

310°C~320°C and the other of which starts at approx. 300°C and continues up to around 360°C. (8) In the light of the corrosion curves and the D. T. A. curves of the alloy steel tempered between 250°C and 310°C, the theory that transition precipitate consists of ϵ -carbide only is difficult to be approved. (9) In order to explain the above-mentioned phenomena it is necessary to introduce a new phase of another kind which is tentatively called χ factor by the author as was pointed out in the previous reports. (10) When the tempering temperature is raised higher than 250°C ϵ -carbide turns into χ factor irreversibly, accompanied with decrease in hardness and corrosion rate and with exothermic reaction. According to the magnetic analysis χ factor shows the same Curie point with Hägg-carbide. What the author calle χ factor can be surmised as χ carbide itself.

Introduction

In this report the author has shown the results of the investigations on the tempering processes of high chromium steel through the methods of the corrosion proof test and the differential thermal analysis. It has generally been accepted that the corrosion test is very effective in the study on the carbide reactions of plain carbon steels and one of the import-factors influencing the corrosion of chromium steels is the carbide contained in them. The reasons why the author adopted D. T. A. method are (1) very few reports and studies on this problem through thermal analysis have been published so far, and (2) in view of the instances where thermal analysis gave powerful bases to the studies on ageing and recovery of aluminum alloy the author considered that it is the same with the case of chromium steels.

Materials and Procedure

The samples used in the experiments are chromium steels with 8%, 11% and 13% Cr (with 0.6% carbon content), and were taken out of the same materials used in the study reported in the first thesis.⁽¹⁾

The measure of the test pieces used in the corrosion-resistance test is 5mm ϕ \times 30mm; they were polished up to 05 grade with Emery paper before the tempering, and again they were polished with Emery paper after the tempering and just before the beginning of corrosion tests. The corrosive reagent used was 400 cm³ of 10% HCl solution; a large-mouthed bottle of 500 cm³ was used as bath. The samples were suspended with No. 1 type glass hook used by H. Endo and S. Morioka⁽²⁾ respectively and each piece was inserted vertically into the center of each bath. The decrease in weight was measured up to 0.1 mgr with a precision balance.

The thermal analyses were carried on with the aid of the differential thermal analysis apparatus of automatic temperature control style manufactured by 'Rigaku-Denki' company. The test piece used for D. T. A. has a cylindrical form of the size 4.5mm ϕ \times 20mm and has a hole drilled lengthwise in the the core for containing a thermo-couple. The container of the sample is of nickel. Generally a metal test piece has a good thermal conductivity and so a little difference in setting condition

has a serious influence upon the result. After various preliminary experiments it was found out that good results can be obtained by insulating thermally the test piece from its container with the aid of a porcelain tube for thermo-couple. The measurement with continuous heating was found to be most stable when it was done in argon gas. The results in this report were measured through the above-mentioned methods, having the nickel piece of the same form and mass with that of the test piece as a standard. The endothermic and exothermic phenomena which are essentially involved in the tempering process were observed and measured in the following way. First hardened chromium steel was put into one hole of the container and standard sample of nickel was put into the other hole, and then the first D.T.A. was done. This D.T.A. was made up to around A_3 point of chromium steel and thus the carbide reaction in the tempering process was made to finish. Next, after cooling it down to the room temperature, the second D.T.A. was carried on in the same setting. The difference between the curve described by the first D.T.A. and that obtained through the second D.T.A. is nothing less than what the author tried to find out.

The hardening condition of the samples is the same with that in the first report.⁽¹⁾ The austenitizing treatment at the time of hardening and the tempering treatment were all carried on in vacuum.

Results and Discussion

Corrosion proof test :

Fig. 1 and Fig. 2 show the corrosion rate of R80C6 steel after the tempering for 20 hours at various temperatures. Where the results shown in Fig. 1 are those of the tempered material with much martensite content after subzero treatment, and the results in Fig. 2 are of the tempered samples containing plenty of retained austenite (γ_R) as oil quenched. Corrosive reagent is 10% HCl solution, time needed for corrosion is 80 hours ; temperature is room temperature ; the temperatures shown in the diagrams are the average one throughout the tests. Both of the corrosion curves mentioned above show an abrupt rise around and after 500°C, but a reversal between 600°C and 650°C, showing a low corrosion rate again. This resulted from the increased amount of austenite caused by A_3 transformation beginning at this temperature range partly, but it has no direct relation with this study and so was omitted in the diagrams ; the results of the corrosion proof tests after the tempering up to 550°C are shown in the diagrams. It is natural that the corrosion curve of the tempered material with plenty of γ_R content should show lower value than that of the tempered sample with plenty of martensite content, but both the curves show nearly the same trend except the following point. The marked difference between these two curves is that the curve of the sample with plenty of martensite shows a remarkable peak in the neighborhood of the tempering tempera-

ture 250°C while the curve of the sample with plenty of γ_R has not shown clearly such a peak as corresponds with the above-mentioned peak. This shows that the peak of the former was not due to the decomposition of γ_R .

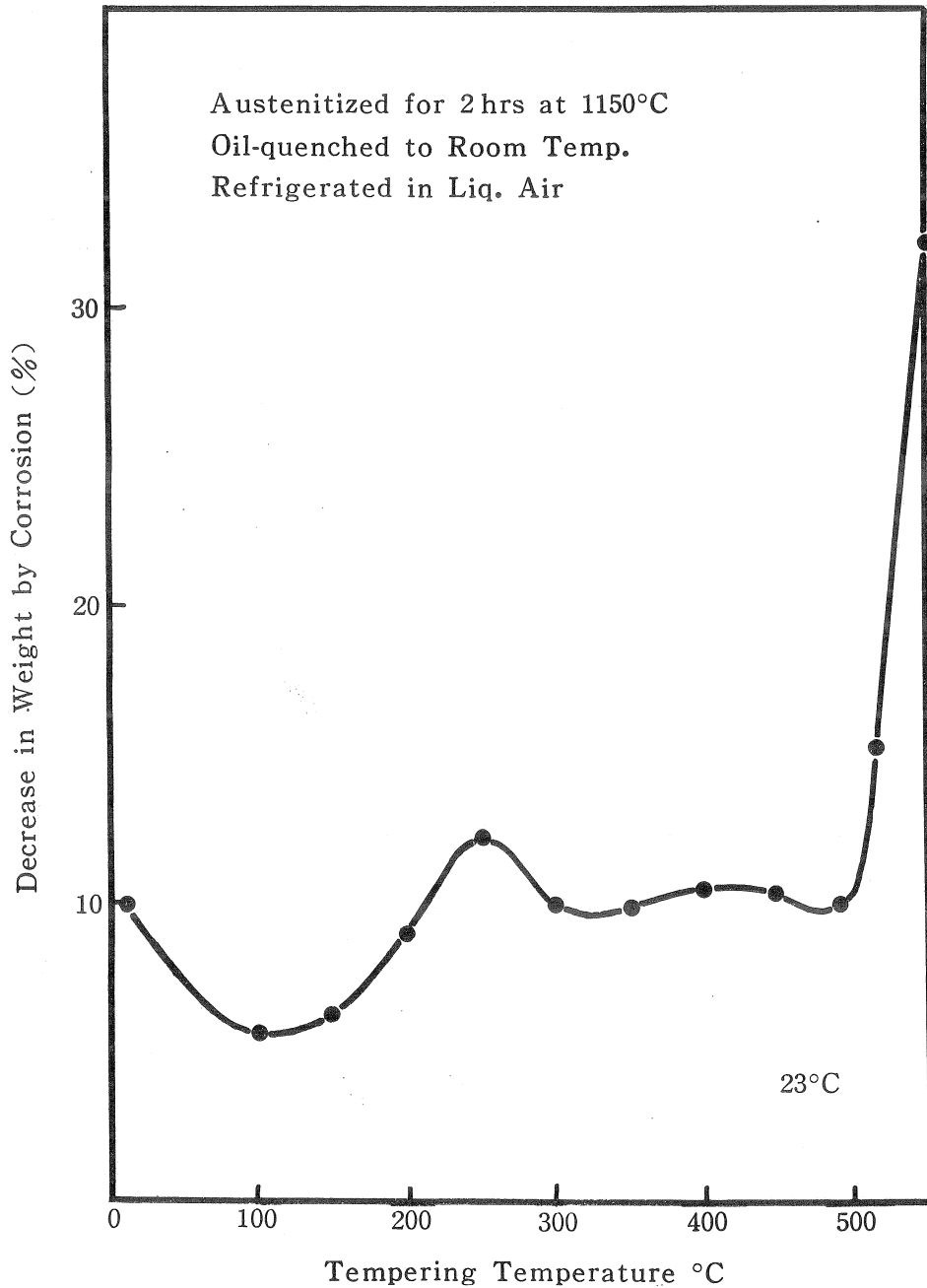


Fig. 1 Corrosion of R80C6 Steel Tempered for 20 hrs,
Dipped in 10% HCl for 80 hrs

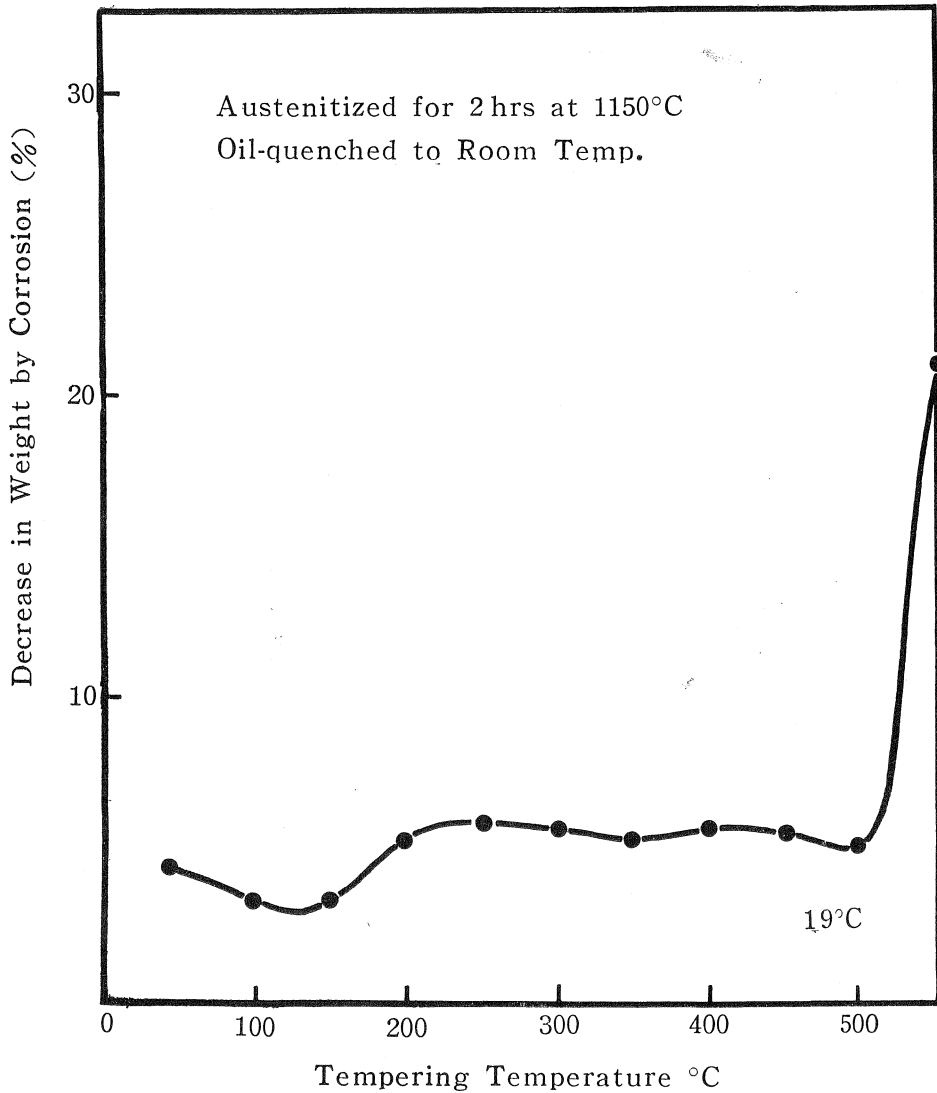


Fig 2. Corrosion of R80C6 Steel Tempered for 20 hrs,
Dipped in 10% HCl for 80 hrs

By considering the relation between the tempering temperature and the corrosion rate in the light of Fig. 1, the following results were obtained.

The corrosion rate before tempering is greater in the case of the subzero-treated sample with smaller content of γ_R . Within the tempering between the room temperature and 100°C, the corrosion rate shows a little decrease, and this trend is also remarkable with the sample with less γ_R . It can be surmised that this is probably due to the release of a part of the internal stress between crystal grains, which was caused by hardening, with the aid of thermal energy.

Within the tempering between 120°C and 240°C the corrosion rate shows a nearly uniform increase and the corrosion curve shows a small peak in the neighborhood

of 250°C. This peak is not due to the decomposition of r_B as was mentioned above. This phenomenon can be explained from the results obtained from the data furnished through magnetic analyses and hardness tests as was described in the previous reports⁽¹⁾⁽³⁾: that is, the growth of ϵ -carbide begins at around 120°C and it gets to the saturation point at around 250°C, and the corrosion rate increases with this growth. The peak seen in the neighborhood of 250°C in the corrosion curve denotes that the growth of ϵ -carbide has reached the maximum.

Within the tempering range between 260°C and 310°C the corrosion rate shows a measure of decrease as the temperature increases. This temperature range corresponds with the area in which χ factor (probably χ -carbide) exists as was shown in the previous reports.⁽¹⁾⁽³⁾ According to the results of the magnetic analyses⁽¹⁾ θ phase has not been formed within this temperature range. In the light of the other reports which have been published so far, it is conceivably impossible that magnetic analysis has less sensitivity than hardness test or corrosion test. To consider that transition precipitate consists of only ϵ -carbide makes it extremely difficult to explain the peak in the neighborhood of 250°C of the corrosion curve: that is, in view of the results of the corrosion tests it is more appropriate to consider that transition precipitate consists of ϵ -carbide and χ factor.

Within the tempering range between around 330°C and 450°C the corrosion rate shows a little increase but can be said nearly regular and fixed: this coincides with the result of the previous report⁽³⁾ that θ phase remains meta-stable within this temperature range. Again, the slight increase in the corrosion rate within this temperature range corresponds with the secondary hardening accompanying the precipitation of θ phase.

The rapid increase of corrosion rate seen in the tempering higher than 480°C corresponds with the growth of θ phase in the earlier stage, and the nucleation and growth of η phase in the later stage; this again agrees with proceeding of softening in this temperature range.

In the neighborhood of the transitional temperature 320°C from χ factor to θ phase and at around 500°C where the transition from θ phase to η phase is supposed to begin, the corrosion rate of the tempered samples shows a nearly fixed value or the corrosion curve shows even a trend to denote a slight valley in the neighborhood of these temperatures: this can be considered to have connection with transitional mechanism between these carbides, and this is an interesting problem.

Differential Thermal Analysis (D. T. A)

Fig. 3 shows the D.T.A. curve (with the standard sample of Ni) of hardened RL30C6 steel while it was being heated at the rate of 10°C/min and Fig. 4 denoted the D. T. A. curve when it was heated again in the same setting after the first test (D. T. A.) was through. The differences between these curves make exothermic and

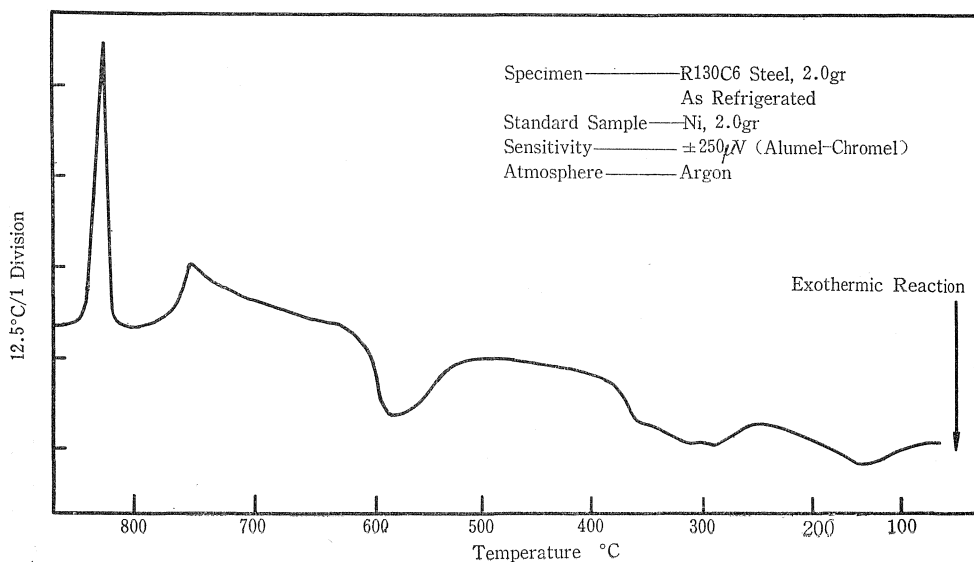


Fig. 3. D. T. A. Curve of hardened R130C6 Steel

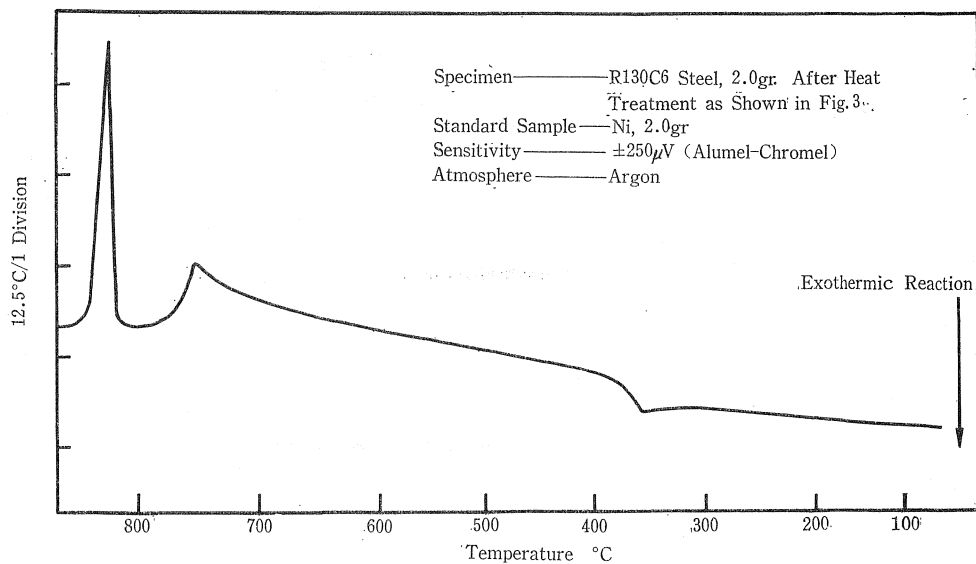


Fig. 4. D. T. A. Curve of tempered R130C6 Steel

endothermic proper to the tempering process. In the D.T.A. curve shown in Fig. 4, the peak of λ type seen in the neighborhood of 360°C and 760°C denotes the Curie point of the standard sample (Ni) and of chromium steel respectively, and the sharp peak around 824°C corresponds with A_3 transformation of chromium steel; none of these phenomena are peculiar to the tempering process.

In Fig. 5 these two successive D. T. A. curves of R110C6 steel mentioned above

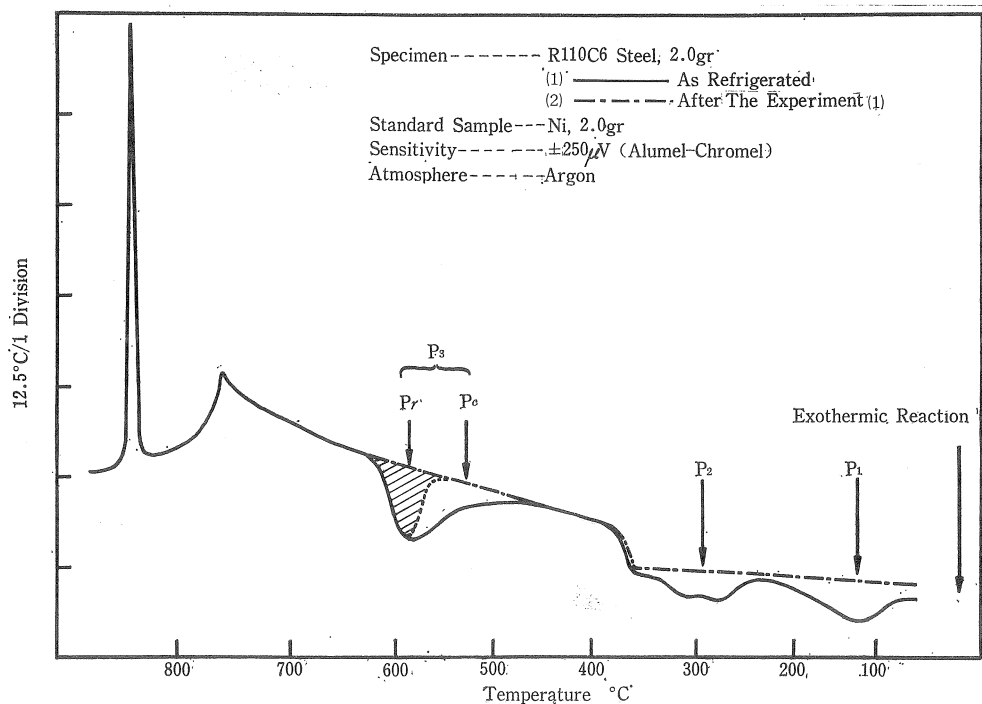


Fig. 5. D. T. A. Curve of R110C6 Steel

are put together for convenience' sake. The D. T. A. curve of the first test is given in solid line and that of the second test in chained line. (The temperature range which is denoted with only a solid line shows that both these two curves overlap here within the limit of experimental error.) The tests were carried on in such a way as the case where the solid line comes under the chained line denotes exothermic reaction; and the results of the tests show that there are three distinct exothermic reactions in the tempering process of this steel as is seen in Fig. 5. These peaks denoting exothermic reactions were named P_1 , P_2 , P_3 in the order of low temperature by the author.

P_3 is the most remarkable exothermic reaction which begins to be noticeable at about 480°C and reaches the culmination at and around 590°C and ends in the neighborhood of 620°C. As was pointed out in the first report⁽¹⁾, in this alloy steel γ_R is decomposed between 550°C and 600°C of the tempering temperature at the heating rate 3°C/min. And the decomposition of γ_R is accompanied with exothermic reaction as is well known. As the heating rate in the D. T. A. test was 10°C/min the decomposition temperature range of γ_R is to be shifted to the side of high temperature. In the tempering higher than 500°C the exothermic reaction accompanying the reaction $(Fe, Cr)_3C \rightarrow (Cr, Fe)_7C_3$ and the growth of $(Cr, Fe)_7C_3$ occurs naturally; but judging from the proportion of the amount of carbide in the sample to the amount of γ_R , it can be considered that in the tempering higher than 550°C the exothermic reaction by the decomposition of γ_R is far greater than

that by the carbide reaction. Consequently, reversing the curve of P_3 on high temperature side to the low temperature side having the ordinate passing on the highest peak as symmetrical axis (shown with a dotted line in the diagram) the author named the space which is enclosed with the dotted curve, the solid curve, and the chained base line (which is filled with hatching lines in the diagram) P_γ ; it would be permissible to consider as the first approximation that the generation of heat in P_γ part is due to the decomposition of γ_R . P_c which denotes the balance of P_3 minus P_γ , shows the generation of heat by carbide reaction. The exothermic reaction in P_c part is getting noticeable in the neighborhood of the tempering temperature 480°C and the calorific value gradually increase with the rise of the temperature and reaching the culmination around 550°C , falls gradually. The final stage of P_c is indistinct owing to the formation of P_γ . Even if judging from these points only it is certain that P_c is due to the aggregation of θ phase and the nucleation and growth of η phase as was pointed out in the previous reports⁽¹⁾⁽³⁾.

In view of the results in the previous report and its temperature range, exothermic reaction P_1 which starts at around 80°C and ends at about 250°C of the tempering temperature is considered to be due to the transformation as follows:

martensite \rightarrow ϵ -carbide+less tetragonal martensite.

P_2 is the exothermic reaction which begins at the tempering temperature around 250°C and continues up to around 360°C . The exothermic reaction at higher tempering temperature than 320°C can be considered to be due to the precipitation of θ phase judging from the results of our previous reports and other various reports. At the tempering lower than 300°C θ phase does not exist as was referred to at the part of corrosion test: unlike P_1 and P_3 , the peak of P_2 is flat or rather might be said to be divided into 2 small, gently sloping hills having around 300°C as the boundary. Moreover at this tempering range of this alloy steel, decomposition of γ_R does not occur. The view point that transition precipitate consists of ϵ -carbide phase only, cannot explain the low-temperature part of P_2 . The author's conclusion that transition precipitate is composed of ϵ -carbide and χ factor (probably χ -carbide), as was pointed out in the previous reports⁽¹⁾⁽³⁾, seems more appropriate. The fact that no noticeable exothermic reaction can be seen within the tempering between 360°C and 450°C coincides with the author's view that θ phase in the early period remains meta-stable.

Conclusion

The author studied the tempering process of chromium steels through the methods of corrosion proof test and differential thermal analysis (D. T. A.), and considering the results together with those of the magnetic analyses and the hardness tests which were put forward in the previous reports, obtained the following conclusions.

(1) The growth of ϵ -carbide accompanied with the tempering begins at around

100°C, and along with it the corrosion rate increases and exothermic reaction occurs; but the growth of ϵ -carbide reaches its saturation at about 250°C and with it both the increase of corrosion rate and exothermic reaction comes to a standstill.

(2) Within the tempering between 330°C and 450°C, corrosion rate shows no noticeable change and between 360°C and 450°C no discernible exothermic reaction occurs; this fact endorses the author's view-point that θ phase remains meta-stable in the early stage of precipitation. The difference between the tempering ranges in the results of both these tests can be considered rather natural when we take into account the fact that the former is the data after isothermal tempering for 20 hours and the latter is the data measured while being heated at the rate of 10°C/min.

(3) In the tempering range from around 480°C up to around 600°C, the corrosion rate shows a remarkable increase and exothermic reactions occur; in the earlier stage these are caused by the growth of θ phase particles and in the later stage by the nucleation and growth of $(\text{Cr, Fe})_7\text{C}_3$.

(4) The corrosion proof curves of the tempered chromium steels show a slight peak in the tempering range between 400°C and 450°C and this corresponds with some secondary hardening within this temperature range.

(5) With the idea that transition precipitate is composed of only ϵ -carbide it is difficult to explain the results shown in the corrosion curve and D. T. A. The author's view that transition precipitate is composed of ϵ -carbide and χ factor (probably χ -carbide) and ϵ -carbide turns into χ factor irreversibly having approx. 250°C as boundary, in the light of not only the magnetic analysis and hardness test but also the results of corrosion proof test and D. T. A., seems to be appropriate.

(6) Within the transitional tempering temperature ranges from χ factor to θ phase and from θ phase to η phase the corrosion rate shows a trend to decrease slightly; this can be considered to be related with transitional mechanisms between these carbides, and stimulates our interest.

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