SPONTANEOUS GENERATION OF HEAT IN RECENTLY HARDENED STEEL. III.

By CHARLES F. BRUSH.

(Read April 13, 1917.)

The present paper is the third of a series under this title. In the first paper it was shown that a specimen of carbon tool steel, and also a specimen of "high-speed" tungsten-chromium steel after hardening by water quenching at a high temperature, spontaneously generated heat in appreciable quantity for at least several weeks, the rate of generation steadily diminishing. It was also shown that the carbon steel, after hardening, shrank progressively when tempered to "straw" color, to "light blue" and finally annealed. It was further shown that another specimen of high-carbon steel, after hardening, spontaneously shrank in measurable amount for many days, the rate of shrinking steadily diminishing. The plotted curve of spontaneous shrinkage was strikingly similar to a curve (not plotted) of total heat spontaneously generated in the other specimen of carbon steel, showing an apparent relationship between the two phenomena. But it was pointed out that spontaneous shrinking could not possibly be the prime cause of the spontaneous generation of heat observed because it was wholly inadequate in amount. This conclusion was afterward confirmed (second paper) in the cases of two specimens of nickel-chromium steel which, after quenching just above the temperature of decalescence, spontaneously generated heat freely but did not shrink at all.

The second paper, after reviewing the first, treated principally of two specimens of nickel-chromium steel furnished for this investigation by Sir Robert Hadfield. Each specimen consisted of twelve


PROC. AMER. PHIL. SOC., VOL. LVI, X, JULY 31, 1917.

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half-inch round bars five inches long, like in size and number those of each of the steels of the first paper, so that results obtained were quantitatively comparable with the earlier ones. Each specimen was first hardened by quenching at a temperature just above that of decalescence as indicated by almost complete loss of magnetic susceptibility.

For observing the magnetic behavior of the steel while being heated or cooled in the gas furnace employed, the bundle of bars was surrounded by a single turn of asbestos-insulated platinum wire, the ends of which were connected with a ballistic galvanometer having the usual mirror and scale. The furnace was surrounded by a large coil of heavy copper wire through which a direct electric current could be established and broken at will by means of a switch and storage battery. Before the steel bars were placed within the platinum loop inside the furnace, closure of the outer copper coil circuit caused a brief electric pulse in the loop and a "kick" in the galvanometer, giving a definite minimum deflection easily observed with considerable precision. With the steel bars inside the platinum loop the galvanometer deflection was, of course, many times greater until, with rising temperature, the decalescent point was approached; then the deflection fell rapidly to the minimum value as above, or very near it. This simple induction apparatus was found entirely reliable and satisfactory.

Each of the nickel-chromium steels exhibited good generation of heat after hardening as above.

They were again heated, to a temperature considerably above decalescence, and quenched as before. This second hardening induced a greater generation of heat than the first hardening, especially in the case of specimen B.

Specimen B was slowly heated a third time, somewhat above the temperature of complete loss of magnetic susceptibility, and allowed to cool very slowly in the furnace until complete recovery of magnetic susceptibility was attained; then it was immediately quenched. A very fair generation of heat followed this treatment. This was quite unexpected because it was thought that true hardening of the steel could not have taken place. In the absence of suitable appa-
ratus no test of hardness was at that time made. The twelve bars (specimen B) were next annealed by slowly heating to full decalescence and then allowing to cool very slowly in the furnace. As expected, no trace of heat generation followed this treatment which was made for checking purposes.

Before commencing the experiments with specimens A and B, a test bar of each lot was prepared for accurate length measurements which followed each treatment. The very interesting results of these measurements, differing materially in the two specimens, were tabulated and compared.

The present (third) paper deals with some later experiments prompted by the anomalous behavior of specimen B of the Hadfield nickel-chromium steel after its third quenching described above.

In conducting these experiments an electric furnace was employed for heating, instead of the less convenient gas furnace formerly used, and the latest form of “scleroscope” for testing hardness was installed; also, a most modern industrial thermo-electric pyrometer. The latter was used as it came from the maker, without further calibration; hence the temperatures recorded in this paper may be several degrees in error, though they are thought to be relatively consistent.

The apparatus employed in detecting, measuring and following the progress of heat generation in the steels under treatment was fully described and illustrated in each of the former papers, and it is thought best to omit another description here.

It will be recalled that “specimen B” was left in the annealed condition. In this condition it was subsequently found to have a scleroscope hardness of 31. This is the mean of many consistent measurements. Each scleroscope hardness cited in this paper is the mean of at least ten consistent measurements, each measurement made on a fresh spot of surface carefully made smooth and flat.

In order to ascertain the critical temperatures of decalescence and recalescence of “specimen B,” three of the twelve bars were very gradually heated until almost complete loss of magnetic susceptibility was reached. This occurred rather abruptly at about
777° C. One of the bars was quenched at this temperature, and its scleroscope hardness was found to be 74. This may be taken as the hardness of "specimen B" after the first quenching described in connection with the second paper.

The remaining two bars were allowed to cool very slowly in the furnace until complete recovery of magnetic susceptibility took place at about 660°. Recovery was abrupt in temperature. One of these bars was quenched at this temperature, and its hardness was found to be only 37, which is not much above annealed hardness (31). This seems to me conclusive evidence that true hardening did not take place in "specimen B" on its third quenching already described above, although good spontaneous generation of heat followed the quenching.

The three bars were again heated to complete decalescence and annealed in the furnace so as to leave all twelve bars of "specimen B" in annealed condition.

Fig. 1 is the curve sheet of "specimen B." "Galvanometer deflection" measures temperature difference, indicated thermo-electrically, between the steel under examination and a thermally equivalent quantity of water, contained separately in silvered Dewar
真空罐。两者都很常被带到相同的室温下，然后被放入热量计。55个刻度表示温度差为1°C。

温度计的正常冷却曲线在图中的右上角结束，很容易与其它曲线区分开来。这条曲线是用等重量的未处理钢制成，其温度在被放入热量计前已经高于室温。它显示出正常的失热，即由于不良热绝缘单引起的，是所有其它曲线的基础。显然，这条曲线可以进一步向右或左延伸而不会影响其有效性；而且它可以被绘制到任何其它曲线的任何一点，以方便研究其它曲线及其与本曲线的交点。为了我的便利，我已经制作了正常冷却曲线的金属模板，发现它非常有用。

当然，这只模板的底座必须始终与曲线纸的基线对齐。

“第一硬化”曲线显示了在大约777°C时，磁性导磁率完全消失后首次淬火所引起的自发热量生成。随后 scleroscope 硬度可能约为74。

第二硬化曲线(“2h”)显示出明显较大的热量生成。淬火温度和硬度未被观察到；但已知淬火温度明显高于777°C。

到目前为止讨论过的三条曲线在第二篇论文中已有说明，但未绘制。第二篇论文中已描述的此曲线的淬火温度必须稍低于660°C，硬度约为37。

“标本 B”，保持在退火状态直到接近
former experiments, with a hardness of 31, was next gradually heated to 554°, allowed to cool slowly to 532° and quenched. It was then purposely brought to a temperature slightly above room temperature and placed in the calorimeter. The progress of cooling is plotted in the curve “4q” (fourth quenching). For easy comparison the normal cooling curve is drawn as a dotted line through the first station of the 4q curve. Beyond this point the 4q curve lies everywhere below the normal cooling curve, showing conclusively that the steel cooled abnormally fast. In other words, there was spontaneous disappearance or absorption of heat in the steel, most notable during the first few hours after quenching. Hardness was 35.5.

The result of this experiment is remarkable, and was quite unlooked for. I had expected to find a small generation of heat, if anything.

The steel was next heated to 562° and quenched. The result of this treatment is shown in the curve “5q,” with its own dotted normal cooling curve. Absorption of heat is again indicated, even greater than in 4q but somewhat differently distributed. Hardness was now 34.5.

Again the steel was heated, this time to 594°, and quenched. Again there was marked absorption of heat. The curve, 6q, was almost identical with 4q, and is not plotted, to avoid confusion of lines. Hardness was again 34.5.

The seventh heating was carried to 667° for quenching. This was a much larger temperature advance than in either of the preceding experiments, and was above the temperature of the third quenching, which was followed by very considerable generation of heat. But now there was very considerable absorption of heat, as shown in curve “7q.” Hardness was now 34.

It should be noted that the quenchings which were followed by absorption of heat were made at rising temperatures which had not been exceeded (except slightly in the case of 4q) since the steel was annealed. But in the case of third quenching the quenching temperature was a falling one, reached by cooling from the much higher temperature of decalescence. I can think of no other cause than
this for the radically different results of the third and seventh quenchings, which were made at substantially the same temperature. The temperature difference between complete loss and complete recovery of magnetic susceptibility, 117°, was unusually large; but while this temperature drop brought about almost annealed softness, and full restoration of magnetic qualities, it did not very greatly affect that quality of the steel, whatever it is, which is responsible for the spontaneous generation of heat. Seemingly, one or more of the several unstable compounds or mixtures of the constituents of the steel which were formed at the upper critical temperature did not have time to wholly revert to normal annealed condition while the metal was cooling to and passing through recalescence. The time of this cooling was about half an hour.

To confirm the curious result of the third quenching, i.e., generation of heat without hardening, the bars were quenched the eighth time as follows: Slowly heated (nearly two hours) to 819°, slowly cooled (nearly one hour) to 680° and quenched. During the heating complete loss of magnetic susceptibility occurred at 779°, which was an excellent confirmation of the former finding (777°). But in cooling, full recovery of magnetic susceptibility came at 680°, which is 20° higher than before. The five intermediate treatments

RÉSUMÉ OF SPECIMEN B.

Temperature of complete loss of magnetic susceptibility, 777° C.
Temperature of complete recovery of magnetic susceptibility, 660/680.

<table>
<thead>
<tr>
<th>Quenching Temp.</th>
<th>Hardness</th>
<th>Remarks</th>
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</thead>
<tbody>
<tr>
<td>First hardening . . .</td>
<td>About 777° C.</td>
<td>74</td>
</tr>
<tr>
<td>Second &quot; . . .</td>
<td>Much higher temp.</td>
<td>—</td>
</tr>
<tr>
<td>Third quenching . . .</td>
<td>About 780°/660°</td>
<td>37</td>
</tr>
<tr>
<td>Annealing . . .</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Fourth quenching . . .</td>
<td>554°/532°</td>
<td>35.5</td>
</tr>
<tr>
<td>Fifth &quot; . . .</td>
<td>562</td>
<td>34.5</td>
</tr>
<tr>
<td>Sixth &quot; . . .</td>
<td>594</td>
<td>34.5</td>
</tr>
<tr>
<td>Seventh &quot; . . .</td>
<td>667</td>
<td>34</td>
</tr>
<tr>
<td>Eighth &quot; . . .</td>
<td>819°/680°</td>
<td>47</td>
</tr>
</tbody>
</table>

may, perhaps, account for this. And this higher quenching temperature may account for the somewhat greater hardness produced, which was later found to be 47, as against 37 for the third quenching (74 for true hardening above decalescent temperature).
Following the eighth quenching there was good *generation of heat*, better than after third quenching, but differently distributed in time—not so rapid at first, but much better sustained (curve not plotted). This appears to confirm the third experiment.

I cannot, thus far, offer any promising explanation of the absorption of heat in the fourth, fifth, sixth and seventh experiments.

It may be seen that absorption was rapid during the first few hours, and nearly (not quite) ceased at the end of 50 or 60 hours; while generation was well marked up to 150 hours. In earlier experiments generation of heat was easily detected at the end of a month.

As it seemed desirable to learn whether plain carbon steel would show, like the nickel-chromium steel, generation of heat without hardening, or absorption of heat when quenched at rising tempera-

![Graph](attachment:image)

**Fig. 2.**

The normal cooling curve and upper curve of heat generation shown in Fig. 2 are taken from that paper.

Following is a résumé of the early and recent experiments with the carbon steel:

<table>
<thead>
<tr>
<th>Analysis of Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
</tr>
<tr>
<td>Sulphur</td>
</tr>
<tr>
<td>Silicon</td>
</tr>
<tr>
<td>Manganese</td>
</tr>
<tr>
<td>Carbon</td>
</tr>
</tbody>
</table>

Galvanometer Deflection in Scale Divisions

Hours After Hardening
First (Original) Hardening.—Quenched at very high temperature. Temperature and hardness not then observed. Large generation of heat, as shown in upper curve of Fig. 2. Scleroscope hardness, recently observed, 79.

Second (Recent) Hardening.—Quenched at 802°, considerably above decalescence, but much lower than in first hardening. Complete loss of magnetic susceptibility occurred at 765°. Good generation of heat, but very much less than in first, as shown by the lower curve of Fig. 2. For convenient comparison with this curve the normal cooling curve is shown as a dotted line appropriately located. Hardness was now 73.

Third Quenching.—Heated to 815°, somewhat above preceding quenching temperature, allowed to cool slowly to 720° and quenched. This was a little below the temperature of complete recovery of magnetic susceptibility, which had occurred at 729°. Hardness was now only 28.5, and there was no generation of heat. (The nickel-chromium steel had shown good generation of heat under similar circumstances.) Note the small temperature difference, 36°, between complete loss and complete recovery of magnetic susceptibility. Annealed by heating to 822°, to obliterate previous quenching effects, and cooling slowly in furnace. Hardness was now 25.5.

Fourth Quenching.—Heated slowly, from annealed condition, to 633° (considerably below the lower critical temperature) and quenched. Hardness was again 28.5, and there was no trace of absorption of heat. (The nickel-chromium steel had shown good absorption of heat under similar circumstances.)

Fifth Quenching.—Heated slowly to 732°, just above the temperature of complete recovery of magnetic susceptibility, and quenched. No generation or absorption of heat, nor change in hardness (28.5).

Clearly, the carbon steel showed none of the excentricities of the nickel-chromium steel when quenched below the hardening temperature. But when quenched a little above, as well as far beyond this temperature, they behaved very much alike.

While considering plain carbon steel, I thought it worth while to observe heat generation in some steel (or white cast iron) very high in combined carbon, and very pure otherwise, which I happened
to have in my laboratory. Fig. 3 shows the composition of this metal, which is hard and very brittle. The carbon is all combined, and remains so after heating and quenching.

An induction experiment with a large lump of the metal showed:

Temperature of complete loss of magnetic susceptibility $757^\circ$.

![Graph showing magnetic susceptibility over time]

Temperature of complete recovery of magnetic susceptibility $704^\circ$:

Slowly heated many fragments, aggregating in weight that of the usual twelve bars of steel, to $906^\circ$ and quenched.

Very moderate generation of heat followed the quenching, as shown in Fig. 3, and it was much less persistent than usual, as indicated by its small value at the end of 150 hours. Hardness was 76.

The behavior of this specimen of steel, or white cast iron, was not thought sufficiently encouraging to warrant further experiments with it.

For a general check on the performance of the apparatus, twelve half inch round bars of Swedish charcoal iron, of the aggregate weight of the steel usually employed, were slowly heated to $960^\circ$ and quenched. Complete loss of magnetic susceptibility had occurred at $801^\circ$. The bars were warmed about three degrees just before being placed in the calorimeter.

There was no trace of heat generation following the quenching. Indeed, the curve of cooling followed the normal cooling curve with such fidelity that nowhere did they differ as much as the width of
the curve line. This was very gratifying in view of the fact that observations for the normal cooling curve were made more than two years ago, and checked only once since that time.

Hardness was 18.5.

Again heated above decalescence and annealed by cooling in the furnace.

Hardness remained 18.5, showing that the previous heating and quenching had no effect whatever on the hardness of this, presumably, very pure iron.

Spontaneous generation and absorption of heat in recently quenched nickel-chromium steel, would be a better descriptive title for the present paper; but the subject matter is so intimately related to that of the former papers, that it is thought best to retain the former title for the sake of continuity.

In conclusion, I can only express the hope that contemplated experiments, on somewhat different lines, may throw more light on these interesting phenomena.

Cleveland, O.,
April, 1917.