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Tempering of Chromium Steels
(The Second Report)
Mainly by Means of Hardness Tests*

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The tempering process of chromium steels was studied mainly through hardness tests, and through these observations together with the results of the magnetic analyses published in the previous report(1) the following results were obtained. (1) Accompanied with the early period of precipitation of ε–carbide, some measure of hardening is observed in the neighborhood of the tempering temperature 100°C. In the isothermal tempering at 100°C and 150°C, the increase of hardness reaches its culmination in the early period of the tempering and after that a measure of softening due to the growth of ε–carbide is observed. (2) In the hardness curve after the tempering for 20 hours, at 125°C∼225°C sudden and rapid softening due to the growth of ε–carbide is observed. The growth of ε–carbide is saturated in the neighborhood of 250°C. (3) The decrease of hardness between the tempering temperasures 250°C∼325°C, corresponds with χ factor (probably χ–carbide) pointed out in the previous report.(1) (4) In the isothermal tempering at 350°C a measure of hardening is observed after the rapid softening in the earlier period. This can be considered to be related with the carbide–reaction (ε–carbide$\longrightarrow\chi$ factor$\longrightarrow$precipitation of θ phase) proceeding rapidly in this temperature. (5) The point of view that transition precipitate consists of ε–carbide only is hard to be approved in terms of hardness tests. (6) The change from ε–carbide in χ factor is irreversible and not accompanied with the increase of hardness. (7) In the tempering temperature 400°C∼450°C some secondary hardening is discernible. This can be considered to be due to θ phase in the early period of precipitation. (8) The electron micrographs of the impact fracture of the samples tempered at 450°C for 20 hours showed "hard" fractured surfaces. (9) In the hardness curve after the tempering for 20 hours at various temperatures, softening does not proceed between 330°C and 450°C. This shows that θ phase in the early period of precipitation remains meta–stable within this temperature range (330°C∼450°C). (10) In the tempering higher than 460°C, a rapid softening proceeds owing to the growth of $(Fe, Cr)_3C$ in the early period and to the nucleation and growth of $(Fe, Cr)_7C_3$ in the later period.

* A part of this research was presented at the Semiannual Conventions of Japan Institute of Metals, held 8 times between April. 1957 and October, 1960.

Introduction

The author has made a report on the results of the investigations on the tempering procsses of high chromium steel mainly through hardness tests.

Materials and Procedures

The samples used in the experiments are chromium steels (with 0.6% carbon content) having 8 % Cr content and 13% Cr content respectively : and their values of chemical analyses and hardening conditions are shown in the next table.

Designation	Chemical Analyses wt %				Austenitizing and Quenching	Subzerotreatment
	C	Cr	Si	Mn		
R′80C6	0.61	8.15	0.29	0.18	1150°C × 2hrs ⟶W. Q.	Liq. Air
R′130C6	0.63	13.17	0.25	0.15	〃	〃

For the sake of convenient comparison the plain carbon steel used here is the same R0C6 as was used in the previous report(1) and the measure of the samples is 10 mmϕ × 7 mm; the manufacturing processes are also the same with those in the previous report(1). Hardness tests were carried on at the room temperature, after the planned tempering processes treated in vacuo. The impact fractured surfaces of some samples were observed through electron microscope: the measure of the samples used in the above-mentioned test was 8mmϕ×40mm: in order to take electron micrograph, carbon film was evaporated on the impact fractured surface and it was observed through Extraction Replica method.

The Results and Discussion

The diagrams from Fig. 1 to Fig. 6 denote the results of the hardness tests after the tempering for 0.5∼21 hours at 100°C, 150°C, 200°C, 300°C, 350°C and 450°C respectively. In the tempering at 100°C the increase of hardness is remarkable in the early period. However softening began after 1.5 hour in the case of R′80C6 steel and after 2 hours in the case of R′130C6 steel, and in both cases after the tempering for more than 5 hours, approximately the same hardness was derived. The hardness after more than 5 hours′ tempering is lower in degree than that of the sample as subzero-treated in R′80C6 steel; on the contrary, in R′130C6 steel which has more chromium content it shows higher values than that of the sample as subzero-treated. The same tendency can be seen more remarkably in the case of the tempering at 150°C (Fig. 2): in the tempering at 150°C both the hardening in early stage and the rate of softening are greater than those shown in the case of the tempering at 100°C, but after softening the hardness proved lower than that as subzero-treated in the case of R′80C6, while higher than that as subzero-treated in the case of R′130C6. The time of beginning of softening at 150°C is earlier than

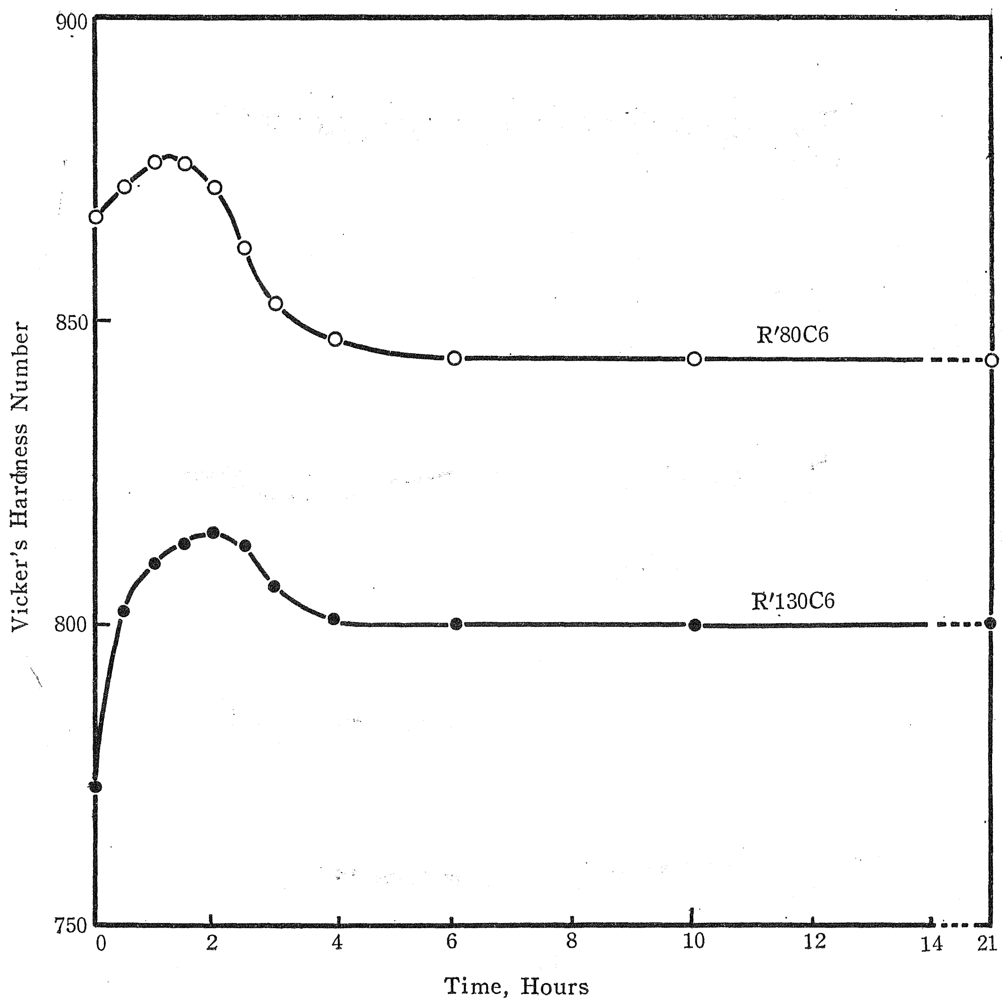

Fig. 1 Vicker's Hardness Number of R′80C6 and R′130C6 Steel After Various Times at 100°C Tempering

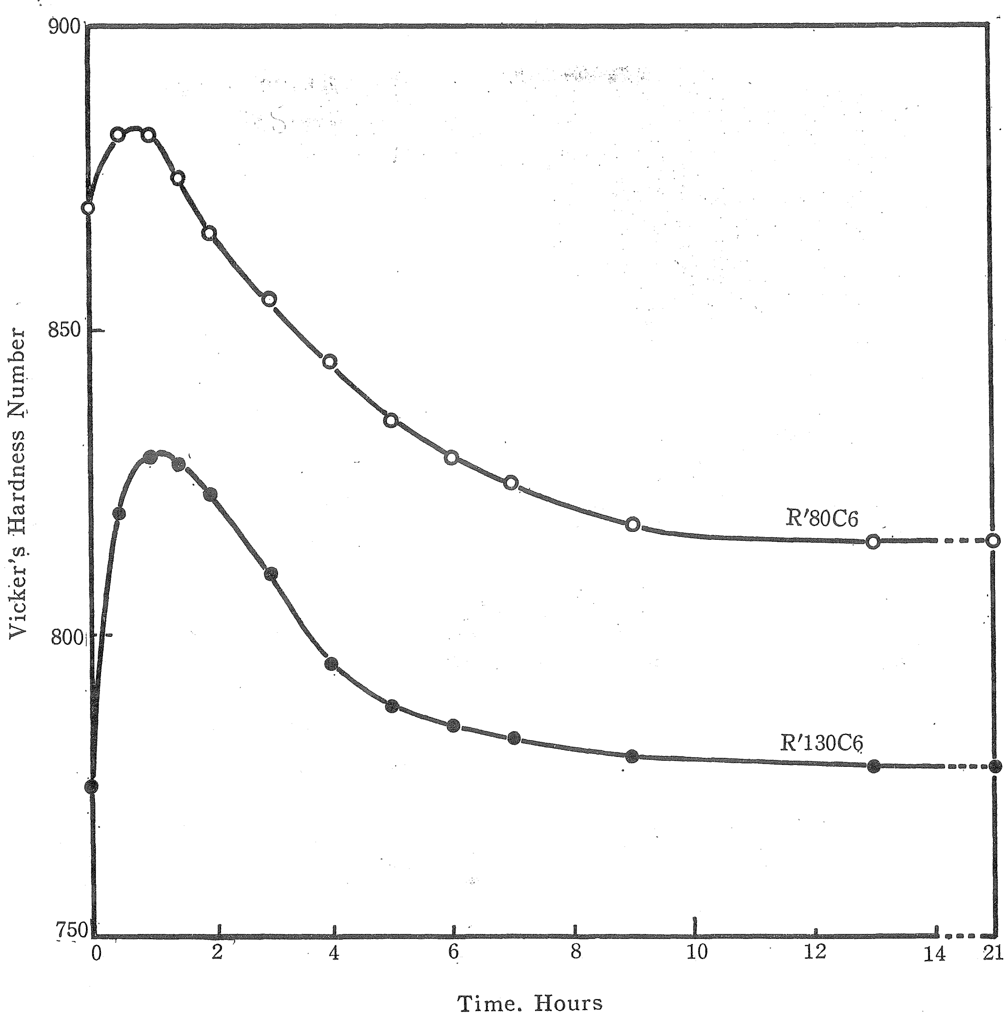

Fig. 2 Vicker's Hardness Number of R'80C6 and R'130C6 Steel
After Various Times at 150°C Tempering

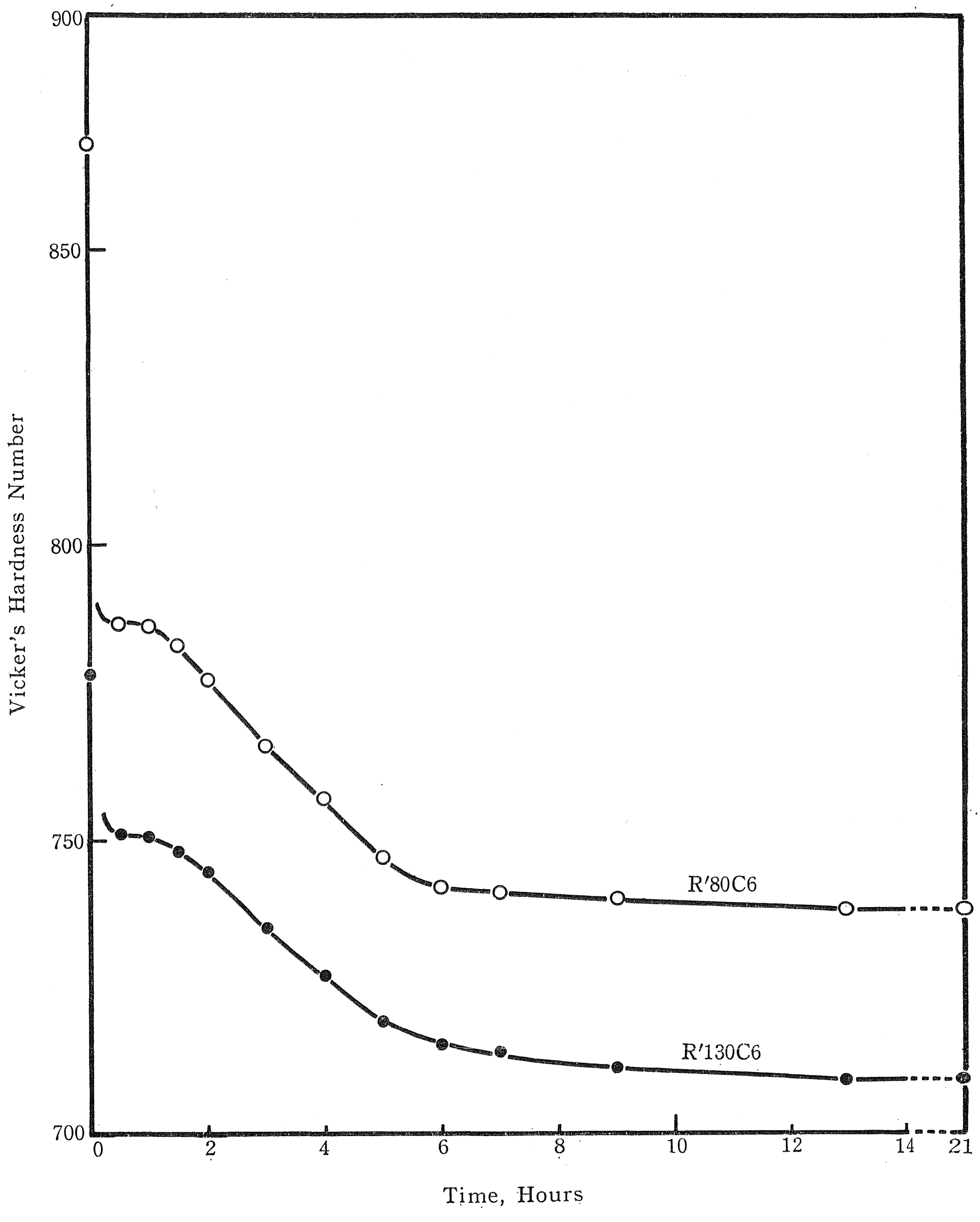

Fig. 3 Vicker's Hardness Number of R'80C6 and R'130C6 Steel After Various Times at 200°C Tempering

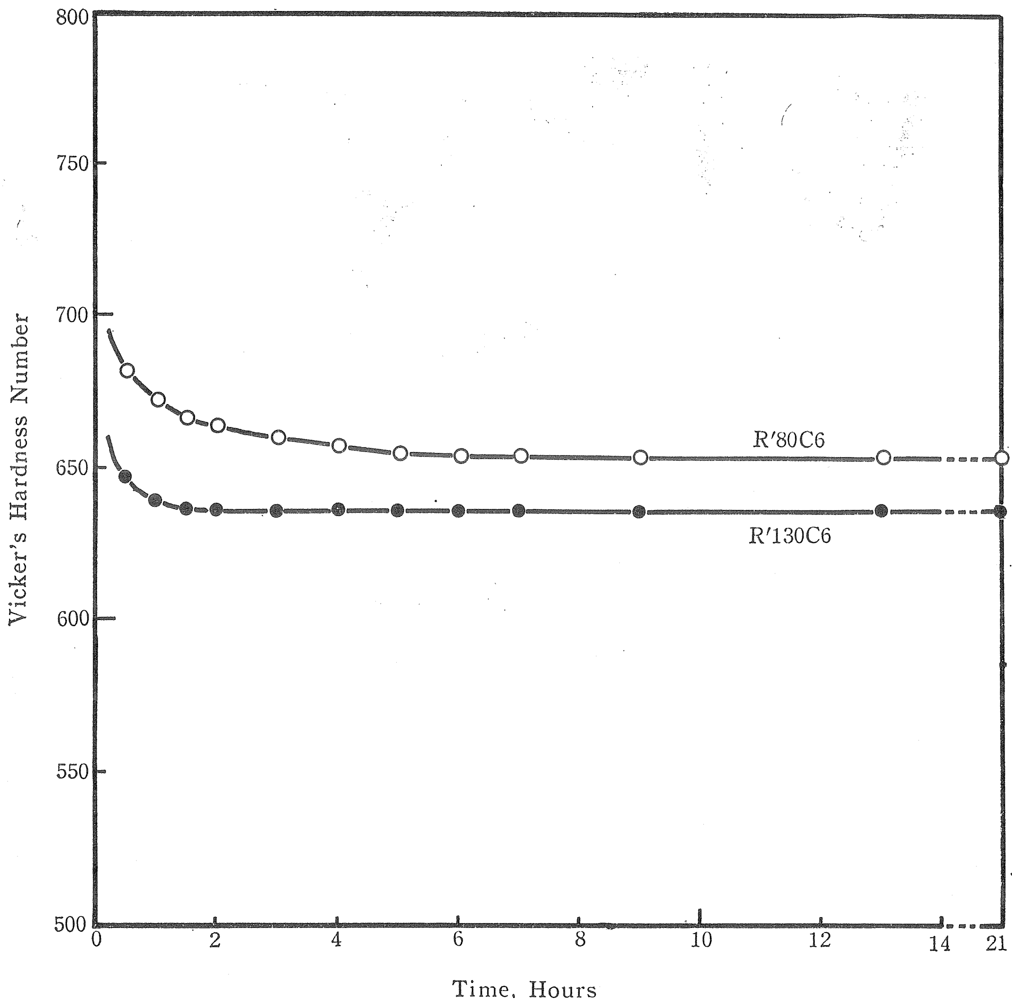

Fig. 4 Vicker's Hardness Number of R'80C6 and R'130C6 Steel After Various Times at 300°C Tempering

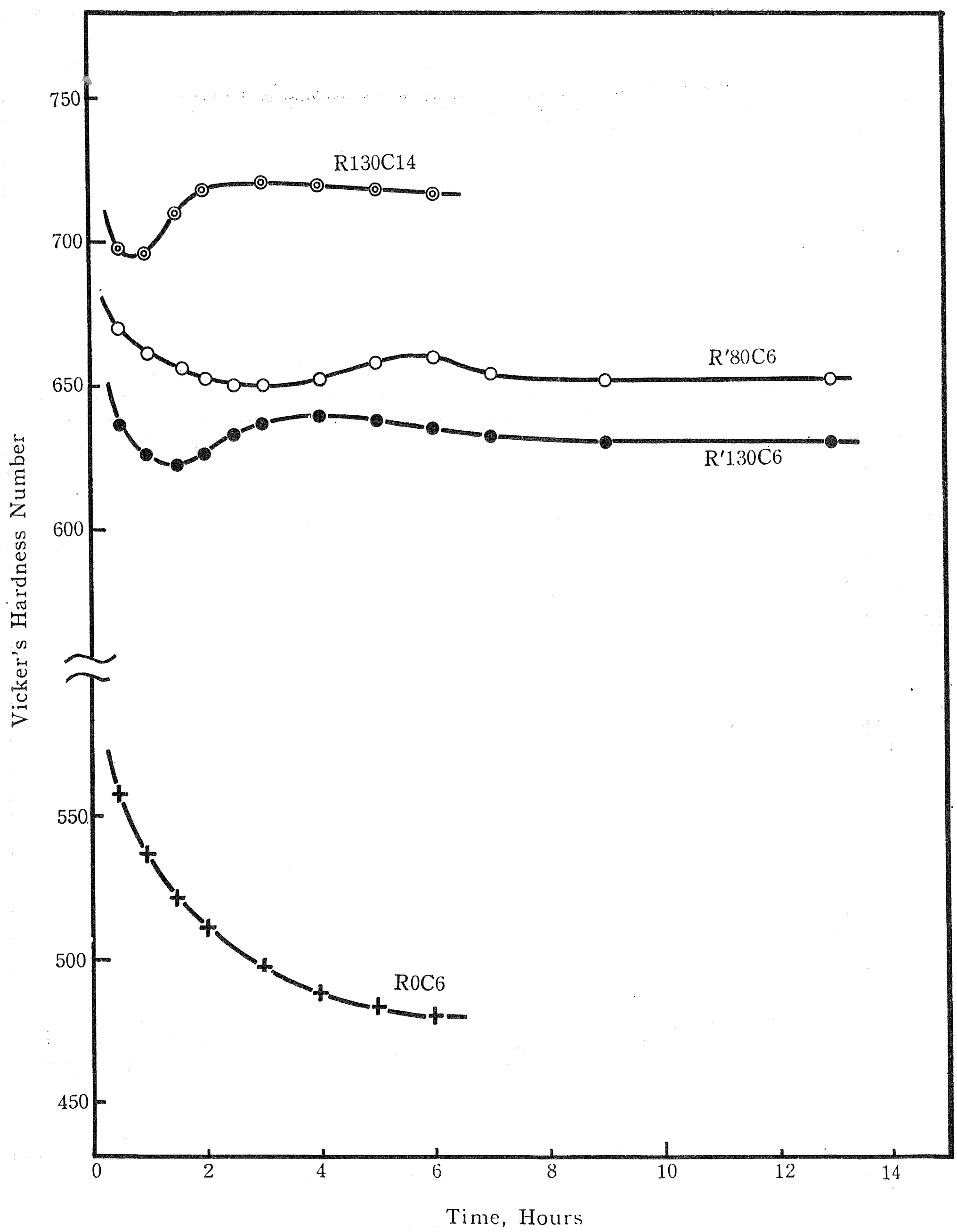

Fig. 5 Vicker's Hardness Number of R'80C6, R'130C6, R0C6 and R130C14 Steel After Various Times at 350°C Tempering

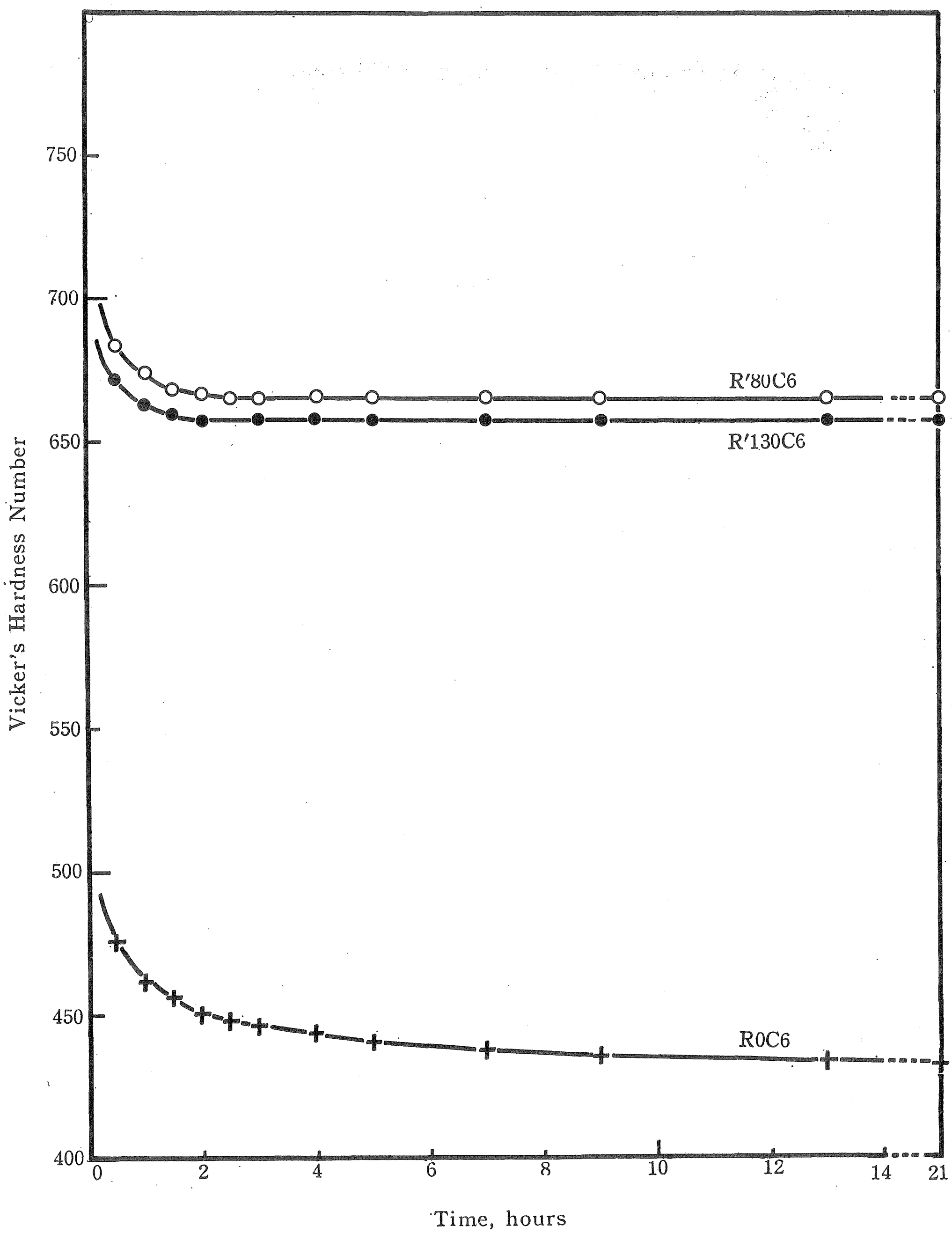

Fig. 6 Vicker's Hardness Number of R'80C6, R'130C6 and R0C6 Steel After Various Times at 450°C Tempering

that at 100°C; softening begins in about 0.7 hours in R′80C6 and in about 1 hour in R′130C6. In view of the conclusion of "the first report"(1) the above-mentioned results can be interpreted as follows: the increase of hardness detected in the early periods of the tempering at 100°C and 150°C respectively is due to the precipitation of ε-carbide, and softening corresponds with the growth of the particles of ε-carbide. When the tempering temperature is raised up to 200°C, the time required for the formation of ε-carbide becomes still shorter and softening also proceeds more rapidly as is shown in Fig. 3. In the hardness curve of the tempering at 300°C, the growth of the precipitated particles proceeds more rapidly, and the degree of softening is also greater, as is shown in Fig. 4 : but the precipitated particles at this temperature are not ε-carbide but χ factor which can be considered to be χ carbide in terms of the magnetic analysis.

The hardness curve after the tempering at 350°C (Fig. 5) shows especially remarkable characteristics : that is, at this temperature softening proceeds rapidly once in the early period, and then some degree of hardening occurs later. But this phenomenon cannot be detected in the plain carbon steel as is shown in the diagram. In order to examine the authenticity of this anomaly, the experiments, at this tempering temperature, of high carbon high chromium steels especially (1.41% C, 13.63% Cr, 0.34% Si, 0.33% Mn: hardening conditions are the same with those of R′80C6 and R′130C6), in addition to those of R0C6, R′80C6 and R′130C6 steels, were carried on. As is discernible in the diagram, the above-mentioned phenomenon is still more remarkable in R130C14 which has much content of carbon : this fact shows that this phenomenon has a close relation with the carbide reaction in alloy steels. As was pointed out in the previous report, in high chromium steels the carbide reaction (ε-carbide$\longrightarrow\chi$ factor$\longrightarrow$precipitation of θ phase) proceeds rapidly having approximate 320°C as a borderline. The peculiarities seen in the above-mentioned hardness curve is considered to be related with this carbide reaction. In the hardness curve of the tempering at 450°C no anomaly can be observed, and it can be surmised that θ phase develops rapidly at this temperature.

Putting all the results shown in the diagrams (from Fig. 1 to Fig. 6) together, it can be seen that in the chromium steels with more than 8 % Cr content, the degree of the tempered hardness proves higher where the chromium content is little, and the resistance to softening shows higher degree where the chromium content is much. The hardness of these steels after the sufficient tempering at the respective temperature proved to be higher than that of plain carbon steel with 0.6% C after the same tempering process.

Fig. 7 and Fig. 8 show the relations between the hardness and the tempering temperatures after the tempering of R′80C6 and R′130C6 steels at various temperatures for 20 hours, and the hardness curve shows approximately the same tendency. In R′130C6 steel a little increase of hardness is noticeable in the noighborhood of 100°C. In R′80C6 steel no increase of hardness corresponding with that just mentioned, but in the same part the retardation of softening can be noted.

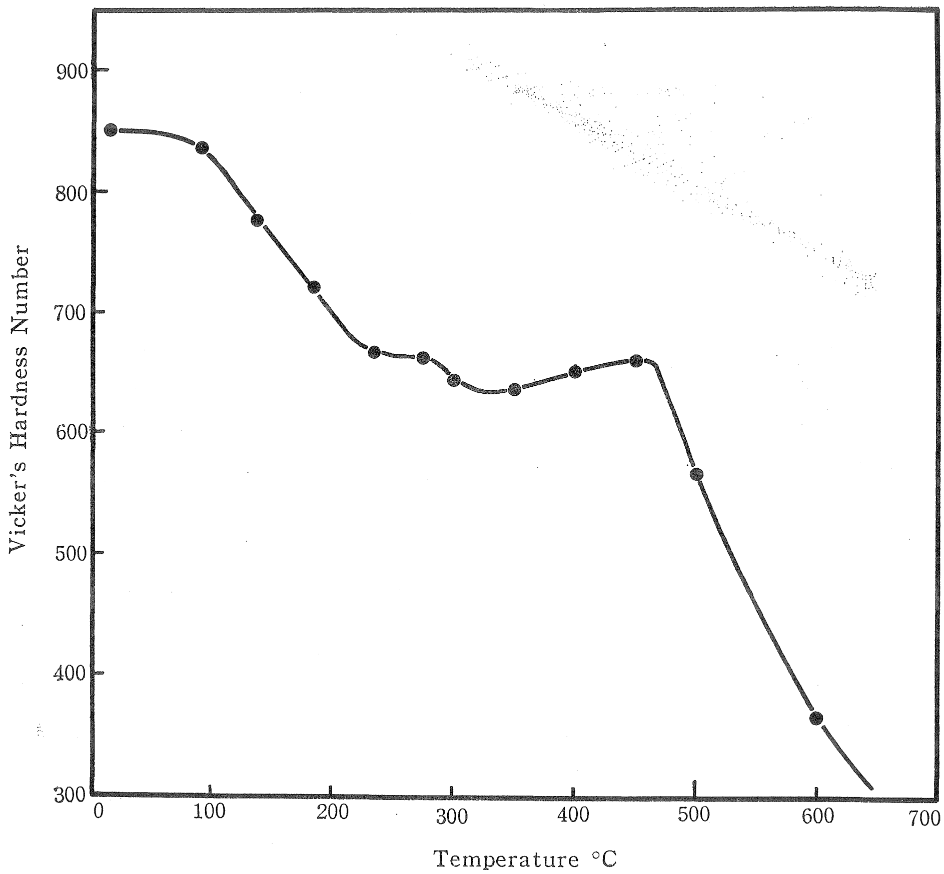

Fig. 7 Vicker's Hardness Number of R′80C6 Steel After 20Hours at Various Tempering Temperature

The indications of the hardness curves in the neighborhood of 100°C shows some differences between both the kinds of alloy steels, but judging from the results of Fig. 1 their essence is completely the same, and the following interpretation can be obtained through the reasoning of the conclusion mentioned in the previous report.(1) The small increase of hardness in the neighborhood of the tempering temperature 100°C comes out accompanied with the early stage of precipitation of ε-carbide, and can be said to be due to the strain hardening caused by the coherency of matrix and precipitated phase. The rapid decline of hardness in tempering at more than about 125°C shows the growth of ε-carbide, but the proceeding of softening falls rapidly in the neighborhood of 225°C, and in the temperature range from 230°C approx. to 275°C approx. the values of the tempered hardness are nearly the same. It can be said with safety that the growth of ε-carbide reaches its limit within this temperature range. And this conclusion is not inconsistent with the results of the magnetic analyses shown in the previous report.(1)

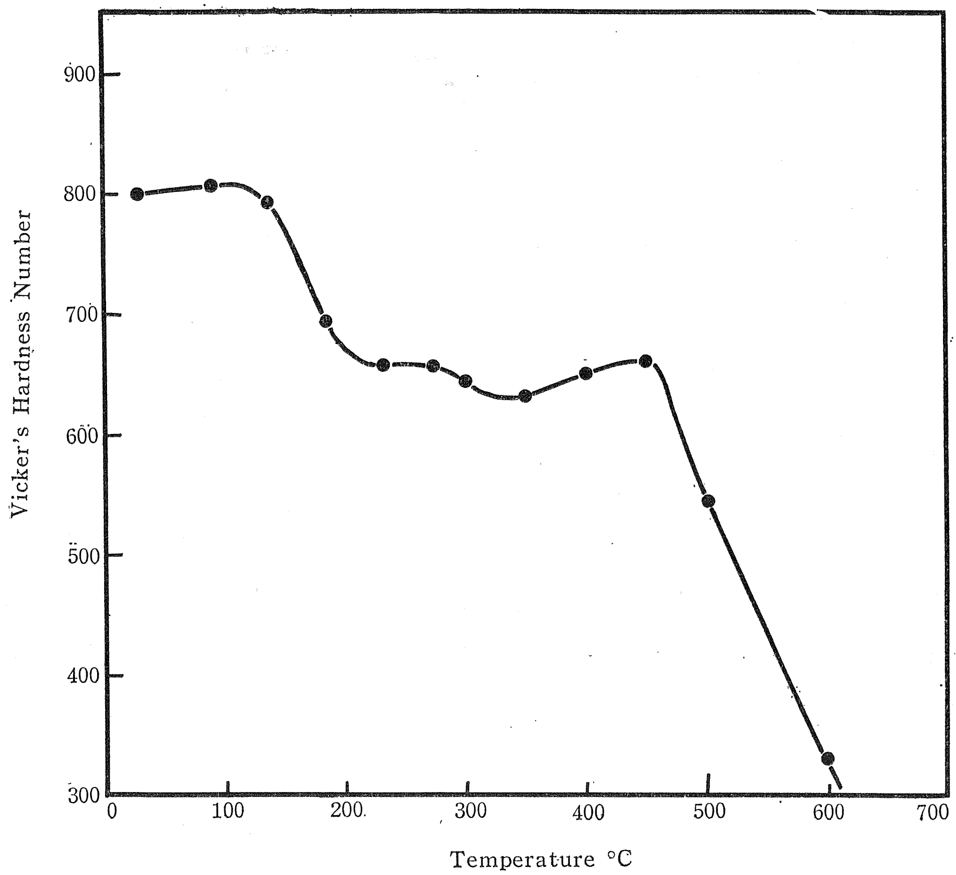

Fig. 8 Vicker's Hardness Number of R′130C6 Steel After 20 Hours at Various Tempering Temperature

Between the tempering temperatures 275°C and 325°C the hardness shows another decline. The results of the magnetic analyses show that within this range of tempering temperature there exists a precipitated thing which the author calls χ factor and it is different from ε-carbide. The proceeding of softening in this temperature range may be considered to be due to the growth of χ factor; what should be especially noticed here is that the change from ε-carbide to χ factor is not accompanied with any noticeable increase of hardness. We have already seen through the results of the magnetic tests that the change from ε-carbide to χ factor goes on gradually in the tempering lower than 380°C. And now again we have seen that the formation of χ factor is not accompanied with hardening. Judging from the results of the magnetic analyses there is no inconsistency in considering that χ factor is Hägg-carbide. The composition of Hägg-carbide approximately coincides with that of ε-carbide. It is generally admitted that the crystal structure of ε-carbide is hexagonal, but that of Hägg-carbide has been said to be orthorhombic or hexagonal, and there has been no established theory about it. Putting all these things and the results of our experiments together and thinking collectively, the change of ε-carbide into χ factor (probably χ-carbide) should be considered as allotropic transformation, it seems to the author. This way of thinking coincides with that of S. Oketani.[2] At any rate the view that transition precipitate consists of only ε-carbide is hard to be approved also in view of the results of hardness tests.

In the tempering range between 330°C and 450°C hardness increases in some measure. As was shown in the previous report[1] θ phase forms within this temperature range. Accordingly the above-mentioned results are the phenomenon of hardening accmpanied with the precipitation of θ phase. In the reports published heretofore the view[3] that in chromium steels the secondary hardening does not take place is prevalent. But some report[4] says that the secondary hardening occurs in chromium steels and even some reports supporting the view that the secondary hardening does not take place admit that a remarkable retardation of softening is noticeable in the neighborhood of 400°C. According to the results of our investigations, "*In high chromium steel* (0.6% C) *a measure of secondary hardening takes place after the tempering at* 400°C～450°C, *accompanied with the precipitation of* θ *phase*": this way of description seems proper. Again judging from the hardness curve the growth of θ phase seems to proceed when the temperature is over 450°C: that is, θ phase in the early stage of precipitation remains metastable within the tempering range between 330°C and 450°C. Rapid softening discernible in tempering over 460°C corresponds with the growth of θ phase in the early period and with the nucleation and growth of alloy carbide $(Cr, Fe)_7C_3$ in the later period.

The photographs from No. 1 to No. 6 show the impact fractured surfaces of some R′130C6 steel seen through electron microscope. The fractured surface of the test piece after the tempering at 450°C for 20 hours shows so-called "*hard fractured surface*" as is seen in No. 5 photograph: this corresponds with the secondary hardening above-mentioned. The black particles which are visible in No. 6 photograph are considered to be $(Cr, Fe)_7C_3$: attention must be paid to the point that the sizes of the particles are less than 1 micron.

Conclusion

The author studied the tempering processes of chromium steels through hardness tests and, putting the results together with the results in the previous report[1], obtained the following conclusion.

(1) In the neighborhood of the tempering temperature 100°C some increase of hardness occurs: this occurs accompanied with ε-carbide in the early period of precipitation and can be considered as strain hardening due to coherency of matrix and precipitation phase.

(2) When the tempering temperature is raised up to higher than 125°C, ε-carbide

grows and develops, and with this a rapid progress of softening is discerned.

(3) Within the tempering range between 230°C and 270°C hardness keeps up approximately a definite value. This seems to be due to the growth of ε-carbide reaching the saturated point in the neighborhood of 250°C.

(4) Within the tempering range between 275°C and 325°C, hardness decreases again. This is probably due to the growth of χ factor which can be considered χ-carbide as was pointed out in the previous report.

(5) The hardness curve of the isothermal tempering at 350°C shows that a measure of hardening occurs right after the rapid softening in the early period of tempering. This trend becomes more noticeable as carbon content increases and has close relations with the carbide reaction in the tempered steel. This can be considered to be due to the rapid proceeding of carbide reaction (ε-carbide$\longrightarrow\chi$ factor $\longrightarrow$precipitation of θ phase) discernible in the neighborhood of 320°C in the continuous heating of hardened alloy steel as was pointed out in the previous report.

(6) The change of ε-carbide into χ factor discernible in the tempering process is irreversible as was pointed out in the previous report, and is accompanied with no perceptible hardening.

(7) The view that transition precipitation consists of only ε phase is hard to be approved in the light of the results of hardness tests.

(8) Within the tempering range between 330°C approx. and 450°C approx. hardness shows a measure of increase. This can be interpreted as hardening phenomenon involved in the precipitation of θ phase : that is, in high chromium steels with 8～13% Cr (0.6% C) the secondary hardening is accompanied with the precipitation of θ phase in the tempering process at 400°C～450°C.

(9) In view of the fact that softening does not occur in tempering range between 350°C and 450°C, it can be said that θ phase in the early period of precipitation remains metastable in this temperature range.

(10) The electron micrographs of the impact fractured surfaces show that the fractured surfaces of the test pieces after the tempering for 20 hours at 450°C are so-called "hard".

(11) It is next to impossible to discuss thoroughly the temperatures and mechanisms of formation of $(Cr, Fe)_7C_3$ (η phase) and so on, but it can be considered that rapid progress of softening discernible in the tempering higher than 450°C corresponds with the growth of θ phase in the early period and with the nucleation and growth of finally stable η phase in the later period.

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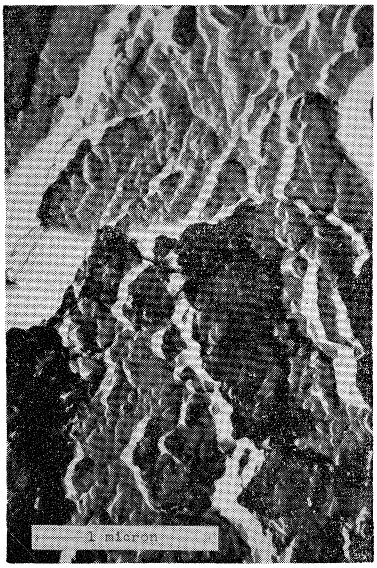
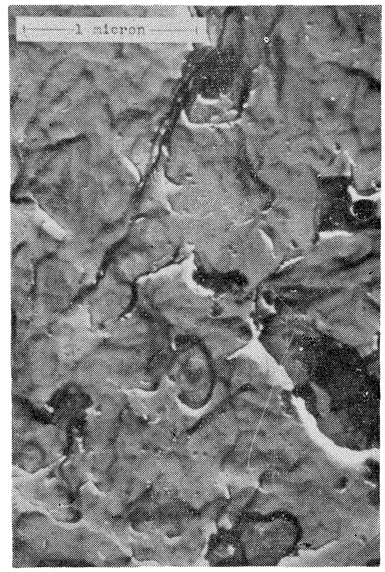


No. 1



No. 2

No. 3

Electron Micrograph of Impact Fractured Surface, 13%Cr—0.6%C Steel. ×5,000.

No. 1. As Refrigerated

No. 2. Tempered at 100° C, for 20 Hrs.

No. 3. Tempered at 150° C, for 20 Hrs.

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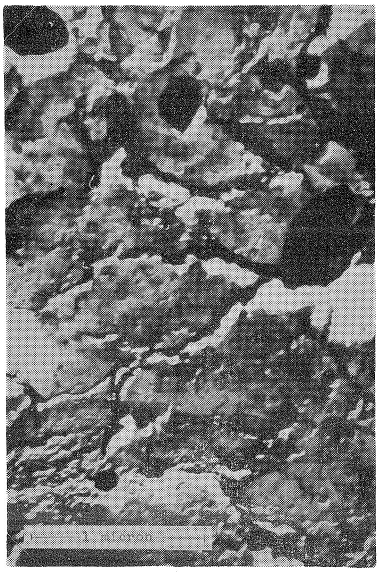

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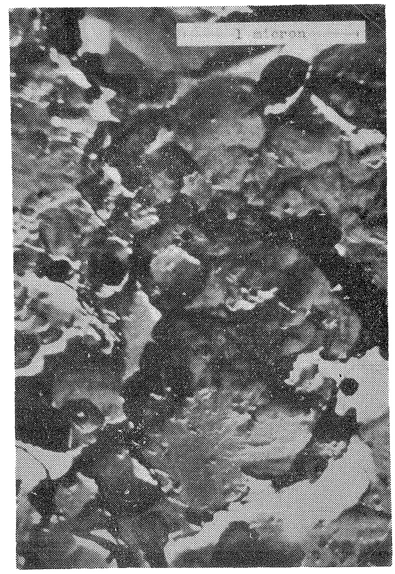

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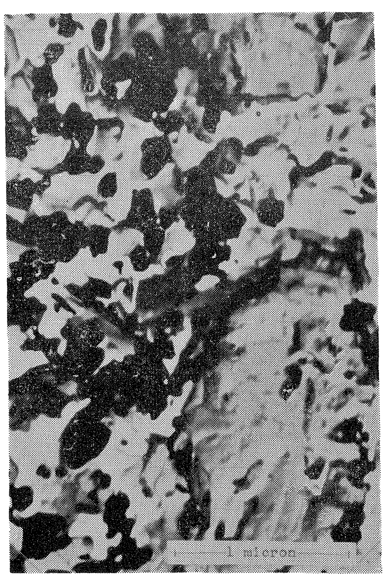

No. 6

Electron Micrograph of Impact Fractured Surface, 13%Cr—0.6%C Steel. ×5,000.

No. 4. Tempered at 400° C, for 20 Hrs.

No. 5. Tempered at 450° C, for 20 Hrs.

No. 6. Tempered at 750° C, for 20 Hrs.

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