Tempering of Chromium Steels

(The Fourth Report)

Qualitative Analysis by X-ray Diffractometer*

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The tempering processes of the chromium steels (Cr–8% or 13%, C–0.6%) were studied through X-ray diffraction method comparing with the tempering process of 1% plain carbon steel, and these and the other results of the magnetic analyses, hardness tests, corrosion proof tests, and differential thermal analyses, were considered synthetically. The conclusions obtained were as follows: (1) It is impossible te explain without any contradtction all the diffraction patterns in each stage of tempering process with the view that the carbide in each stage of the tempering process is respectively ε–carbide, Fe_3C or $(Fe, Cr)_3C$ and $(Cr, Fe)_7C_3$ alone. (2) In the chromium steels after the tempering at 300°C for 20 hours, the diffraction line was recognized where the strongest diffraction line (710) of χ–carbide is due. And the reflection from the atomic plane (612) of χ–carbide was also recognized. (3) It may be hasty to assert the existence of χ–carbide on the sole ground that there exists a diffraction line where (710) line and (612) line of χ–carbide are due : but considering this along with the results in the previous reports, and especially in view of the fact that Curie point of χ–carbide is recognizable at this stage of tempering process, the existence of χ–carbide is nearly positive. (4) Essential diffraction lines, the existence of which was concluded in the previous reports, were dinstinctly recognized at the stage of the tempering process where they were expected.

Introduction

The author has studied the tempering process of chromium steels with the aid of X-ray diffractometer and has put forward the results in this report. It is needless to say that X-ray diffraction is an effective method of the researches on tempering process of steels. However, the X-ray diffraction lines of each carbide which matters much in the tempering process are feeble compared with those of the matrix. Moreover, what are regarded as the strongest diffraction lines of each

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carbide, viz. (101) line of ε-carbide, (710) and (612) lines of χ-carbide, (210) and (103) lines of (Fe, Cr)$_3$C, (202) and (421) lines of (Fe, Cr)$_7$C$_3$, and so on appear so close to the strongest diffraction lines of the matrix, viz. (101) and (110) lines of Martensite, (110) line of α-Fe, (111) line of γ-Fe, etc. that it is difficult to know one from another. Consequently a usual method so far was to take up and study a single crystal of martensite[1][2] and so forth. But in chromium steels, even after subzerotreatment is done, still some amount of austenite is retained, as is well known, so in order to study the tempering process in the proper way "as hardened chromium steel itself" in which martensite and austenite are blended should be dealt with as the object of study. Another method is to extract carbides from the tempered sample with the aid of the electrolytic method and examine the diffraction patterns; but this method is still open to discussin, as was pointed out in the first report[3], and there are some carbide hard to be drawn out by the electrolytic extraction method.[3][4] X-ray diffractometer has pretty high sensitivity because it can make effective use of reflected X-ray from the broad surface of the sample with the aid of para-focussing method and of G. M. counter tube available; accordingly it can be relied upon to detect the carbide reactions produced in the tempering process of chromium steels. The primary object in this report is to follow up the formation and extinction of various carbides accompanying the tempering process through X-ray diffraction method.

Materials and Procedure

The chromium steels used in this investigation are the same with those in the first report, viz. R80C6 and R130C6 (with 8% and 13% chromium content, and 0.6% carbon content); the hardening conditions are also the same with those in the first report. The plain carbon steel which was used for the sake of comparison has such composition as is shown in the following list, and it was austenitized for 2 hours at 1000°C and oil-quenched to room temperature and then it was subzero-treated in liquid air.

(Chemical Analysis of R0C10 Steel: wt %)

C	Si	Mn	Al
0.99	0.45	0.40	0.13

The experiments were made through the following two methods: (1) after the tempering for 20 hours at various temperature, it was measured at the room temperature; (2) the sample was fixed in the apparatus for maintaining high temperature and was measured while it was being heated at the rate of 3°C/min. The size of the sample used in the experiment (1) is 20 mm$\phi \times 5$ mm and its X-ray

diffraction pattern was observed while the sample was being rotated. The size of the sample used in the experiment (2) is $25 \times 20 \times 1mm^3$, and in this case the temperature was measured with Pt-Rh thermo-couple percussion welded to the sample. The X-ray diffractometer used in the experiments is D3-1-F type made by 'Rigaku-Denki' Inc.: the heating treatments higher than the room temperature were all carried on in vacuum. Identifications of the diffraction lines were done with the aid of Diffraction Cards by A. S. T. M. and Handbook by Pearson.[5]

Results and Discussion

Plain carbon steel :

Fig. 1 and Fig. 2 indicate a part of X-ray diffraction patterns continuously recorded of R0C10 steel while being heated at the rate of 3°C/min. The X-ray used was Co-K_α radiation filtered with Fe, and the conditions of the experiment are as follows: acceleration voltage is 30 KVP; beam current 12 mA; count full scale 1600 c/s; divergency 2.5°; receiving slit 0.2mm. The amplitude of scanning was 5° or 6° comprising the main diffraction lines of martensite and various expected carbides: scanning speed was 2°/min.

As the sample was poly-crystal it was impossible to completely resolve the main diffraction line of martensite; viz. (101) line from (110). But it was possible to discern and identify them clearly, as is shown on the top line of Fig. 1. The arrow marks in the diagram, h_1 and h_2 denote the positions of (101) line and (110) line respectively of the martenites of 1% C steel calculated according to the reports by Werner et al[2]. At tempering temperature 72°C a new peak l_1 was born between h_1 and h_2. At the first stage of the tempering the martensite super-saturated with carbon is decomposed into ε-carbide and low carbon less tetragonal martensite, as is generally known. Let us take l_1 the (101) line of less tetragonal martensite tentatively and calculate the amount of the carbon content according to the equations by Werner et al, and the answer 0.3% was worked out which coincided with the value denoted in the reports published up to dats: l_2 is the position of (110) line of martensite with 0.3% C content, but it was difficult to be detected. But it must be affirmed that the carbon content of less tetragonal martensite was 0.3%.

When the tempering temperature was raised to 130°C the several peaks were nearly unified into one, which denotes that M_h, martensite as hardened (1% C), decreases and M_l, low carbon martensite (0.3% C), which is the product by decomposition of M_h, increases. Judging from the diffraction pattern, it can be surmised that approximately equivalent amounts of M_h and M_l exist at this tempering stage. When the tempring temperature was raised still higher, the shape of this peak became sharper gradually and shifted to the side of larger diffraction angle in proportion to the rise of the temperature. This shows that M_h gradually decreases and M_l gradually increases.

As Refrigerated

Austenitizd for 2Hrs at 1000°C
Oil-quenched to Room Temperature
Refrigerated in Liquid Air

at   72°C

at   130 C

at   166 C

at   230 C

at   257 C

With X-Ray Diffractometer
Target,   Co
Filter,   Fe
Voltage,   30 KVP
Current,   12 mA
Count Full Scale,   1600 c/s
Divergency, $2\frac{1}{2}°$
Receiving Slit,   0.2mm
Heating Velocity,   3°C/min

50°   55°
                              2θ

Fig. 1 Continuous Tempering X-Ray Diffraction Pattern
of 1.0%C Steel

At the tempering temperature 562°C this peak became a single, sharp one, which denotes the formation of cubic α-Fe. At the tempering temperature 166°C another new diffraction line came out, which was denoted with ε in the diagram. This diffraction line grows together with the rise of the tempering temperature and exists positively up to 275°C, but again it disappesrs completely at the tempering higher than 350°C. In the case of plain carbon steel, retained austenite γ_R and ε-
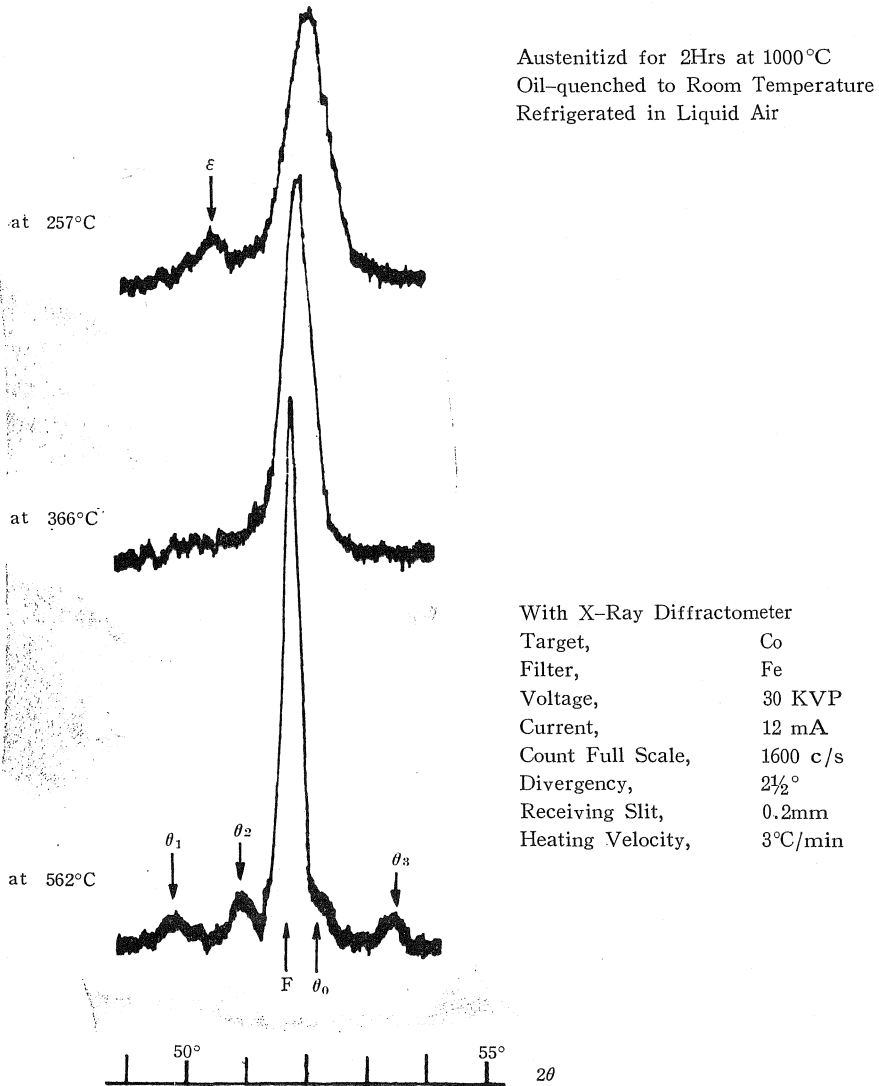
Fig. 2 Continuous Tempering X–Ray Diffraction Pattern
of 1.0%C Steel

carbide are considered as the factors producing the diffraction line at this position. However, taking consideration of the fact that ε line did not exist at the low tempering temperature, it is clear that this is not (111) line of γ_R. Consequently it can be asserted that ε line is (101) line of ε-carbide. This point of view is consistent with the results of the other researches published so far and of our previous reports.

When the carbon steel was tempered with continuous heating, the magnetic analysis showed that the decomposition temperature of ε-carbied is around 385°C as was described in the first report[3]. But in the results through X-ray diffraction

method, the diffraction line of ε-carbide disappeared at the temperature 350°C. These trifle differences can be explained by the following consideration : as was pointed out in the first report[3], the method of magnetic analysis is so sensitive that even fine particles in the esrly period of precipitation and two-dimensional precipitation phase before it can be dected. In order to investigate the condition of the early stage of precipitation through X-ray diffraction method, such a method as small-angle scattering method is indispensable ; wide-angle gonismeter is insufficient. The results of the previous reports show us that ε-carbide ought to have been precipitated at the tempering lower than 150°C. In the present experiment, ε-carbide was not detected through X-ray diffraction method until it had grown to some extent at the tempering higher than 150°C. This fact proves that the above-mentioned way of thinking is right. Consequently and conversely the same reasoning might be allowed about the disappearing stage of ε-carbide. Moreover, the decomposition of ε-carbide gradually proceeds at the tempering higher than 300°C as was pointed out in the first report[3]. The decomposition of ε-carbide proceeds in considerable measure at the tempering temperature around 350°C and its crystal structure deforms so much that it cannot be detected by the common X-ray diffraction method but presumably can up to a little later stage by the magnetic analysis.

Fig. 3 shows the the diffraction pattern of annealed R0C10 steel, and its sharp peak F denotes (110) diffraction line of α-Fe. Furthermore, in this diffraction pattern there are smaller peaks, θ_1, θ_2, θ_3 and θ_0 which partly overlaps the high-angle side of F. What exist in annealed 1% C steel are α-Fe and cementite Fe_3C, and as a matter of fact, θ_0, θ_1, θ_2 and θ_3 denote the diffraction lines of (103), (121), (210) and(211) atomic planes of Fe_3C respectively. And within this diffraction angle range (022) line of Fe_3C ought to exist, but the interplanar spacing for (022) plane of Fe_3C and that for (110) plane of α-Fe approximately coincide and besides, the intensity of (022) line of Fe_3C is low so that it seems to be hidden behind the strong (111) line of α-Fe.

In the diffraction pattern at the tempering temperature 562°C in Fig. 2 are the above-mentioned small peaks θ_0, θ_1, θ_2 and θ_3 discernible, which denotes the secure existence of Fe_3C at this temperature. According to the consecutively recorded heating diffraction patterns, Fe_3C seems to be precipitated at the temperature around 500°C.

Between the tempering around 350°C and 500°C diffraction line which can be consicered to be due to carbides could hardly be discerned as that at 366°C in Fig. 2. As was mentioned above, even when the tempering tempsrature is higher than 350°C, there might possibly be ε-carbide undetectable by X-ray diffraction method up to the temperature around a dozen degrees higher than 350°C. And even when the tempering temperature is lower than 500°C, within the temperatures around a dozen degrees lower than 500°C there may possibly be produced Fe_3C which cannot
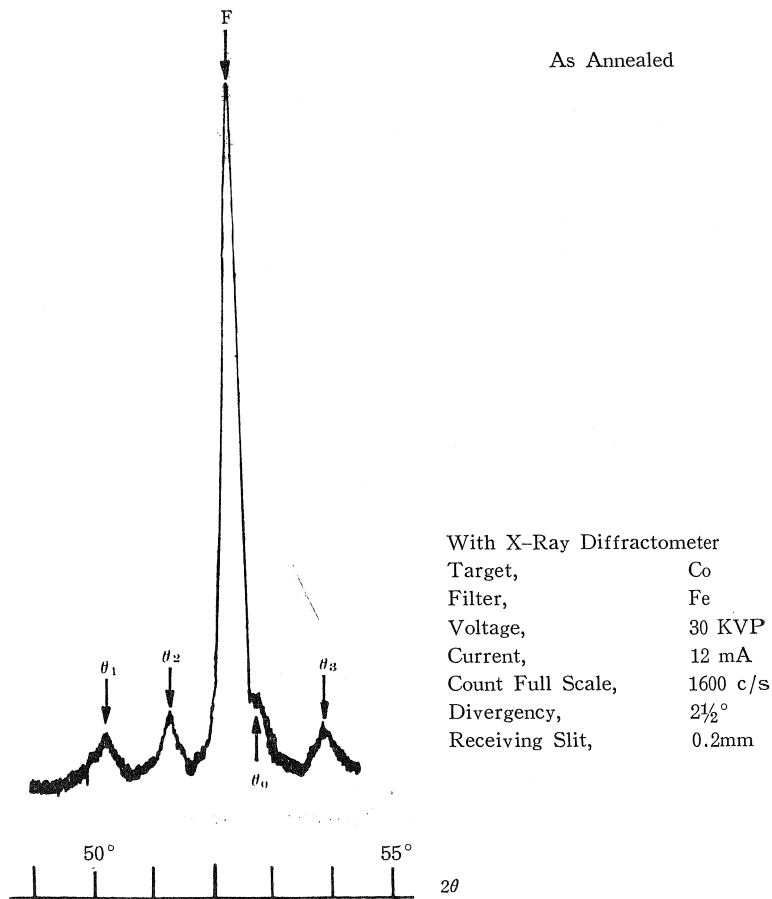
Fig. 3   X–Ray Diffraction Pattern of 1.0%C Steel

be detected by X-ray diffraction method.   But it was after the tempering at 500°C that Fe₃C was detected through magnetic analysis for the first time.   Therefore it is next to impossible to explain the fact that there is no diffraction line of carbides within the wide temperature range between 350°C and 500°C with only ε -carbide and Fe₃C.   The author found out the necessity of introducing another new phase named χ factor by the author into this tempering temperature range after the magnetic analyses.   This χ factor has the same Curie point with that of χ-carbide. Within this diffraction angle range the strongest diffraction lines of χ-carbide, (710) and (612), exist, but neither can be detected because they are within the strong influence of the doublets of martensite which still cover a pretty wide extent.   Thus from only the results of the studies on the tempering process of steel with consecutive heating X-ray diffraction method, χ factor on whose existence the author has insisted cannot be identfied with χ-carbide clearly, but the viewpoint that the carbides which exist in the tempering process are made up of only ε-carbide and Fe₃C must be denied.   In order to explain without any inconsistency

the results of magnetic analyses, hardness tests, corrosion proof tests, differential thermal analyses, etc., it seems more appropriate and valid to admit the existence of χ-carbide and consider that its diffraction lines are hidden benind the doublets of martensite.

Chromium steel :

Fig. 4 and Fig. 5 show the important parts of the X-ray diffraction patterns of R80C6 steel at room temperature after the tempering for 20 hours at various temperatures and Fig. 6 shows that of R130C6 steel at room temperature after the tempering for 20 hours at 700°C. The X-ray used in the experiment is Cr-K$_\alpha$ radiation filtered with V; acceleration voltage is 40 KVP; beam current 8mA; couut full scale 800 c/s; divergency 2.5°; receiving slit 0.2mm.

As is seen in Fig. 4 and Fig. 5, it is difficult and indistinct to record the doublets of martensite separately and distinguish M_h from M_l. However, the general trend that the main peak of the diffraction pattern becomes gradually sharper and its position shifts to the high angle side can be detected clearly. From this result only it might be considered that the amount of C in martensite has gradually decreased but when this result is considered in comparison with the results of studies on plain carbon steel it seems more appropriate to conrider that the amount of M_h has gradually decreased and that of M_l gradually has increased. After the tempering for 20 hours at 250°C the diffraction line corresponding with $d = 2.08$ Å appears newly. Seeing that this diffraction line did not exist at the low temperature it is obvious that this is not (111) line of γ_R; judging this synthetically with the results in the previous reports[3][4][6] of the author this can be considered to denote the strongest diffraction line (101) of ε-carbide.

After the tempering at 300°C for 20 hours the aforesaid diffraction line disappears and the diffraction line of $d \doteqdot 2.07$ Å which is weaker than this appears. It is an important matter this coincides with one of the strongest diffraction lines of χ-carbide, viz. (710). Furthermore, when the main peak of diffraction pattern at each tempering temperature stage is compared with that at other stage, a general trend is that it becomes higher and sharper as the tempering proceeds, but so far as the peaks at 300°C and 350°C are concerned, the trend is reverse—that is, the main pesk at 350°C is lower than that at 300°C. This means that the main peak of X-ray diffraction pattern after the tempering at 300°C for 20 hours has something added other than martensite. Suppose the aforesaid diffraction line corresponding with $d \doteqdot 2.07$ Å represented (710) line of χ-carbide, it would be inevitable that the other main diffraction line (612) of χ-carbide should appear. But (612) line of χ-carbide is within the influence of the main diffraction line of martensite as is denoted with an arrow mark in Fig. 5. Consequently, assuming that χ-carbide existed after this tempering process it would be possible to explain both the coming out of $d \doteqdot 2.07$ Å diffraction line and the anomaly with regard to the intensity of the main diffraction line of martensite without contradiction.

Martensite (101),(110)

As Quenched

Austenitizd for 2Hrs at 1150 °C
Oil–quenched to Room Temperature
Refrigerated in Liquid Air

Tempered for 20Hrs
at 100°C

Tempered for 20Hrs
at 150°C

Tempered for 20Hrs
at 200°C

ε (101)

Tempered for 20Hrs
at 250°C

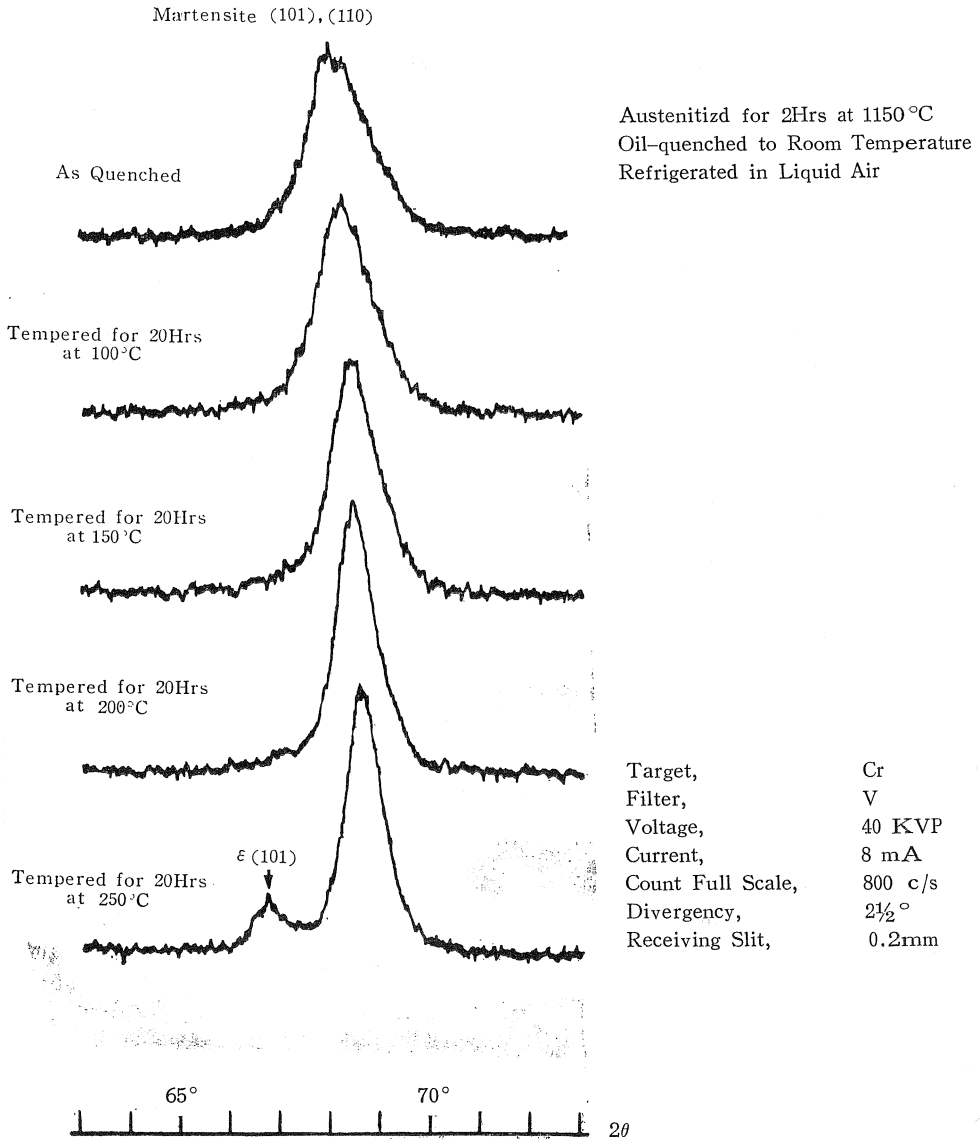|	
Target,	Cr
Filter,	V
Voltage,	40 KVP
Current,	8 mA
Count Full Scale,	800 c/s
Divergency,	$2\frac{1}{2}$ °
Receiving Slit,	0.2mm

65°   70°

2θ

Fig. 4 X–Ray Diffraction Pattern of 8%Cr–0.6%C Steel with Diffractometre

The diffraction line of χ-carbide could not be detected except the strongest diffraction lines (710) and (612). It may be criticized as a hasty conclusion to affirm the existence of χ-carbide with the bare fact that the two weak diffraction lines corresponding with the strongest diffraction lines of χ-carbide exist. It may be open to censure to assert the existence of χ-carbide with the mere fact that there exists something having the same Curie point of χ-carbide on the magnetic curve, as was shown in the previous report[3]. However, it can be affirmed for certainty that in the high chromium steel tempered at 300°C there exists something
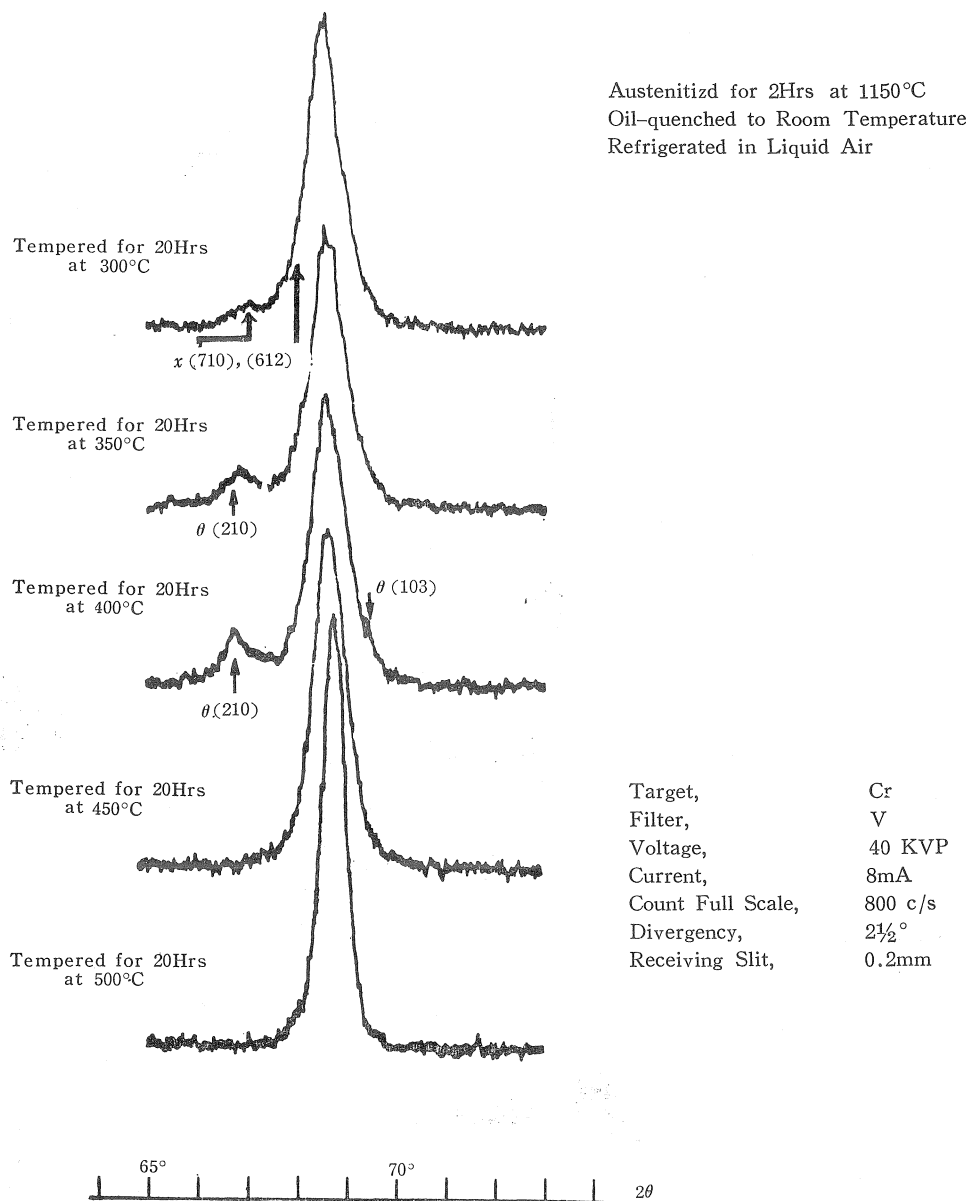
Austenitizd for 2Hrs at 1150°C
Oil–quenched to Room Temperature
Refrigerated in Liquid Air

Tempered for 20Hrs at 300°C

x (710), (612)

Tempered for 20Hrs at 350°C

θ (210)

Tempered for 20Hrs at 400°C

θ (103)

θ (210)

Tempered for 20Hrs at 450°C

Target,	Cr
Filter,	V
Voltage,	40 KVP
Current,	8mA
Count Full Scale,	800 c/s
Divergency,	$2\frac{1}{2}°$
Receiving Slit,	0.2mm

Tempered for 20Hrs at 500°C

65°   70° 2θ

Fig. 5 X–Ray Diffraction Pattern of 8%Cr–0.6%C Steel with Diffractometer

which has magnetic transformation point corresponding with the Curie point of χ-carbide and produces diffraction lines corresponding with X-ray diffraction patterns of χ-carbide. And also the results of hardness tests, corrosion tests, differential thermal analyses, etc. show that the existence of another phase must be admitted in the intermediate process between ε-carbide and θ phase, in order to explain the tempering processes of plain carbon steel and chromium steels. The author has so far called this phase χ-factor. However, judging synthetically from

the above-mentioned results, it would be appropriate and valid to reason that this χ-factor is χ-carbide. The diffraction line of χ-carbide which was indiscernible in the tempering process of plain carbon steel could be discerned in that of chromium steel; this seems to be due to the fact that chromium condensed in carbide as is well-known and as a consequence the lattice constant became larger.

Considered on the basis of certainty of the existence of χ-carbide in the tempering process of chromium steels, the above-mentioned inference of the existence of χ-carbide in the tempering process of plain carbon steel increases in its validity.

After the tempering at 350°C for 20 hours, the main diffraction line of martensite shows a slight decrease in intensity and (710) line of χ-carbide disappears but a more remarkable new diffraction line appears to the low-angle side of (710) line of χ-carbide, and the main diffraction line of martensite leaves a gentle trail to the high-angle side. The former is considered to be (210) line of $(Fe, Cr)_3C$ and the latter is due to the overlapping of its (022) and (103) lines on the main diffraction

Austenitizd for 2Hrs at 1150°C
Oil–quenched to Room Temperature
Refrigerated in Liquid Air

Target,	Cr
Filter,	V
Voltage,	35 KVP
Current,	9mA
Count Full Scale,	400 c/s
Divergency,	$2\frac{1}{2}°$
Receiving Slit,	0.1mm

$(Cr, Fe)_7C_3$ (421)

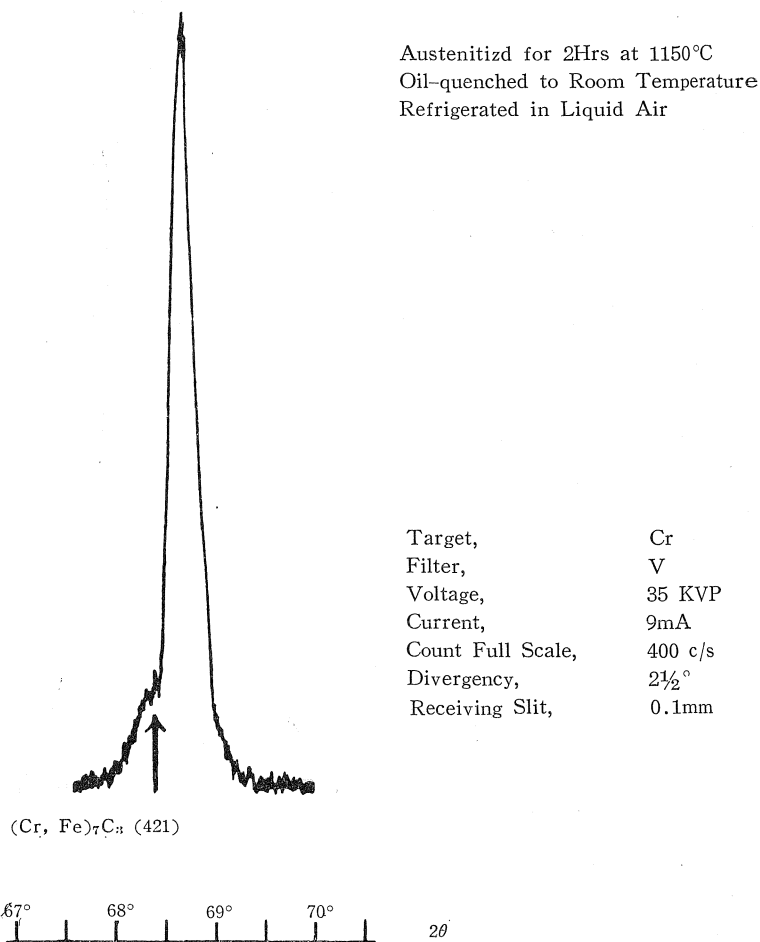67°   68°   69°   70° 2θ

Fig. 6 X–Ray Diffraction Pattern of 13%Cr–0.6%C Steel with Diffractometer
Tempered for 20Hrs at 700°C

line of martensite. The X-ray diffraction pattern of the sample tempered at 400°C for 20 hours shows that θ phase is retained meta-stable within this tempering range.

After the temperings at 450°C for 20 hours and at 500°C for 20 hours, no other diffraction line could be discerned than the main diffraction line of martensite. The representative diffraction line (421) of the ultimately stable alloy carbide (Cr, Fe)$_7$C$_3$ is extremely weak and is so close to (110) line of α-Fe that it is very difficult to distinguish it; this can be seen from Fig. 6 also which shows the X-ray diffraction pattern after the tempering at 700°C for 20 hours where this carbide has fully grown up: it is probably due to this that no diffraction line attributed to carbide can be discerned in the diffraction patterns of the samples tempered at 450°C and 500°C.

Conclusion

The author studied the carbides which exist in the tempering processes of plain carbon steel and chromium steels qualitatively through X-ray diffractometer and putting together these and the other results in the previous reports, obtained the following results :

(1) The reports up to the present that the amount of carbon content of low carbon less tetragonal martensite formed in the 1st stage of the tempering of steels is 0,3% without regard to the amount of carbon content in the matrix, were reaffirmed.

(2) Within the respective tempering stage where ε-carbide, Fe$_3$C or (Fe, Cr)$_3$C, and (Cr, Fe)$_7$C$_3$ are considered to exist, each representative main diffraction line was confirmed.

(3) The X-ray diffraction line which can be considered as reflection from (710) and (612) planes of χ-carbide was detected at the intermediate stage between the range of ε-carbide and that of θ phase in the tempering process of chromium steels.

(4) Indeed it may be hasty to conclude that there is a range where χ-carbide exists in the tempering process of chromium steels from the mere fact that a couple of X-ray diffraction lines can be discerned. But it is extremely difficult to explain these X-ray diffraction patterns with the view that transition precipitate is composed of ε-carbide alone. All the results in the previous reports show that there exists another phase different from these at the intermediate range between ε-carbide and θ phase. Above all, the results of magnetic analyses show that this new phase has a magnetic transformation point at the same temperature with the Curie point of χ-carbide.

Judging synthetically from all the results mentioned above it seems approximately certain that there exists χ-carbide in the tempering process of chromium steels.

(5) In the consecutive heating tempering process of plain carbon steel, the diffraction line of ε-carbide could be discerned distinctly at 257°C and that of Fe_3C at 562°C, but no other diffraction line than that of martensite was recognized between 350°C and 500°C. It seems appropriate to consider that though χ-carbide exists in this range, its strongest diffraction line is hidden behind the doublets of msrtensite.

Reference

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