Chapter VI

EFFECTS OF ALLOYING ELEMENTS IN TEMPERING

It has already been mentioned that relatively little steel enters its service in the fully hardened condition, — as quenched and untempered. The lack of toughness of martensite, except perhaps in low carbon compositions, is of such importance that it is general practice to reheat the quenched products, at least to a moderate temperature, even when the steel is to be used at high hardness. Thus the function of the tempering treatment is best regarded as a means of imparting a degree of plasticity and toughness, which, incidentally, may soften the steel, rather than primarily as a softening treatment. This viewpoint is more in line with the observation that brittleness is in part caused by high internal stress, which is now regarded as inevitably present in quench-hardened steel and which, being intense, is somewhat dissipated by even relatively low temperature of reheating. The tendency to crack after the quench is perhaps a rough measure, or at least a reflection, of the magnitude of internal stress set up during quenching, and, if so, the practice of allowing a coarse-grained austenite to form or the use of quenching baths of exceedingly high power are clearly not favorable to the production of tough parts of high hardness. Rather, steels of adequate hardenability for use with milder quenches and at finer grain size are more widely adaptable. These circumstances are repeated here because cracking is often found to occur shortly after quenching, not immediately, and therefore if the tempering treatment is quickly applied the cracking may be avoided.

When the properties to be sought are acquired only after a reheating which very substantially softens the martensite, no particular interest attaches to the precise hardness of the martensite and accordingly any concern about its as-quenched hardness is unwarranted provided only that—

1. The austenite at heating temperature dissolves the desired amount of carbon and alloy;
2. No pro-eutectoid ferrite or carbide forms during quenching; and,
3. The austenite has transformed *essentially* to martensite or the hard acicular type of structure.

Individual minor variations of initial hardness usually all level off in any particular quenched steel when the tempering is well under way, provided the heating was uniform and the quench adequate for the conditions above.

NATURE OF THE TEMPERING REACTION

There can be little doubt that the process of tempering is involved mainly with the crystallization and coalescence of the carbides of iron and alloying elements. The evidence all points to this conclusion. Through a circumstance unique in steel, a solid-solution is formed at the heating temperature which may easily contain some fifty times as much carbon as is soluble at the temperature reached upon quenching. This tremendous potential supersaturation may be reached in a few seconds. The stable (or at least metastable) form of this carbon is that of carbide crystals; seemingly just after quenching, if it is combined at all, it is in combination with the iron with the maximum possible unit being something in the nature of the molecule. The limited diffusion alone forces this circumstance. That carbon has a diffusivity at various temperatures suitable to explain tempering as a particle-growth phenomenon is well known, and it is quite as well known that, with sufficient tempering temperature, large, individually-recognizable particles do form. The ever-slower rate of softening of carbon steels, held after quenching at constant temperature for prolonged intervals, is likewise characteristic of the diffusion necessary to the increase in size, and decrease in number, of dispersed particles. This broad pattern of behavior is found in every "age-hardening" system once the time at aging temperature has been sufficient to go beyond the maximum hardening effect and inaugurate softening. It was seen in Fig. 27 that increasing temperature of tempering for a constant interval reduces the hardness of carbon steels in a fairly definite manner for a particular hardness scale; the same is largely true for martensitic alloy steels carrying moderate amounts of either manganese, silicon or nickel. The influence of the hardness scale selected upon the shape of the Hardness versus Tempering-Temperature Curve is well shown in Fig. 143, which shows the softening after 1 hour in a quenched 0.62 per cent carbon steel,[45] plotted both on a Rockwell scale and a Brinell scale. The tempering action is seemingly simple and forthright in carbon steels which are so quenched as to consist essentially of martensite and it may be well to become somewhat familiar with the *form* of these curves of the softening effect of tempering.

Time and Temperature Relationships in Tempering — A still better acquaintance with the softening of steels by tempering may be gained by a consideration of the effect of time interval at tempering temperature. Fig. 144 shows the incredibly rapid softening during the first few minutes in an 0.82 per cent carbon, quenched steel at 1200 degrees Fahr. (650 degrees Cent.). It is well known that most of the softening action occurs in the first few minutes and that little further reduction of hardness results from increasing the time of tempering from, say, ½ hour to 2 hours. More rarely, however, data are presented covering a wider range of tempering interval as in Fig. 145. Owing to the vast change in softening velocity it is convenient to employ a logarithmic

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[45] Figs. 143, 144 and 145 are based on data from unpublished work of E. L. Roff and E. C. Bain.

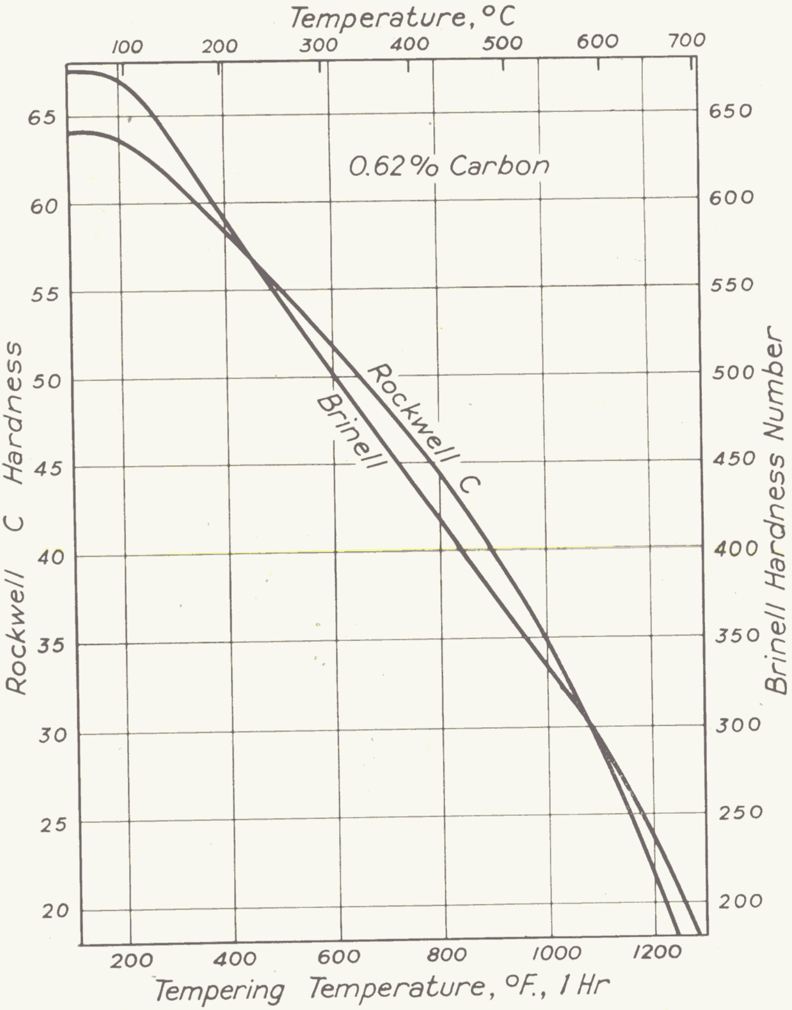

Fig. 143—The Effect of Tempering for 1 Hour at Various Temperatures upon Hardness of a 0.62 Per Cent Carbon Steel. Plotted both upon a Brinell Scale and a Rockwell C Scale. Note Minor Differences in Shape of Softening Curves.

scale for time. As a matter of fact, over the range of tempering time between some 5 minutes and several hours, the rate of softening is diminishing in such a way as to produce essentially a straight line in a plot made in this way. The hardness scale is an arbitrary one and there is no basic reason for this precise pattern of softening; nevertheless the approximation to a logarithmic relation is so close as to permit the prediction of softening effects. Thus the loss of hardness value is fairly constant for the intervals, — 6 minutes to 1 hour, 1 hour to 10 hours and 10 hours to 100 hours, when the temperature is such as to bring the hardness into the range between some 50 and 35 Rockwell C. Actually the quasi-logarithmic pattern of softening is even better reflected in plots wherein Brinell hardness rather than Rockwell hardness is employed, as may be seen in comparing Fig. 146 with Fig. 147.[46] Note that the interval at reheating temperature is prolonged to about 1500 hours.

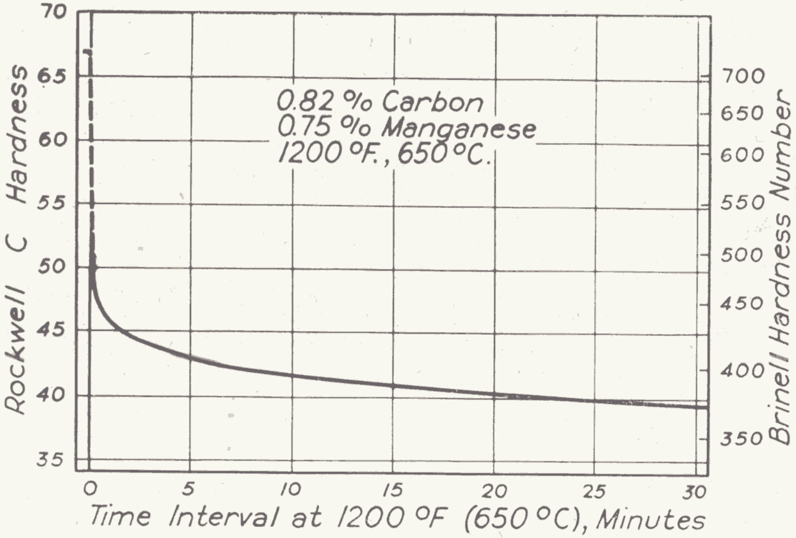

Fig. 144—The Effect of Time-Interval upon the Softening of a Quenched 0.82 Per Cent Carbon Steel as Tempered at 1200 Degrees Fahr. *(E. L. Roff at United States Steel Corporation Research Laboratory).*

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[46] The extensive data on the softening of several 0.35 per cent carbon steels, with chromium, molybdenum and both present at various temperatures and after a wide range of intervals, were secured by J. R. Vilella, H. A. Brown and R. V. Hilkert of the United States Steel Corporation Research Laboratory. These data are presented in Figs. 146, 147, 153, 155, 158, 159, 160, 164, 165, 167, 168, 169, 170, 171, 172, 173 and 174.

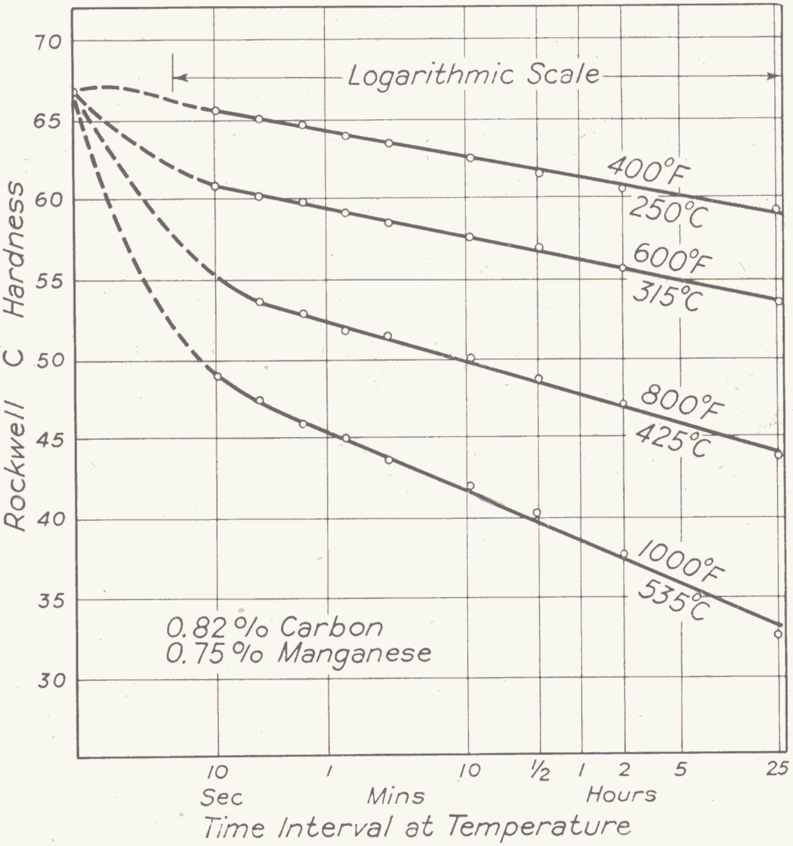

Fig. 145—The Effect of Time-Interval at Four Tempering Temperatures upon the Softening of Quenched 0.82 Per Cent Carbon Steel. Note Nearly Straight Lines on Logarithmic Time Scale. *(E. L. Roff at United States Steel Corporation Research Laboratory).*

There are circumstances, however, which greatly modify the softening pattern of some carbon and alloy steels and these are of outstanding importance in the technology of heat-treated alloy steels. The first of these is austenite retained after quenching and the second is the special carbide-forming tendency of the elements chromium, tungsten, molybdenum, tantalum, vanadium, columbium and titanium.

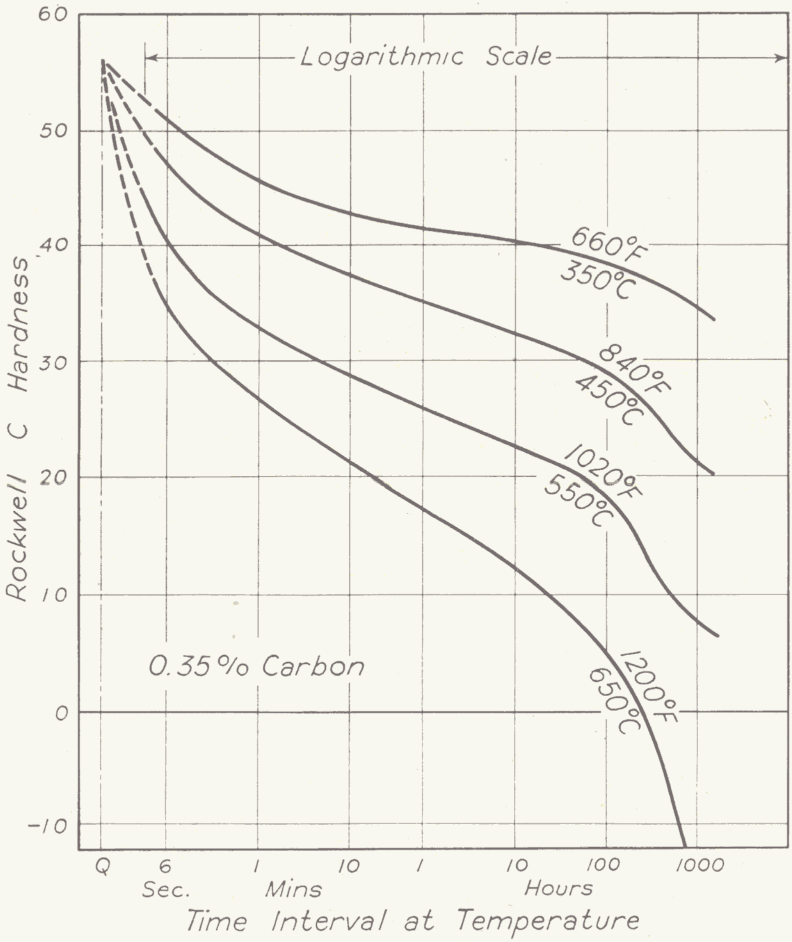

Fig. 146—The Effect of Time-Interval at Four Tempering Temperatures upon the Softening of Quenched 0.35 Per Cent Carbon Steel. Rockwell C Scale for Comparison with Fig. 147. (See Footnote 46).

Retained Austenite During Tempering—In high carbon steels, particularly those containing also nickel or amounts of manganese beyond the normal content, the transformation to martensite is usually not complete; instead some unstable austenite remains permanently. Even after some of

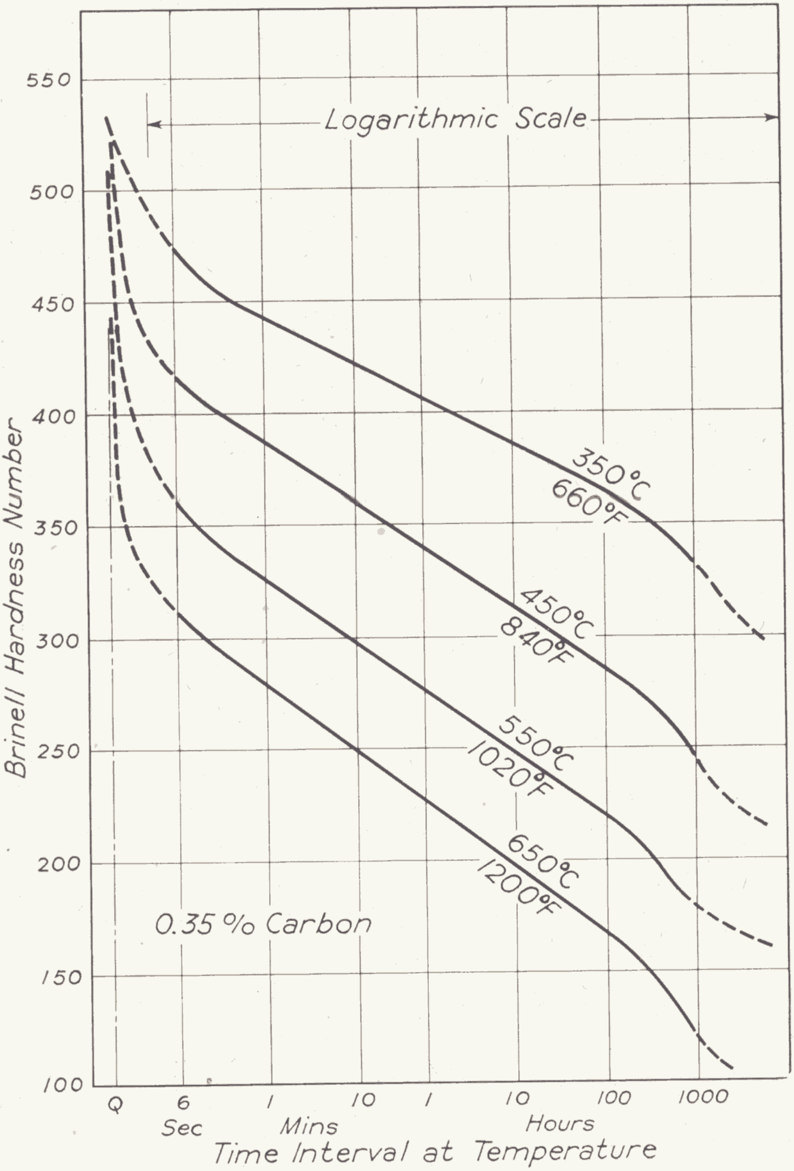

Fig. 147—The Effect of Time-Interval at Four Tempering Temperatures upon the Softening of Quenched 0.35 Per Cent Carbon Steel. Brinell Scale for Comparison with Fig. 146. (See Footnote 46).

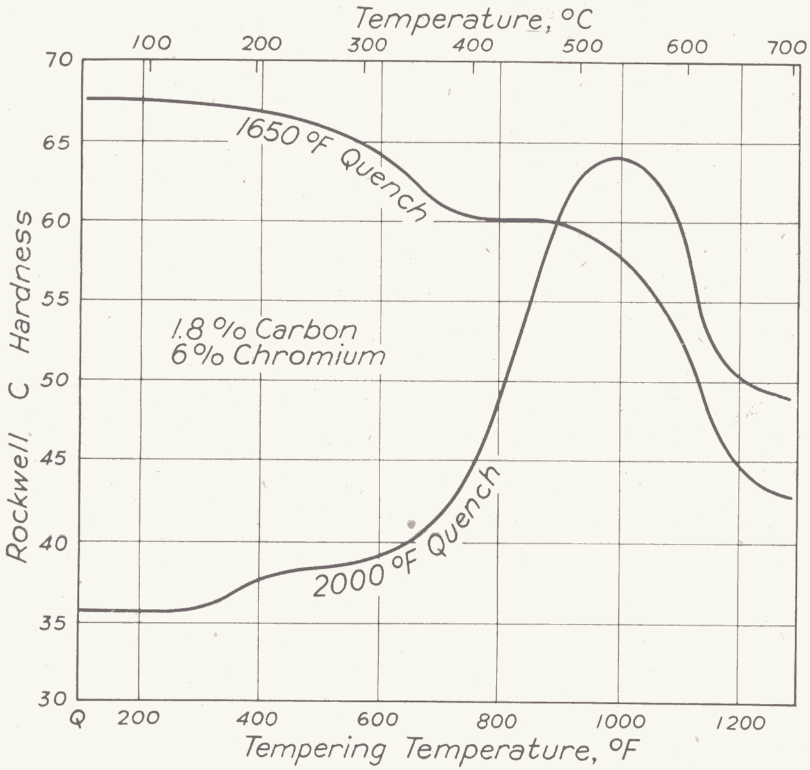

Fig. 148—The Effect of Reheating at Various Temperatures upon Hardness of a Quenched, High-Chromium, High-Carbon Steel. The 1650 Degrees Fahr. Quench Retains Some Austenite; the 2000 Degrees Fahr. Quench Causes Nearly a Wholly Austenitic State. Note Hardening by Tempering.

this residual austenite is induced by refrigeration to form martensite a small proportion persists. The proportion of retained austenite may amount to 10 to 25 per cent even in commercial steels and the behavior of this austenite during tempering should be considered. In many steels the presence of a surprisingly large proportion of austenite scarcely reduces the hardness of the quenched steel perceptibly even though precise hardness measurements may reveal a slight increase of hardness upon further martensitization. Indeed, a fairly

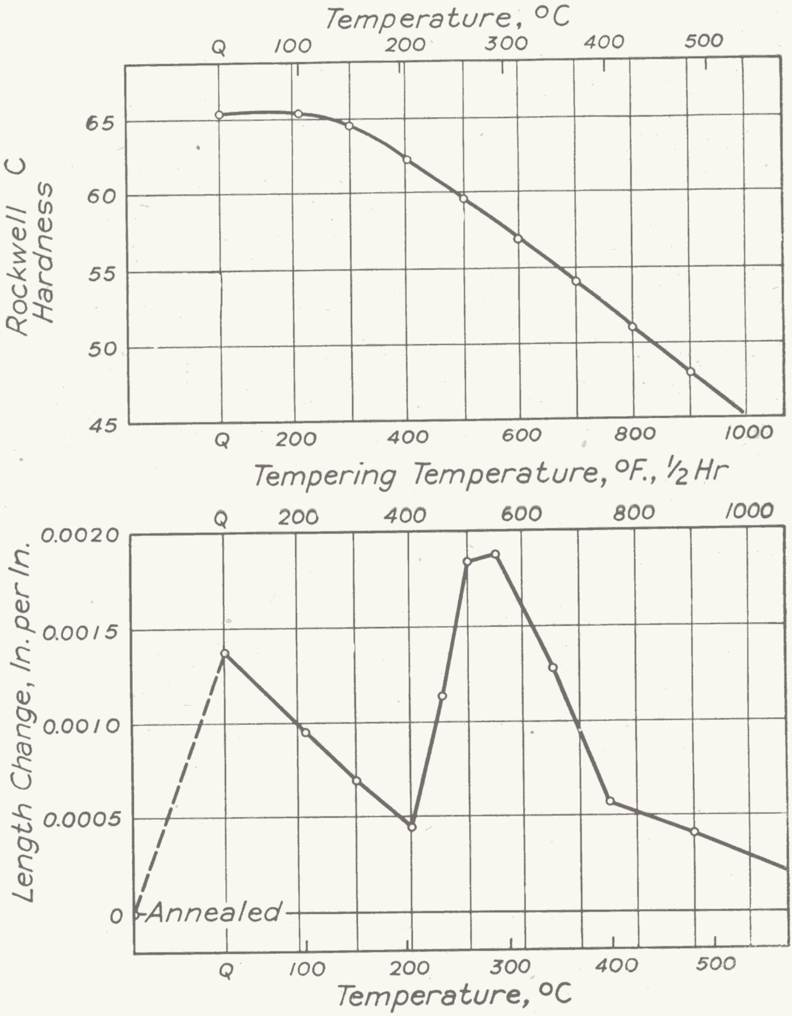

Fig. 149—Tempering Effects in a 0.9 Per Cent Carbon, 1.5 Per Cent Manganese Steel. Above—Hardness versus Tempering Temperature; Below—Length Change versus Tempering Temperature. (See Footnote 48).

large proportion of austenite is required to be retained, along with the martensite, to reduce the hardness by as much as 10 points Rockwell. This may be due to the mode of distribution of the austenite. However this may be, one circumstance is quite clear; while martensite, in general, is softened by brief heatings to as low temperatures as 300 degrees Fahr. (150 degrees Cent.), austenite retained therewith remains substantially unchanged during brief intervals, even in carbon steels, up to a temperature of about 450 degrees Fahr. (240 degrees Cent.). Its presence, and final transformation, after tempering at successively higher temperatures may be verified either by X-ray diffraction or by measurement of density or dimension change with tempering. At one time it was thought that the initial preservation of austenite and its subsequent decomposition upon heating was a primary cause for the anomalous halt in the softening curve of certain steels as increasingly tempered (i.e., "secondary hardening", or "secondary hardness"). That a very large proportion of austenite when preserved may result in a definite hardening of the metal, as well as a halt in softening, when tempering causes transformation, is entirely true as may be seen in the hardness curve of Fig. 148,[47] which has to do with the tempering of a very high carbon (1.8 per cent) steel of 6.4 per cent chromium as quenched from 1650 degrees Fahr. (900 degrees Cent.) and 2000 degrees Fahr. (1100 degrees Cent.). In this case the steel quenched from 2000 degrees Fahr. is doubtless 80 to 90 per cent austenite, and higher tempering temperatures contrive to bring about the transformation to constituents harder than austenite. It is to be observed that no initial softening takes place in the steel of Fig, 148, as quenched from 2000 degrees Fahr. to render it substantially austenitic. When only small proportions of austenite are retained in carbon steel its breakdown is clearly reflected in the increase in dimension, but usually no emphatic effect can be found on the hardness curve. This is exemplified by Fig.

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[47] "Secondary Hardness in Austenitized High Chromium Steels", E. C. Bain, TRANSACTIONS, American Society for Steel Treating (American Society for Metals), Vol. 5, 1924. p. 89.

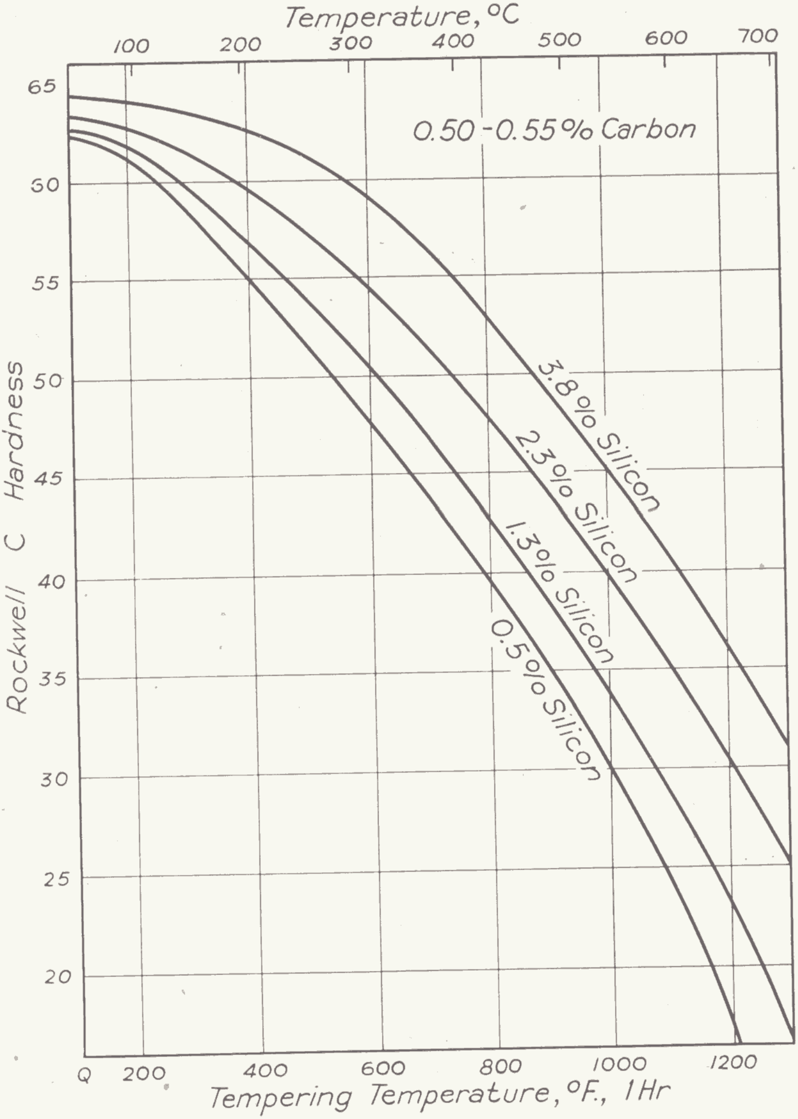

Fig. 150—The Softening, with Increasing Tempering Temperature, of Quenched 0.50-0.55 Per Cent Carbon Steel as Influenced by Silicon Content.

149,[48] which deals with a 0.90 per cent carbon, 1.5 per cent manganese steel as quenched in oil. This record clearly shows that retained austenite does not always result in a "secondary hardening" effect.

Having available now the so-called "S-Curves" of austenite transformation it is quite apparent that retained austenite, upon reaching a suitable tempering temperature, merely sets about its transformation in accord with its characteristic rate at that temperature. These S-Curves show how it is that in the customary tempering interval of 30 to 60 minutes, a temperature well above 400 degrees Fahr. (200 degrees Cent.) may be required for the destruction of the retained austenite. Such studies of isothermal transformation reveal also that the product of austenite transformation at tempering temperature will not be hard martensite, but rather one of the softer structures of the so-called bainite family, with a hardness little greater than that of the associated tempered martensite. In the case illustrated in Fig. 149, the transformation product of the vanishing retained austenite would be about 54 Rockwell C. In short, retained austenite, *per se*, in quenched steel behaves as though it were just cooled to the tempering temperature, except insofar as internal stress may alter its mode of transformation or its effect upon the remaining structure. Practically, it seems certain that retained austenite exerts only an auxiliary effect upon the abnormalities of the softening effect of tempering in any steels, and in medium-carbon, low-alloy steels it is not a contributor to "secondary hardness" at all because it is present, if at all, in far too small proportion. It cannot be doubted, however, that it plays an important role in dimensional changes and perhaps also in the baffling toughness minimum of quenched steels tempered in the vicinity of 500 to

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[48] "The Nature of Oil-Hardening, Non-Deforming Tool Steels", by E. C. Bain and M. A. Grossmann. TRANSACTIONS, American Society for Steel Treating (American Society for Metals), Vol. 10, 1926, p. 883.

600 degrees Fahr. (260 to 315 degrees Cent.).

In this general discussion of the tempering of carbon steels one more anomalous behavior should be mentioned. Many quenched, high-carbon steels become slightly harder following quenching with the lapse of some days at ordinary temperature or of some hours at 212 degrees Fahr. (100 degrees Cent.) and similarly at intermediate temperatures for intermediate intervals. It is as though martensite itself could undergo aging, for still longer intervals bring about some softening. It is mentioned here especially because some curves of hardness versus tempering temperature indicate (and quite correctly) a slight rise at about 200 degrees Fahr. (100 degrees Cent.).

Since this effect is most pronounced in the higher carbon steels the possible transformation of some additional austenite suggests itself as a possible cause, and this may well be the explanation since it is now known that austenite transforms in the low temperature range at a rapidly decreasing rate and that the product immediately after the quench is by no means necessarily at a standstill. Possibly some of the carbon is yet in a state which is less effective than that of the great preponderance of it at the moment the quench is effected, though this would seem less probable.

The author proposes that if any further special explanation is required for this phenomenon of hardness-increase (over that of a lingering transformation of austenite) it may be found in the mere dissipation of stress. It is to be expected that the plastic deformation of the metal, as accomplished in the act of measuring penetration hardness, would be facilitated by the presence of high internal stress of the well distributed variety. Any period of time at a temperature allowing the gradual reduction of stress through slight movements within the metal would raise its apparent hardness just as the stress-relief of certain steels raises their yield point. This

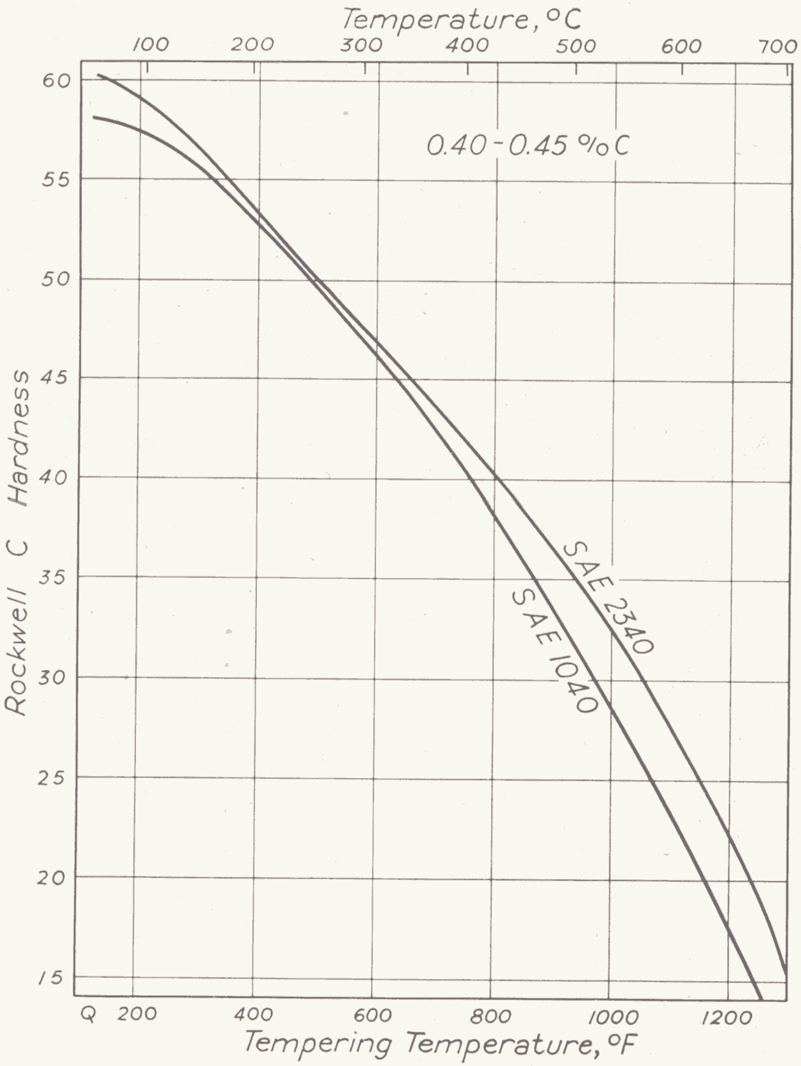

Fig. 151—The Softening, with Increasing Tempering Temperature, of Quenched 0.40-0.45 Per Cent Carbon Steels as Influenced by about 3.5 Per Cent Nickel. (See Footnote 49).

slight hardening effect of an "aging period" upon freshly quenched steel is of academic, rather than of practical interest. The effects of the alloying elements, particularly those which

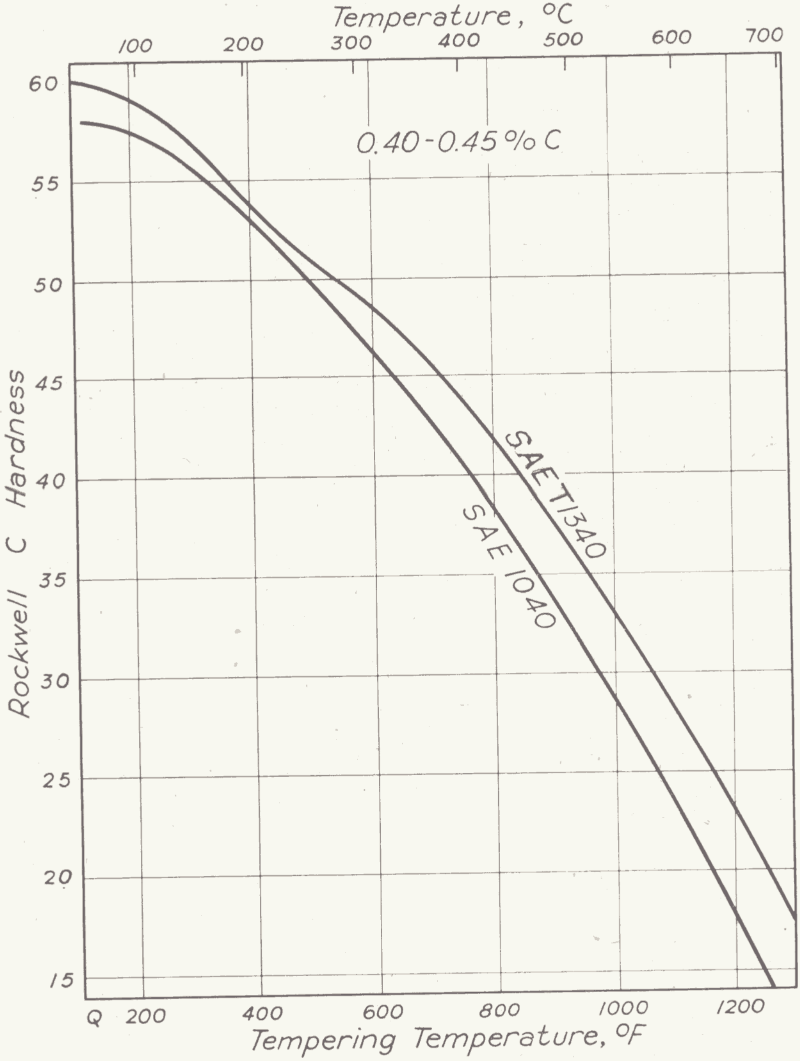

Fig. 152—The Softening, with Increasing Tempering Temperature, of Quenched 0.40-0.45 Per Cent Carbon Steels as Influenced by an Incease of Manganese from about 0.75 to 1.75 Per Cent. (See Footnote 49).

are strongly carbide-forming, upon tempering are of much greater interest.

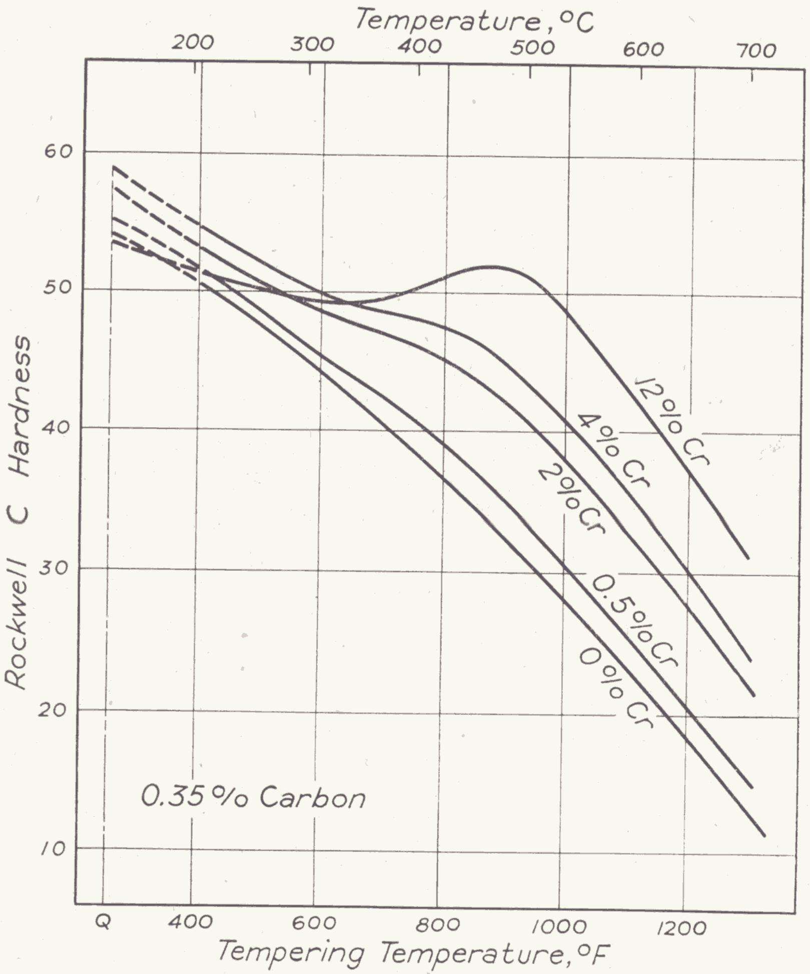

Fig. 153—The Softening, with Increasing Tempering Temperature, of Quenched 0.35 Per Cent Carbon Steels as Influenced by Chromium Content. (See Footnote 46).

Alloying Elements and Softening — In the case of steels of low and medium carbon content, moderate amounts of alloying elements may slightly increase the initial maximum hardness incurred by effective quenching. In the presence of higher carbon they are likely to reduce slightly the hardness achieved through an increase of the proportion of retained austenite. Otherwise the elements have little effect upon hardness; probably no wrought steel ever exceeds the maximum hardness attainable in a high carbon steel, as measured at ordinary temperatures. Except the proportion of austenite be very high, a tempering at about 400 degrees Fahr. (200 degrees Cent.) reduces the hardness of all ordinary alloy steels but, seemingly, the presence of any element retards, at least slightly, the loss of hardness and strength. Fig. 150 shows how silicon, in increasing proportion, acts to elevate the hardness of tempered steels which have been suitably quenched. One may assume, since silicon is not present in any large proportion in the carbide, that its effect is to strengthen the ferrite in which the gradually coarsening carbide particles are dispersed. The elements, nickel and manganese, also largely dissolved in the iron rather than in the carbide, act similarly though they are less effective at the same percentage content, and nickel is particularly moderate in this one respect. This is illustrated[49] in the softening curve of Fig. 151 in which the softening of an ordinary 0.45 per cent carbon steel is compared with a steel carrying about the same manganese and carbon but, in addition, 3.5 per cent nickel. Similarly the slightly more marked effect of an increase from 0.76 per cent to 1.78 per cent of manganese is shown in Fig. 152.

In the case of carbon content much above 0.90 per cent, and particularly in the presence of over 1 per cent manganese or considerable nickel, the tempering curve may possibly reflect the release of retained austenite by a slight retardation of softening. This effect is so small with moderate amounts of retained austenite, that it is probably usually attributed to error in hardness measurement. However marked the effect

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[49] The data on the softening in tempering of a number of alloy steels of 0.40 to 0.45 per cent carbon content were furnished by W. M. Lindsey and E. L. Roff of the South Chicago Works of Carnegie-Illinois Steel Corporation and are gratefully acknowledged. The data are presented in Figs. 151, 152, 154, 156, 157, 161 and 162.

of retained austenite, which is fostered by nickel and manganese, may be upon other properties, the hardness and strength in ordinary steels with these elements fall off very smoothly with increase in tempering temperature. This is not true of another class of elements.

RETARDATION OF SOFTENING AND SECONDARY HARDNESS

In order to study the influence of various elements upon the course of softening during tempering it is desirable, at least in approaching the subject, to avoid the consideration of steels carrying a great deal of retained austenite. This circumstance would confuse the issue and reflect a behavior of high carbon rather than that of the alloying element alone. Accordingly there are shown here a few examples of medium carbon, alloy steels in which retained austenite is at a minimum.

Tempering in the Presence of Carbide-Forming Elements — Fig. 153 illustrates the softening patterns of a series of chromium steels along with a plain carbon steel otherwise similar with respect to the uniform carbon content of about 0.35 per cent. The chromium content of the series is 0, 0.50, 2.0, 4.0 and 12 per cent. The heating for quenching was such as to insure the solution of substantially all the carbide; the quenching developed nearly, though not quite, the maximum martensitic hardness possible for the compositions. It will be noted that even a half per cent of chromium suffices to resist softening, particularly at the higher temperatures. Four per cent chromium produces a definite "secondary hardening". The 12 per cent chromium steel, a typical cutlery stainless steel, is particularly interesting because it definitely preserves a moderate amount of retained austenite, — sufficient, however, to lower the initial hardness below that of the other members of the series. The release of this retained austenite

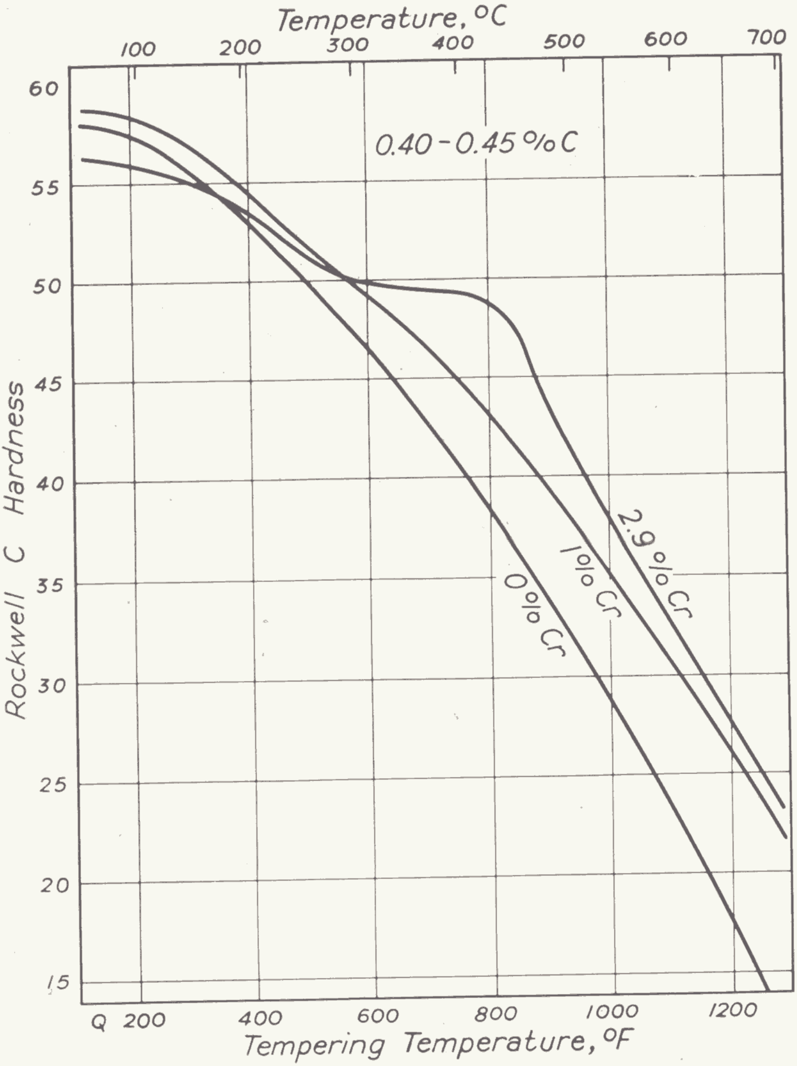

Fig. 154—The Softening, with Increasing Tempering Temperature, of Quenched 0.40-0.45 Per Cent Carbon Steels as Influenced by Chromium Content. (See Footnote 49).

may possibly have augmented the effect of secondary hardness. Similar effects of chromium, even in small proportions,

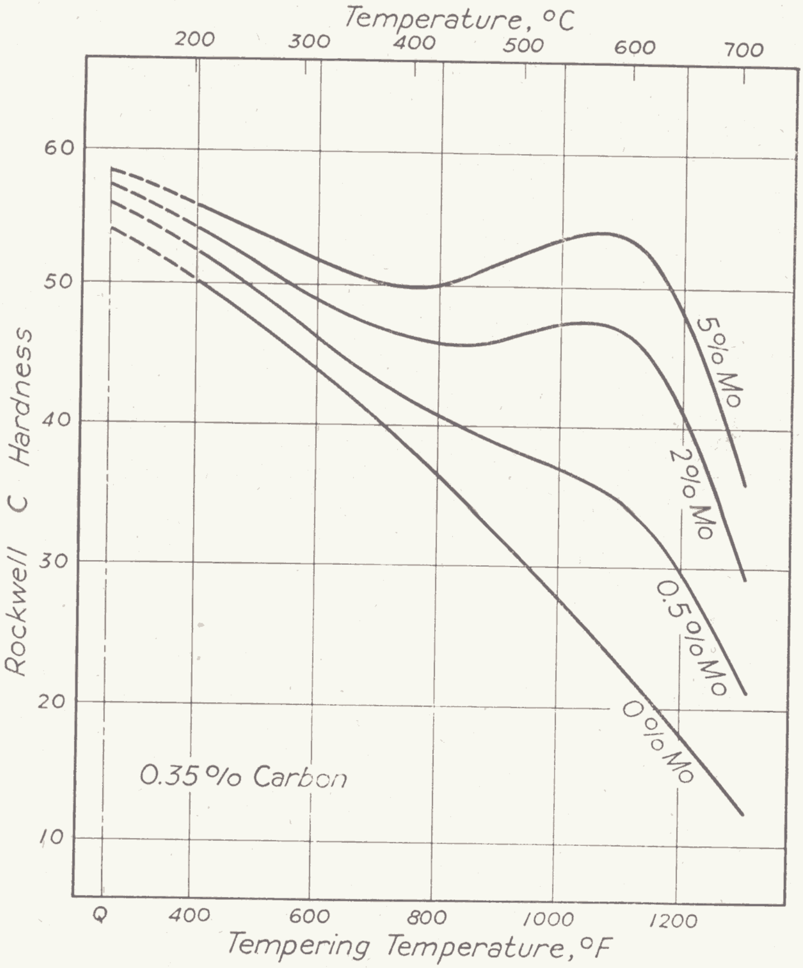

Fig. 155—The Softening, with Increasing Tempering Temperature, of Quenched 0.35 Per Cent Carbon Steels as Influenced by Molybdenum Content. (See Footnote 46).

are observed in 0.40 to 0.45 per cent carbon steels, as in Fig. 154.

The carbide elements in general, while powerful in deep-hardening influence, are not so effective in retaining austenite as are nickel and manganese, yet they produce this retarda-

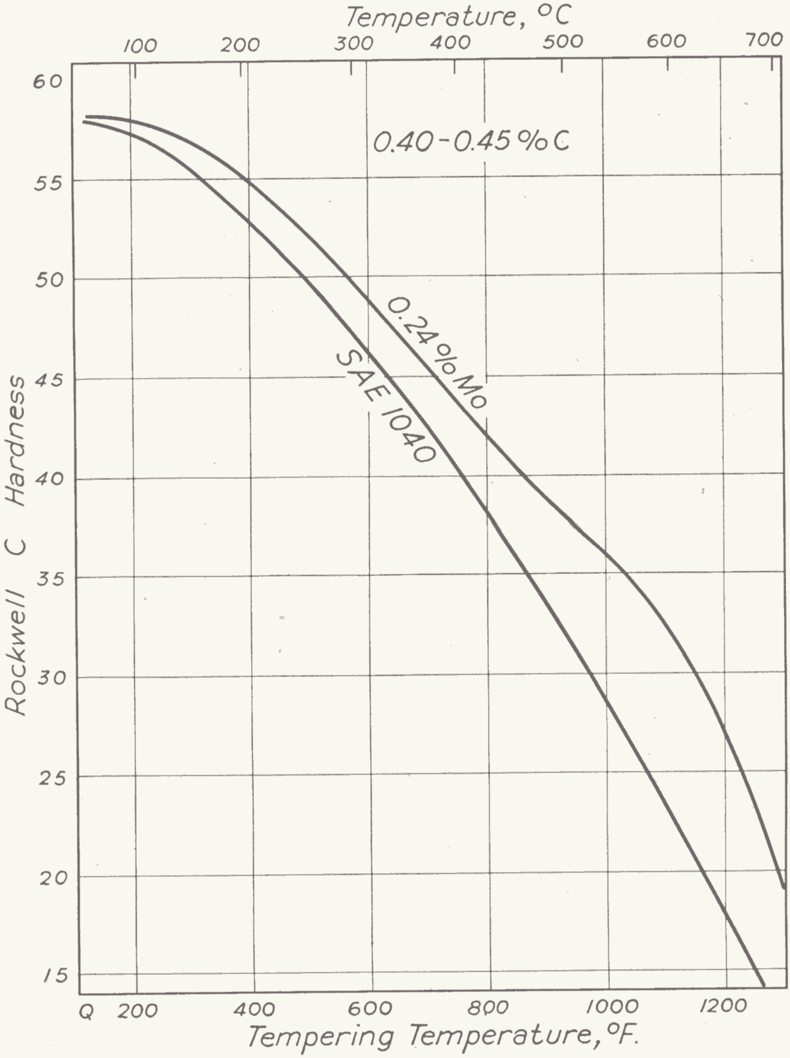

Fig. 156—The Softening, with Increasing Tempering Temperature, of Quenched 0.40-0.45 Per Cent Carbon Steels as Influenced by about ¼ Per Cent Molybdenum. (See Footnote 49).

tion of softening or secondary hardness. It is interesting therefore to inquire into the effect of a stronger carbide-former such as molybdenum. In Fig. 155 are shown the soft-

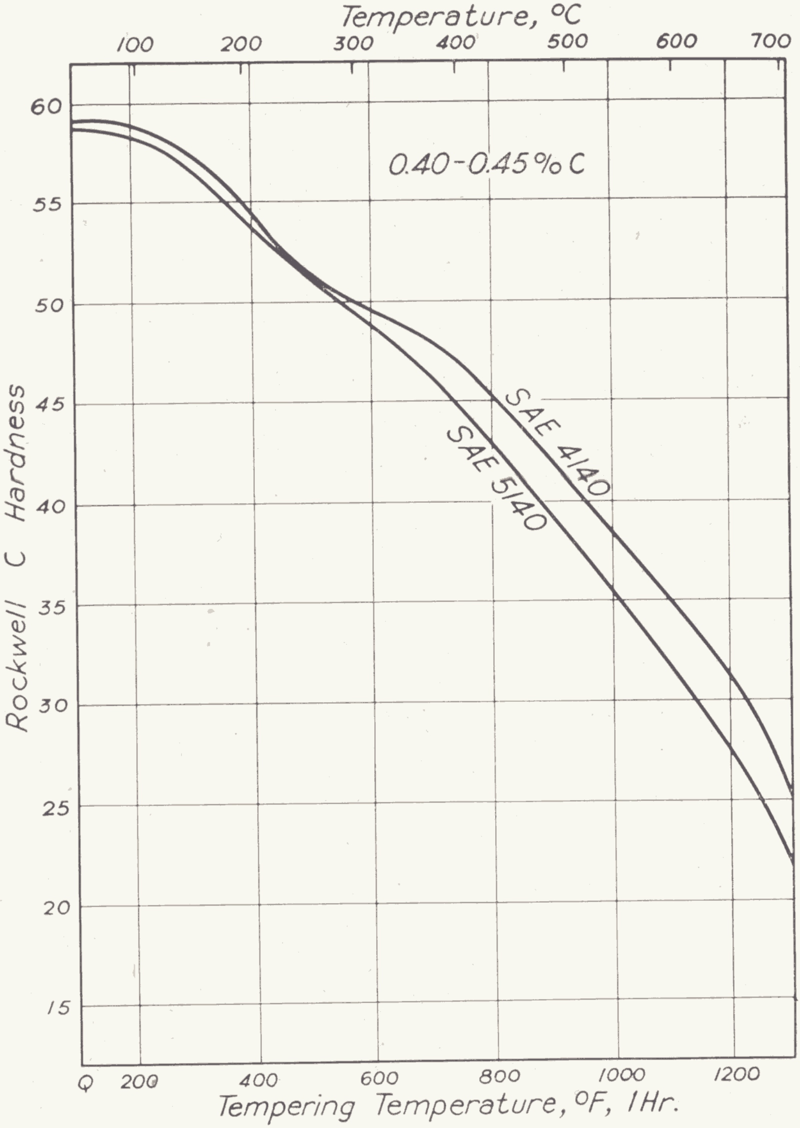

Fig. 157—The Softening, with Increasing Tempering Temperature, of Quenched 1.0 Per Cent Chromium, 0.40-0.45 Per Cent Carbon Steels as Influenced by 0.20 Per Cent Molybdenum. (See Footnote 49).

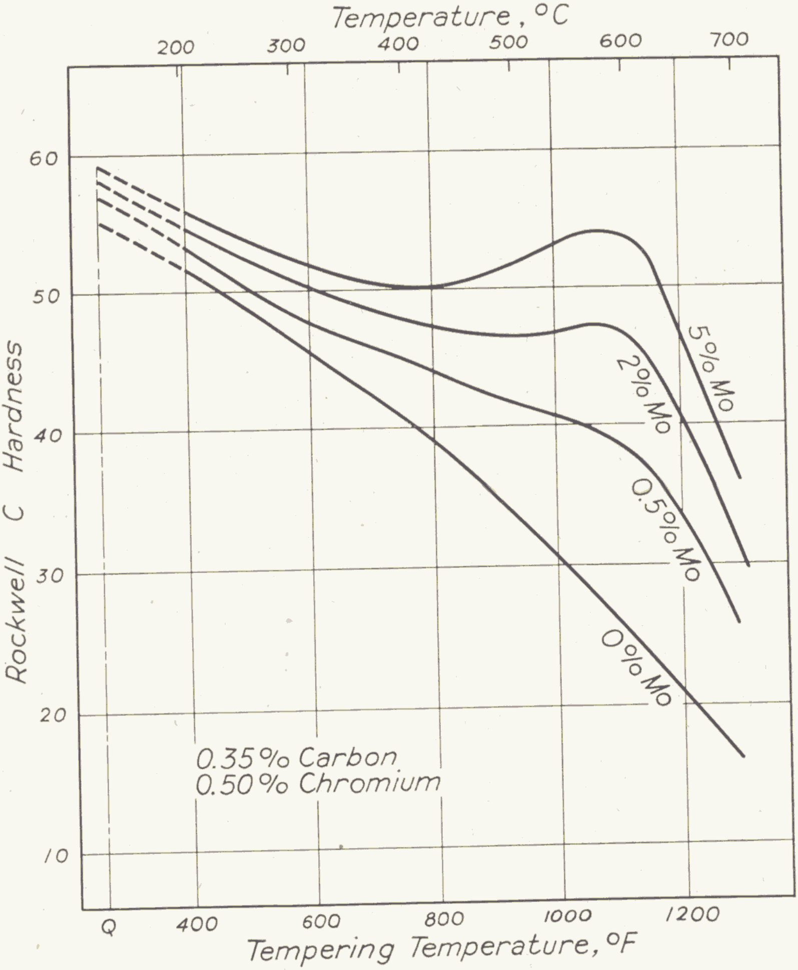

Fig. 158—The Softening, with Increasing Tempering Temperature, of Quenched 0.5 Per Cent Chromium, 0.35 Per Cent Carbon Steels as Influenced by Molybdenum Content. (See Footnote 46).

ening curves for a series of 0.35 per cent carbon steels of increasing molybdenum content, again with a straight 0.35 per cent carbon steel for comparison. It is observed that molybdenum is even more effective than chromium in preserving high strength and hardness after reheating at high

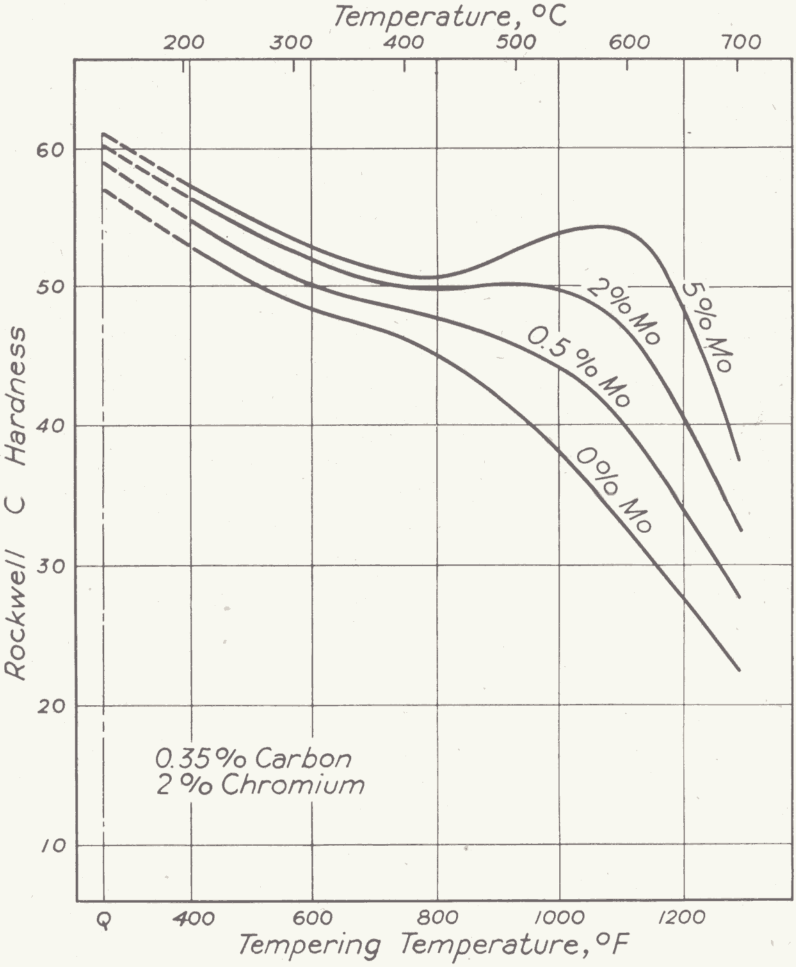

Fig. 159—The Softening, with Increasing Tempering Temperature, of 2.0 Per Cent Chromium, 0.35 Per Cent Carbon Steels as Influenced by Molybdenum Content. (See Footnote 46).

temperature. It is interesting to note that the full effect of the hardening increment is reached at a slightly higher temperature in the molybdenum steels than it is in the chromium steels.

The effect of a still smaller addition of molybdenum (0.24

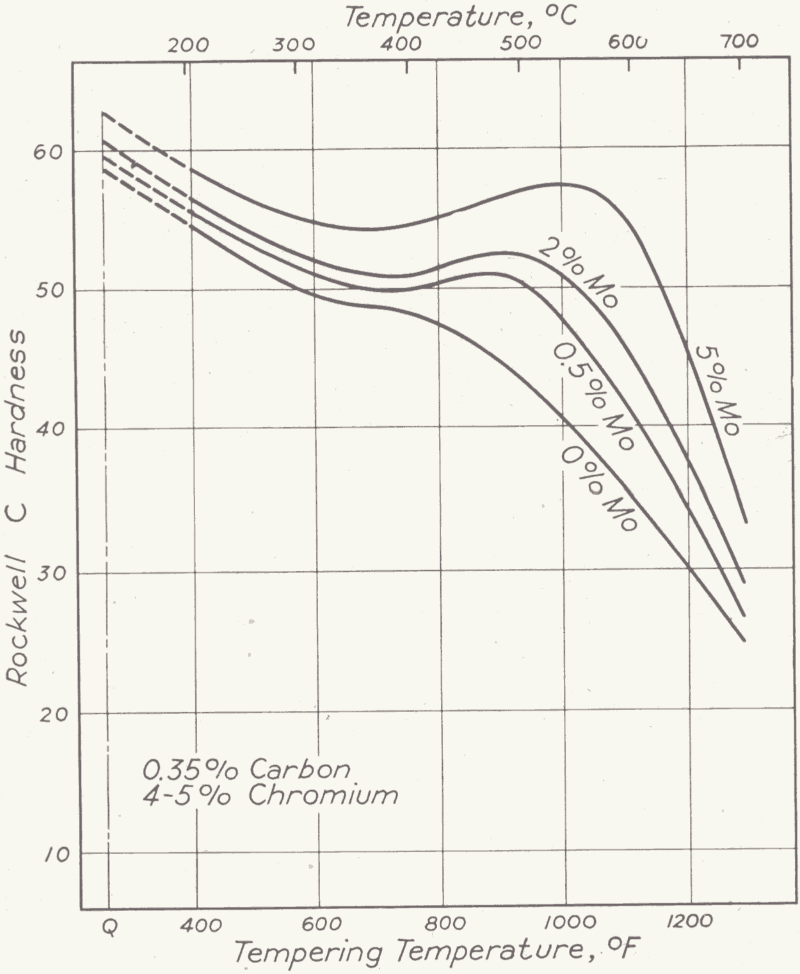

Fig. 160—The Softening, with Increasing Tempering Temperature, of 4.0-5.0 Per Cent Chromium, 0.35 Per Cent Carbon Steels as Influenced by Molybdenum Content. (See Footnote 46).

per cent) in a 0.40-0.45 per cent fine-grain carbon steel is at least detectable in the softening characteristics as seen in Fig. 156. Even in the presence of about 1 per cent chromium, as small a proportion of molybdenum as 0.20 per cent makes its presence felt in tempering as may be observed in Fig. 157,

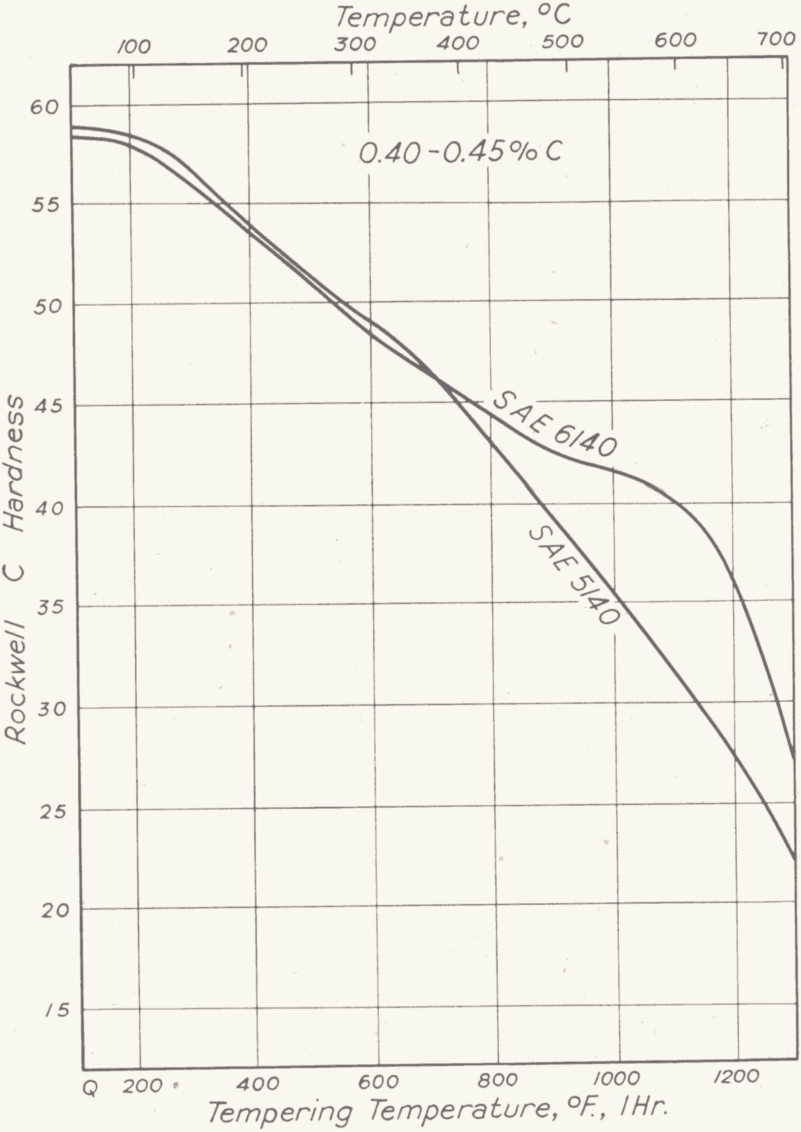

Fig. 161—The Softening, with Increasing Tempering Temperature, of 1.0 Per Cent Chromium, 0.40-0.45 Per Cent Carbon Steels as Influenced by 0.16 Per Cent Vanadium. High Quenching Temperature Applied to the Vanadium Steel. (See Footnote 49).

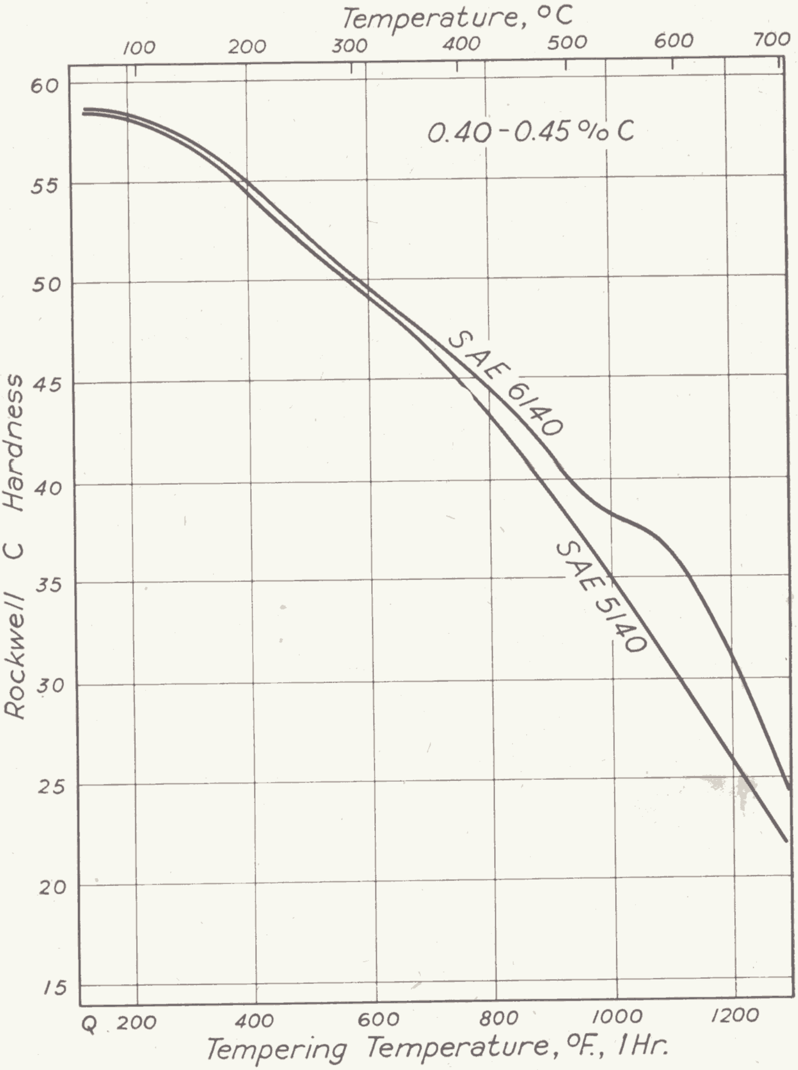

Fig. 162—The Softening, with Increasing Tempering Temperature, of 1.0 Per Cent Chromium. 0.40-0.45 Per Cent Carbon Steels as Influenced by 0.16 Per Cent Vanadium. Both Steels Quenched from 1625 Degrees Fahr. (See Footnote 49).

which compares two steels, S.A.E. 5140 and 4140, with all elements, excepting molybdenum, at almost indentical values.

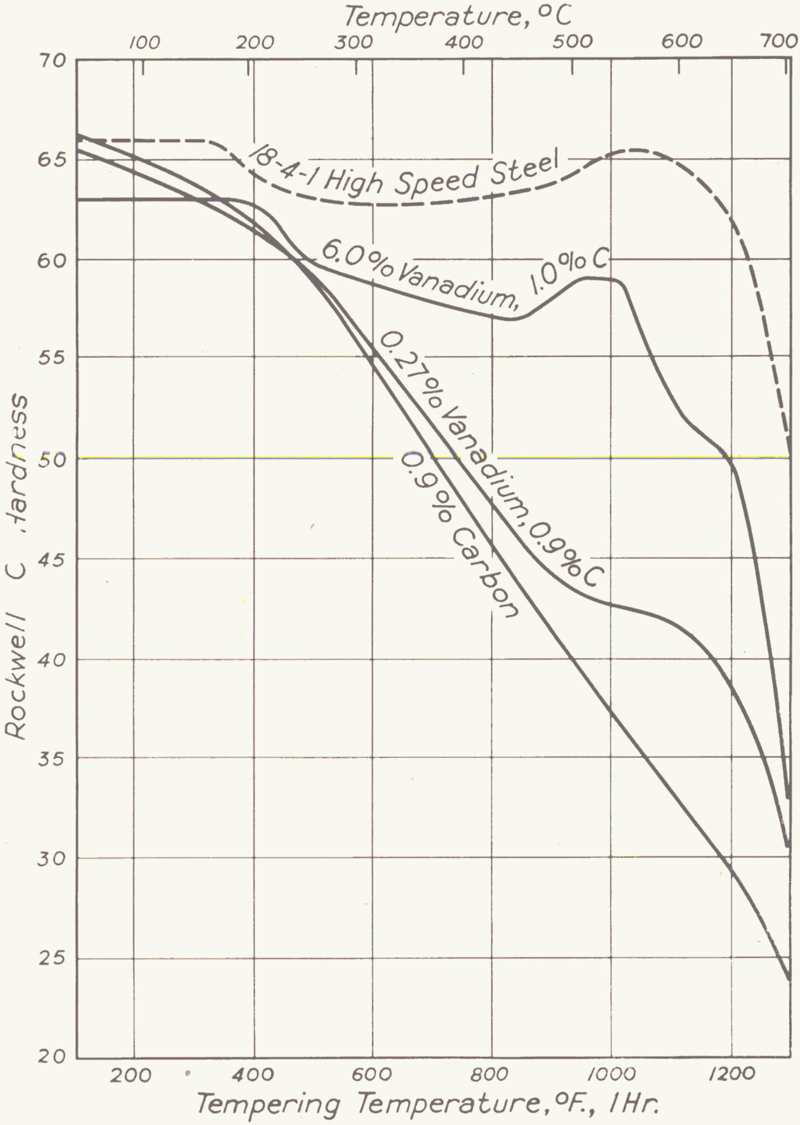

Fig. 163—The Softening, with Increasing Tempering Temperature, of 0.9 Per Cent Carbon Steels as Influenced by 0.27 Per Cent Vanadium. For comparison the Softening of a 6.0 Per Cent Vanadium, 1.0 Per Cent Carbon Steel and a Typical High Speed Steel are also shown. *(Data on 6 Per Cent Vanadium Steel from Houdremont, Bennek and Schrader).*

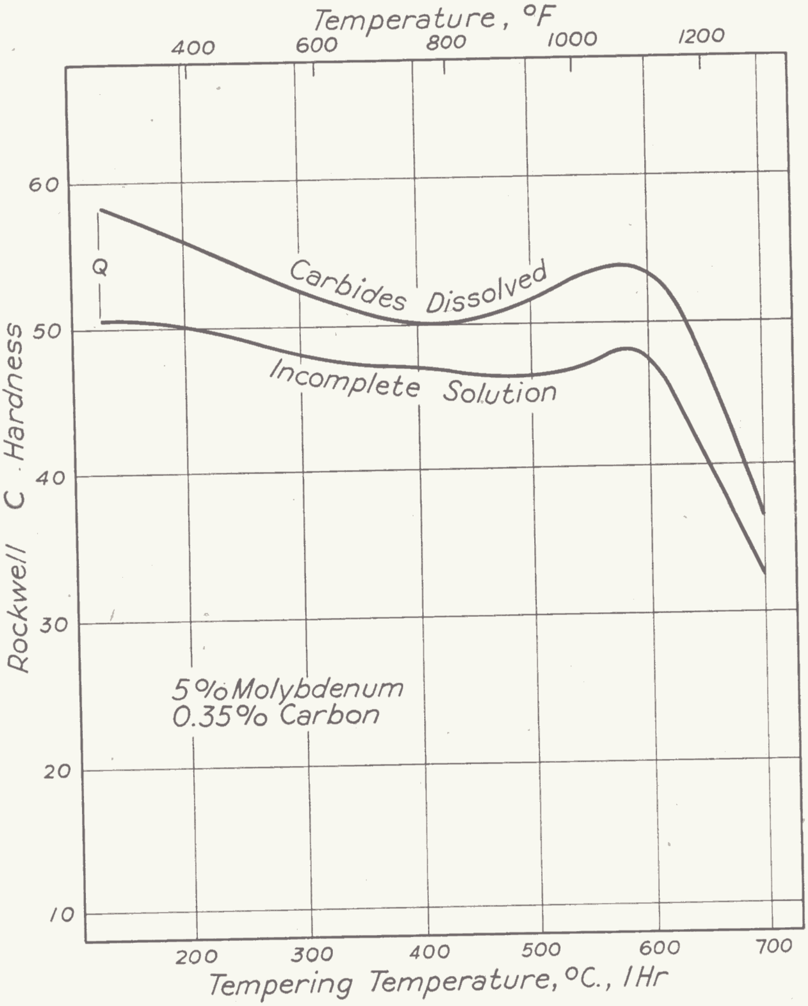

Fig. 164—The Softening, with Increasing Tempering Temperature, of Quenched 5.0 Per Cent Molybdenum Steel as Influenced by the Extent of Carbide Solution. Upper Curve 2200 Degrees Fahr. Quench; Lower Curve 1740 Degrees Fahr. Quench. (See Footnote 46).

In all these instances the steel was quenched after a heating which sufficed to dissolve substantially all the carbide in the austenite.

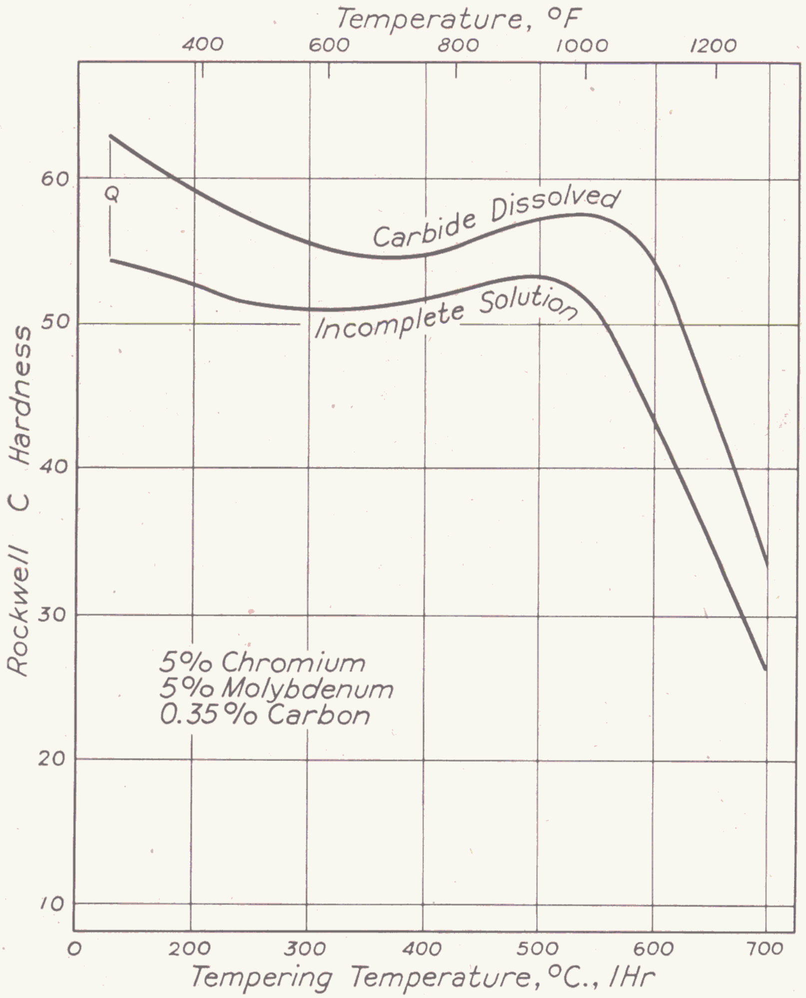

Fig. 165—The Softening, with Increasing Tempering Temperature, of Quenched 5.0 Per Cent Molybdenum, 5.0 Per Cent Chromium Steels as Influenced by the Extent of Carbide Solution. Upper Curve 2200 Degrees Fahr. Quench; Lower Curve 1740 Degrees Fahr. Quench. (See Footnote 46).

The superimposition of the molybdenum effect upon that of 0.50 per cent chromium is shown in Fig. 158. The small proportion of chromium does not alter the trend of softening

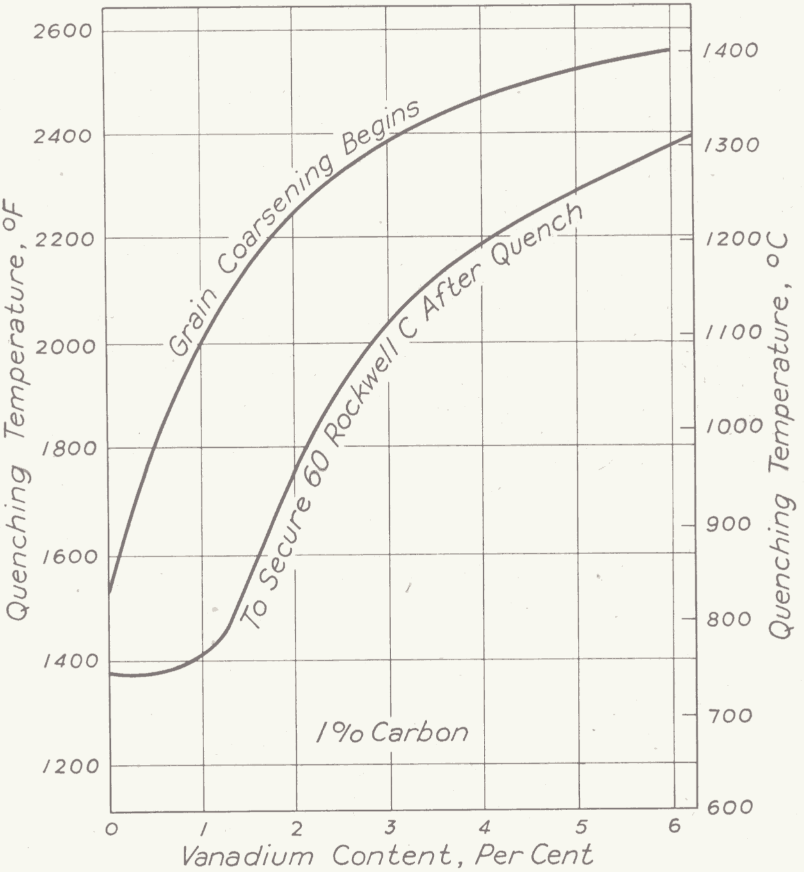

Fig. 166—The Heating Temperature Range for 1.0 Per Cent Carbon Steels of Indicated Vanadium Content. Upper Curve, Maximum to Just Avoid Undue Coarsening; Lower Curve, Minimum to Secure 60 Rockwell C Hardness with Drastic Quench. *(After Houdremont, Bennek and Schrader).*

greatly, but tends however to cause "secondary hardening" to be inaugurated at a somewhat lower temperature. With a uniform 2 per cent chromium with 0.35 per cent carbon the reluctance to soften is very marked indeed as the molybdenum content increases as shown in Fig. 159. The alloys bearing 4 per cent chromium sustain a high hardness, in pro-

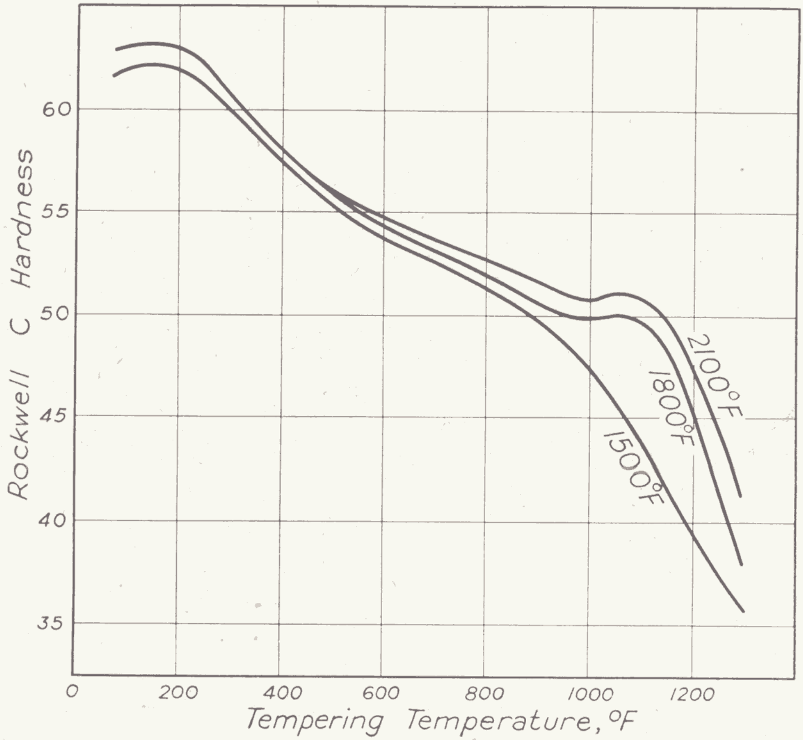

Fig. 167—The Softening, with Increasing Tempering Temperature, of a Quenched Chromium-Molybdenum-Vanadium Steel, as Influenced by the Degree of Carbide Solution in turn Dependent upon Heating Temperature. (See Footnote 46).

portion to the molybdenum, and present a series of steels with exceptional retention of strength after high reheating temperature, as may be inferred from Fig. 160.

A surprisingly strong resistance to softening in the temperature range about 1000 degrees Fahr. (550 degrees Cent.) is offered by small proportions of the element vanadium, if, however, the vanadium-rich carbide is first largely dissolved. Referring again to the 0.40-0.45 per cent carbon, 1 per cent chromium steel employed in Fig. 157, the comparative softening pattern of a similar steel with 0.16 per cent vanadium may be observed in Fig. 161. The elements other

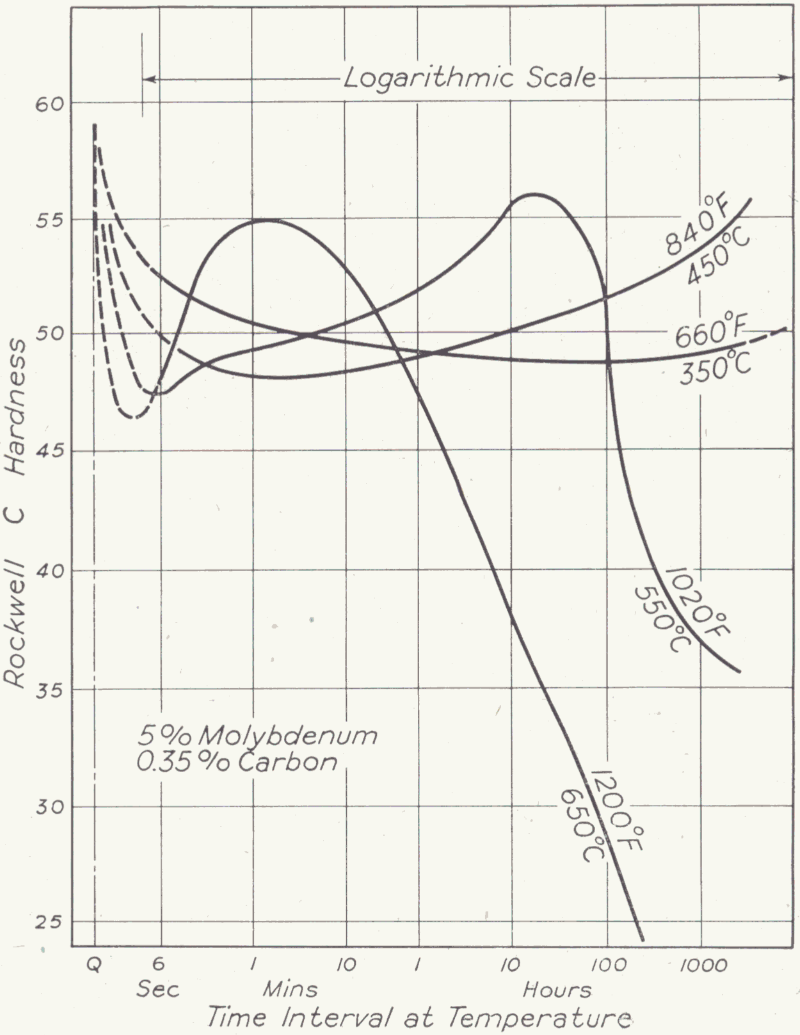

Fig. 168—The Softening, with Increase of Time Interval, at Four Temperatures in a Quenched 5 Per Cent Molybdenum Steel. Note Great Difference Between Figs. 146 and 168. (See Footnote 46).

than vanadium are present in almost identical amount. In this instance a temperature well above 1800 degrees Fahr. (1000 degrees Cent.) was required to bring nearly the whole of the vanadium-rich carbide into solution. The grain size, however, remained uncoarsened above 1725 degrees Fahr. (940 degrees Cent.) and at 1925 degrees Fahr. (1050 degrees Cent.) the grain size was only about No. 5 (A.S.T.M.). The vanadium effect is observable even when the two steels, as shown in Fig. 162, are quenched from 1625 degrees Fahr. The remarkable resistance to softening contributed by vanadium is well illustrated in Fig. 163, which shows a comparison between two tool steels, essentially alike except for the 0.27 per cent vanadium in the one. In the same chart the hardness versus tempering temperature curves are also plotted for a 6 per cent vanadium steel[50] and "18-4-1" high speed steel.

The significance of actually dissolving the vanadium-bearing carbide and thereby insuring the solution of vanadium in the austenite before quenching is well illustrated in the softening curves of Figs. 161 and 162, in which heating temperatures differing by some 250 degrees Fahr. were employed for the vanadium-bearing steel, S.A.E. 6140. Similar effects relating to the solution of molybdenum in austenite are reflected in the comparison curves of Figs. 164 and 165, which relate to certain 0.35 per cent carbon, molybdenum and chromium-molybdenum steels.

With respect to the necessity, as well as the possibility, for high heating temperature for properly hardening the steels carrying a considerable proportion of carbide-forming elements, the data of Houdremont, Bennek and Schrader,[51] as shown in Fig. 166, are of considerable interest insofar as the element vanadium is representative of the group.

Finally, the significance of the degree of solution of carbide-forming elements with respect to tempering behavior is specially well exemplified in a certain chromium steel carrying both molybdenum and vanadium, as set forth in Fig. 167.

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[50] "Hartbarkeit und Anlassbeständigkeit von Stählen mit schwerlöslichen Sonderkarbiden", by E. Houdremont, H. Bennek and H. Schrader, *Archiv für das Eisenhüttenwesen*, April 1932, No. 122, Group E.

[51] See Footnote 50.

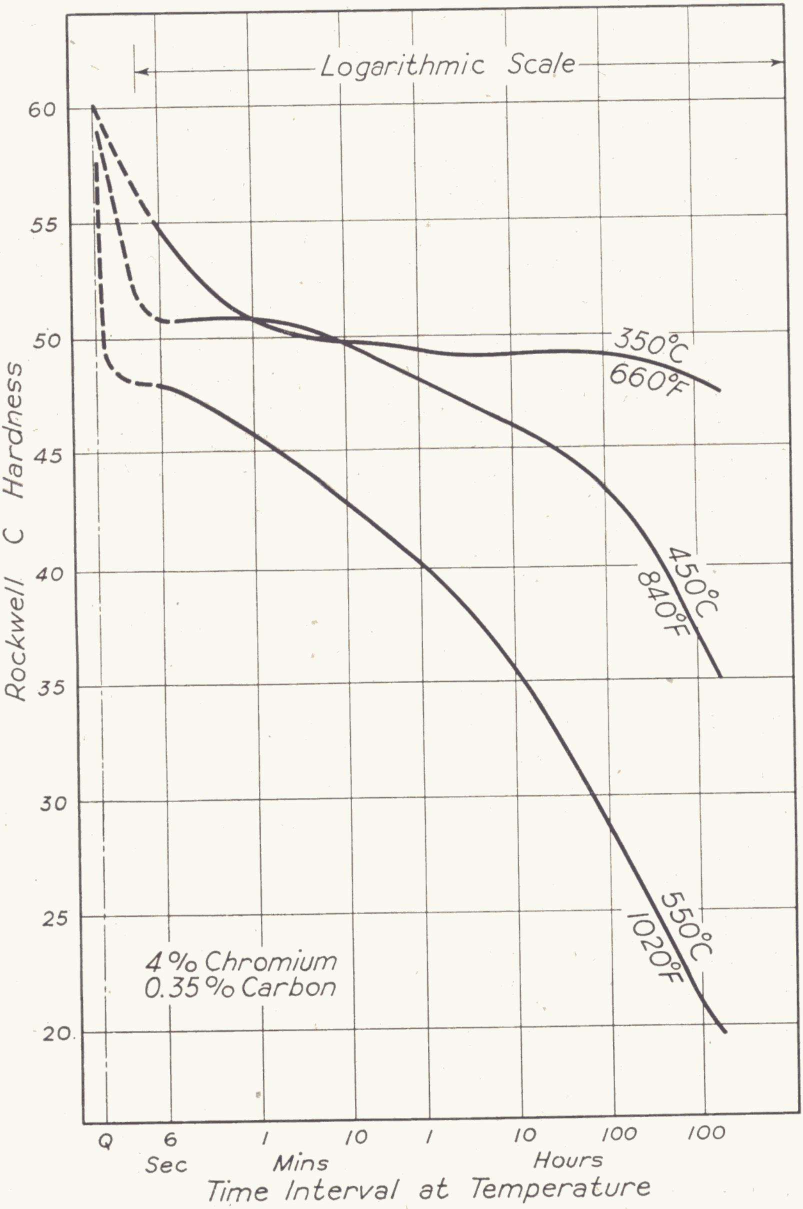

Fig. 169—The Softening, with Increase of Time Interval, at Three Temperatures in a Quenched 4 Per Cent Chromium Steel. (See Footnote 46).

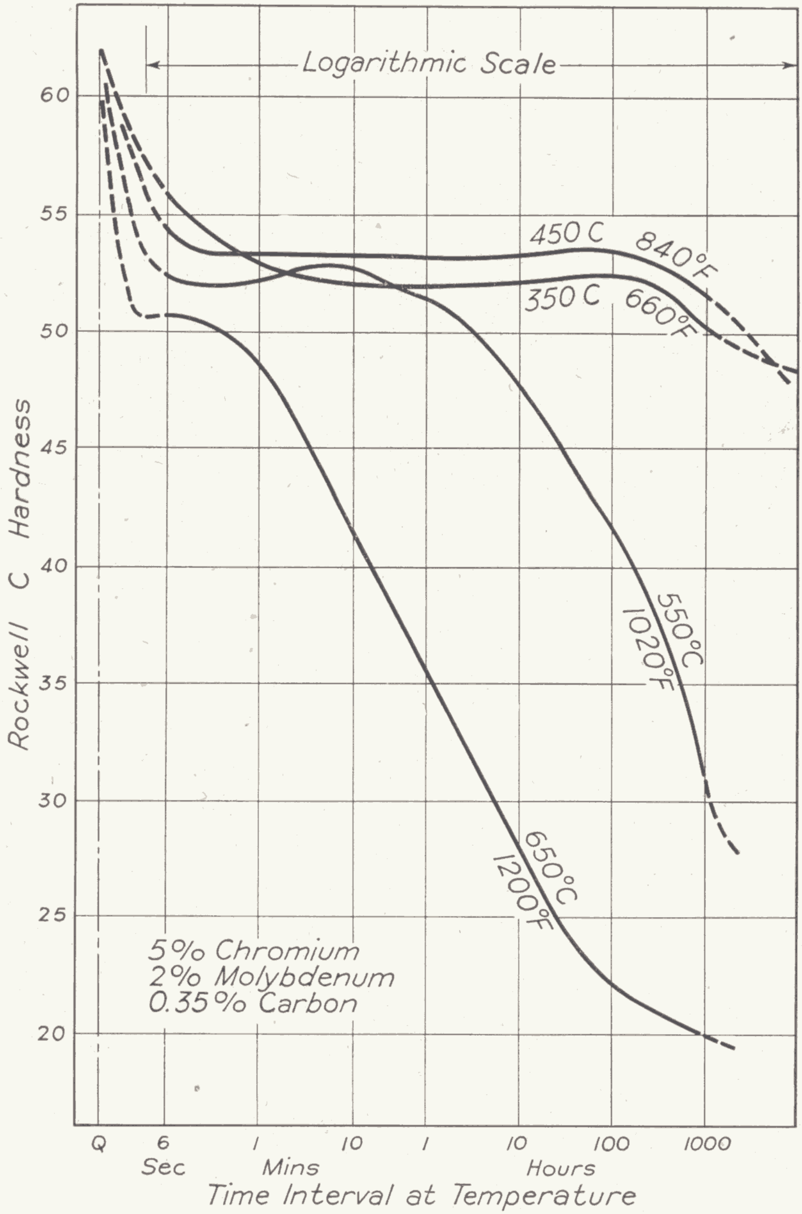

Fig. 170—The Softening, with Increase of Time Interval, at Four Temperatures in a Quenched 5 Per Cent Chromium, 2 Per Cent Molybdenum Steel. (See Footnote 46).

As quenched from 1500 degrees Fahr. (815 degrees Cent.) the fully hardened steel softens rapidly, revealing only the retardation caused by chromium, which, in the presence of molybdenum and vanadium, is readily dissolved. However, when the elements are increasingly dissolved at 1800 degrees Fahr. (980 degrees Cent.) and 2100 degrees Fahr. (1150 degrees Cent.) the strong retardation of softening, or "secondary hardness" becomes prominent.

The cause of the secondary hardness in the medium carbon steels can scarcely relate in any considerable part to retained austenite, for the proportion of such retention is scarcely sufficient to account for the effect. Furthermore, the temperature of the release of the austenite is not precisely in agreement with that of the retardation of softening or, as seen in some cases, an actual gain in hardness. Even in higher carbon alloy steels it is probable that "secondary hardness" can be brought about without the co-operation of the transformation of retained austenite; the latter is almost certainly only an auxiliary minor cause at any time, for the carbide-forming elements are the most effective in retarding softening but not in retaining austenite.

Time Interval and Secondary Hardening—The circumstances under which chromium, molybdenum, tungsten, vanadium and (in certain ranges) titanium retard softening (or even elevate hardness after some softening has occurred) is most easily conjectured by regarding tempering as comparable to an "over-aging" process in precipitation effects. In the presence of a dissolved element, martensite softens upon heating to some 500 to 600 degrees Fahr. (about 300 degrees Cent.) in much the same manner as in the case of corresponding carbon steel, though often to a less degree. At some higher reheating temperature the characteristic softening behavior of carbon steel is prevented, and depending upon the particular element, its proportion in solution, and the carbon content, the softening is retarded or prevented entirely and replaced by a hardening effect. This process becomes clearer when instead of reheating for constant intervals at increasing temperature, the hardened steel is studied after increasing intervals at some constant temperature of draw-back. It is illuminating to follow the course of softening over periods of hundreds of hours, even though the technique of securing reliable surfaces for accurate hardness numbers is laborious. This softening with lapse of time was shown for a carbon steel in Figs. 146 and 147, and it was observed that no unexpected behavior was reflected. Consider now the softening of a 5 per cent molybdenum steel (0.35 per cent carbon) at several temperatures, as in Fig. 168. The hardness was measured at appropriate intervals from 10 seconds to 1500 hours. The actual change in hardness during the first 10 seconds is not known but is inferred and plotted in a manner compatible with the subsequent observations. It is to be noted that the time-scale is logarithmic and that for carbon steel such a plotting was advantageously chosen, at least over a considerable range, in which the hardness graph is nearly rectilinear. In brief, it will be seen that, between about 2 hours and 1500 hours of reheating, the specimen held at 660 degrees Fahr. (350 degrees Cent.) was more softened than the one tempered 180 degrees Fahr. higher at 840 degrees Fahr. (450 degrees Cent.). Indeed, the specimens tempered at 1020 degrees Fahr. (550 degrees Cent.) were harder than those heated only to 660 degrees Fahr. (350 degrees Cent.) when the tempering period was between 5 minutes and 100 hours. Finally, heating at 1200 degrees Fahr. (650 degrees Cent.) produced a harder product than 660 degrees Fahr. (350 degrees Cent.) when the tempering interval ranged between about 10 seconds and 20 minutes. These observations may be explainable in terms of precipitation effects but probably not on the basis of retained austenite alone. It will surely be necessary to

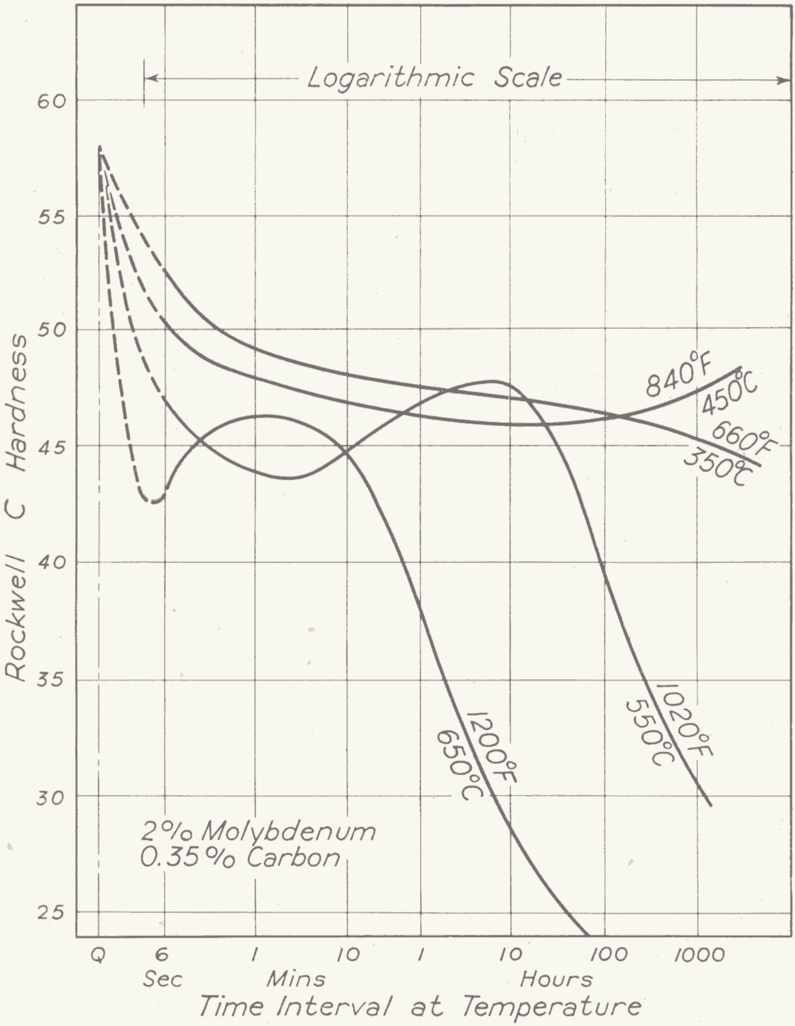

Fig. 171—The Softening, with Increase of Time Interval, at Four Temperatures in a Quenched 2 Per Cent Molybdenum Steel. (See Footnote 46).

recognize a precipitation effect other than that of iron carbide, and in the presence of carbide-forming elements there is the possibility of forming a second dispersion of particles which in their nature must remain at effectively fine size at

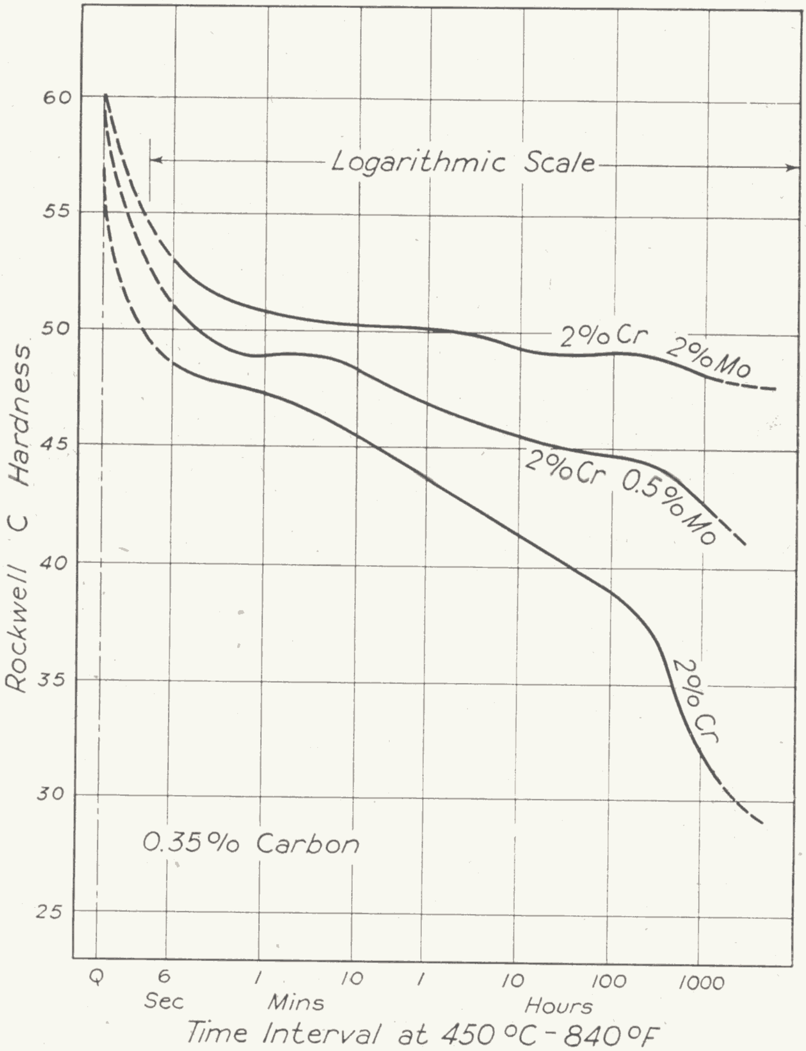

Fig. 172—The Softening, with Increase of Time Interval, at 840 Degrees Fahr. in Three Quenched 2 Per Cent Chromium Steels, with 0, 0.5 and 2.0 Per Cent Molybdenum. Compare with Fig. 173. (See Footnote 46).

more elevated temperatures.

Before attempting an explanation for the retardation of softening and secondary hardness during tempering in the

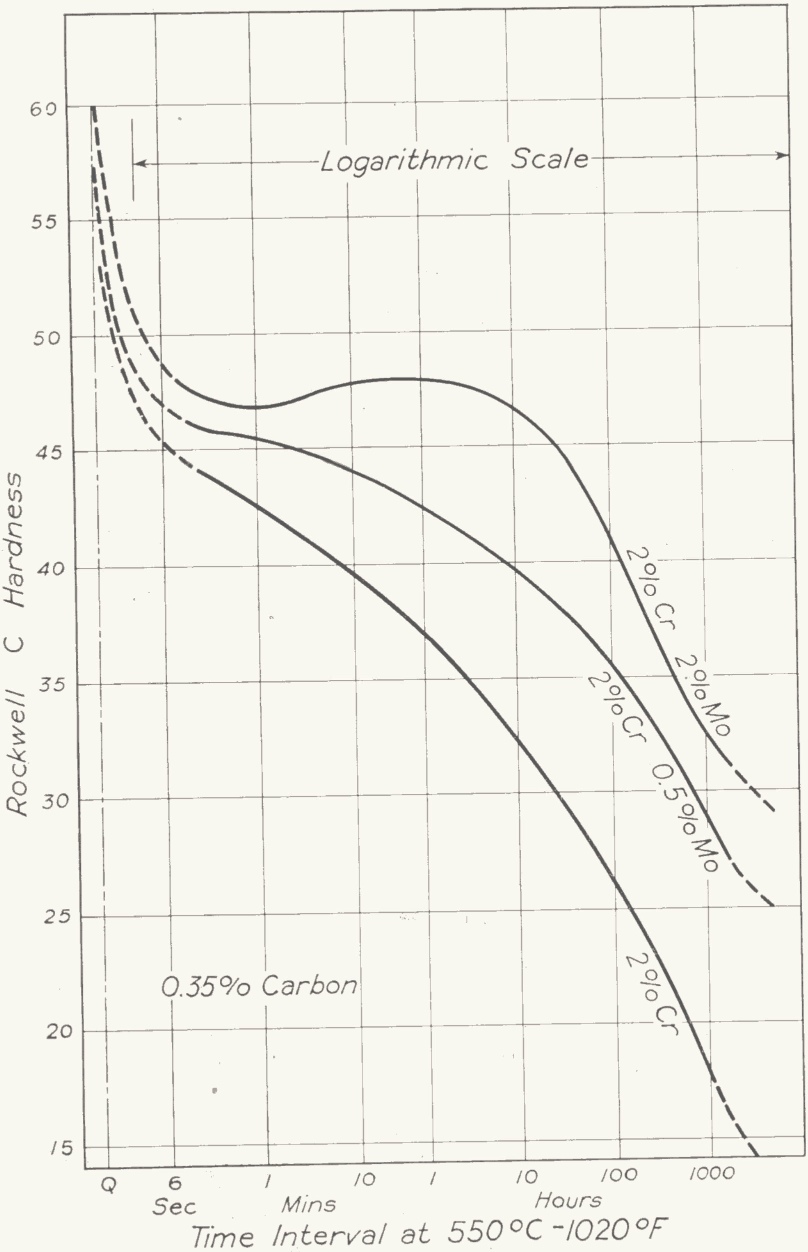

Fig. 173—The Softening, with Increase of Time Interval, at 1020 Degrees Fahr. in Three Quenched 2 Per Cent Chromium Steels, with 0, 0.5 and 2.0 Per Cent Molybdenum. Compare with Fig. 172. (See Footnote 46).

presence of carbide-forming elements, a brief consideration of these effects in other compositions may be useful. Thus, in the 4 per cent chromium steel of Fig. 169 some considerable retardation is clearly in evidence. Tempering for a few minutes at 840 degrees Fahr. contrives to retain (or induce) a hardness greater than that for the same interval at 660 degrees Fahr. The secondary hardness contributed by chromium alone is mild, though very definite. When 2 per cent molybdenum is present along with about 5 per cent chromium, the different retarding effects of the two elements appear to supplement one another and result in the softening effects recorded in Fig. 170 in which tempering at 840 degrees Fahr. is seen to bring about a hardness superior to that at 660 degrees Fahr. over a wide range of time intervals. The more or less constant level of hardness maintained over long periods is seemingly a feature of the combination of two or more alloying elements, for 2 per cent molybdenum alone brings out a sharper rise in secondary hardness, as may be seen in Fig. 171. In the presence of 2 per cent chromium, even ½ per cent of molybdenum contributes a marked reluctance to the tendency to soften either at 840 degrees Fahr. or at 1020 degrees Fahr., as may be seen in Figs. 172 and 173 respectively. In the same figures the potent retention of hardness for hundreds of hours, particularly at 840 degrees Fahr., may be observed in the top curves for 2 per cent chromium with 2 per cent molybdenum. Finally, in Fig. 174 it may be seen that a hardness in excess of 55 Rockwell C (room temperature) is found in a 5 per cent chromium, 5 per cent molybdenum steel after 1000 hours at 840 degrees Fahr., whereas, the same quenched steel, held at only 660 degrees Fahr., is considerably softer because the temperature is too low to develop the secondary hardening in 1000 hours. Probably a hardness well in excess of 55 Rockwell C could be induced in, let us say, 10,000 hours at 700 to 750 degrees Fahr.

The Secondary Hardness Mechanism—It is clear that carbon diffuses fairly rapidly at temperatures as low as 660 degrees Fahr. (350 degrees Cent.), for a plain carbon steel loses some 15 Rockwell C Hardness Numbers in 10 hours at this temperature. Such softening is the result of particle growth far beyond any very effective size, whatever it may be. There is no need for any diffusion save that of carbon, for the carbon atoms are surrounded on all sides by the iron atoms among which it diffuses. Indeed, the softening slows up only as the distances between the growing particles (on the one hand) and the disappearing ones (on the other) increase. No reversal in softening could occur.

The 5 per cent molybdenum steel of Fig. 168 contains the following proportions of atoms per 1000 atom cube (i.e., of a 10 atom edge): iron, silicon and manganese 945, molybdenum 29, carbon 17. To bring about the growth of iron carbide particles it is only necessary for a carbon atom to migrate the average distance separating the disappearing particle and the growing particle even though the mechanism of particle growth, in detail, may be somewhat complicated. Beyond doubt many particles increase in size for a time because fortuitously they were able early to achieve a slightly superior size while the surrounding particles were small. Later, however, many of these medium sized particles are in turn redissolved and vanish, their material becoming incorporated into fewer, larger ones. This sequence continues either as the steel is heated to higher temperature or for a greatly extended period. It may well be that there is a certain coarseness of particle which is ultimately stable for any given temperature, as though a certain threshold value of local energy were required to propel any carbon from one particle. This is a purely academic question however, and at temperatures wherein initial softening may be detected in a few hours, there is apparently continued softening in subsequent intervals provided vastly longer intervals at temperature are studied. The elements which are not carbide-formers alter this carbon migration and carbide coalescence little if any, except the temperature of reheating be such as ultimately to result in graphite formation.

We have then to explain the phenomenon which retards, halts or reverses the softening action when carbide elements are present. This behavior undoubtedly falls into a category similar to that of complex aging systems. The most probable explanation lies in the formation of a *second* precipitated compound after the iron carbide has coalesced to a degree no longer very effective as a hardener. One may visualize carbon atoms combining with the ubiquitous iron to form carbide particles of substantial and increasing size; but to form a crystallite, however small, of a special carbide implies a degree of mobility sufficient for the alloying element to leave the ferritic lattice and migrate as required to form at least the simplest molecule of its special carbide. This will be accomplished, rightly enough, but only when diffusivity is possible as provided by an adequately high temperature; for the diffusivity of the metallic elements in iron, unlike that of carbon, is exceedingly small at temperatures up even to 1800 degrees Fahr. (1000 degrees Cent.). The special carbides generally require the presence of more than one atom of the carbide-forming element in the simplest molecule, but even this circumstance is not the only one requiring diffusion of the sluggish elements, for even the most minute crystallite must contain a number of the atoms of alloying element. As a result of this slow diffusion at ordinary tempering temperatures the special carbide particles are able to remain exceedingly small, and hence an exceedingly effective hardening dispersion, when the first-formed iron carbide has lost its resistance to softening effects and has already formed large particles. Since only at such relatively high temperatures is the second system of dispersed particles formed, it is not unreasonable or surprising that the characteristic halt in softening in such steels as high-speed steel, for example, is referred to as "secondary" hardness. That it is still reflected in the tempering curves of lower alloy steel is perhaps not so well recognized. At any rate the new dispersion, formed when mobility admits of an approach to equilibrium, coarsens similarly to any other dispersion except that a higher level of temperature is required than for iron carbide, since in this case an element of low diffusivity must migrate instead of the highly mobile carbon.

It will become apparent from this explanation of secondary hardening by the special carbide-forming elements that the effect will depend largely upon the homogeneity of the austenite as quenched. The carbide particles of the annealed material clearly contain a very high proportion of the alloying element. As first formed upon heating for hardening, the austenite in the vicinity of such former particles will likewise be disproportionately rich in the carbide-forming element. If time and heating temperature do not succeed in a homogenization it will result in some regions of the martensite having no possibility of secondary hardness, while in the alloy-rich regions no great amount of diffusion will be required to reform the special carbide. Both conditions reduce the secondary hardness potentially inherent in the composition and cause a softening pattern in tempering more nearly like that of carbon steels. Where the greatest retention of hardness and strength after high tempering are required, the composition should first of all include one of the carbide-forming elements and, almost equally important, the heating temperature should bring about the maximum solution of this element and distribute it likewise with a fair degree of uniformity. It appears further that for many services these points are properly observed.

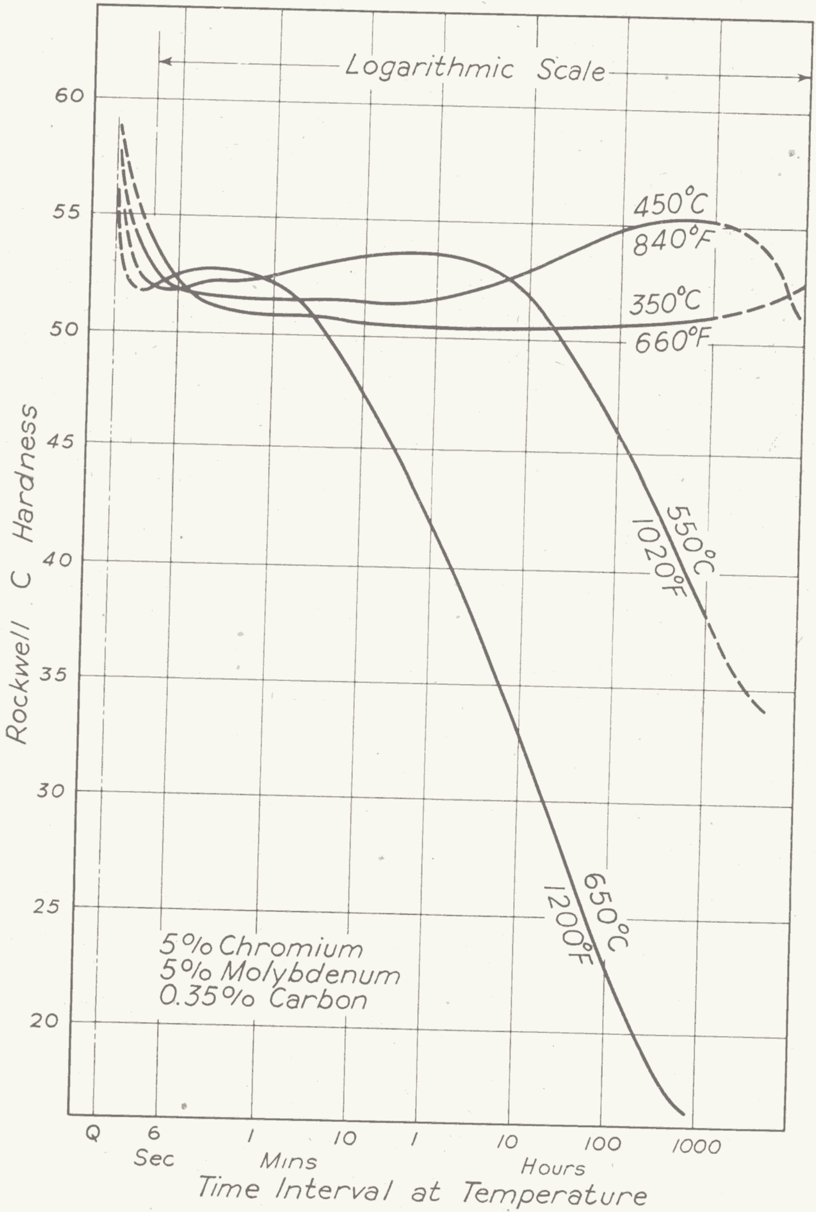

Fig. 174—The Softening, with Increase of Time Interval, at Four Temperatures in a 5 Per Cent Chromium, 5 Per Cent Molybdenum Steel. (See Footnote 46).

Strength at Elevated Temperature — In all metals, seemingly, there is a purely reversible change in strength which takes place with temperature even though, by preheating, all permanent changes are eliminated. For this reason metals are weaker and softer at high temperatures than at low. There is further no simple law available describing this change. Accordingly one may not predict the strength of a material at, say 800 degrees Fahr., from its room temperature test results. Only a test at the elevated temperature will suffice. Indeed, the selection of steels is still more difficult because of the phenomenon of high-temperature creep, — a slow deformation of metal which continues indefinitely at constant temperature and under constant load. That creep occurs more and more readily as the temperature of the metal under load is increased is well illustrated by the fact that creep is pronounced in all steels at 1200 degrees Fahr. (650 degrees Cent.) but at room temperature many steels may bear loads only a little under the elastic limit for exceedingly long periods with no visible change in dimension.

In spite of these circumstances one observation may be relied upon. If a structure in any steel is greatly softened and weakened with respect to its room temperature tests by a heating at some elevated temperature, then it is certainly not suited for use at that temperature under loads even approaching those of room temperature. In other words, unless a steel shows considerable resistance to softening with high-temperature tempering it is probably not a creep-resisting steel. The various diagrams of Figs. 155 to 174 show the resistance to permanent softening at elevated temperature brought about by the carbide-forming elements in small proportion. It is most unlikely that it is a coincidence that these elements are found in the low or medium alloy steels having considerable creep resistance. Indeed, without the presence of sufficient (but not too much) carbon to form a hardening dispersion a very considerable proportion of dissolved elements is necessary to develop similar creep resistance. In the latter case, however, the difference between properties at high and low temperatures may be less.

Another example of the need for strength at high temperature is found in economical cutting tools. Most steels for efficient cutting carry very hard, sizable particles imbedded in a matrix of at least some plasticity. This matrix, itself generally hardened by a dispersion, must not soften unduly at a "red heat", say 1100 degrees Fahr. (600 degrees Cent.), otherwise the hard particles cannot be held rigidly. Now, in steels the hard particles are provided by a well adjusted proportion of carbon and carbide-forming element so that the resulting special carbide is not ever wholly dissolved in the solid state after solidification. A sufficient amount, however, is dissolved to develop marked resistance to softening even at 1100 degrees Fahr. (600 degrees Cent.) and not uncommonly the vanadium and tungsten or molybdenum contrive to furnish a marked secondary hardness revealed as an increase in hardness after tempering. A steel without such effect could probably not serve as a modern cutting tool, for the high operating temperature is a necessary and desirable condition of high speed machining.

Advantages of Special Dispersions — An inspection of any of the charts showing softening by increasing tempering temperature will reveal that the alloy steels, containing any of the carbide-forming elements, may be tempered at higher temperatures for the same retention of strength. The primary function of tempering is to develop toughness, and in no small measure this is the result of stress liberation. The stress resides in the ferrite matrix, which is much the same in the carbon steel and in the alloy steel once the special alloy-rich carbide is formed. The higher tempering temperature permissible in the latter case would be expected to materially reduce the internal stress and should then substantially improve the degree of plasticity and notch toughness of the alloy steel, at a given hardness, over that of equally hard carbon steel. This is, of course, well known in practice, particularly when the hardness level chosen for comparison is such as to just permit a moderate coalescence of the second dispersion. Herein lies a great advantage of the alloy steels; the elements which do not form carbides, and which strengthen the ferrite matrix, would not be expected to detract much from the toughness of heat-treated steel, but it is perhaps only through the circumstance of higher necessary tempering temperature that the carbide-forming elements operate to improve this property.

SIMILARITIES IN TEMPERED ALLOY STEELS

While it has been preferable to consider the differences among the several common alloy steels in order to develop the individual characteristics of the alloying additions, it is also necessary to regard certain properties and behaviors which are similar in nature among a number of alloy steels. Thus the room-temperature tensile test results of a number of the automotive steels show a most interesting correlation.

Hardness and Tensile Properties—Janitzky and Baeyertz[52] have found a remarkably small deviation from a constant relationship between hardness and ultimate strength, yield point and elongation in a number of oil-quenched or water-quenched steels when tempered to various identical hardness values. The relation holds only when the prior quenched structure is substantially martensitic. Surprisingly, their observations cover both some 0.30 per cent carbon as well as some 0.45 per cent carbon steels, the former water-quenched and the latter oil-quenched. The steels investigated

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[52] "The Marked Similarity in Tensile Properties of Several Heat Treated S.A.E. Steels", by E. J. Janitzky and Miss M. Baeyertz, Metals Handbook, American Society for Metals, 1939, p. 515.

are as follows, according to the S.A.E. designation (though some are not listed as S.A.E. steels) :

	Carbon	Manganese	Nickel	Chromium	Molybdenum	Vanadium
1. Oil 4340	0.35-0.45	0.50-0.80	1.5 -2.0	0.50-0.80	0.30-0.40	....
2. Oil 4145	0.40-0.50	0.60-0.90	....	0.80-1.10	0.15-0.25	....
3. Oil 6145	0.40-0.50	0.60-0.90	....	0.80-1.10	....	0.15 Min.
4. Oil 3240	0.35-0.45	0.30-0.60	1.5 -2.0	0.90-1.25	....	....
5. Oil 5145	0.40-0.50	0.60-0.90	....	0.80-1.10	....	....
6. Oil 4645	0.40-0.50	0.50-0.80	1.65-2.0	....	0.20-0.30	....
7. Oil 3145	0.40-0.50	0.60-0.90	1.0 -1.5	0.45-0.75	....	....
8. Water 6130	0.25-0.35	0.60-0.90	....	0.80-1.10	....	0.15 Min.
9. Water 5130	0.25-0.35	0.45-0.75	....	0.70-1.00	....	....
10. Oil 2345	0.40-0.50	0.60-0.90	3.25-3.75	....	....	....
11. Water 3130	0.25-0.35	0.50-0.80	1.0 -1.5	0.45-0.75	....	
12. Water 4130	0.25-0.35	0.50-0.80	0.50-0.80	....	0.15-0.25	Sulphur
13. Water 1330	0.25-0.35	1.35-1.65	....	....	....	0.07-0.15
14. Water 2330	0.25-0.35	0.50-0.80	3.25-3.75	....	....	....

First of all Janitzky shows that the steels do not drop to the same hardness and strength when tempered at the same temperature; on the contrary some of them must be heated as much as 200 degrees Fahr. (95 degrees Cent.) higher to reach the same tensile strength or hardness. The several steels studied resist softening by tempering about in the order shown above, — the first preserving the greatest strength after a given tempering. This response to tempering is shown in Fig. 175. When the several steels are carefully compared at the same hardnesses by the choice of appropriate tempering temperature, the tensile properties are amazingly similar as shown in Fig. 176, which summarizes the extensive study. The bands include all but one or two data which, seemingly, may be in error experimentally, since they are somewhat inconsistent in themselves. This is indeed a remarkable similarity and justifies not only the prediction of ultimate tensile strength from hardness measurements but also supports the contention that microscopic structure, rather than precise composition of phases, determines many mechanical properties. With respect, however, to the tensile test value of reduction in cross-section, Fig. 177, a close similarity for the several steels at the same strength exists only when they are tempered below about 400 B.H.N. (about 200,000 pounds per square inch tensile strength). This property begins to reflect some of the fundamental characteristics of the steels which may control notch toughness after a great deal of deformation has occurred, and in this respect it is clear that steels differ due to such factors as (1) the elements in solution in ferrite and (2) the residual stress. As might now be anticipated, some of the steels which show the higher reduction of area at some constant value of high hardness (400-600 B.H.N.) are those which permit a high temperature of drawback without undue softening. The nickel-bearing steels are likewise able to withstand a high reduction of area prior to rupture at a given strength. High reduction of area generally connotes a steel of poor machinability. It is believed that the bands of Figs. 176 and 177 would be narrowed considerably if steels only of a similar carbon content and grain size were compared and especially if, furthermore, the degree of homogeneity of the austenite were carefully controlled to secure uniformity. Janitzky believes that the value for reduc-

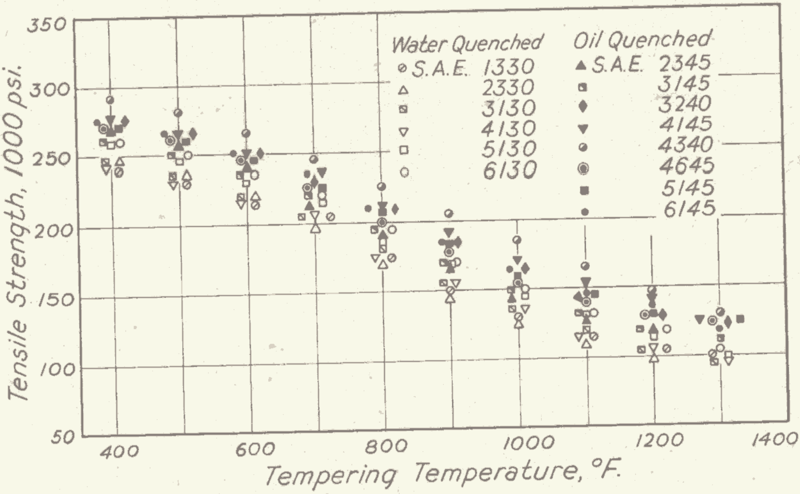

Fig. 175—The Hardness in Various Quenched S.A.E. Steels as a Function of Tempering Temperature. *(Janitzky and Baeyertz).*

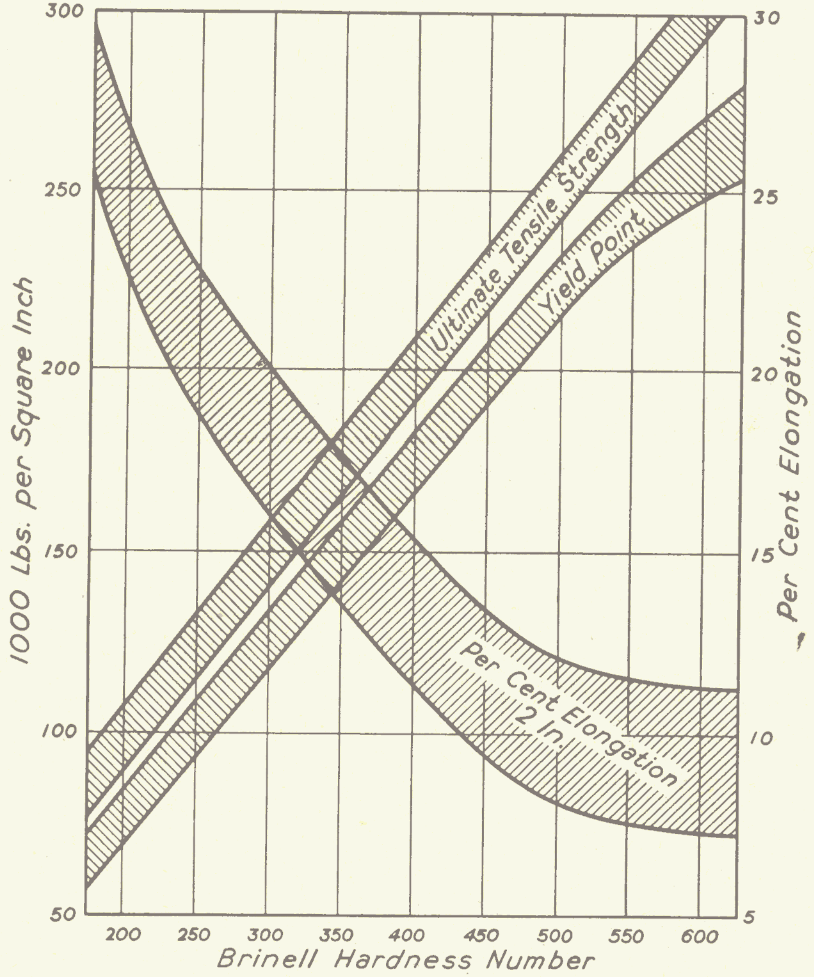

Fig. 176—The Range of Tensile Properties in Several Quenched and Tempered S.A.E. Steels at Various Hardness Values alike for All. *(Janitzky and Baeyertz).*

tion of area is in part controlled by the proportion of retained austenite and this view is certainly compatible with the results. At any rate, the scatter for the several steels is greatly reduced when the steels are so tempered as to eliminate such austenite if present after the quench.

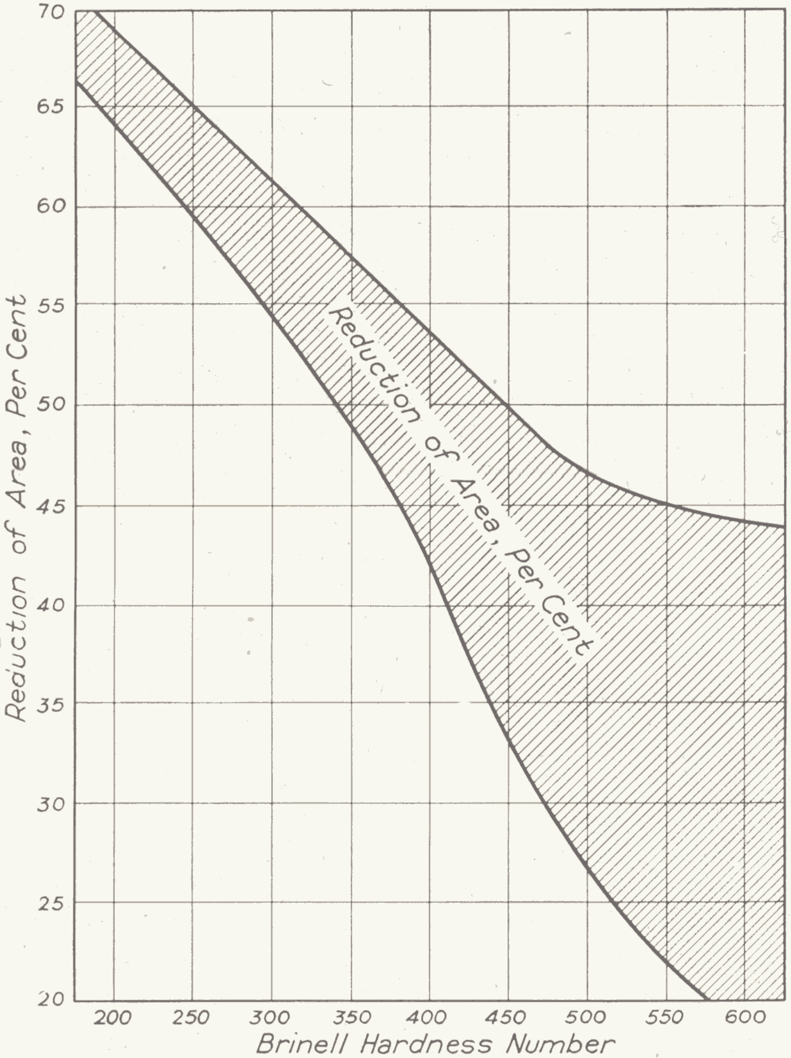

Fig. 177—The Range of Values of Reduction of Area in Several Quenched and Tempered S.A.E. Steels at a Variety of Hardness Values alike for All. Note Spread at High Hardness. *(Janitzky and Baeyertz).*

LOSS OF TOUGHNESS IN INTERMEDIATE TEMPERING

Low Temperature Tempering — The function of tempering to increase the plasticity and notch toughness of hardened

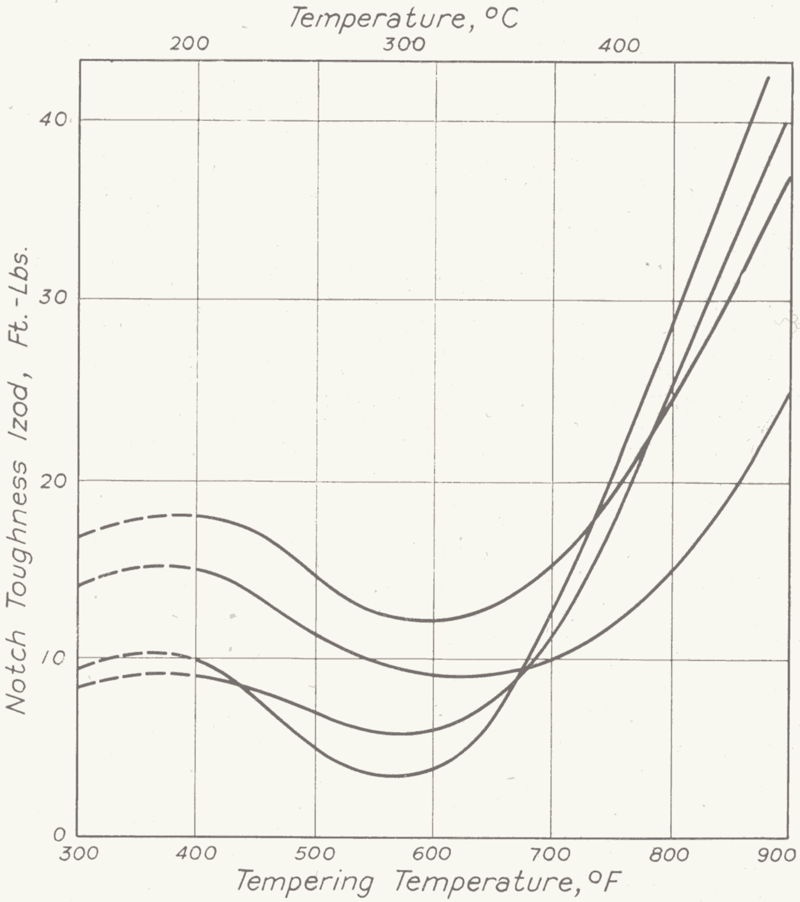

Fig. 178—The Loss of Notch Toughness in Izod Test in Several Alloy Steels after Tempering at about 600 Degrees Fahr.

steel has thus far been spoken of as a continuous effect, becoming more marked as the tempering temperature is raised. This is not strictly in accord with the fact, for carbon steel and many low-alloy steels do not always acquire augmented notch toughness after tempering in a certain low range of tempering temperature. The elongation in the tensile test generally increases slowly with any tempering increment but in the vicinity of 500-600 degrees Fahr. (260-315

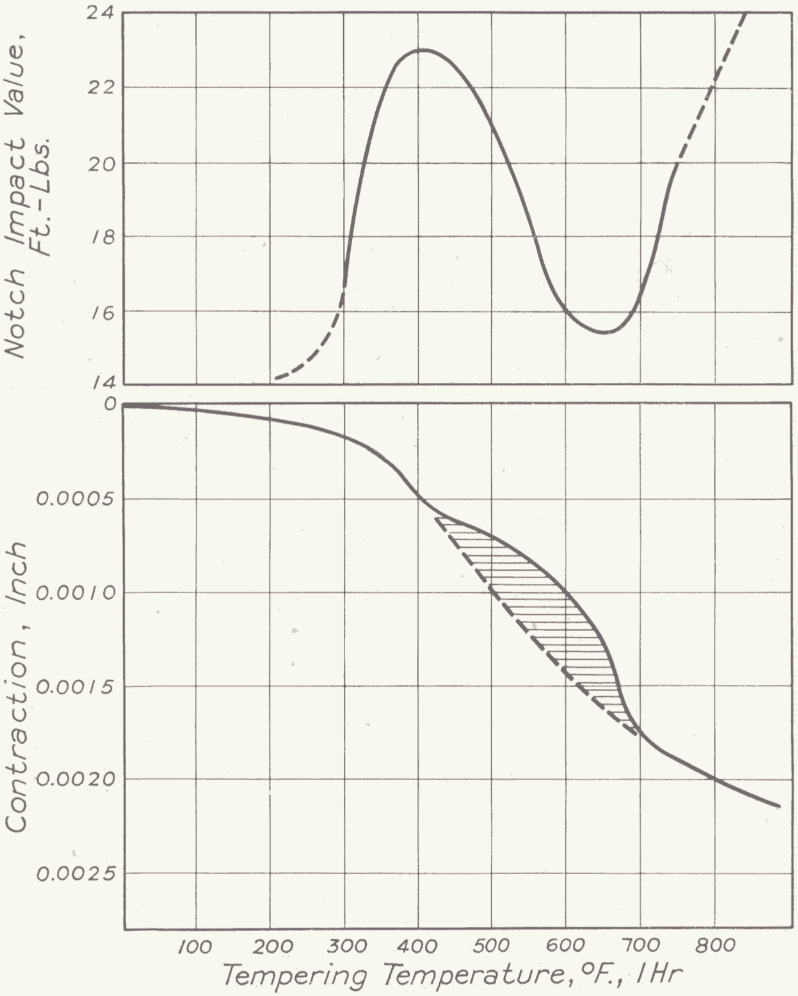

Fig. 179—Relative Notch Impact Values (Above) and Change in Length (Below) Resulting from Tempering at Various Temperatures. Note Effects at about 600 Degrees Fahr. *(Grossmann).*

degrees Cent.) the tempering treatment often results in a notch toughness lower than that of the steel when tempered only at 300 degrees Fahr. (150 degrees Cent.) or perhaps scarcely greater than that of the untempered steel. Higher tempering temperatures usually effectively raise the notch toughness to much higher values. The curves of Fig. 178 are thoroughly typical of many steels. The phenomenon of an unexpected lowering of notch toughness, or the inability to undergo deformation under adverse conditions, has been the subject of much discussion. Grossmann in 1924 offered what is perhaps the most probable explanation of this reduced toughness in steels tempered at about 550 to 600 degrees Fahr. (285 to 315 degrees Cent.). In Fig. 179 some data of Grossmann[53] are presented. The upper chart shows the characteristic minimum in notch toughness and below is shown the length change accompanying the tempering. An anomalous retardation of the shrinkage corresponds to the lowered toughness. This failure to contract uniformly with increased tempering effect amounts to a definite expansion in the same steel when the heating for hardening is at a higher temperature such as 1800 degrees Fahr. (980 degrees Cent.). These circumstances point to the preservation of austenite upon quenching and its subsequent transformation during tempering. The concurrence of the two phenomena is regarded by many as a case of cause and effect.

The same temperature range of tempering has been found adversely to affect the capacity of the steel to flow in shear during a torsion test. Luerssen and Greene[54] show a variety of observations of a much reduced angle of twist in their torsion impact test and attribute the effect to the same cause as did Grossmann, i.e., that of the release of retained austenite. Fig. 180 indicates a simultaneous change in the trend of other properties as a function of tempering temperature. All are compatible with the austenite hypothesis. It is interesting to note that in Luerssen's 1.0 per cent carbon tool steel even the hardness shows the effect of some retained austenite.

It is admittedly difficult to accept the proposal that steels

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[53] "Brittle Range in Low-Alloy Steels", by M. A. Grossmann, *Iron Age,* July 17, 1924.

[54] "Interpretation of Torsion Impact Properties of Carbon Tool Steels", by G. V. Luerssen and O. V. Greene, TRANSACTIONS, American Society for Metals, Vol. 23, 1935, p. 861.

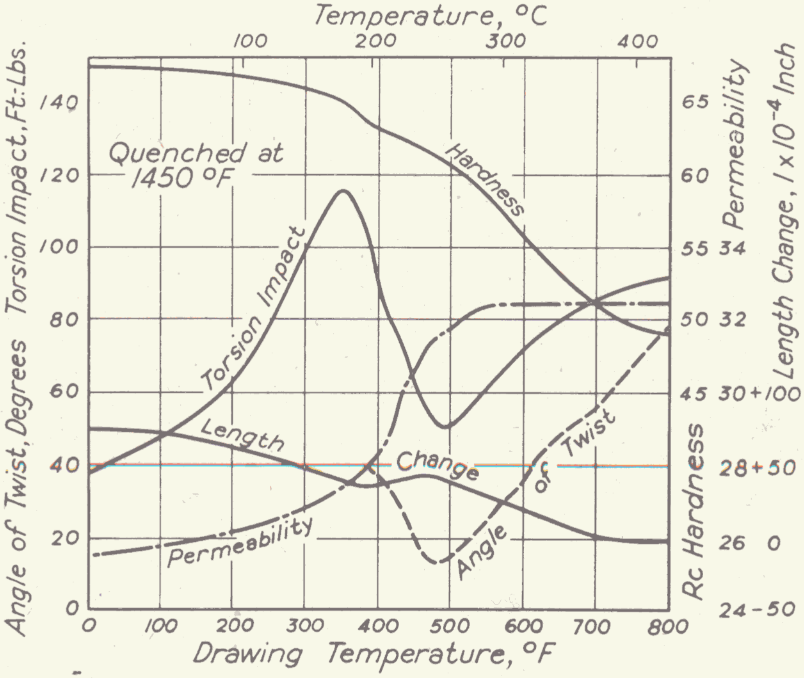

Fig. 180—Irregularities in Property Changes Accompanying Tempering in Vicinity of 500 Degrees Fahr. *(Luerssen and Greene).*

with a carbon content as low as some which exhibit this tempering effect should preserve much austenite. Nevertheless it seems that no other explanation has been offered which is more attractive. One possibility, however, presents itself for consideration. If one attributes the low plasticity in the notch toughness test (Charpy or Izod test) to the presence of internal stress, one might reason that strength falls off in the early stages of tempering faster than the effective internal stress is dissipated; if this were true it might explain a minimum value through which the notch toughness passes with increase of tempering temperature. An interesting circumstance in this connection is the nearly complete freedom of "austempered" specimens from this kind of temper brittleness in the range of hardness which manifests it in quenched

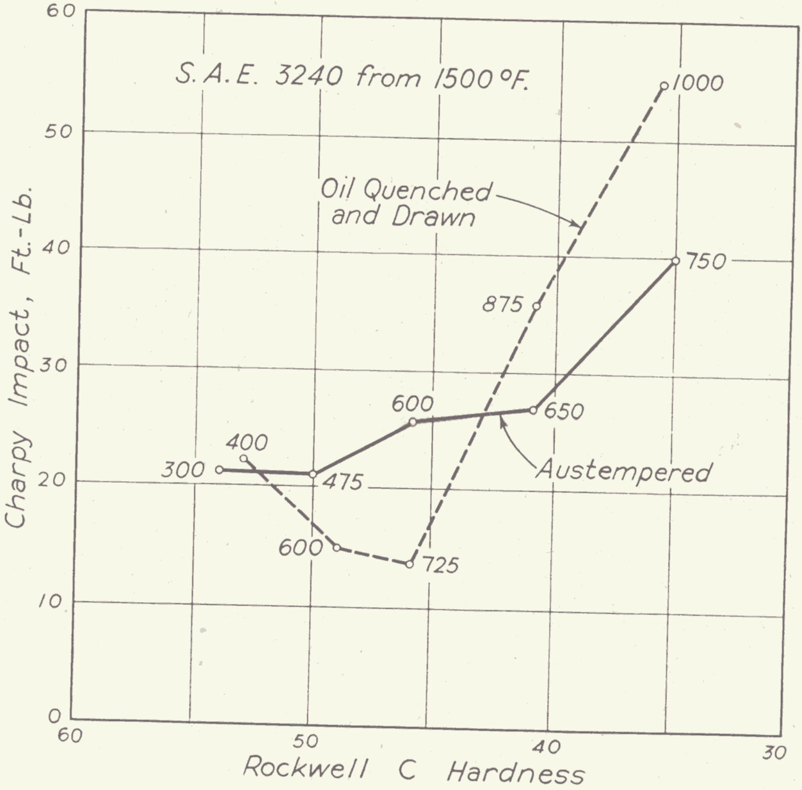

Fig. 181—The Charpy Impact Value of S.A.E. 3240 Steel Accompanying Various Decreasing Hardnesses. Solid Line, as Austempered; Dotted Line, as Quenched and Tempered. *(Payson and Hodapp)*.

and tempered specimens of the same steels. This is well illustrated[55] in the work of Payson and Hodapp, of which Fig. 181 is characteristic. One can imagine that lower stress would reside in a specimen which had transformed *slowly* at some 600 degrees Fahr. (315 degrees Cent.) than in one which had been, at one stage, comprised of highly stressed martensite, — even though later tempered to the same 46 Rockwell C hardness number. Again the evidence is inconclusive, for

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[55] "Austempering of S.A.E. Alloy Steels not Always Advantageous", by P. Payson and W. Hodapp, *Metal Progress,* Vol. 35, No. 4, April 1939, p. 358.

there would admittedly also be less probability of any deleterious residual austenite effect in a properly austempered specimen than in a quenched and tempered specimen.

Heat Evolutions in Tempering — In the study of phenomena and reactions which may relate thereto, in connection with tempering steel, one useful method of experimentation seems not to have been much used of late. The occurrence of a reaction may often be verified and its temperature ascertained by a full heating curve, taken under such conditions as accentuate the absorption or evolution of heat. Thus a specimen of quenched steel may be surrounded by an inert body with thermocouples in each and the whole slowly heated. When the heating rate is at an optimum and the relative masses well selected, as well as the slight thermal insulation between steel and neutral body, a plot of temperature difference versus steel temperature is very informative. Almost any real change is announced by a fairly abrupt change in the slope of the differential curve, which, in the absence of reaction, lies fairly uniformly near zero.

Thus Esser and Cornelius[56] have shown three seemingly separate heat evolutions in the course of heating the martensite of carbon steel up to about 1000 degrees Fahr. (540 degrees Cent.) as shown by the regions *a, b* and *c* in the curve of Fig. 182. The heat evolution at *a* is thought to be associated with the restoration of a cubic lattice from the relaxation of the tetragonal martensite; that at *b* is definitely the heat of transformation of retained austenite to an acicular, ferrite-carbide constituent. The evolution at *c* is sometimes thought of as marking the formation of larger units of carbide, but the author ventures the suggestion that it may relate to the recrystallization of the ferrite matrix as it changes from the "disregistered platelet" form to the polyhedral form.

At any rate, the heat given off in tempering some steels

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[56] See *Archiv für das Eisenhüttenwesen,* Vol. 7, 1933-34, p. 693.

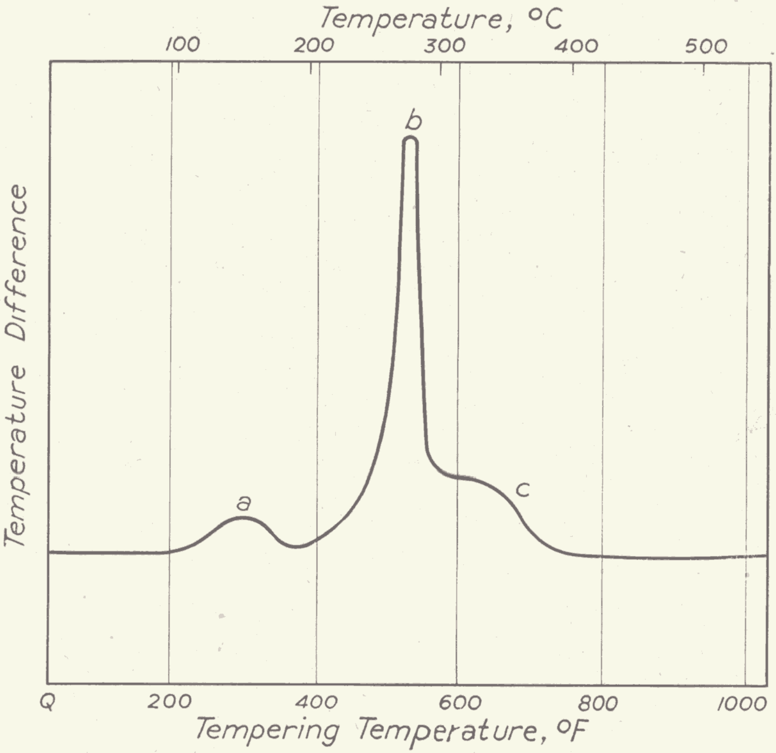

Fig. 182—Heat Evolution in Tempering at Increasing Temperatures as Reflected in Differential Heating Curve Method. *(Esser and Cornelius).*

is sufficient to cause the specimens to rise in temperature far above that of the furnace in which they are being heated; even glowing faintly in a black furnace. It is doubtful if carbide formation, even of the special carbides, is responsible for as much of the heat evolution as is the transformation of retained austenite.

Loss of Toughness at Higher Tempering Temperatures — Another form of lowered notch toughness is developed particularly in the deep-hardening chromium-nickel steels in the course of cooling from the tempering operation. The loss of toughness is pronounced when they linger in the vicinity of

900 to 1000 degrees Fahr. (480 to 540 degrees Cent.) for considerable time following tempering at a temperature near, but below, the Ac_1 temperature. Thus an ordinary air-cooling from 1160 to 1200 degrees Fahr. (625 to 650 degrees Cent.), for example, will often result in a severe loss of toughness, while a quench from the same tempering temperature produces a tough product. The work of Greaves and Jones[57] suggests that something is dissolved above 1100 degrees Fahr. (600 degrees Cent.) which may be precipitated at a slightly lower temperature in a damaging form. The ultimate nature of the phenomenon has not been adequately explained, but high manganese and phosphorus appear to accentuate the effect. Generally speaking, it is of little practical significance since it is not usually inconvenient to quench the material from the draw-back. Since molybdenum acts very definitely to reduce the severity of the effect, it is generally supposed that carbon plays a part in the action; presumably the molybdenum greatly lowers the solubility of carbon in ferrite. A surprising feature of this temper brittleness is that both brittle (as a result of slow cooling) specimens and tough, tempered and quenched specimens can be brought to the same notch impact rating if held for sufficient time (16-40 hours) at the same temperature. This holding temperature appears to bring about a kind of equilibrium, for the degree of notch susceptibility reached alike by the two specimens is low when the holding temperature is in the vicinity of 1100 degrees Fahr. (600 degrees Cent.) and high for the pairs of specimens held (a somewhat longer interval) at about 800 degrees Fahr. (425 degrees Cent.). Intermediate temperatures achieve "equilibrium" at intermediate toughness. Holding for short intervals at temperature below about 900 degrees Fahr.

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[57] "Temper Brittleness of Nickel-Chromium Steels", by R. H. Greaves and J. J. A. Jones, *Journal,* Iron and Steel Institute, Vol. CII, No. 2, 1920, p. 171-222.

"Temper Brittleness of Steel; Susceptibility to Temper-Brittleness in Relation to Chemical Composition", by R. H. Greaves and J. J. A. Jones, *Journal,* Iron and Steel Institute. Vol. CXI, No. 1, 1925, p. 231-262.

(480 degrees Cent.) does not alter the toughness established in the former cooling from the draw-back. These circumstances would be explainable on the basis of mere *quantity* alone of some partially soluble phase, — as though its *form* were always alike and its presence damaging to plasticity.

TEMPERING OF STRUCTURES OTHER THAN MARTENSITE

The tempering operation, to improve plasticity and toughness in hardened steels, is usually applied to material in the martensitic condition, — martensitic at least in surface layers. Closely akin to the fully martensitic structure is the acicular constituent formed at temperatures somewhat higher than that which results in full martensitic hardness. This structure, sometimes called pseudo-martensite in alloy steels cooled at a moderate rate, is analogous to the bainite of carbon and low-alloy steel, of necessity developed in these latter compositions by an initial rapid cooling and a period at the somewhat elevated transformation temperature. So long as the hardness of these various acicular structures differs only a little, tempering proceeds similarly in all. Minor differences appear to exist in respect to the precise rate of softening of the several initial structures securable in the same steel.

Occasionally a fine lamellar (or pearlitic) structure is reheated or tempered. It will be apparent at once that a tempering operation upon such structures can consist only of a spheroidizing action upon the lamellae of carbide. Unless the tempering temperature (and time interval) be high enough to produce spheroids with a mean diameter at least in the order of magnitude of the thickness of the lamellae, then little or no action may take place. Hence low reheating temperatures scarcely soften the pearlitic structures in which the lamellae are coarse enough to be easily visible in the microscope. At the same time the tempering may be beneficial as a means of dissipating internal stress, both general stress distributed over large zones and any microscopically distributed stress. In some instances the ductility of the steel may be raised without lowering the yield strength. As the lamellae of carbide become coarser in softer, slowly cooled steels, a change of structure by heating below the critical temperature becomes more and more improbable, as is well exemplified by the difficulty experienced in spheroidizing without heating somewhat into the temperature range of austenite formation. This latter method tends to leave a part of the carbide undissolved but at a temperature of easy migration; very slow cooling then permits spheroids to form upon nuclei consisting of the undissolved portions of the former lamellae.

Rates of Softening in Three Structures—The peculiarities of tempering characteristics of the various initial structures have been studied by Engel.[58] His data show that a variety of structures, typified by martensite, bainite and fine pearlite quickly come to a similar hardness at a fairly high tempering temperature, — more slowly at low temperature. Thus in the 0.75 per cent carbon steel employed the three constituents had respectively the following initial Rockwell C hardness:

Martensite	64.6	(684 B.H.N.)
Bainite	53.5	(527 B.H.N.)
Fine Pearlite	44.5	(421 B.H.N.)

In about ½ minute at 1200 degrees Fahr. (650 degrees Cent.) the specimens had all softened to about 34.5 ± 1.5 Rockwell C (330 B.H.N.) but were persistently slightly different in *precise* hardness. This is shown in Fig. 183, in which it may be discovered also that a hardness value of, say, 350 B.H.N., 37.0 Rockwell C, is reached in an incredibly short

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[58] "The Softening Rate of a Steel when Tempered from Different Initial Structures", by E. H. Engel, Transactions, American Society for Metals, 1939. Presented October 1938.

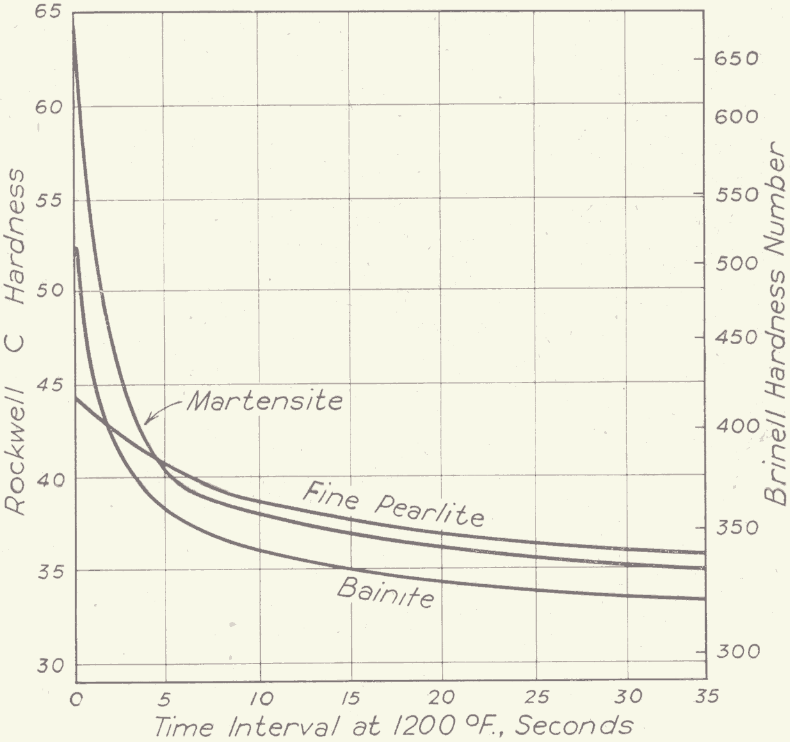

Fig. 183—The Softening, with Increase of Short Time Interval, at 1200 Degrees Fahr. in Three Characteristic Structures of Carbon Steel. *(Engel).*

time; 16 seconds for the martensite, 7 seconds for the bainite, and 20 seconds for the fine pearlite.

The three specimens, after these three short intervals of tempering, have been materially softened and they are then at the same hardness. It might be supposed that from this time on they would soften equally and identically during subsequent holding at 1200 degrees Fahr. (650 degrees Cent.). This is not true, however, as may be seen in Fig. 184. The equally hard specimens (arbitrarily shown as beginning the tempering period at 1 second, about the time required to reach temperature in a lead bath) are seen to soften at different rates; the difference in initial structure is still exerting an

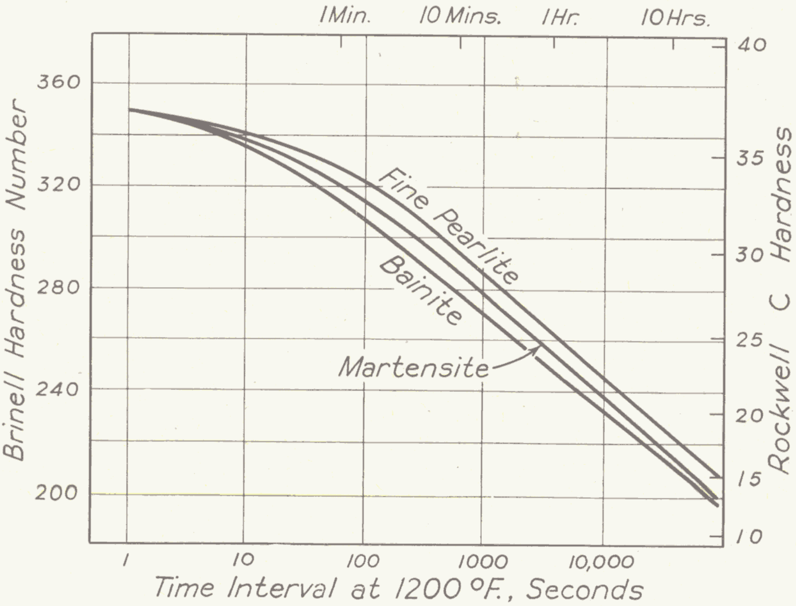

Fig. 184—The Softening, with Increase of Long Time Interval, at 1200 Degrees Fahr. of Three Characteristic Structures all of same Initial Hardness. *(Data of Engel).*

effect after 22 hours 13 minutes (80,000 seconds) to cause a greater hardness to remain in the pearlitic specimen than in the originally martensitic one and the bainite specimen to soften most. This actual difference is of course small and after a far-reaching spheroidization might possibly vanish entirely. The point is of interest, however, as a matter of unpredictable scientific fact.

Engel predicted from these observations that in a properly chosen time interval and temperature of tempering, it should be possible to reverse the hardness gradient in a round bar hardened only in the surface layers. This he was able to do, as shown in Fig. 185.

VALUE OF TEMPERING DATA

It has been stressed that hardness values correlate very

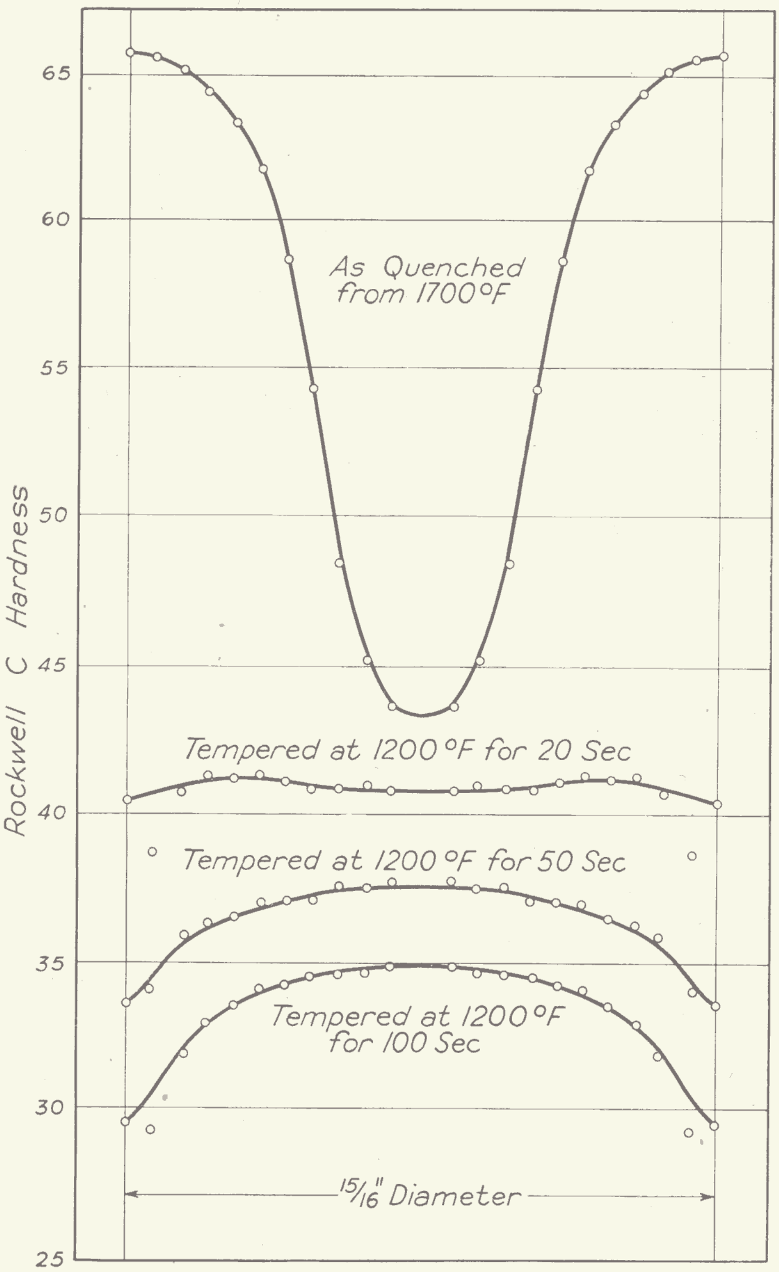

Fig. 185—Hardness Distribution across Mean Diameter of Quenched and Variously Tempered Round of Carbon Steel. *(Engel).*

well indeed with tensile strength in many steels as determined in the tensile test. The ease with which the changes in hardness of steels may be followed after tempering operations makes studies of this phenomenon very attractive. The information derived therefrom is unequaled as a means of securing an intimate acquaintance with the internal rearrangement of the constituents of the steel, as well as the factors which promote high temperature strength. It would appear that such a sensitive and positive *reflection* of diffusion, as softening during tempering undoubtedly is, would prove to be an excellent measurement of diffusivity. This has not proven to be the case, because the increase of carbide particle size, — the basic cause of softening, — is an exceedingly complex phenomenon, — an intrinsic manifestation of diffusion, — for which a workable mathematical concept is as yet almost impossible of achievement. Until such agglomeration of carbides has occurred as to permit microscopic measurement of size and a statistical treatment of the classification of such sizes and their occurrence, no accurate basis for assigning a dimension to the particles is possible. Less probable is it that one could assign a certain hardening power to a certain size of particle; the attempt to do so might have as little meaning as the concept of a "critical size" of particle. When similar quantities of similar dispersions have the same hardening influence in the same matrix, one might safely conclude that the same effective size of particles existed in both dispersions; beyond this the reasoning must largely remain comparative rather than rigidly quantitative.

STEELS RENDERED INHOMOGENEOUS

Much has been said of the hard surface, soft interior, combination found in hardened, shallow-hardening steels. This condition is often advantageous, and in homogeneous compositions it is the result of the natural and inevitable disparity in cooling rate as between surface and interior of a piece during quenching. Only occasionally is it found desirable to retain the full difference in hardness; more often some tempering is applied which reduces surface hardness. Instead of depending upon the range of cooling rates, the heating temperature may be raised to a suitably higher temperature on the surface than in the interior by an exceedingly high rate of heat input. Even a greater degree of difference in properties is sometimes sought, in which case other means of producing the dissimilarity are called upon.

When, however, great differences are contemplated the inhomogeneity is introduced in the composition itself, especially in respect to carbon. This may range from the thin, hardenable layer of high carbon (and increased nitrogen) easily imparted by cyaniding, to the heavy case of high carbon introduced more frequently by pack or gas carburizing. Intermediate depths of carburization (with some little nitrogen introduction) are conveniently accomplished in so-called activated baths. Hard surfaces, to be sure, may be laid down on the steel by electrolytic chromium plating, or even in hard-surfacing by the melting-on of hard alloys through an adaptation of the welding processes, but these do not concern us here. Rather, we shall restrict ourselves to carburized and nitrided steels.

Carburized Steels — The processes of case-carburizing serve to produce a composite steel in which the composition of the steel is very significantly altered at the surface. The alteration is primarily one of an increased carbon content, but at the same time nitrogen may be significantly augmented in long treatments in the cyanide-bearing baths. Of some import, however, is the introduction of oxygen in pack-carburizing. In typical killed steels oxygen diffuses inwardly along with the carbon, though generally to a lesser depth than carbon. It appears probable that, even in pack-carburizing, little or no oxygen is absorbed in rimming steels low in manganese, since the steel, in solidification, was already saturated with respect to CO. Indeed, highly oxidized, low-metalloid steels might be expected to lose oxygen during carburizing in CO, — the agent in pack-carburizing. As the total oxygen (in any form) content of the agent in gas-carburizing is lowered, the tendency toward raising the oxygen content of the steel decreases; methane-carburizing introduces no oxygen and probably often removes it from the steel.

The relation between oxygen content and inclusions is so inevitable, and the dependence of grain growth upon inclusions is likewise so marked, that it is not surprising that the grain growth pattern of the carburized case is often distinctly different from that of the unaltered core. For this reason a determination of the grain growth characteristics of a steel for carburizing must be made upon properly carburized material for the case, and upon uncarburized material for the core.

The effect of oxygen absorption from the CO of the pack-carburizing environment is exceedingly marked in steels carrying a small proportion of dissolved aluminum. It so elevates the coarsening temperature of this type of steel that an abrupt change in subsequent grain size at the limit of oxygen penetration provides an ideal indicator of the rate of oxygen migration. By this method the author's associates have accurately measured the relative rate of carbon and oxygen penetration into certain steels.

While it is universally realized that carburization provides only a higher-carbon steel at the surface of the work (and a frequent alteration of grain growth behavior), the implications may sometimes be disregarded. It has been shown that the increase in hardenability as between medium- and high-carbon steel is only a certain modest increment. Hence the capacity to acquire martensitic hardness in the carburized case is not greater (and generally less) than would be found in the surface layers of a high carbon steel. Excessive sections in carburized steel will fail to harden at the surface exactly as in homogeneous high-carbon steels. The resorting to alloying elements for adequate hardenability in exterior zones is just as imperative for carburized steels as for homogeneous steels.

The utilization of coarsened austenite for improving hardenability is subject to much the same rule as in homogeneous steel. If the accompanying reduced ductility and impairment due to stress effects is not a controlling factor, coarsening may be allowable in the case as ready for quenching. Otherwise the steel and the hardening practice should be such as to produce full martensitic hardening at the surface in a fine-grained austenite. One sometimes observes a fine-grained carbon steel, so constituted as to retain a fine austenite grain at the conclusion of carburizing, spoken of as of inferior carburizing quality and prone to soft spots. At worst, such steel is merely ill-chosen (if intended for a size of part for which its composition supplies insufficient hardenability) and its *quality* is really not in question at all.

Hardening Case-Carburized Steels — The distribution of the augmented carbon content, or the carbon gradient, as a function of temperature, time and method of carburizing has been well studied and reported in excellent literature. High surface carbon and steep gradient are characteristic of lower carburizing temperatures, while higher temperatures favor lower surface carbon and a more gradual falling off toward the interior. The steels low in all alloying elements tend to consist only of austenite at the conclusion of the carburizing period at the higher range of temperature, just prior to quenching. Steels carrying carbide-forming elements tend to build up microscopically-sizable, disconnected particles of carbide during the carburizing period. The surface is generally hyper-eutectoid and, depending upon the carbon concentration of the austenite, a tendency exists for adverse envelopes of carbide to form about the austenite grains during cooling. This may be prevented by quenching from the carburizing treatment, whereafter spheroidization may readily be brought about.

Reheating for hardening provides an opportunity for producing a martensite of about eutectoid composition in itself, in which well distributed particles of carbide are present in the outer highest carbon zone. While parts may be slowly cooled from the carburizing treatment and then given an extra heating and quenching for homogenization, this is not generally economical except when light machining or finishing operations figure in determining the economy of the procedure. In any event, one may be certain that (1) a low final heating for hardening causes a fine-grained austenite to form, and (2) rarely, if ever, are undissolved carbide envelopes desirable. It is recommended to verify that surface decarburization does not occur during any slow cooling, even in the carburizing box.

It should be pointed out that there is often an opportunity for ingenuity in devising heating and hardening schedules to bring about an optimum combination of case and core properties, and advantage is usually taken of this opportunity.

Nitrided Steels — Surface layers of certain steels may be intensely hardened by the introduction of nitrogen by means of the decomposition of ammonia upon the surface. The steels employed for nitriding carry aluminum (about 1 per cent) or other elements which presumably form nitrides, and the outstanding feature of the treatment is the low temperature which will serve to permit nitrogen diffusion to useful depths. Nitriding may be carried out at temperatures as low as 850 degrees Fahr. (455 degrees Cent.) although temperatures up to 1000 degrees Fahr. (540 degrees Cent.) are recommended. A phenomenal hardness, represented by a

Vickers number of over 1100, may be developed. The high abrasion resistance of these surfaces is accompanied by considerable resistance to several types of corrosion.

Since the nitriding temperature is low, mechanical properties corresponding to fairly high strength are retained through the nitriding treatment applied after the steel articles themselves are appropriately heat-treated. The varieties of steel suited to nitriding are such as to provide a wide variety of basic properties limited only by the softening, which the nitriding temperatures (as a tempering operation) incurs. The nitriding process is interesting, metallurgically, in that diffusion of the agent imparting the hardness may occur at a temperature at which an excellent array of mechanical properties in the steel itself still persist. It may be repeated here that the effectiveness of this treatment apparently depends upon the formation of the finest conceivable units of a hard compound, finer than any crystallite might be. This dispersion, of maximum effectiveness, maintains itself at its temperature of formation because only one component of the compound has significant diffusivity at that temperature; hence coalescence and attendant softening may occur only at higher temperatures.

The inhomogeneous steels introduce no entirely novel fundamentals, but, instead, require merely the selection of an optimum schedule of treatments to secure desired structure and properties in both interior and surface.

RECAPITULATION

This series of discussions has shown that alloying elements accomplish improvements in steel properties through comparatively few fundamental influences; these influences are most effectively exerted when a closely controlled heat-treatment is applied to the steels, a heat-treatment appropriate to the composition of the steel and its final purpose.

Indeed, unless the heat-treatment is selected and applied the alloying elements may be of little avail. As has been said, the heat-treatment may, in some instances, be no more than a simple cooling from rolling, but it must be suited to the steel and its intended function.

With respect to mechanical properties at ordinary temperatures, the demand appears to be greatest for a combination of high strength and considerable plasticity or toughness. This combination is sometimes not described in terms of the tensile test alone, but includes a test requiring a capacity to flow under the adverse conditions of a notch. That such tests are really appropriately applied to material to be used in members free from notches or notch effects may be questioned. But the fact remains that with respect to mechanical properties the metallurgist is more and more concerned with securing simultaneously a high degree of strength and a greater and greater capacity to flow under adverse conditions, be it designated ductility or notch insensitivity. This objective is approached through heat-treatment primarily, and secondarily through alloying elements, because they both extend the possibilities of heat-treatment and also exert direct influence. The heat-treatment is effective through the establishment of a favorable microstructure.

If carbon steels were all finished at sizes corresponding to shapes from ½ inch to ¾ inch in thickness and no heat-treatment were applied save that of simple cooling from the rolling or forging temperature, the tensile properties would be substantially those shown in Fig. 186 as a function of the carbon content. The improvements in tensile properties brought about by alloying and heat-treatment may in effect be approximately measured by reference to this chart. The carbon steel compositions with manganese not exceeding 1 per cent may be so heat-treated as to acquire a splendid array of mechanical properties at room temperature; — that is in

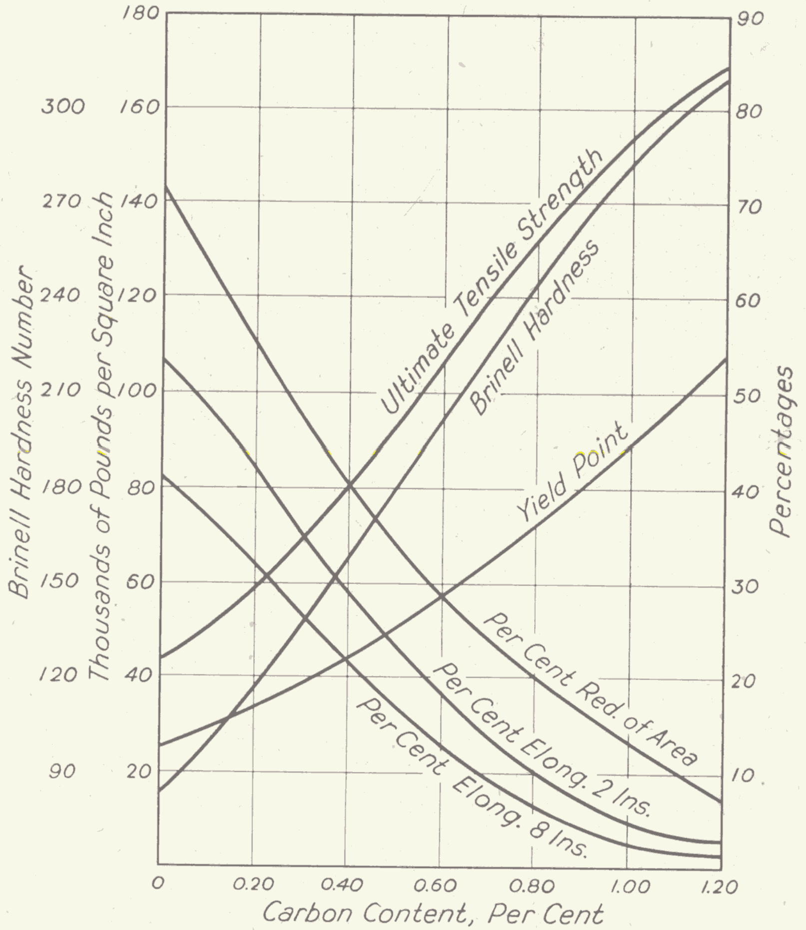

Fig. 186—Approximate Influence of Carbon Content upon Tensile Properties of Carbon Steels in the As-Rolled Condition. Applicable to Sections in the Vicinity of ½ to ¾-Inch Thickness.

small section. Entirely uniform structures throughout can scarcely be produced in such carbon steels if heat-treated in the form of rounds larger than about ⅞ to 1 inch in diameter. The greatest toughness at the high strengths results when the austenite grain size is fine, a condition which also restricts hardenability.

We come then to the foremost function of alloying elements, — that of increasing hardenability, or the size of sections hardenable throughout. Scarcely less valuable than the increase of maximum heat-treatable size is the other aspect of increased hardenability; the possibility of using milder quenches on all sections, thereby reducing internal stress. Through increased alloy content the grain need not be coarsened to secure almost unlimited hardenability, but the added alloying elements must be dissolved in the austenite. Elements remaining undissolved in the form of carbides generally restrict grain growth and accordingly it is not usual to dissolve the whole of the carbide-forming elements; indeed, exceedingly high temperatures might be required to do so. Curiously enough, the carbide-forming elements when dissolved increase hardenability very greatly, more than equal weight of other elements, generally speaking. The undissolved particles remain unchanged during quenching and tempering and serve to resist abrasion and enhance cutting capacity in tools.

Suppose elements have been dissolved to enhance hardenability and are accordingly located in the quenched and martensitic steel in the form of an atomic dispersion. They may still exert a profound further influence upon the properties of the steel. During tempering the noncarbide-forming elements remain dissolved in ferrite to add some strength thereto and in this condition detract relatively little from the plasticity of the ferrite, nickel being especially favorable in this respect. But the carbide-forming elements contribute a still more striking influence in tempering.

During tempering a second fine dispersion of alloy-rich carbide forms which retards softening by tempering and greatly enhances high-temperature strength. For any particular final strength or hardness, quenched steels carrying such elements must be heated at considerably higher temperature in tempering and this circumstance presumably enables a greater dissipation of internal stress. This stress resides mainly in the ferrite matrix which, in itself, may not be greatly different in many alloy steels from that in carbon steels, and a further relaxation of internal stress increases the net external stress which may be endured under adverse conditions of loading; hence toughness. This slowly-diffusing, special carbide dispersion contributes, by the same token, to the preservation of strength at elevated temperature.

It will have been noted that the behavior of the individual elements emphasizes a division into two groups: (1) the elements which are only mildly carbide-forming, or do not combine in the carbide and (2) the carbide-forming elements. This classification is useful in distinguishing the behavior of the elements in alloy steels in a fundamental way. The other obvious classification, referred to in Fig. 2, based upon the relative solubility in alpha and gamma iron, is of practically no importance in the medium and high carbon steels treated in these discussions. Thus, silicon and vanadium having similar characteristics in phase formation in pure iron alloys fall into the same (B-I) classification; but how different in alloying influence, because they stand almost at the opposite extremes with respect to carbide-forming tendency! If one were considering only low carbon compositions carrying relatively large alloy contents, then some interest would attach to the tendency of the elements to dissolve more in ferrite or in austenite, and ultimately to eliminate one or the other solid-solution at higher concentration.

Any of the elements as dissolved in alpha iron contribute strength to the ferrite matrix in steel, conforming to the usual solid-solution effect. They vary in intensity of hardening weight for weight, and differ also in the extent to which they reduce plasticity in adding a certain increment to strength. The noncarbide-forming elements in steel are almost wholly dissolved in the ferrite in either pearlitic steels or in the structures of tempered martensite. The carbide-forming elements are to be found extensively in ferrite only when the carbon content is insufficient to combine with them; the excess carbon required to substantially withdraw the element from ferrite being the less the stronger the carbide-forming tendency. The mildly carbide-forming elements, chromium and manganese, are generally divided between carbide and ferrite even with relatively high carbon content.

The principle of partition of these carbide-forming elements follows the same general trend when the steel is heated to form austenite except that the solubility of these elements may be high in austenite and, since the carbon itself is often largely dissolved, there is frequently no carbide phase left. Only with the stronger carbide-forming elements or in high-carbon steels are persistently insoluble carbide particles left remaining at high heating temperatures. Vanadium, columbium and titanium withhold carbon from solution even at relatively low excess concentration.

It should be possible to enumerate the more common alloying elements and to place them in proper categories, at least approximately, on the basis of their fundamental characteristics and influences.

Aluminum. Maximum solubility in pure gamma iron about 1.1 per cent; somewhat higher in presence of carbon.

Solubility in pure alpha iron about 30 per cent.

Carbide-forming tendency less than iron, i.e., promotes graphitization.

Mild contribution to hardenability as dissolved in austenite.

Principal functions: (1) to form an effective fine dispersion with oxygen (or nitrogen) which restricts austenite grain growth, and (2) to form, by relatively low-temperature diffusion of nitrogen, an exceedingly effective surface-hardened layer, i.e., nitriding. Excellent deoxidizer.

Chromium. Maximum solubility in pure gamma iron about 12.8 per cent; in presence of about 0.5 per cent carbon maximum solubility in austenite about 20 per cent.

Solubility in pure alpha iron, infinite.

Carbide-forming tendency greater than manganese; less than tungsten.

Moderate contribution toward hardenability; in proportions up to about 1 per cent more effective than manganese. Mild carbide effect in tempering to resist softening.

Principal functions: (1) to increase corrosion and oxidation resistance; (2) increase hardenability; (3) contribute some high temperature strength, and (4) abrasion resistance in high carbon compositions.

Cobalt. Maximum solubility in pure gamma iron, infinite.

Maximum solubility in pure alpha iron nearly 80 per cent.

Carbide-forming tendency about that of iron or slightly stronger.

Contribution toward hardenability negative.

Principal functions: to resist softening with elevation in temperature when dissolved in ferrite which is considerably hardened thereby.

Manganese. Maximum solubility in pure gamma iron, infinite.

Maximum solubility in pure alpha iron about 15 to 18 per cent.

Carbide-forming tendency slightly greater than iron; less than chromium.

Moderate contribution to hardenability; in ordinary amounts greater than nickel, less than chromium. Favors retention of austenite after quench in high carbon steels.

Principal functions: (1) specific to form sulphide in relatively unharmful form but favoring machinability; (2) increase hardenability moderately at moderate cost, and (3) produce a high-carbon, austenitic steel. Increases strength in ferrite but reduces plasticity.

Molybdenum. Maximum solubility in pure gamma iron about 3 per cent; in presence of 0.25-0.30 per cent carbon maximum solubility in austenite is about 8 per cent.

Maximum solubility in pure alpha iron about 32 per cent, falling off at lower temperatures; Fe_3Mo_2 is rejected and an age-hardening system results.

Carbide-forming tendency strong, more effective than chromium or tungsten, although in resisting softening in tempering the secondary hardness may occur at slightly lower temperature than in tungsten steels at appropriately higher concentration of tungsten.

Contributes greatly to hardenability as dissolved; in proportions up to about 1 per cent, more effective than chromium or tungsten.

Principal functions: (1) raises austenite coarsening temperature; (2) contributes to deep-hardening; (3) raises high-temperature strength and creep resistance, and (4) enhances corrosion resistance in stainless steel.

Nickel. Maximum solubility in pure gamma iron, infinite.

Maximum solubility in pure alpha iron about 25-30 per cent; remains in ferrite in presence of high carbon.

Carbide-forming tendency less than iron, i.e., promotes graphitization.

Contribution to hardenability mild and hence useful in compositions intended to be insensitive to rapid cooling. In effective amounts tends to retain austenite after quenching medium and high carbon compositions.

Largely dissolved in ferrite even in presence of high carbon and hence useful in strengthening unhardened steels by solid-solution effect.

Principal functions: (1) rendering high chromium compositions austenitic; (2) producing steels of moderate or high hardenability (depending upon other elements) having relatively low required heating temperature and high toughness as tempered, especially at low testing temperature, and (3) promoting toughness in pearlitic-ferritic steels. (Very high nickel-iron alloys have special thermal expansion and magnetic characteristics).

Phosphorus. Maximum solubility in pure gamma iron about 0.5 per cent.

Maximum solubility in pure alpha iron about 2.5 per cent, not decreased by carbon content.

Carbide-forming tendency probably nil.

Contribution to hardenability surprisingly great considering small contents found in steel. Not known to increase retained austenite after quenching.

Very effective hardener as dissolved in ferrite up to some 0.20 per cent, in which proportions it is largely so located.

Principal functions: (1) strengthener in low carbon steel to which (2) it confers corrosion resistance; (3) improves machinability in high-sulphur, free-machining steels, and by the same token, restricted to 0.05 per cent in certain other higher-carbon steels in the interest of maximum plasticity.

Silicon. Maximum solubility in pure gamma iron about 2 per cent; in presence of about 0.35 per cent carbon, maximum solubility in austenite about 9 per cent.

Maximum solubility in pure alpha iron about 18.5 per cent; even in presence of carbon solubility remains high.

Carbide-forming tendency negative, i.e., promotes graphitization.

Contribution to hardenability only moderate, with little increase in retained austenite.

Fairly effective hardener of ferrite, probably more potent than manganese; certainly much less than phosphorus; strengthening accompanied by only moderate reduction in plasticity at concentrations up to about 1 per cent.

Principal functions: (1) almost universally present in magnetic sheet, in which low carbon compositions it aids in regularity of crystallization and raises electrical resistivity; (2) contributes oxidation resistance in several heat-resisting compositions; (3) moderately increases hardenability in steels carrying other nongraphitizing elements; (4) increases strength in quenched and tempered steels and pearlitic steels wherein added plasticity is not sought, and (5) is a general-purpose deoxidizer.

Titanium. Maximum solubility in pure gamma iron about 0.75 per cent; in the presence of about 0.18 per cent carbon solubility in austenite increases to about 1.0 per cent.

Maximum solubility in pure alpha iron may be about 6 per cent. Falling solubility and rejection of Fe-titanide makes possible strongly precipitation-hardening ferritic iron-titanium alloys with some 7 per cent titanium.

Carbide-forming tendency greatest observed with any alloying element. Even small proportions reduce the carbon content of the austenite appreciably, and at 1.5 to 2.0 per cent titanium even 0.50 per cent carbon steels have practically no tendency to quench harden. A 1 per cent titanium, 0.2 per cent carbon alloy quenched from high temperature is martensitic and presumably reluctant to soften by tempering, but the secondary hardening effect is less than in molybdenum and tungsten steels because of the small amount of titanium and carbon dissolvable.

The contribution of titanium, as dissolved, to hardenability may be considerable but since it may only be dissolvable in minute amounts in the presence of considerable carbon, the over-all effect is generally negative. Persistent carbide particles restrict grain growth and thereby reduce hardenability.

Principal functions: (1) to withdraw carbon from solution and reduce martensitic hardness and hardenability in medium chromium steels; (2) similarly, to prevent austenite formation in high chromium steels; (3) to withdraw carbon from solution at elevated temperature in austenitic stainless steels and thereby prevent intergranular deterioration through chromium carbide formation at grain boundaries and attendant local chromium depletion. Used as deoxidizer.

Tungsten. Maximum solubility in pure gamma iron about 6 per cent; in the presence of about 0.25 per cent carbon maximum solubility in austenite is increased to about 11 per cent.

Maximum solubility in pure alpha iron about 32 per cent, falling off with decreasing temperature; Fe_3W_2 is rejected and an age-hardening system results.

Carbide-forming tendency strong, slightly more vigorous than molybdenum when present in twice the proportion by weight. Special carbide, as of molybdenum, opposes softening in tempering.

Contribution to hardenability very considerable as dissolved, small proportions relatively more effective than large additions.

Principal functions: (1) formation of hard, abrasion-resisting, permanent carbide particles in tools together with (2) development of high-temperature ("red") hardness in quenched and tempered steels. Generally similar to molybdenum.

Vanadium. Maximum solubility in pure gamma iron about 1 to 2 per cent; in the presence of about 0.2 per cent carbon, solubility in austenite is increased to about 4 per cent.

Maximum solubility in pure alpha iron infinite, although compound FeV may form at above some 30 per cent vanadium; age-hardening not described, probably similar to FeCr in the iron-chromium system.

Carbide-forming tendency very strong but less than titanium or columbium. Sufficient carbon and vanadium soluble at elevated temperature to cause maximum observed secondary hardness effects. Special carbide formation during tempering exceedingly effective. Carbide rich in vanadium appears to restrict austenitic grain growth since vanadium steels coarsen only at elevated temperature; other mechanisms possibly contribute to fineness of grain.

Contribution to hardenability very marked when dissolved even in small amount.

Principal functions: (1) elevation of coarsening temperature of austenite with advantages of fine grain, and, as partially dissolved, (2) increase in hardenability, and (3) resistance to softening in tempering amounting, in moderate concentration, to marked secondary hardness.

It will have been observed how smoothly and gradually the influences of alloying elements are altered by increasing proportions of the elements, even though some influence may pass through a maximum or minimum. It is equally obvious that these influences are rarely, if ever, exerted strictly proportionately, that is, as a linear function, even of a single element. Accordingly, simple formulae for computing behaviors or characteristics from composition are of little value except for very narrow ranges or very restricted conditions. Similarly, there is no evidence that any certain mechanical properties are abruptly brought to a sharp optimum by a certain so-called balanced composition or ratio of alloying elements. More fruitful is the concept that the alloying elements alter the properties of steel by (1) making certain structures possible or convenient, and by (2) altering moderately the properties of the structure. The composition is adjusted to meet these needs. By way of contrast, in the case of corrosion characteristics, — a matter of the chemical properties of the steel, — it is not surprising to find that certain compositions need be changed only a little to modify properties.

In the selection of an alloy steel for a specific application, it frequently happens that some particular requirement determines the type of steel. Thus, high-temperature strength or creep resistance might at once restrict the selection to a narrow range of compositions or resistance to oxidation might similarly dictate the choice. When a good combination of mechanical properties at ordinary temperature is desired the selection may often be made from a wider list. There are, too, a variety of means for securing enhanced hardenability. Economy is in considerable part influenced by machinability, depending upon the amount of machining involved. Broad principles governing selection of steels will scarcely avoid some recognition of the facts that (1) mild quenches applied to steels of high hardenability are usually more advantageous than the use of steels of minimum hardenability for which drastic quenches only are adequate, and (2) that it is difficult indeed to secure simultaneously the properties needed for easy machining and those usually sought in construction steels entering service, except insofar as an intervening heat-treatment may alter the characteristics sufficiently.