Some Problems on Quenched Steels. II : On the Mechanism of Temper Hardening in Quenched High Speed Steel

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Some Problems on Quenched Steels. II
On the Mechanism of Temper Hardening in Quenched High Speed Steel*

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Synopsis

The cause of the secondary hardening in a quenched high speed steel was studied by measuring dilatation, high temperature hardness and electric resistance, and the following conclusions were obtained : (1) The cause of the decrease in hardness by tempering at the temperature $100 \sim 350°$ is the relief of the internal stresses induced by the structural change during quenching. (2) The secondary hardening is due to the precipitation of a special carbide from the residual austenite, and the martensitization of the residual austenite give the phenomenon a small effect.

I. Introduction

As well known, the hardness of a quenched high speed steel is decreased by tempering at the temperature 100~350°, and increased by tempering at the temperature 400~550°, and the best cutting quallity can be obtained by quenching at about 1300° and then tempering at about 550°. Many investigations on the heat treatments of high speed steels had hitherto been reported, but the causes of these hardness changes were not throughly explained. The author studied these problems by means of several physico-metallurgical methods. The present investigation was substantially completed many years ago**, although its publication was delayed owing to some unavoidable circumstances. Nowadays the greater part of the results is widely known, and yet the author decided to publish the pressent report, because it is directly connected with those which will be put out successively.

II Results of experiments and considerations

(1) Hardness change by tempering

The specimen used in this research was of the following composition:

0.56 % C 19.66 % W 4.61 % Cr 7.1 % Co Fe Bal.

The sample, $10 \times 10 \times 50\,mm^3$ in dimension, was heated in Elema furnace for 10 mins. to the required temperature, and then quenched in oil. After quenching, each surface of the samples was ground off about 1 mm in thickness in order to remove decarburized zone.

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* The 636 th report of the Research Institute for Iron, Steel and Other Metals.

** This paper was read at the 15 th meeting (1935) of Iron and Steel Institute of Japan, and quoted in prof. T. Ishiwara's lecture in N. K. G. -Shi (J. Jap. Inst. Metals), 4 (1940). 80

The samples were successively tempered for 30 mins. at the following temperatures: 100~300° in oil: 300~800° in vacuum furnace and cooled slowly. The hardness was measured by the Rockwell "C" scale. Curves (I), (III), (IV) in Fig. 1 are the results of the samples quenched at 1300°, 1130° and 950°, respectively.

As shown in curve (I), the hardness of the specimen quenched at 1300° was slightly increased by tempering at 100°, but in the case of the tempering at 100~350° it decreased gradually. When the tempering temperature was higher than 350°, it increased and showed a maximum at 550°. This increase in hardness within the temperature range 350~550° was the so-called temper hardening. In the case of the tempering at the temperature higher than 550°, the hardness gradually decreased. So the temper hardness curve has a minimum point at about 350°. Curve (III) is similar to (I), but quantitatively it has a lower maximum hardness and the degree of the hardness decrease in the range 100~350° is small.

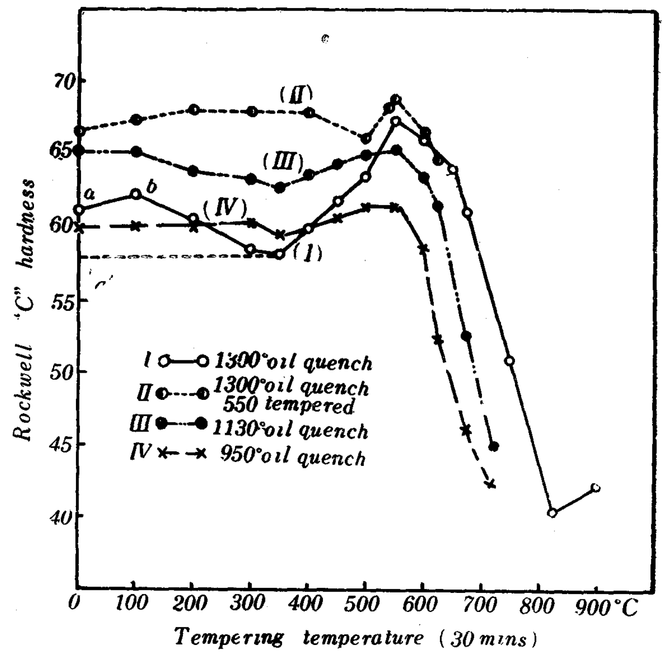

Fig. 1. Temper hardness curves of quenched high speed steel.

Curve (IV) shows no decrease of hardness in the range 100~350°, and the degree of temper hardening is also very small, and, consequently, the maximum hardness is much lower than those in the former examples.

The decrease of hardness in the range 100~350° is the wellknown phenomenon in the tempering of a quenched high speed steel, but its exact cause is still uncertain. It was sometimes said that this softening was the temper softening of the quenched martensite. If this explanation is adopted, we can not explain the cause of temper hardening by the martensitization of the residual austenite, because the temperature at which the hardening occurs is higher than the softening temperature of martensite.

As above stated, the decrease of hardness became small as the quenching temperature fell, and in the case of the quenching at 950°, the decrease almost disappeared. As the quenching temperature becomes low, the sample should contain smaller amount of the retained austenite, and, the martensite itself may have a lesser resistivity to softening. Therefore, if we adopt the martensite tempering theory to explain this softening, the sample quenched at the lower temperature should show a greater degree of softening than that quenched at the higher temperature. This is, however, contrary to the results shown in Fig. 1.

Curve (II) in Fig. 1 shows the hardness change in the successive tempering of a sample formerly tempered at 550° for 30 mins. In this case, the martensitization of the retained austenite should occur in the previous tempering as shown in the previous report[1] or in Fig. 4 of this paper. As seen from the curve, no softening is observable in the range 100～350°, which shows that the martensite formed by the previous tempering is not softened by the tempering at the temperature lower than 550°. This fact also contradicts the above-stated martensite softening theory.

How can, we then, explain these facts? As will be shown later, the sample quenched at 1300° contains a large amount of retained austenite. Now, the greater part of martensite is formed at the abrupt expansion of Ar″ during quenching, and the other part retained as austenite do not expand, shrinking smoothly with temperature drop. In other words, some part of the sample abruptly expands at a relatively low temperature, say 200～100°, and the other part do not expand. In the quenched state, therefore, the retained austenite recieves a severe hydrostatic pressure from the surrounding martensite. These structural internal stresses increase the hardness of the sample, as in the case of a cold-working. Such a sample is gradually softened by tempering. This is the author's explanation of the temper softening at 100～350°.

In the curve (1) of Fig. 1, the area occupied by *a b c a′* represents the quantity of hardening due to the structural internal stress. Therefore, the curve of the temper hardness change is the resultant curve of the essential hardness change of quenched state and of the internal stress. In the case of the quenching at 1130°, both the retained austenite and the induced internal stress should be smaller than those in the case at 1300°, and hence, the softening in the range 100～350° should be smaller in the former case than in the latter case. In the case of the quenching at 950°, there exists only a slight austenite, and, consequently, almost no change appears by tempering at 100～350° as shown in curve (IV).

The author's structural internal stress relief theory can be proved by the X-ray investigation. Photo. (1) in Fig. 2 is the X-ray photograph of the sample quenched at 1300°, and photo. (2) is that of the same sample tempered for 30 mins. at 300°. In photo. (1) the lines of austenite (A) and martensite (M) are diffused into each other,

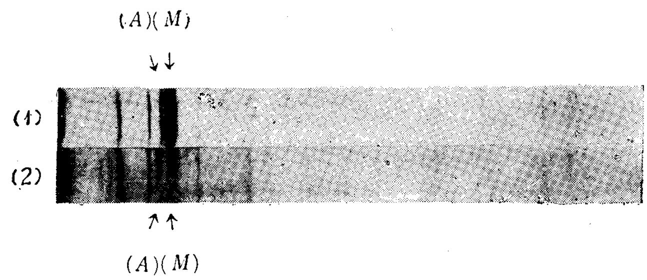

Fig. 2. X-Ray photographs.
(1) as quenched at 1300°
(2) tempered at 300° for 30 mins.

but in photo. (2) the austenite line is clearly shifted toward the left side, namely, toward the side of the larger lattice constant. This shows that the greater part of

(1) K. Monma, Sci. Rep. Tohoku. Imp. Univ. series 1 28 (1939) 128.

the austenite is relieved from that stress by tempering at 300°. This result of X-ray investigation may be said to be the direct verification of the author's theory.

(2) Dilatometric experiments

As previously stated, the martensitization of the retained austenite occurs in the cooling course of tempering. So the dilatometric study was carried out more systematically. The sample, 5 mm in diameter and 50 mm in length, was quenched in oil at 1300°. The rate of heating or cooling in the dilatometric mesurements was about 10°/10 mins. The specimen was kept at the maximum temperature of tempering for 30 mins. and then cooled, in order to obtain results corresponding to those of the hardness measurements shown in Fig. 1.

Curve (1) in Fig. 3 is the heating and cooling curve for the tempering at 500°. They are very smooth showing no change in the sample. It was the same also in the case of the tempering at a temperature lower than 500°.

Curve (2) is the result of successive heating to 525° and cooling. In the heating, there was no change and the curve was smooth as in the former, but in the course of cooling an abrupt expansion appeared at about 100°. In the repeated heating of the same sample to 550°, no change appeared as shown in curve (3), but in cooling a large expansion appeared at the range of temperature 300~200°. Therefore, the stepwisely tempered sample was expanded by *c g* as indicated in Fig., compared with the quenched condition. This expansion was, of course, due to the martensite formation from the retained austenite.

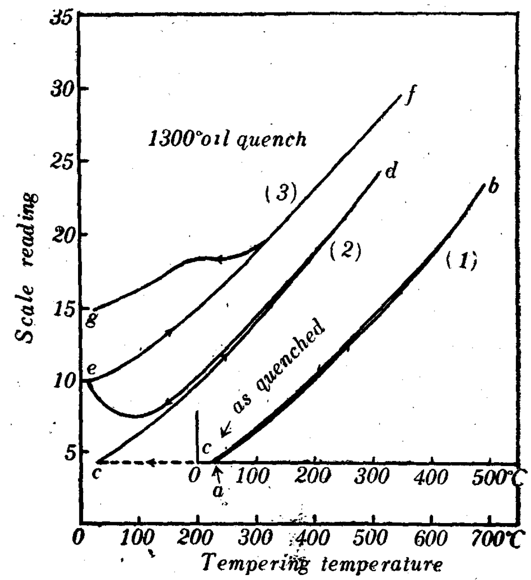

Fig. 3. Dilatometric curves of tempering.

Curve (1) in Fig. 4 shows the result of the heating of a quenched specimen to 950°. It was smooth up to 700°, but an expansion appeared in the range of 700~750°. Hence, this indicates that, in case the heating velocity is moderately quick, the retained austenite changes into α-state or troostite at the temperature range of 700~800°. The small shrinkage observable in the range of 800~820° may be due to the recrystallization. The A_3 transformation began at about 850° in heating.

A virgin sample was heated at 680° and the result was as follows: in the course of heating some parts of the retained austenite changed into α-state and, consequently, an expansion took place from 600 to 680°, and, therefore, the cooling curve was somewhat higher than the heating curve as shown in (2). In the course of cooling a large amount of expansion, owing to the Ar'' transformation, appeared at about 420°. Comparing this example with the two curves in Fig. 3, it will be seen that the higher the heating temperature is, the higher the Ar'' point in cooling becomes.

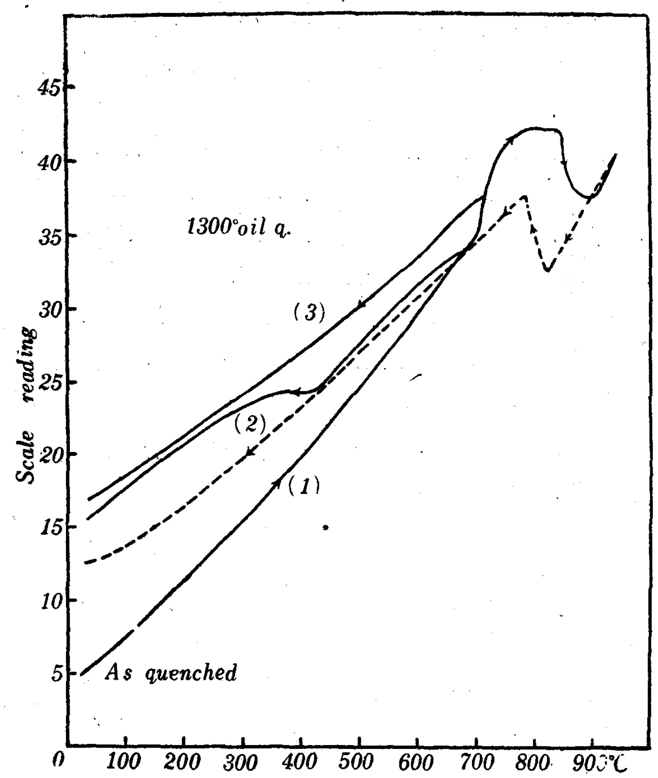

Fig. 4. Dilatometric curves of tempering.

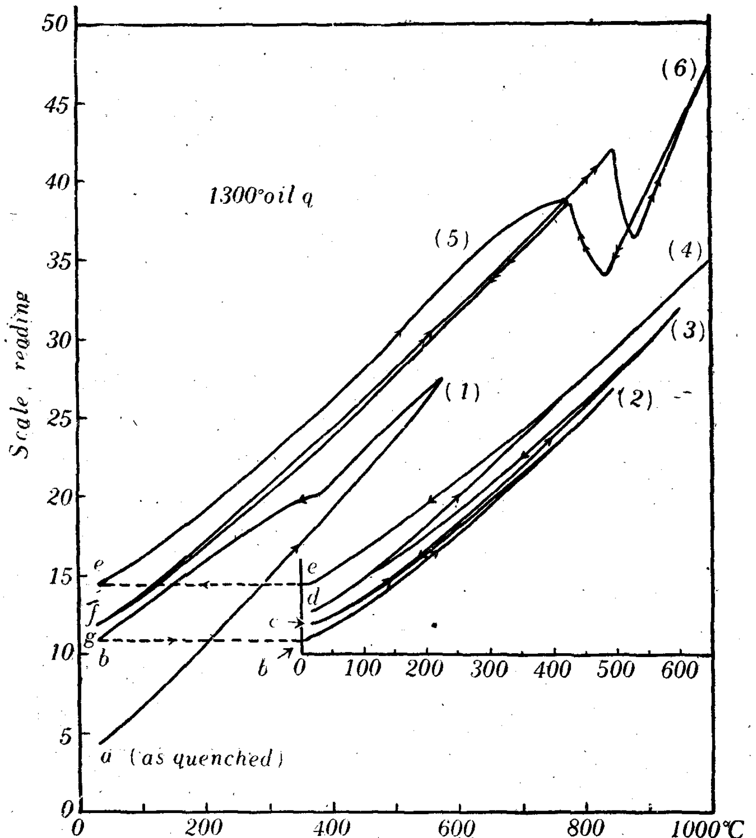

Fig. 5. Dilatometric curves of tempering.

The curve (3) is the result of the cooling of a virgin sample at 725°: in this case, almost all the retained austenites transformed into α-state in heating course and, consequently, only a slight expansion appeared in cooling. The curve (1) in Fig. 5 is that of tempering at 580°. In this case, the Ar$''$ transformation occurred. The curves (2), (3) and (4) are the results of the successive heatings of the same specimen to 505°, 605° and 650°, respectively. These experiments were carried out in order to examine the tempering of martensite which was formed from the retained austenite by tempering. As shown in Fig. 5, the change of martensite did not appear, being different from the case of a carbón steel. As to the curves (5) and (6), there will be no need for explanation.

On what ground, then, does the martensitization of the retained austenite in cooling occur?

If we consider the retained austenite as a state which was caused by the circumstance in which the cooling velocity was too rapid to transform all the austenite into martensite, the transformation should have taken place in heating course.

In reality, however, the change was observable only in cooling but not in heating, provided that the tempering temperature is in proper range, as shown in Fig. 3.

Now, comparing the curve (1) in Fig. 1 with the curve (1) in Fig. 3, the following extraordinary fact will be seen: the hardness of a quenched sample tempered at 500° was distinctly increased, but the dilatometric curve did not show such a change either in heating or in cooling. Judging from this fact, the increase of hardness after the tempering is not caused by the martensitization of retained austenite; in other words, the martensitization of retained austenite can not be accepted as the cause of a temper hardening.

As to this fact, the author has the following opinion: in heating a quenched sample at the temperature range 350~500°, a certain change will occur in the retained austenite and, with the development of this change, the austenite gradually becomes unstable and, on subsequent cooling, transformation of the unstable austenite takes place at Ar″ point. In the case of the tempering at 500°, this unknown change seems to have been in progress in some degree and, consequently, the hardness was increased, but the degree was not sufficient to induce the Ar″ transformation. What is, then, the nature of this unknown change? According to the author's opinion, this is the precipitation of carbide from the supersaturated retained austenite.

As well known, a high speed steel is usually quenched at the temperature as high as or higher than 1300°, to dissolve the carbide as much as possible in austenite before quenching. Therefore, it is natural to consider the retained austenite to be supersaturated with carbide. The supersaturated austenite will, then, precipitate carbide on tempering, which may be the origin of the temper hardening in the range of 350~500°, though the retained austenite is not transformed into martensite. As temperature becomes higher, the larger amount of carbide will precipitate, and though the degree of the unstableness is not sufficient to transform the retained austenite into α-state or into troostite at that temperature, the tendency of transformation in cooling becomes more powerful with the temperature fall, and at last the transformation takes place as shown in curve (3) in Fig. 3. When the specimen was heated to temperatures highei than 500°, an expansion occurred at about 700° as shown in the curve (1) in Fig. 4. The reason for this is as follows: the precipitation of carbide so proceeded that the austenite could not hold its own phase any longer. The expansion observable in heating was due to this transformation.

By the author's theory, the results of the dilatometric experiments and the hardness change can be explained without any contradiction. The dilatometer used in this experiments, however, was not so sensible as to indicate the precipitation. Hence, the hardness testing at high temperatures and the measurement of electric resistance were carried out to ascertain the carbide precipitation.

(3) Measurement of high temperature hardness

According to the author's theory, in the tempering of a high speed steel, the precipitation of carbide from retained austenite will occur first, causing the hardening and the unstableness of the austenite matrix. Therefore, the hardness of a tempered sample may be a resultant of the hardening due to the precipitation and that due to the martensitization. This is the reason why many researchers believed the martensitization of retained austenite to be the only cause of the temper hardening.

If we can measure a high temperature hardness and trace its change at tempering, we can ascertain the mechanism of the temper hardening more clearly. Some results of measurements of the high temperature hardness of a high speed steel were reported, but all of them were examined to ascertain the resistivity to softening at high temperatures, and, accordingly, the samples were not merely quenched but tempered at temperatures at which maximum hardness was attained. Therefore, these results were useless for the proof of the author's theory. R. A. Page[(1)] reported his experiments on the change of high temperature hardness in heating a quenched high speed steel. He stated that there were a minimum and a maximum in hardness at about 400° and 550°, respectively, and that, when the temperature became higher than 600°, the hardness rapidly decreased. He did not, however, examine the hardness change in cooling course.

The author used Honda-Sato's high temperature hardness testing machine with some modifications. The sample, 60 mm in diameter and 15 mm in thickness, was quenched in oil at 1300°, the surface was ground off about 1 mm. In order to compare this results with that in Fig. 1, the sample was kept for 30 mins. at the required temperature and then the hardness was measured. To prevent the sample from being oxidized, the heating furnace was filled with purified nitrogen gas, and the oxidation was so slight that the surface of the sample was slightly coloured yellow when heated at 500~600°.

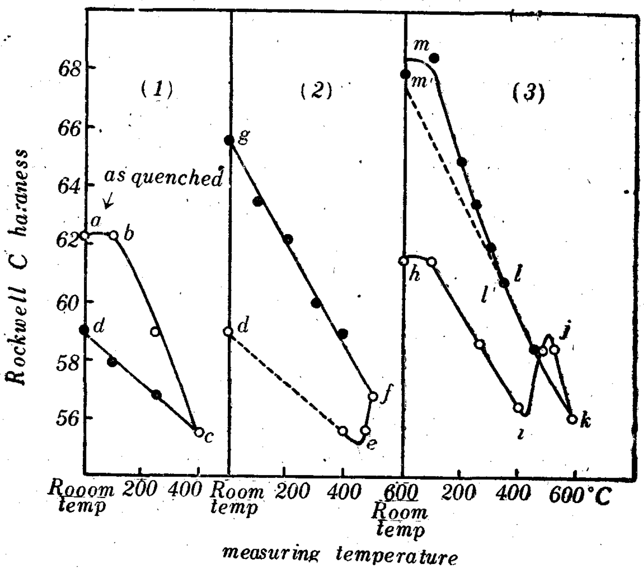

Fig. 6. High temperature hardness change in tempering (1300° oil q.)

Fig. 6 represents the results of the measurements, in which the hardness number is, for conveniency, converted into the Rockwell "C" scale. As seen from Fig. 6, the hardness of a quenched specimen did not change at 100° and then rapidly decreased. On cooling from 400°, it increased almost linearly as indicated by *c d*, showing somewhat great irreversibility of increasing difference with the temperature fall. In other words, by tempering at 400°, hardness decreased by *a d* at ordinary temperature, and these results coincided with that of curve (1) in Fig. 1.

Curve (2) is the result of the same sample heated twice at 500°, and shows an increase of hardness by *e f* at the temperature 480 ~ 500°. On cooling, the hardness

(1) R. A. Page, Metallurgia, 3 (1931), 85

increased linearly with the temperature coefficient of hardness, which showed no change in hardness during cooling. Thus, after the heating the hardness became much higher than that of the initial state, which corresponded to the hardness increase at 500° in curve (1) in Fig. 1. As previously stated, the origin of this hradening could not be explained only from dilatometric measurement, but it is now ascertained that the cause of the hardening lies in the heating at the range 450~500° as predicted by the author.

Curve (3) represents the result of the hardness measurement of a virgin sample heated to 580°. As shown in the dilatometric researches, this curve corresponded to the case in which abnormal expansion appeared in cooling process. As seen obviously from the figure, the heating curve is similar to curve (1) up to 400° and as the temperature was raised, the hardness first increased as in the case of curve (2), showing a maximum at 500°, and then rapidly decreased to 580°. On cooling from 580°, the hardness increased as shown in the curve ***k l m***, the inclination of which was steeper and concave upward, compared with the former two examples. According to the dilatometric curve (1) in Fig. 5, when the tempering temperature was 580°, the Ar″ expansion took place at about 375° in cooling, and, it is now known that the cooling course ***k l m*** of curve (3) began to deflect gradually toward the higher hardness side from the straight line ***k l′ m′*** at about the same temperature. From these facts, it may be concluded that the increase of hardness due to the transformation of the retained austenite is so small as represented by the difference between the curve ***l m*** and the straight line ***l′ m′***. This is an extraordinarily important fact which shows that the main cause of the temper hardening in a quenched high speed steel lies in a certain change due to the heating at the temperature 400~500° and that the hardening due to the martensitization of the retained austenite is of minor importance. Hence, it will be concluded that the cause of hardening, apparently concealed in the heating of the range 400~500°, is the dispersed precipitation of special carbide from residual austenite.

(4) Measurement of electric resistance

In general, a supersaturated phase has a higher electric resistance than the normal state and the resistance diminishes as the precipitation goes on. Hence, in order to ascertain the carbide precipitation in tempering of a quenched high speed steel, the author measured the electric resistance of a quenched sample during tempering.

The sample was 4 mm in diameter and 100 mm in length, and the leading wires were welded at the position, 10 mm inside from the both ends, and the potential difference between them was measured by a potentiometer, the current being kept at just 1.000 Amp. The heating of the sample was made in vacuum to avoid oxidation.

Fig. 7 and 8 are the results of the measurements. As shown by curve (1) in Fig 7, the resistance of a quenched sample increased with the rise of temperature, in accordance with the temperature coefficient of resistance. But, in the range 350~500°, the rate of increase became small, and in the range 450~700° a distinct decrease appeared and then the resistance again increased. In cooling course, there was no change, but the inclination of the curve was very steep, and, accordingly, the resistance at ordinary temperature became very small, compared with that of the quenched state.

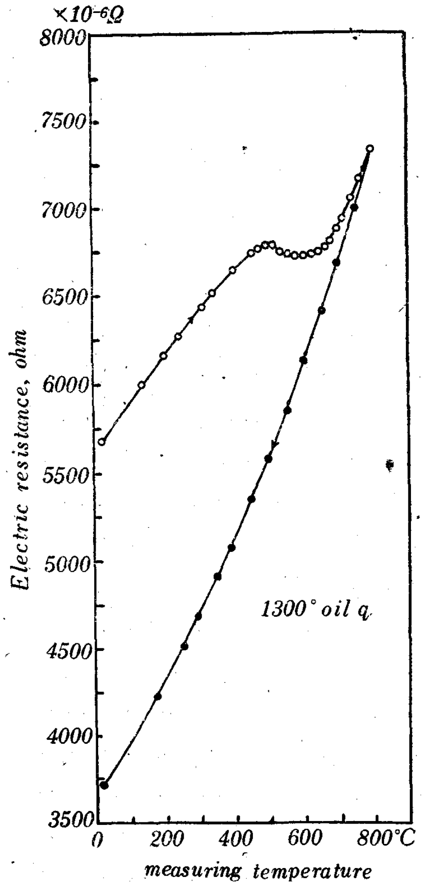

Fig. 7. Electric resistance change in tempering.

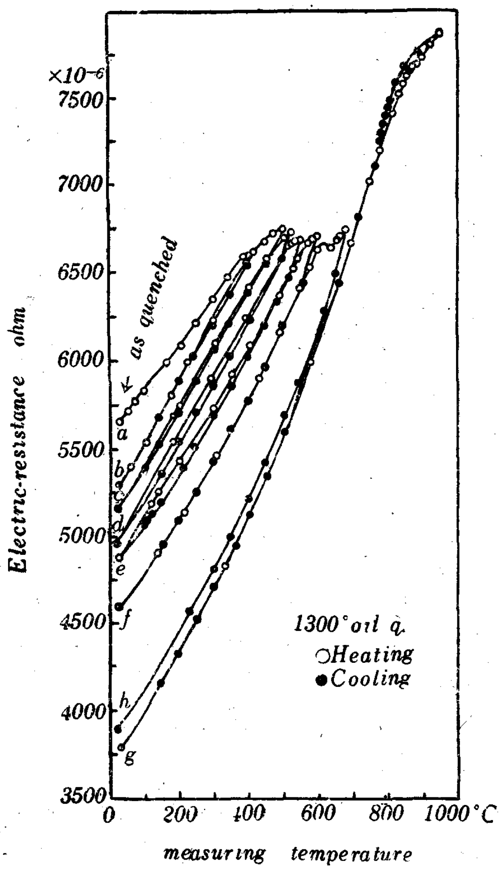

Fig. 8. Electric resistance change in tempering.

Comparing this result with that of curve (1) in Fig. 4, it will be seen that in the resistance curve, a decrease appears at 450°～700°, whereas the dilatometric curve is smooth from ordinary temperature up to 700°, and that in the latter curve a distinct expansion due to the formation of trootite from residual austenite appears at 700～750°, whereas in the former curve there is no change in that range. From these facts, it may be said that in the tempering of a quenched high speed steel, two processes will take place, one influencing the electric resistance and the other giving rise to a change in dilatometric curve. Moreover, it is a significant fact that after the former has occurred, the latter begins to take place. Hence, it may safely be concluded that the cause of the decrease in electiric resitance is no other than the carbide precipitation from the supersaturated residual austenite, whereas the expansion of the dilatometric curve is caused by the transformation of the retained austenite, or that the γ-α transformation of the residual austenite begins to occur after the supersaturated carbide precipitates to a certain extent.

Fig. 8 shows the resistance change during repeated heatings and coolings of a quenched high speed steel. In the course of heating, the resistance increased linearly up to 100° in accordance with the temperature coefficient and then the inclination of curve slightly dimimished, and a slight decrease began to appear at 400~430°. On cooling from 430°, no change occurred, but the inclination was steeper than that of heating, and, accordingly, came to *b* at ordinary temperature. The small decrease in the inclination of heating curve within the range 100 ~ 400° indicates a gradual decrease of resistance, which corresponds to the decrease in hardness due to the relief of internal stresses in that temperature range.

As shown in Fig. 8, on subsequent heating to 500°, the curve was reversible to the former cooling curve up to 400° and then somewhat decreased. This decrease of resistance corresponded to the increase of high temperature hardness indicated by *e f* and *i j* of curve (2) and (3) in Fig. 6, respectively, and was the proof for the carbide precipitation occurring in that temperature range. The cooling curve from 500° was smooth without special change.

When the same sample was reheated to 530°, the curve was similar to that in the former case, and on the cooling no change occurred as shown in the figure. Considering from the dilatometric curves in Fig. 4, when the sample was heated at the temperature higher than 525°, Ar'' transformation should occur in cooling course. But, as seen from Fig. 8 no remarkable change in electric resistance was observable. The curve for the reheating at 550° was similar to the former, indicating no particular change in cooling, contrary to the above stated consideration of the dilatometric result. The only difference between the cooling curves with and without the Ar'' transformation was as follows: in the one case, the cooling and its adjacent reheating curves make a narrow loop, the latter having a slightly higher resistance, the other case the two curves almost coincide with each other while in as shown in Fig. 8.

From the above, the following significant fact will be recognized: by the measurement of electric resistance, the carbide precipitation from retained austenite can clearly be ascertained, whereas by the dilatometric measurement, the lattice transformation or the martensitization of the retained austenite is mainly observable.

Summary

The results of the present investigation may be summarized as follows:

(1) In the tempering of a quenched high speed steel, the decrease in hardness appears in the range 100 to 350°, and then the so-called "temper hardening" occurs in the range 350~550°, and, with the further rise of temperature, the decrease again takes place gradually. Therefore, the temper hardness curve has the minimum and maximum at 350°, and 550°, respectively.

(2) When the quenching temperature is low, the degree of hardness decrease in the range 100 to 350° and those of temper hardening are both small.

(3) The cause of softening at 100 to 350° is not the decomposition of martensite, but is the relief of stresses induced by the Ar'' transformation during quenching.

(4) When the tempering temperature is in a certain range, the Ar'' transformation occurs only in cooling course.

(5) When the carbide is precipitated to a certain extent, the retained austenite becomes unstable and the transformation will occur. In this case the martensitization of the retained austenite scarcely influences the temper hardening, the main cause being the precipitation of carbide from the retained austenite.

In conclusion the author expresses his cordial thanks to professor T. Ishiwara, the ex-Director of the Research Institute for Iron, Steel and Other Metals, Tohoku University, for his kind guidance.