for reactions accompanied by reduction of volume.

Examples were selected in which a large part of the total mass is affected and the reactions take place preferably in substituted mixed crystals and not in intercalated mixed crystals (e.g., austenitic manganese steel). Where the increased pressure appreciably influences the diffusion of the alloyed partners, it was to be expected that this influence is not so easily obscured for reactions in substituted mixed crystals by the influence of the magnitude and of the sign of the change of volume. Alloys of iron and nickel containing 25-35% nickel appeared suitable for such experiments. This concerns substituted mixed crystals which can be transformed extensively into the body-centered cubic crystal form and should produce a reduction of volume upon return to the face-centered form. The  $\alpha \rightarrow \gamma$  conversion starts partly already immediately above 200° C. This circumstance is very useful from the metallurgical viewpoint because continuous measurements in a high-pressure vessel above 400° C are rather difficult. In regard to diffusion, it should be kept in mind that the adjustment of the phase equilibria between  $\alpha$ - and  $\gamma$ - mixed crystals below 500° C requires prolonged intervals.

The  $\gamma = \alpha$  conversion in the iron-nickel system has been investigated in detail by many researchers. For our present task, it is sufficient to know that the two-phase field  $\alpha + \gamma$  has an appreciable width already at 500° C which further increases with lower temperatures. The conversion inertia of the face-centered  $\gamma$ -mixed crystals is sufficiently great, however, to preserve the composition of the mixed crystals

(2) Arch. Eisenhüttenwes. 32 (1961) P. 843/50 (Werkstoffaussch. 1302). --Also Dr.-Ing. Diss. (Extract) by W. Biermann, Techn. Hochsch. Aachen.

unchanged by quenching to 20 or 0° C. Upon deep-cooling in liquid air or other agents, demixing also does not need to be expected. The face-centered mixed crystals quenched to 20° C are supersaturated with iron in regard to the phase equilibrium. The body-centered mixed crystals with 25-35 % nickel obtained by low-temperature cooling are supersaturated with nickel. On the basis of the balanced system, there should be present simultaneously, both at 20 and at 400° C, body-centered mixed crystals with a low content of nickel and face-centered mixed crystals with a high content of nickel. According to E. A. Owen and Y. H. Liu (3), the body-centered limit mixed crystal contains 6.6 % nickel and the face-centered crystal contains 43 % nickel at 400° C. In an alloy with 35 % nickel, the  $\alpha \rightarrow \gamma$  conversion allegedly does not become complete below 450° C under customary pressure. The remaining  $\alpha$ -mixed crystals are said to contain less and the newly formed  $\gamma$ -mixed crystals more than 35 % nickel. Our task consisted in transforming the crystals without demixing into the body-centered crystal form and, upon heating of the  $\alpha$ -mixed crystals supersaturated with nickel to measure the formation of  $\gamma$ -mixed crystals in consideration of temperature, quantity, time and nickel content both under customary as well as high pressure.

#### Sample Preparation, Pressure Apparatus and

#### Measurement Procedure

The samples were prepared by mixing, compacting and sintering of powdered carbonyl iron and carbonyl nickel. From data of the manufacturer, carbonyl nickel contains not less than 99.8 % nickel and not more than 0.05 % iron, and carbonyl iron contains not less than 99.7 % iron and not more than 0.04 % nickel. After sintering, the content of carbon was 0.002 %. Sintering was carried out at 1,350° C for 48 hours. The samples were cooled in the furnace and subsequently cut into cylinders with a diameter of 4.5 mm and a length of 35 mm. Upon measurement of the electric resistance in the  $\gamma$ -state, the samples were converted through deep-cooling in liquid nitrogen into a primarily ferritic state.

(3) J. Iron Steel Inst. 163 (1949) p.132/37 & 1 table; see esp. p. 136.

Table 1. Measurements of resistance for determining  $\alpha \rightarrow \delta$  conversion in iron-nickel alloys.

| heat treatments;   | pressure in $\text{kg/cm}^2$ ; | 54.8%-nickel alloy:                                |  |  |
|--|--------------------------------|--|--|--|
|  |                                | electric resistance $\rho(1)$ $\mu\Omega\text{cm}$ | amount of $\delta$ -phase from experiments | amount of $\delta$ -phase from equilibrium diagram (3) |
| I. pure $\alpha$ -phase, 1350° C, 48 hours furnace cooling (5); 1 $\nabla$ 15 min deep-cooling (6) | --                             | 33 <sup>4)</sup>                                   | --   | --   |
| II. 1 $\nabla$ 11 $\nabla$ annealing at 250° C, 22 hours, furnace cooling; 5000                    | --                             | 86   | 100  | --   |
| III. 1 $\nabla$ 11 $\nabla$ annealing at 300° C, 20 hours, furnace cooling; 5000                   | 1                              | 43   | 19   | 45,8<br>(with 66,5% Ni)                                |
| IV. 1 $\nabla$ 11 $\nabla$ annealing at 350° C, 20 hours, furnace cooling; 5000                    | 1                              | 44   | 20,8                                       | 54,0<br>(with 57,8% Ni)                                |
| V. 1 $\nabla$ 11 $\nabla$ annealing at 400° C, 19 hours, furnace cooling; 5000                     | 1                              | 46   | 24,5                                       | 64,6<br>(with 49,8% Ni)                                |
| VI. 1 $\nabla$ 11 $\nabla$ annealing at 400° C, 19 hours, furnace cooling; 5000                    | 1                              | 49   | 30,2                                       | 78,0<br>(with 43,0% Ni)                                |
|  |                                | 57,7   | 46,6                                       |  |
|  |                                | 55,7   | 42,8                                       |  |
|  |                                | 68,4   | 66,8                                       |  |
|  |                                | --   | --   |  |
|  |                                | --   | --   |  |
|  |                                | --   | --   |  |

|     | 29.9%-nickel alloy:                          |  |  |
|-----|--|--|--|
|     | electric resistance (1) $\mu\Omega\text{cm}$ | amount of $\delta$ -phase from experiments | amount of $\delta$ -phase from equilibrium diagram (3) |
| I.  | 31 <sup>4)</sup>                             | --   | --   |
| II. | 85   | 100  | --   |
|     | 33,0   | 3,7  | --   |
| V.  | 37,3   | 4,3  | 11,6<br>(with 49,8% Ni)                                |
| VI. | 41,0   | 8,0  | 18,5<br>21,8<br>35,5<br>(with 43% Ni)                  |
|     | 42,8   | 9,8  | 64,0   |
|     | 50,2   | 17,2                                       |  |
|     |  | --   | --   |

Footnotes for Table 1.

- (1) electric resistance at room temperature and  $p = 1 \text{ kg/cm}^2$ ; (2) difference of electric resistance at room temperature and  $p = 1 \text{ kg/cm}^2$  before and after annealing;
- (3) diagram of equilibrium according to Wren and Liu; (4) extrapolated from measurements by Shirakawa; (5) pure  $\chi$ -phase in this state; (6) in liquid nitrogen.

For the experiments under high pressure, we utilized the high-pressure apparatus described by U. Jellinghaus and H. Friedewold (1). A hollow cylinder, closed at one end, of tempered chrome-nickel-molybdenum steel with a tensile strength of  $100 \text{ kg/mm}^2$  served as high-pressure vessel. The effective working space has a diameter of 25 mm and a length of 100 mm with a wall thickness of 28 mm. Pressure is produced by a two-stage high-pressure pump employing as pressure fluid "silicon-oil" with a viscosity of 3 cSt at room temperature. The apparatus is capable of pressures up to  $6,000 \text{ kg/cm}^2$ . Pressure is controlled with a steel-tube spring-pressure gauge. The pressure vessel is heated to the starting temperature by a vertically adjustable furnace and temperature is measured with a nickel-chrome/nickel thermocouple element whose hot-soldered junction is located in a bore, 12 mm deep, in the middle of the cylinder wall. An automatic regulator was utilized for the isothermal experiments which maintains temperature constant with  $\pm 2^\circ \text{ C}$ . About two hours are required to heat the unit from room temperature to  $400^\circ \text{ C}$ .

The  $\alpha \rightarrow \gamma$  conversion was observed primarily by measurement of electric resistance. Power leads and potential terminals consisting of copper wire with a diameter of 0.4 mm were silver-soldered at the extremities of the samples. The samples and the electric leads were isolated by ceramic tubes. In order to seal the bushings of the measuring wires from the high-pressure vessel to the outside, we utilized the method of Ebert and Gielessen (4). A Thomson bridge served for measurement of resistance.

For the complementary magnetic measurements as far as determination at room temperature was concerned, we utilized an electromagnet with axially drilled poles as developed by Stablein and Schroeter (5). Concentration of nickel in the  $\gamma$ -mixed crystal with the aid of the Curie temperature was determined by a magnetic scale according to Mathieu (6). Further uses of the scale will be described later.

#### Experimental Findings

Upon heating, an  $\alpha \rightarrow \gamma$  Conversion up to  $400^\circ \text{ C}$  increase of electric resistance occurs which is due in part

(4) Ann. Phys., 6. Folge, 1 (1947) P. 229/40. see esp. P. 230

(5) Z. anorg. allg. Chem. 174 (1928) P. 193/215.

(6) Arch. Eisenhüttenwes. 16 (1942/43) p. 415/23.

to the increased temperature but in part also due to the  $\alpha \rightarrow \gamma$  phase conversion. This non-reversible part of the increase of resistance is found above 235° C for the alloy with 34.8 % nickel. If heating is arrested by transition to a constant temperature, the increase of resistance is also practically arrested. In several experiments with constant temperatures between 250 and 400° C, no appreciable increase of resistance was found after 20 hours. During cooling, resistance decreases but the decrease is less than the increase upon heating due to the non-reversible  $\alpha \rightarrow \gamma$  conversion.

Table 1 groups the values of electric resistance measured at room temperature before and after the experiment. These measurements were also made for the samples heated under high pressure without stress. The conditions of measurement consequently concord for both groups of annealing experiments (at pressures of 1,000 and 5,000 kg/cm<sup>2</sup>; ref. 2).

The quantitative proportion of the newly formed  $\gamma$  phase was calculated from the changes of resistance. We assumed here that elastic stresses in the mixture of the two types of crystals did not have any appreciable influence on electric resistance. On this assumption, the volume ratio  $x$  of the  $\gamma$ -phase was calculated according

to the mixing rule 
$$x = \frac{\rho_{100\% \alpha} - \rho_{leg.}}{\rho_{100\% \alpha} - \rho_{100\% \gamma}} \quad (1)$$

from the specific resistances of the pure  $\alpha$ -phase  $\rho_{100\% \alpha}$  and of the phase mixture  $\rho_{leg.}$

The specific resistance of the pure  $\alpha$ -phase of the iron alloy with 34.8 % nickel was extrapolated according to measurements by Shirakawa (7) from the resistances of alloys with 25 and with 30 % nickel. In the experiments performed under high pressures, the increases in the quantitative ratio of the  $\gamma$ -phase are 2 to 3 times as high as in experiments under customary pressure. Figure 1 shows the increase of the specific electric resistance under annealing. The curves extrapolated from low annealing temperatures intersect in the vicinity of the initial resistance.

(7) Sci. Rep. Tohoku Univ. 27 (1939) P, 485/531.



An appreciable influence of pressure on the temperature at the start of non-reversible changes can not be observed.

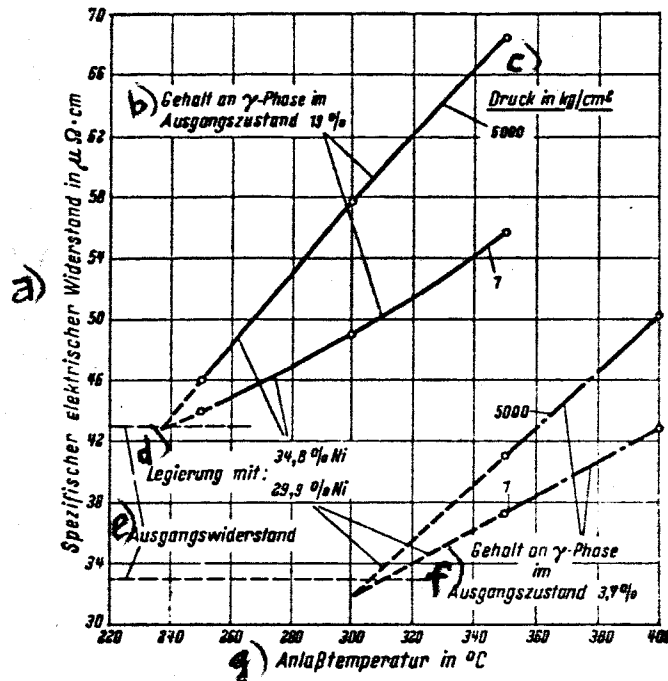


Fig. 1 - Increase of electric resistance due to incomplete re-formation of  $\alpha$ -phase into  $\gamma$ -phase in iron alloys with 29.9 and 34.8% nickel under customary and under high pressure.

Legend: a) specific electric resistance in ...; b) content of  $\gamma$ -phase in initial state 19%; c) pressure in  $\text{kg/cm}^2$ ; d) alloy content: ...; e) initial resistance; f) content of  $\gamma$ -phase in initial state 3.9%; g) annealing temperature in  $^{\circ}\text{C}$ .

Measurements of magnetic saturation can be utilized in the same manner for the determination of the quantitative ratio of the  $\delta$ -phase if the saturation values are known for  $\alpha = 100\%$  and  $\gamma = 100\%$ . They were carried out for the iron alloy with 29.9% nickel. According to formula 1, there is valid 
$$x = \frac{4\pi J_{\infty, 100\% \alpha} - 4\pi J_{\infty, \text{Lex.}}}{4\pi J_{\infty, 100\% \alpha} - 4\pi J_{\infty, 100\% \gamma}} \quad (2)$$

For the 29.9% nickel alloy, it is difficult to find a saturation value in literature which can be ascribed reliably to a state of the alloy completely free of austenite. The saturation value required in formula 2 for the pure body-centered state was therefore provisionally derived through calculation by assuming as known, from the measurements of resistance in the same alloy, the ratio of the  $\gamma$ -phase in the deep-cooled state. For the further treatment of the 29.9% nickel alloy, there resulted approximately the same increases in the share of the  $\gamma$ -phase as from the

the measurements of resistance (cf. Table 2).

Table 2--Measurements of magnetization for determining  $\alpha \rightarrow \gamma$  conversion of 29.9 %--nickel alloy.

| heat treatments  | pressure in kg/cm <sup>2</sup> ; | magnetization $4\pi I_{\infty}$ at 20° C <sup>1,2</sup> in Gauss; | ratio of $\gamma$ -phase; measured; | calculated from Peschard; Vol.-% |
|--|----------------------------------|---|-------------------------------------|----------------------------------|
| I. pure $\alpha$ -phase, 1350° C, 48 hours, furnace cooling; | ---                              | 19370 <sup>3)</sup>   | 0                                   | ---                              |
|  | ---                              | 4800  | 100                                 | ---                              |
| II. 1 / 15 min deep-cooling <sup>(4)</sup> ;                 | ---                              | 18840   | 3,7                                 | 0,3                              |
|  | ---                              | 18830   | 3,9                                 | 0,35                             |
|  | ---                              | 18810   | 4,1                                 | 0,5                              |
| III. 1 / 11 / annealing at 350° C,                           | 1                                | 17640   | 11,9                                | 8,8                              |
|  | 5000                             | (18840)   |                                     |                                  |
|  | 5000                             | 16610   | 18,9                                | 16,1                             |
| IV. 1 / 11 / annealing at 400° C, 19 hours, furnace cooling. | 1                                | 16310   | 21,0                                | 18,3                             |
|  | 5000                             | (18830)   |                                     |                                  |
|  | 5000                             | 14300   | 34,8                                | 32,5                             |
|  |                                  | (18810)   |                                     |                                  |

(1) pressure = 1 kg/cm<sup>2</sup>; (2) data in parentheses: values measured in initial state; (3)  $4\pi I_{\infty}$  for  $\alpha$ -state from Peschard = 18,880; (4) in liquid nitrogen.

Table 2 further lists the volume ratios of the  $\gamma$ -phase obtained if we introduce 18,880 Gauss for  $4\pi J_{00,100\% \alpha}$  as basis for calculation in accordance with Peschard (8). Since this value is lower by 490 Gauss than the one calculated from formula 2 with a given  $x$ , there results a correspondingly lower volume ratio of the  $\gamma$ -phase.

Subsequent to the annealing treatment, temperature/magnetization curves were plotted from samples of both alloys and the Curie-temperatures determined were compared with the Curie-temperatures of the pure  $\gamma$ -phase. There were found only minor divergences. The concentration of nickel in the re-formed  $\gamma$ -mixed crystal is consequently still approximately the same as earlier in the initial homogeneous austenitic state. Since, according to Peschard (9), the Curie temperature rises,

(8) Rev. Metallurg., Mem., 22 (1925) P. 490/514, 581/609 and 663/85; cf. esp p. 670.

(9) cf. ref. 8, p. 594.

at about 30 % nickel, by 25° C per 1 % nickel, the increases found of 8° C (pressure = 1 kg/cm<sup>2</sup>) and 10° C (pressure = 5,000 kg/cm<sup>2</sup>) and under 400° C treatment of the 29.9 % nickel alloy can be equated with an increase of the nickel content by 0.3 and 0.4 %. According to the equilibrium, we should have found, at 400° C, an increase to 43 %, i.e., an increase to 13.1 % nickel.

Table 3 - Measurements of hardness on samples of 29.9 %-nickel alloy.

| heat treatment;  | pressure in kg/cm <sup>2</sup> ; | hardness, HV 10; | volume ratio of $\delta$ -phase (1) in %; |
|--|----------------------------------|------------------|---|
| I. 1300° C, 48 hours, furnace cooling;                         |                                  | 125              | 100                                       |
| II. 1 / 15 min deep-cooling (2);                               |                                  | 200              | 3,7                                       |
| III. 1 / 11 / annealing at 350° C, 20 hours, cooling to 20° C, | 1<br>5000                        | 197<br>207       | 11,9<br>18,9                              |
| IV. 1 / 11 / annealing at 400° C, 19 hours, cooling to 20° C.  | 1<br>5000                        | 204<br>183       | 21,0<br>34,8                              |

(1) = calculated on the basis of measurements of magnetization; (2) = in liquid nitrogen.

In alloying the iron with 29.9 % nickel, we also measured the Vickers hardness on samples with different pre-and/or annealing treatment (Table 3). Under conversion from  $\gamma$  to  $\alpha$ , an increase of hardness occurs upon cooling to low temperatures. Annealing treatment at 350° C did not yet produce any measurable diminution of hardness. However, after annealing at 400° C under increased pressure, hardness has become appreciably reduced.

Prolonged experiments at 400° C for  $\alpha \rightarrow \delta$  Conversion

At higher temperatures and appreciably longer duration of annealing, the expectance for coming closer to equilibrium is greater. Experiments on an iron alloy with 29.7 % nickel were carried out at 430° C for 528 hours (22 days), both under customary pressure and under a pressure of 10,000 kg/cm<sup>2</sup>. The pressure was created in this case through heating of the sample in a closed steel vessel filled with mer-

cury (1). According to the diagram of equilibrium of Owen and Liu (3), we should have obtained, at  $430^{\circ}\text{C}$ , a volume ratio of the  $\gamma$ -phase of 71 % and nickel concentration of about 39 % for a sample with a nickel content of 29.7 %. Subsequently, there was found a ratio of the  $\gamma$ -phase of 19 % under customary pressure and a ratio of 31 % under high pressure. On the basis of quantity, equilibrium is far from being reached. From the temperature-magnetization curves, there resulted Curie-points of the  $\gamma$ -phase of  $318^{\circ}\text{C}$  for  $p = 1 \text{ kg/cm}^2$  and  $272^{\circ}\text{C}$  for  $p = 10,000 \text{ kg/cm}^2$ . Since, according to Peschard (8), the Curie point for the homogeneous mixed crystal with 29.7 % nickel lies at  $120^{\circ}\text{C}$ , the nickel concentrations of the  $\gamma$ -phase have, under these conditions, increased appreciably in the direction of the equilibrium. According to Peschard, we calculate, from the Curie temperatures, the nickel content of the  $\gamma$ -phase as about 30 % in the experiment under customary pressure and as 36.2 % for the experiment under high pressure. Consequently, the quantity of the  $\gamma$ -phase is higher under high pressure but the adaptation of the concentration to equilibrium is less complete.

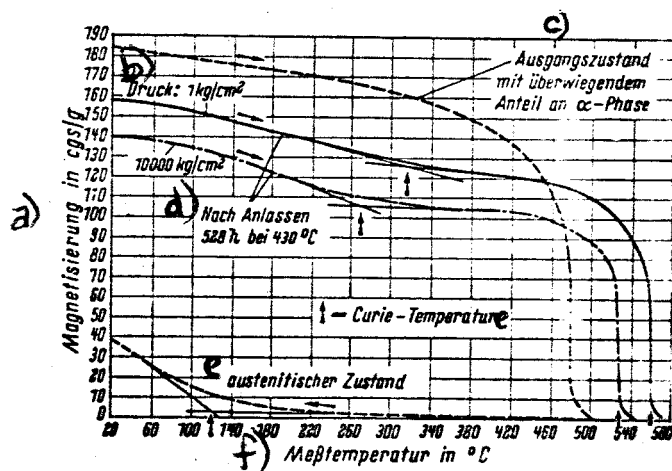


Fig. 2--Temperature-magnetization curves for determining nickel concentration of  $\alpha$ - and  $\gamma$ -phase after prolonged annealing at  $430^{\circ}\text{C}$  under customary and under high pressure.

Legend: a) magnetization in cgs/g; b) pressure:...; c) initial state with predominant share of  $\alpha$ -phase; d) after annealing for 528 hours at  $430^{\circ}\text{C}$ ; e) austenitic state; f) measuring temperature in  $^{\circ}\text{C}$ .

After prolonged treatment at 430° C, a change of the nickel content can also be noted in the  $\alpha$ -phase. Temperature-magnetization curves were plotted as demonstration (fig. 2). The conversion of the  $\alpha$ -phase which is still constant at 430° C, to the  $\gamma$ -phase at higher temperatures can be determined from the regression of the specific magnetization. The comparison of the respective temperatures with the actual diagram furnishes mean values for the nickel content of the  $\alpha$ -mixed crystals. These temperatures (530° C at  $p = 10,000 \text{ kg/cm}^2$  and 560° C at  $p = 1 \text{ kg/cm}^2$ ) correspond to a nickel content of 26.5 and/or 24.5 %. The nickel content has therefore dropped but still lies far above the content of equilibrium of 6.3 % nickel valid for 430° C.

Two brief-interval experiments at 430° C for 2.5 hours of the same alloy resulted in a volume ratio of the  $\gamma$ -phase of 27% under high pressure and in a ratio of 16 % under customary pressure. The Curie temperatures in both cases were the same as for the initial homogeneous austenitic alloy so that the nickel concentrations consequently did not change appreciably. These findings correspond to expectations. The  $\alpha \rightarrow \gamma$  conversion has occurred in greater part already during heating. On the other hand, the composition of the mixed crystals has not undergone any appreciable change at the terminal temperature of the experiment after 2.5 hours.

#### Discussion of Findings

The experiments performed at low temperatures produced a re-formation, favored by pressure, of the face-centered from the body-centered crystals. This did not change the nickel concentration. The result consequently was an instable state in which the quantitative ratio of the  $\gamma$ -phase was increased. The changes of concentration demanded by the diagram of equilibrium, however, had not occurred. Apparently, there exists for temperatures below 400° C only the possibility of a displacement conversion but not the possibility of adaptation of the concentration to the equilibrium. It is noteworthy that the displacement conversion from  $\alpha$  to  $\gamma$  starts at approximately the same temperature, regardless of whether customary or highly increased

pressure is employed. According to the Clausius-Clapeyron equation, there should have been a drop of the equilibrium temperature for the conversion accompanied by reduction of volume. A corresponding drop of the  $\alpha \rightarrow \gamma$  conversion temperatures through pressure was observed in the iron-chrome system by Kaufmann, Leyenaar and Harvey (10). In the iron-nickel system, the same authors investigated an alloy with 9.5 %-atom (10.5 %-vol.) nickel and found a drop of the conversion temperature of  $2 \times 10^{-3} \text{ }^{\circ} \text{C}/\text{kg}/\text{cm}^2$  at pressures up to  $60,000 \text{ kg}/\text{cm}^2$ . At  $p = 1 \text{ kg}/\text{cm}^2$ , the starting temperature of the  $\alpha \rightarrow \gamma$  conversion lies at  $680^{\circ} \text{C}$ .

If we did not find, in our own experiments on iron-nickel alloys, any difference in the temperatures at which the  $\alpha \rightarrow \gamma$  conversion starts, then there must be a special reason for this. The reaction of the iron-nickel alloys in a  $\gamma \rightarrow \alpha$  conversion still corresponds approximately to the theoretical requirements that the "Ms"-temperature, i.e., the temperature of the start of conversion, is reduced by high pressure as observed by Patel and Cohen (11). Why does this not occur in the  $\alpha \rightarrow \gamma$  conversion? The initial state in the  $\gamma \rightarrow \alpha$  conversion, i.e., the homogeneous austenitic mixed crystal, should mechanically still have been in an isotropic state of stress. In the nickel-martensite and/or the mixture of nickel-martensite and residual austenite which represents the initial state for the  $\alpha \rightarrow \gamma$  conversion, no further mention is made of a low-stress or isotropic state. In the displacement conversion from  $\gamma$  toward  $\alpha$ , the atom distances are shortened in certain directions in the crystal lattice but lengthened in other directions. The increase of volume leads to anisotropic state because a uniform hydrostatic pressure in all directions would increase the pressure in all directions would increase the pressure stresses in some directions but more or less equalize the existing tensile stresses in other directions. However this leads, at least for pressure stresses, which lie in the same order of magnitude as the internal stresses existing in the material, only to a changed spatial distri-

(10) Kaufman, L., A. Leyenaar and J. S. Harvey: Progress in very high pressure research. New York 1961

(11) Acta metallurg., New York, 1 (1953) P. 531/38.

tribution of the stresses but not yet to a state with a uniform amount of stress in arbitrary directions. We are also justified in recalling that the Clausius-Clapeyron equation was derived from the states of stress of gases and liquids, i.e., from relations in which anisotropy of the stresses does not occur.

At the time of completing this communication, there was published a report by Melnikov, Sokolov and Stregulin (12) which discusses the influence of pressure on the temperature of the  $\alpha \rightarrow \gamma$  conversion in an alloy with 27.6 % nickel and 0.046 % carbon. At  $p = 1 \text{ kg/cm}^2$ , this temperature lies at  $465^\circ \text{C}$ . Experiments with pressures of 1, 10,000, 20,000 and 30,000  $\text{kg/cm}^2$  showed a displacement by  $0.0025^\circ \text{C/at } p = 30,000 \text{ kg/cm}^2$ . This finding consequently differs considerably from the result of the present investigation in which we found an appreciable difference between the quantities converted with or without pressure but no notable displacement of the start of conversion.

However, the deviation is entirely justifiable both by the lower nickel and higher carbon content of the alloy employed by the Russian investigators (12) which increases the conversion temperature by about  $160^\circ \text{C}$  as compared to the alloy with 29.9 % nickel utilized by us and because of the considerably higher pressures employed by them. It is understandable that 20,000  $\text{kg/cm}^2$  are superior to the internal stresses whereas 5,000  $\text{kg/cm}^2$  do not yet produce any appreciable effect.

The experiments at  $430^\circ \text{C}$  have demonstrated that changes of concentration are effected by increase of temperature and duration which do not occur at  $400^\circ \text{C}$  and with brief intervals. However, the high nickel content of the  $\alpha$ -mixed crystals after the prolonged experiment at  $430^\circ \text{C}$  is still very far from the state of equilibrium. This is understandable inasmuch as the composition of the alloy with 29.7 % nickel lies appreciably closer to the nickel content of the  $\gamma$ -limit mixed crystal (according to the equilibrium, 38.8 % nickel) than to that of the  $\alpha$ -limit mixed crystal which allegedly contains only 6.3 % nickel. In order to reach the concen-

(12) Mel'nikov, L. A., B. K. Sololov and A. I. Stregulin: Phys. Metals Metallogr. 5 (1933) Nr. 3, P. 31/36.

tration of equilibrium in the  $\alpha$  -phase, there is consequently necessary a much more extensive diffusion. The experiments produced a lesser change of concentration in the  $\gamma$  -mixed crystal under high pressure than under customary pressure. It would be premature to attempt to interpret this finding. We might conceive both of an inhibition of diffusion through pressure as well as a displacement of the line of equilibrium of the  $\gamma$  -mixed crystal toward lower temperatures or lesser nickel content.

#### Summary

The  $\alpha \rightarrow \gamma$  conversion of two non-reversible alloys of iron with 29.7 and/or 54.8 % nickel is observed at temperatures up to  $430^{\circ}$  C and customary pressure and under pressure of  $5,000 \text{ kg/cm}^2$ . In both cases, conversion begins during steady heating at approximately the same temperatures. If heating is arrested at 250, 300, 350, or  $400^{\circ}$  C, we then find in the experiments under pressure 2 to 3 times the amount of newly formed  $\gamma$  -phase. Continuation at the temperatures indicated beyond 20 hours does not produce any increase of the  $\gamma$  -phase and the concentrations of the mixed crystals remain almost unchanged. Diffusion can be demonstrated at  $430^{\circ}$  C after continuation for 22 days. In the experiment under customary pressure, the nickel contents come closer to the value required by the diagram of state than in the experiment under high pressure. However, in both cases the nickel content of the  $\alpha$  -mixed crystals remains higher than required by the equilibrium. The start of  $\alpha \rightarrow \gamma$  conversion at the same temperature independently of the amount of pressure is explained by the highly stressed initial state.