

《Special Lecture》

Strengthening of Steel by Small Addition of Nb. V. etc

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Part I

1. Introduction

Lower yield stress, σ_y , is generally related to grain diameter, d , by the well-known Hall-Petch relation¹⁾²⁾:

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

where σ_0 is the frictional stress for moving dislocations and k_y is the material constant. On the other hand, the yield stress of metal containing finely dispersed precipitates is controlled by interparticle spacing λ according to the Orowan³⁾ or Ansell-Lenel⁴⁾ relation.

In a preliminary test with steels each containing niobium, titanium, vanadium and zirconium, it has been revealed that steels containing small amounts of carbon and vanadium are most suited to obtaining a wide range of grain sizes having an equal fine dispersion of carbides.

What effects have the matrix grain size and very fine dispersion of carbides on the lower yield stress of these vanadium steels? To clarify this point, it is necessary to compare the yield stress of steels having fine dispersed particles with that of steels with the same grain size having no such fine particles. From this point of view, the effect of grain size and of very fine dispersion of V_4C_3 on the lower yield stress of vanadium steels were examined, and comparisons were made with the results on low carbon steels containing only a

small number of large particles of Fe_3C having the same grain size range as that of vanadium steels.

2. Experimental Procedure

Chemical compositions of standard carbon steels are shown in Table 1, and those of vanadium steels in Table 2.

Grain sizes of the standard low carbon steels were controlled by varying both austenitizing temperature and heating time. Cooling rates near the A_3 point were fixed at 100°C/min and 1000°C/min for annealing and normalizing, respectively. A small amount of V_4C_3 in low carbon austenite was completely resolved at about 900°C, which is a somewhat lower temperature than that in commercial steels containing vanadium. In case of vanadium steels the grain sizes were controlled by heating at 1000°C for 15 min~120 hr, and subsequently cooled at a rate of about 10°C/min for perfect annealing and 100°C/min for ordinary annealing. The grain size of ferrite was measured by the linear analysis method, and the dispersion state of V_4C_3 and its diameter were observed by transmission electron microscopy.

The lower yield stress at room temperature was determined by the Instron-type testing machine at a strain rate of 6.4×10^{-4} /sec.

3. Results

The relationship between lower yield stress, σ_y ,

and grain diameter, d , for the annealed low carbon steel is shown in Fig. 1. As clearly seen in the figure, the relation is expressed as

$$\sigma_y (kg/mm^2) = 1.9 + 2.7d^{-\frac{1}{2}}$$

For the normalized low carbon steels it is

$$\sigma_y (kg/mm^2) = 5.3 + 2.5d^{-\frac{1}{2}}$$

as shown in Fig. 2.

Thus, the relation between σ_y and d in low carbon steels perfectly satisfied the Hall-Petch relation.

The dispersion state and particle size of vanadium carbide V_4C_3 in the perfectly annealed and the ordinary annealed vanadium steel were fairly uniform. The mean planer interparticle spacing and the mean diameter of carbide are 3000\AA and 2500\AA , and 120\AA and 100\AA , respectively. Phot. 1 shows the carbide precipitation of 0.19%V, 0.15% C steel and Phot. 2 shows that of the same steel showing an especially good coherency with the matrix.

As shown in Fig. 3, the change in lower yield stress σ_y , with grain diameter d , in vanadium steel also agrees with the Hall-Petch relation. The value of material constant, k_y , is nearly equal to that for the low carbon steel, and σ_y has the following value:

$\sigma_y (kg/mm^2) = 4.0 + 3.1d^{-\frac{1}{2}}$ for the fully annealed steel,

$\sigma_y (kg/mm^2) = 8.3 + 2.7d^{-\frac{1}{2}}$ for the ordinary annealed steel.

The value of σ_0 in a group of specimens increases as the cooling rate becomes faster and the particles of carbide are finer, that is, the state of dispersion precipitates has a clear effect on σ_0 also in vanadium steel.

If the lower yield stress of steels having fine dispersed particles mainly depends on precipitation strengthening and less depends on grain diameter, these lines in Fig. 3 should come up in a direction parallel with the co-ordinate axis. On the other hand, if σ_y depends mainly on grain size, the experimental plots for the vanadium steel should fall on the same line for the stan-

dard low carbon steel.

The experimental results shown in Fig. 3 reveals that the line for vanadium steel and that of carbon steel are in a parallel relation. This fact clearly shows that both dispersion of precipitates and grain boundaries contribute independently to the lower yield stress of the vanadium steel. Therefore, as shown in Fig. 4, in case of carbon steel or low alloy strengthened steels having little solid solution strengthening, we can divide the increment in lower yield stress into two parts, one due to grain size σ_{yg} and the other due to precipitates σ_{yp} . So, measurement of the lower yield stress and grain size of the steel would enable us to determine the dispersion states of carbides in them.

Since we could not get a more wide ranges of grain diameters and particle spacings, the mutual effect of λ and d on the lower yield stress remained unclear. However, it is evident that, when λ is $2500 \sim 3000\text{\AA}$ and $d^{-\frac{1}{2}}$ is $3 \sim 8\text{mm}^{-\frac{1}{2}}$, both λ and d have an independent effects on the lower yield stress of the steel.

The increase in σ_0 , by the dispersed precipitates, is somewhat less than the value expected by Orowan's mechanism. Therefore, it must be said that the details of the strengthening mechanism in the steels are yet to be further studied.

Part 2

1. Introduction

In the recent years, low carbon steels containing a small amount of carbide-forming elements such as Nb and V have been drawing attention as a non-heat treated high strength steels. Formerly the strength of the steel increased by the addition of a small amount of these elements was considered subject to fine grain size^(5,6), but at present fine precipitates are assessed more important as initiating factors^(7,8). With this respect, we have carried out investigations^(9~11) and confirmed that the increase in strength of steel by this process is caused by an additional contribution of grain refining and precipitation as above mentioned. On

this basis, the strengthening mechanisms of non-heat treated high strength steel were examined and discussed in the present study with low carbon steels containing one or more of carbide-forming elements from each of Nb, V, Ti, Zr, Cr and Mo.

2. Experimentals

Standard low carbon steels and low carbon steels containing one or more of carbide-forming elements were prepared with electrolytic iron, high-purity carbon and pure metals by vacuum induction melting. Table 3 is the chemical composition of specimens. The amount of alloying elements is 0.07 at% for single element treated steels and is 0.1 at% for two or three elements treated steels, of 0.01% each.

Impurities such as Si, Mn, P, S and so on are less

These steels were austenitized for 1 hr. at 925–1200°C for grain size control and for solution treatment then cooled at a mean cooling rate at A_3 transformation temperature of about 1000°C/min (normalizing) and 100°C/min (annealing).

The experimental conditions were the same as of Part 1.

3. Results and discussion.

Fig. 5 shows lower yield strength σ_{ly} of annealed or normalized single element treated steels at various austenitizing temperatures. Relationships between σ_{ly} and reciprocal square root of grain diameter $D^{-1/2}$ of specimens are collected into Fig. 6. On standard low carbon steels, Hall-Petch lineal relationship is observed. On the other hand, specimens containing carbide-forming element are included into curved lines as shown in this figure. All the results of Nb treated steels are included into hatched areas. The height of each point of alloyed steels from the strait line of carbon steels would correspond to strengthening by the precipitation of fine carbides in the matrix, and strengthening by grain refining could be calculated by comparing the grain size of alloyed steel with that of equally heat treated carbon steel. According to these analytical methods, increments of lower yield strength $\Delta\sigma_{ly}$ of carbon steel by containing of a small amount of carbide-forming

element, could be separated to the increments by precipitation of fine carbides $\Delta\sigma_{yp}$ and that by grain refining $\Delta\sigma_{yg}$. Figs. 7 and 8 are the result of annealed or normalized single element treated steels. As seen in the figures, the increments of lower yield strength by Nb addition is the most, and the higher the austenitizing temperature is, the more the increments is, then $\Delta\sigma_{ly}$ of 0.09% Nb treated steel normalized at 1200°C reached to 19kg/mm². Almost all increments of lower yield strength by heat treatment at the elevated temperatures is due to precipitation strengthening, but that by heat treatment at lower temperatures is due to grain refine strengthening. Transmission electron micrography of specimens treated at the lower temperatures indicates that primary fine carbides NbC which had been precipitated in specimens slightly coarsen and lose the coherency with matrix, but for the specimens treated at higher temperatures than 1100°C the primary precipitates have dissolved into austenite matrix and very finely reprecipitated on cooling, forming secondary coherent precipitates NbC which bring remarkable precipitation strengthening.

In the case of the steels containing Ti, the strengthening mechanisms may be the same as the steels containing Nb, but grain refine strengthening effect may be less because titanium carbide TiC may be more unstable than niobium carbide NbC and agglomerative coarsening of primary precipitates may be easier on austenitizing, while precipitation strengthening effect of TiC may be a little greater because of large solubility of TiC in austenite when the steel treated at the elevated temperatures.

On the other hand, the steels containing V show the maximum grain refine strengthening by lower temperature treating because the solubility products of V_4C_3 in austenite is quite large. But the preventing effect of grain coarsening may be little. Then the coordinated strength is rather small.

For Zr treated steels, precipitation strengthening is the minimum, for primary precipitates ZrC is large and stable and solution treating of them is difficult.

The effects of austenitizing temperatures on

lower yield strength σ_{ly} of the first group of two elements treated steels are shown in Fig.9. σ_{ly} of specimens No.1 (Nb+V), 2 (Nb+Ti), 4 (Nb+Mo) and 7 (Ti+Zr) are very high, especially σ_{ly} of specimen No.1 treated at the elevated temperatures is about 50 kg/mm². The tendencies of tensile strength of these steels are the same as this figure, and that of specimen No.1 reaches to about 62 kg/mm².

Fig.10 is the results of the second group. These steels contain smaller amount of carbide-forming elements than the steels of the first group contain, then the strength of them reaches to the peak at about 1050°C. Even if the steels treated at higher temperatures, the strength never increases and rather decreases, by coarsening of grain size as seen in this figure.

The results of three elements treated steels are shown in Fig. 11. The strength of them reaches to the peak at 1150~1200°C treating.

Fig. 12 shows the results of the analysis of the increments of lower yield strengths $\Delta\sigma_{ly}$ in Fig. 9 into two parts, that is, strengthening by precipitation $\Delta\sigma_{yp}$, and strengthening by grain refining $\Delta\sigma_{yg}$. It reveals that in the best specimens Nos. 1, 2, 3, and 7 about 70% of the total increments is due to the precipitation strengthening.

Summary

As an element vanadium is most effective and next is niobium to strengthening the low carbon steels by small addition both on fine precipitation and fine grain.

The combination effect of vanadium plus niobium or vanadium plus molybdenum is much more effective than adding one element.

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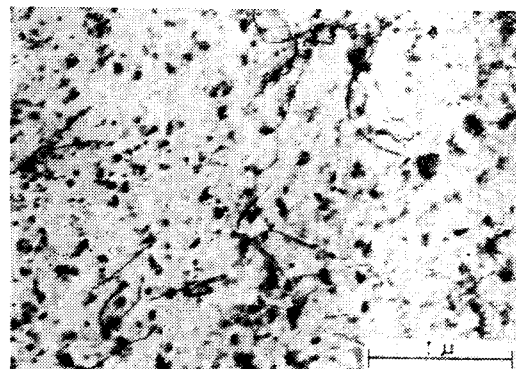


Photo. 1. Carbide precipitation of 0.19%V, 0.15%C steel austenitized at 1000°C for 3 hours and cooled at the rate of 10°C/min,

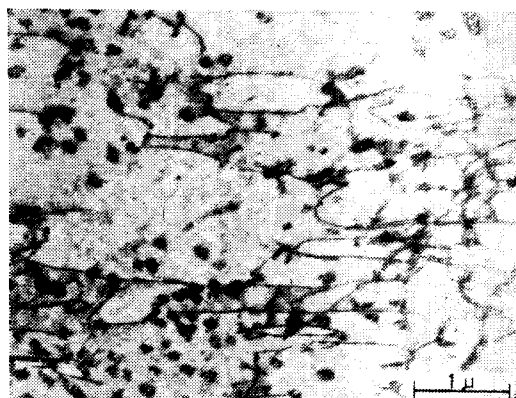


Photo. 2. Carbide precipitation having a good coherency with the matrix of 0.19%V, 0.15%C steel austenitized at 1000°C for 120 hours and at cooled the rate of 10°C/min.

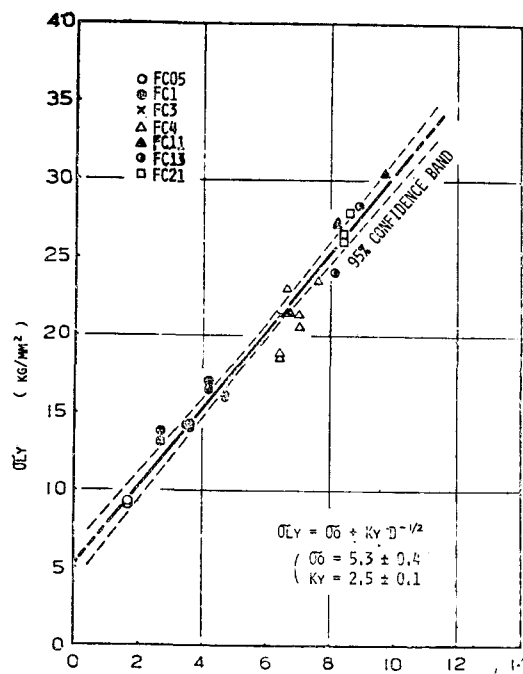


Fig. 1. Relationship between lower yield strength σ_{LY} and reciprocal square root of grain diameter $D^{-1/2}$ for annealed carbon steel tested at a strain rate of $6.4 \times 10^{-4} \text{ sec}^{-1}$

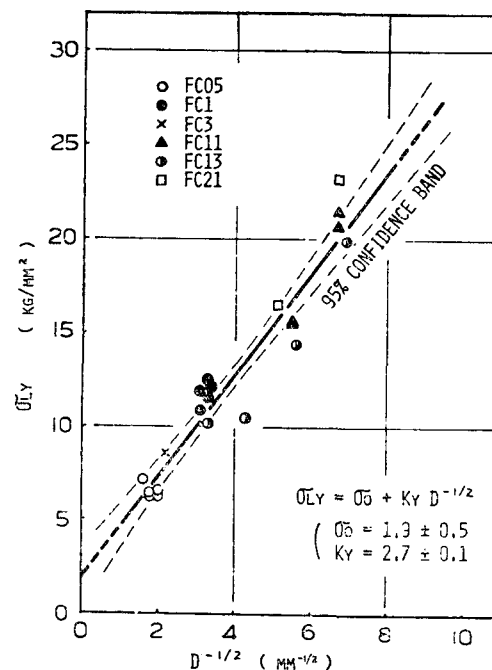


Fig. 2. Relationship between lower yield strength σ_{LY} and reciprocal square root of grain diameter $D^{-1/2}$ for normalized carbon steel tested at a strain rate of $6.4 \times 10^{-4} \text{ sec}^{-1}$

Table 1

Chemical Compositions of Carbon Steels

(Wt%)

Mark	C	N	O	Si	Mn	P	S
FC05	0.005	0.003	0.059	0.005	0.001	0.002	0.009
FC1	0.012	0.001	0.003	—	—	—	—
FC3	0.031	0.001	0.002	—	—	—	—
FC4	0.037	0.001	0.004	0.007	0.001	0.002	0.005
FC11	0.11	0.002	0.001	—	—	—	—
FC13	0.13	0.002	0.001	—	—	—	—
FC21	0.21	0.003	0.002	—	—	—	—

Table 2

Chemical Compositions of Vanadium Steels

(Wt%)

MARK	C	N	O	V	Si	Mn	P	S
VC190	0.15	0.001	0.002	0.19	0.014	0.001	0.003	0.008
VC200	0.12	0.001	0.001	0.20	0.012	0.001	0.004	0.008

Table 3 **Chemical Composition of specimens** **(Wt%)**
(A) Single Element Treated Steels

Mark	C	N	Nb	Ti	V	Zr
FC21	0.21	0.003	—	—	—	—
NC23	0.20	0.007	0.023	—	—	—
NC35	0.19	0.004	0.035	—	—	—
NC90	0.20	0.005	0.090	—	—	—
TC57	0.19	0.004	—	0.057	—	—
VC66	0.20	0.006	—	—	00.66	—
ZC34	0.18	0.003	—	—	—	0.034
ZC131	0.16	0.002	—	—	—	0.131

(B) Two Elements Treated Steels

Mark	C	N	O	Nb	V	Ti	Zr	Mo	Cr
FC4	0.037	0.001	0.003	—	—	—	—	—	—
NC50	0.042	0.002	0.006	0.050	—	—	—	—	—
1-NV1	0.057	0.007	0.008	0.092	0.048	—	—	—	—
2-NT1	0.052	0.009	0.014	0.088	—	0.047	—	—	—
3-NZ1	0.023	0.006	0.074	0.073	—	—	0.086	—	—
4-NM1	0.075	0.004	0.016	0.092	—	—	—	0.11	—
5-NC1	0.059	0.005	0.047	0.083	—	—	—	—	0.055
6-TV1	0.086	0.003	0.018	—	0.048	0.054	—	—	—
7-TZ1	0.094	0.007	0.021	—	—	0.043	0.13	—	—
8-ZV1	0.067	0.005	0.034	—	0.043	—	0.13	—	—
9-ZV2	0.040	0.002	0.001	0.026	0.051	—	—	—	—
10-NT2	0.023	0.002	0.001	0.026	—	0.047	—	—	—
11-NZ2	0.045	0.002	0.002	0.026	—	—	0.11	—	—
12-NM2	0.021	0.002	0.006	0.027	—	—	—	0.12	—
13-NC2	0.018	0.002	0.009	0.022	—	—	—	—	0.065

Table 3 **(C) Three Elements Treated Steels**

Mark	C	N	O	Nb	V	Ti	Zr	Mo
14-NVT	0.051	0.001	0.002	0.046	0.038	0.037	—	—
15-NTZ	0.047	0.001	0.001	0.046	—	0.038	0.031	—
16-NVZ	0.041	0.002	0.002	0.043	0.034	—	0.035	—
17-NTM	0.057	0.001	0.002	0.054	—	0.040	—	0.053
18-NVM	0.054	0.001	0.001	0.050	0.034	—	—	0.051

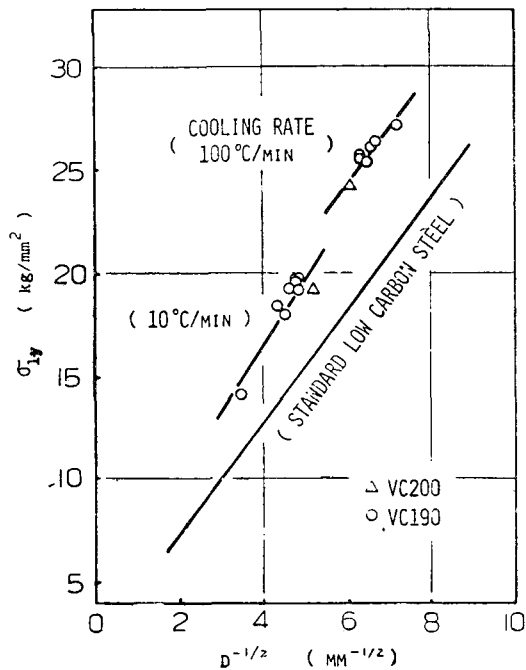


Fig. 3. Relationship between lower yield strength σ_{ly} and reciprocal square root of grain diameter $D^{-1/2}$ of vanadium steels

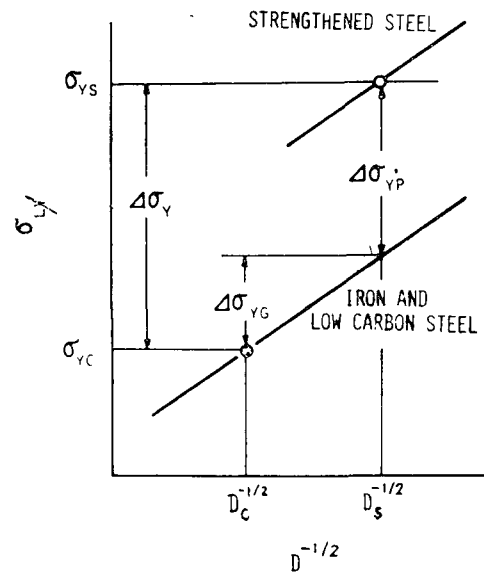


Fig. 4. Relationship between strengthening by precipitation, $\Delta\sigma_{yp}$ and by grain refining $\Delta\sigma_{yg}$

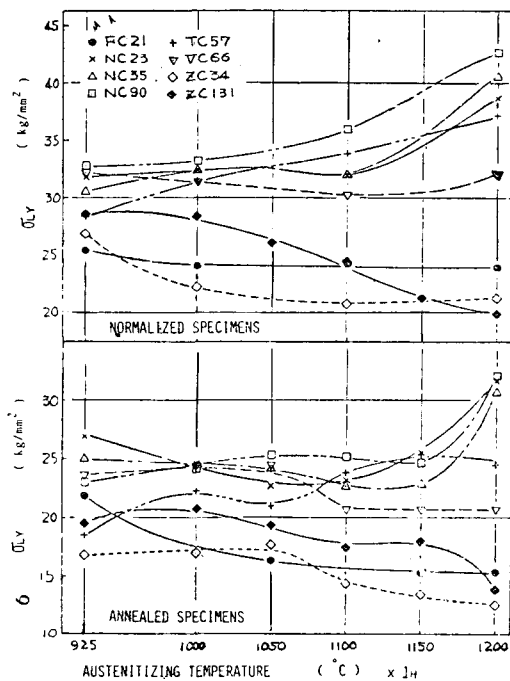


Fig. 5. Lower yield strength σ_{ly} of annealed and normalized single element treated steels at various austenitizing temperatures

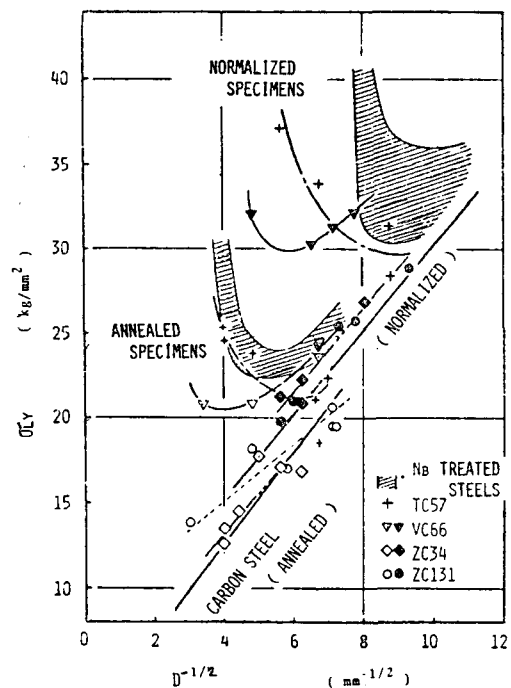


Fig. 6. Relationship between σ_{ly} and D for single element treated steels at annealed or normalized state

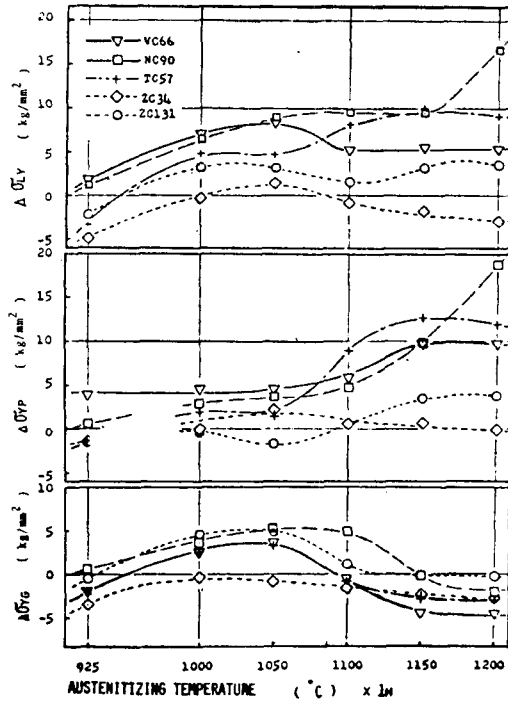


Fig. 7. Increments of lower yield strength, $\Delta\sigma_{LY}$, $\Delta\sigma_{YP}$, and $\Delta\sigma_{YG}$ of annealed single element treated steels at various austenitizing temperatures

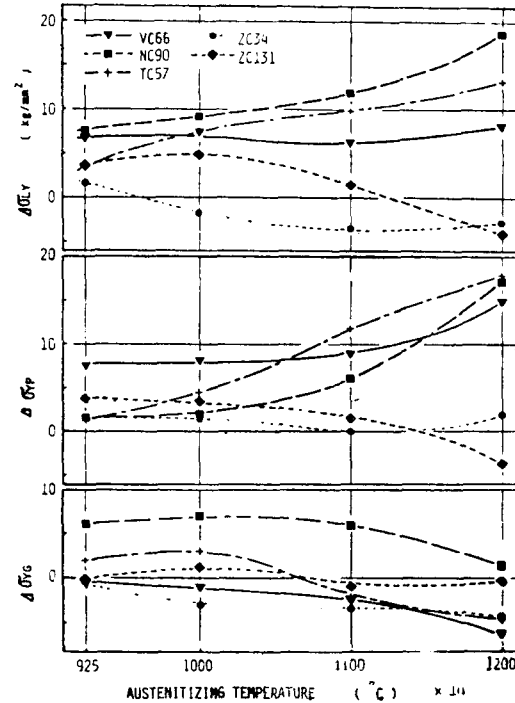


Fig. 8. Increments of lower yield strength $\Delta\sigma_{LY}$, $\Delta\sigma_{YP}$ and $\Delta\sigma_{YG}$ of normalized single element treated steels at various austenitizing temperatures

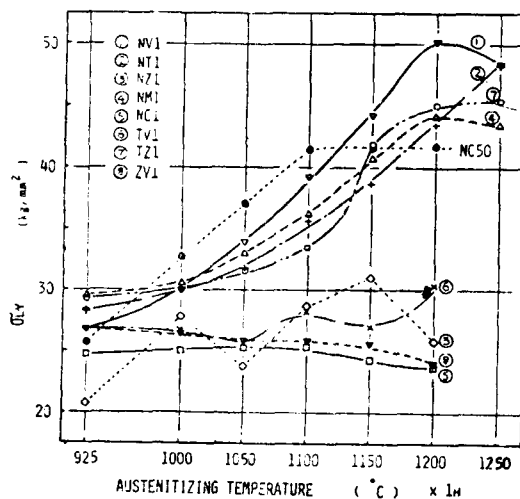


Fig. 9. Effect of austenitizing temperature on lower yield strength σ_{LY} of two elements treated steels at normalized state

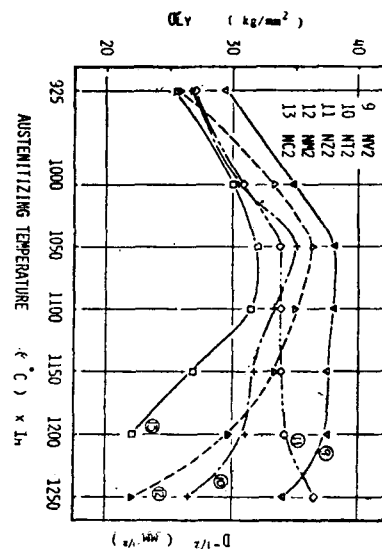


Fig. 10. Effect of austenitizing temperature on lower yield strength σ_{LY} of two elements treated steels at normalized state

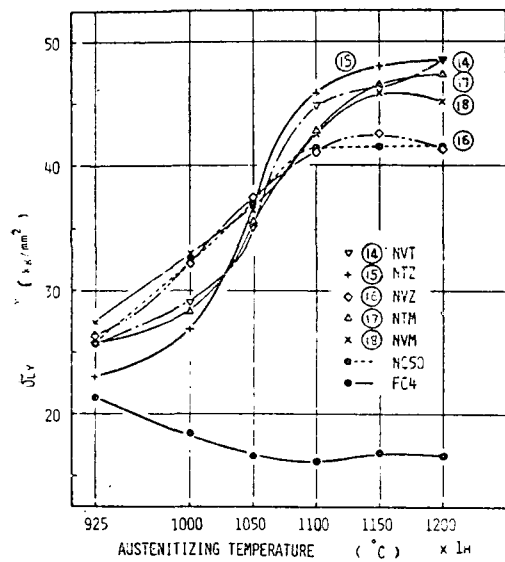


Fig. 11. Effect of austenitizing temperature on lower yield strength σ_{ly} of three elements treated steels at normalized state

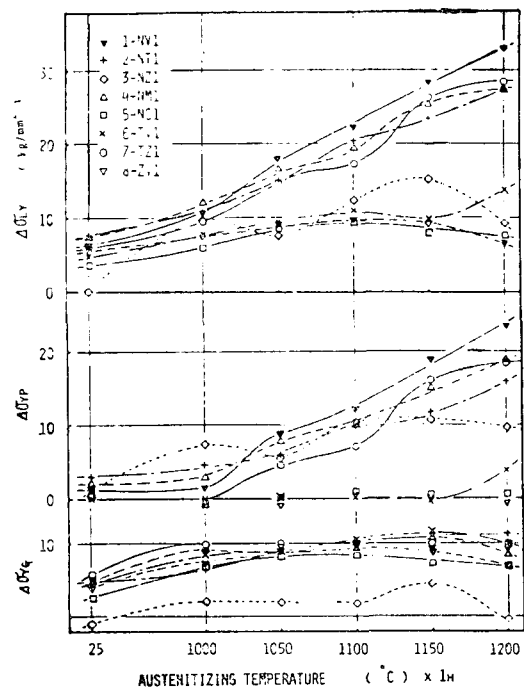


Fig. 12. Increments of lower yield strength $\Delta\sigma_{ly}$, $\Delta\sigma_{yp}$ and $\Delta\sigma_{yg}$ of normalized two elements treated steels at various austenitizing temperatures