Temper Brittleness—An Interpretive Review


ABSTRACTS: The history of the problem of temper brittleness is surveyed; the reviews of Hollomon, Woodfine, and Low are reexamined in the light of recent developments, and the work carried out since 1959 is reviewed. Included in the latter is a model which has been proposed to explain the phenomenon. The problem of “500 F embrittlement” and its connection with temper brittleness are discussed, and a rudimentary model is proposed. Suggested directions for future research are indicated.

KEY WORDS: temper embrittlement, mechanical properties, steel, metallography, evaluation, history

The problem of temper brittleness of alloy steels has been with us for more than seven decades, and the study of it now appears to be entering the most sophisticated and, hopefully, final stage. It is therefore appropriate to examine the history of the problem, as well as its later development, so that the early work can be interpreted in the light of more recent knowledge. To this end an attempt is made to review all of the major advances that have been made in the study of temper brittleness. The task is made easier by the general reviews of Hollomon [1] in 1946 and Woodfine [2] in 1953, and the recent review by Low [3] in 1959.

Early History of the Problem

Temper brittleness, one of the classical problems of physical metallurgy, refers to the decrease in notch toughness which often occurs in alloy steels when heated in, or cooled slowly through, the temperature range about 375 to 575 C. The term was coined by Dickenson [4] in 1917, but the phenomenon was recognized at least several decades

2 The italic numbers in brackets refer to the list of references appended to this paper. Actually, the upward shift of the ductile-brittle transition temperature.
before that. The problem became critical in the period around World War I with the widespread use of alloy steels in thick sections for armor and ordnance.

Significant progress in understanding and combating the problem was made in the period 1917 to 1925, particularly in England. Brearley [7] had recognized by 1917 that the decreases in toughness resulting both from slowly cooling through, and tempering (or retempering) in, the critical temperature range were related phenomena. In 1919 Greaves [8] reported several now-well-known characteristics:

1. Steels of apparently similar compositions could exhibit wide variations of susceptibility under the same conditions of heat treatment.

2. Notch toughness decreased as austenitizing temperature increased.

3. Reheating in the temperature region around 500°C always resulted in embrittlement, regardless of the subsequent cooling rate.

4. An initially tough steel could be embrittled by reheating in, or slowly cooling through, the critical range, while an embrittled steel could be made tough by reheating above 600°C and rapidly cooling, that is, embrittlement was reversible.

Howe [5] noted in 1919 that blacksmiths realized as early as 1883 that it was often necessary to water quench after tempering above 600°C to avoid the brittleness that resulted from slow cooling. They called the treatment "water annealing."

Krupp armor steels became notorious for brittle failures under impact, so much so that the early name for temper brittleness was "Krupp krankheit." Krupp patents issued in 1900 prescribe a water quench after tempering of nickel-chromium steels as a remedy for this "sickness." [6] This, of course, was not practicable for thick sections.

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**FIG. 1—** Schematic impact curves showing shift due to temper brittleness and dependence of susceptibility ratio, \( SR \), on test temperature. If test temperature were \( T_1 \) or \( T_2 \), \( SR \) would be small, indicating nonsusceptibility; if test temperature were \( T_3 \), \( SR \) would be large.
Later work by Greaves and Jones [9] revealed in 1920 that the degree of embrittlement increased with time in the critical region, and in 1925 they reported that, while manganese and chromium increased the embrittlement susceptibility in the presence of phosphorus in a nickel steel, the problem could be reduced and often eliminated by additions of molybdenum [10]. This latter discovery was viewed as a practical remedy for the problem, and intensity of research slackened for some time.

The standard test to determine a steel's susceptibility to temper brittleness was to compare the fracture energies of two specimens in a notched-bar impact test at room temperature. Both specimens were oil-hardened from 900 C and tempered for 2 h at 650 C; one specimen was then water quenched, while the other was slowly cooled (0.3 C/min between 600 and 400 C). The fracture energy of the quenched specimen divided by that of the slowly cooled specimen was called the susceptibility ratio.

Virtually all work prior to 1944 utilized this susceptibility ratio test. This was unfortunate, because the test is actually of little value as a quantitative measure of embrittlement susceptibility, and its use probably contributed significantly to the lack of progress in understanding the mechanisms of the phenomenon. Jolivet and Vidal [11] showed in 1944 that the fundamental characteristic of temper brittleness was the shift of the ductile-brittle transition curve to higher temperatures, and that the use of the susceptibility ratio could be quite misleading, as illustrated in Fig. 1. Hence, it was necessary to establish the fracture transition curves by tests over a range of temperatures before a meaningful measure of embrittlement could be obtained. This same conclusion was reached independently by Hollomon [1].

Status of the Problem in 1946—Hollomon's Review

Hollomon recognized that the earlier work based on measurements of susceptibility ratio had to be interpreted with caution; however, some
fairly well-founded conclusions had been drawn. In addition to those of Greaves and Jones, already mentioned above, it appeared that plain carbon steel with less than 0.6 to 0.7 per cent manganese was not susceptible. Whether molybdenum actually eliminated all or part of the embrittlement susceptibility, or whether it merely delayed the attainment of full embrittlement, was still unclear. There was unanimous agreement by that time that fracture of embrittled steel occurred mainly along prior austenitic grain boundaries. This had been accepted by many since the turn of the century; however, debate continued on this point as late as 1920 [9].

Hollomon [1] replotted the data of Greaves and Jones [9] to show the apparent C-curve nature of the embrittlement behavior (Fig. 2). In view of the similarity between this and many phase transformations, he concluded that temper brittleness is caused by a precipitation from alpha iron, which occurs preferentially at prior austenitic grain boundaries. The precipitate was assumed to be soluble above about 600 C, and the rate of (diffusion controlled) precipitation was a maximum at about 500 C. The nature of the precipitate was a mystery; oxides, phosphides, carbides, and nitrides had been suggested [1]. Hollomon tentatively favored nitrides and suggested that alloying elements acted by changing the nitrogen solubility in ferrite.

**Status of the Problem in 1953—Woodfine's Review**

An important benchmark in the history of this problem is the astute critical review published by Woodfine in 1953 [2]. It is still essential reading for anyone with serious interest in temper brittleness. Without hoping to do it justice, its main conclusions are summarized here.

**Testing Methods**

After reviewing many attempts at detecting the presence of temper brittleness by the measurement of other mechanical and physical properties, Woodfine concluded that the notched-bar impact test was still the only reliable method. The importance of using the shift in transition temperature as the criterion was re-emphasized. It was noted that in some extreme cases temper embrittlement could be detected in tension tests by a drop-off in reduction of area values and deviations from cup-and-cone fracture, but these indications were usually not very dramatic.

**Metallographic Tests**

It had been discovered by Cohen et al [12] that grain boundaries in an embrittled steel could be revealed by etching with an ethereal picric

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6 It will be shown later that the temper brittleness C-curve is due to a set of phenomena different from those of a nucleation-and-growth type of phase transformation. The term, "C-curve," is used here in conformity with past references, but is not meant to imply its more common meaning.
FIG. 3—(left) Results of Vidal [16] for a chromium steel (0.25 per cent carbon, 0.030 per cent manganese, 1.38 per cent chromium, 0.044 per cent phosphorus) originally quenched and tempered at 650 °C. Transition temperature, determined by arbitrary fracture energy, versus time of embrittlement at various temperatures. (right) Same replotted to show rough C-curve behavior; rise in transition temperature indicated on each curve in deg C.

FIG. 4—Isoembrittlement curves of Jaffe and Buffum [17] plotted as a time-temperature diagram, for a Ni-Cr steel (0.39 per cent carbon, 0.79 per cent manganese, 0.77 per cent chromium, 1.26 per cent nickel, 0.015 per cent phosphorus), incorporating later correction [18].

acid solution containing Zephiran chloride. Later McLean and Northcott [13] showed that other solutions based on picric acid gave similar results; in particular, aqueous picric acid seemed to work almost as well as a common germicide, one of several surface-active agents which enhances the action of picric acid etches.
as any, and it was the easiest to prepare. These etchants were found to differentiate between the embrittled and tough conditions of steels containing phosphorus. The main attack appeared to occur along prior austenite grain boundaries, although ferrite boundaries within the prior austenite grains were sometimes revealed. Woodfine showed in a succeeding paper [14] that etching produced grooves along austenitic and ferritic boundaries, as if due to segregated impurities, but no precipitate was revealed.

Woodfine noted that temper brittleness, per se, was often confused with other forms of loss of toughness after quenching, and that this only helped to obscure the real nature of temper brittleness. He suggested that the term be applied only to the phenomenon originally observed in nickel-chromium steels and that such effects as “500 F embrittlement” and the rise in transition temperature due to simple structural coarsening at high temperatures be excluded.

Effects of Time and Temperature

The ‘C-curve’ nature of temper embrittlement had been confirmed by the work of Vidal [16] (Fig. 3) and Jaffe and Buffum [17] (Fig. 4). Both the rate of embrittlement and the maximum temperature at which embrittlement can occur are expected to vary somewhat with the composition of the steel. For example, Jaffe and Buffum’s results for their nickel-chromium steel (Fig. 4) show that initial embrittlement is most rapid at about 550 C, whereas at a later stage the rate is greatest at about 500 C. Vidal’s results for a 1.4 per cent chromium steel, although less extensive, show that the rate is greatest initially at 575 C and later at 525 C (Fig. 3).

Data on the maximum temperature at which temper embrittlement can occur are less clear, since in most of the steels studied, tempering at high temperatures led to coarsening of the ferrite grain size and agglomeration of carbides, with a concomitant rise in transition temperature. This “embrittlement” was often confused with temper embrittlement, and the practice of checking the fracture appearance to see whether intergranular fracture was actually present was not yet universally adopted. Hence, the conclusion by Jaffe and Buffum [17] that embrittlement could occur in their nickel-chromium steel up to the A1 line can be questioned; however, they do seem to make a case for some embrittlement occurring up to 650 C. Cohen et al [12] showed that the Zephiran chloride etch produced slight grain boundary attack in a steel tempered at 630 C, which might have indicated embrittlement; however, they did not present any transition temperature evidence to support this.

They do not work on susceptible steels which do not contain phosphorus (J. R. Low, Jr., private communication).
Several workers have observed “overaging effects” in which the amount of embrittlement passes through a maximum at higher temperatures (see Fig. 3). These observations are summarized in Table 1. (Some of these data appeared just subsequent to Woodfine’s review but are included for completeness.) It still does not seem possible to reach any conclusions about the influences of various alloying elements; however, Preece and Carter [19] did conclude that in their phosphorus-containing high-purity steels the overaging effect was enhanced by the presence of chromium.

### TABLE 1—Summary of “overaging” observations.

<table>
<thead>
<tr>
<th>Composition of Steel</th>
<th>Temperature at Which Overaging Observed, deg C</th>
<th>Tempering Time at Maximum, h</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 0.25 Mn 0.30 Ni 1.38 Cr 0.044 P 0.30</td>
<td>575</td>
<td>1</td>
<td>Vidal [16]</td>
</tr>
<tr>
<td>C 0.39 Mn 0.77 Ni 0.015 Cr 0.30 P 0.01</td>
<td>550</td>
<td>~48</td>
<td>Jaffe and Buffum [17]</td>
</tr>
<tr>
<td>C 0.33 Mn 2.92 Ni 0.87 Cr 0.037 P 0.27</td>
<td>550</td>
<td>8</td>
<td>Woodfine [14]</td>
</tr>
<tr>
<td>C 0.21 &lt;0.01 Mn 2.40 Ni 0.044 Cr 0.01 P 0.1</td>
<td>525</td>
<td>~48</td>
<td>Preece and Carter [19]</td>
</tr>
<tr>
<td>C 0.19 Mn 1.36 Ni 0.01 Cr 0.048 P 0.1</td>
<td>600</td>
<td>10</td>
<td>Preece and Carter [19]</td>
</tr>
<tr>
<td>C 0.19 Mn 0.99 Ni 0.1 Cr 0.053 P 0.1</td>
<td>600</td>
<td>&lt;10</td>
<td>Preece and Carter [19]</td>
</tr>
<tr>
<td>C 0.19 Mn 3.2 Ni 2.13 Cr 0.058 P 0.05</td>
<td>500</td>
<td>168</td>
<td>Preece and Carter [19]</td>
</tr>
<tr>
<td>C 525 Mn &lt;48 Ni 550 Cr &lt;48 P 575</td>
<td>48</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>C 575 Mn &lt;48 Ni 600 Cr &lt;48 P 600</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 600 Mn &lt;48 Ni 600 Cr &lt;48 P 600</td>
<td>48</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Effect of Composition**

At the time of Woodfine’s review, knowledge of the effects of various elements on the susceptibility to temper brittleness was still quite incomplete; the work of Steven and Balajiva [20], which finally identified the impurities responsible for the problem, was not to appear until 1959. In fact, the effects of the various alloying elements are still being unravelled at the present time. Nevertheless, certain aspects had become clear by that time, and these will be summarized at this point.
Plain Carbon Steels

A consensus had been reached, based mainly on the work of Greaves and Jones [10] and Hollomon [1], that plain carbon steels containing less than 0.5 per cent manganese are not susceptible. This view was challenged by Jaffe and Buffum [21] and by Libsch et al [15], who took the position that embrittlement occurs so rapidly in plain carbon steels that it cannot be prevented by quenching. The "plain carbon steel" used by Jaffe and Buffum actually contained 0.8 per cent manganese, and it is now fairly clear that this is enough (with the 0.013 per cent phosphorus also present) to produce the slight embrittlement observed (see Fig. 6). Entwisle and Smith [22] later showed that a 0.4 per cent carbon, 0.65 per cent manganese steel of unspecified purity treated at 480 C for 24 h showed only about 5 per cent intergranular fracture, and thus was not susceptible to temper brittleness in the usual sense of the term. Woodfine carefully reviewed the paper by Libsch et al [15] and was able to show that their "embrittlement" was due to structural coarsening and could be correlated with the decrease in hardness during tempering. Since the embrittlement kinetics did not match those of temper embrittlement, and no evidence could be found of their grain boundary attack by the Zephiran chloride etch or intergranular fracture, it was concluded that their results had nothing to do with temper brittleness. Thus, the original conclusion about plain carbon steels remained intact.

Carbon

Jolivet and Vidal [11] showed that a reduction of carbon content from 0.22 to 0.73 per cent in a chromium steel led to a reduction in embrittlement. Buffum et al [23] later reported that a high-purity alloy containing 0.003 per cent carbon, 0.0004 per cent nitrogen, 0.8 per cent manganese, 1.5 per cent nickel, and 0.6 per cent chromium was not susceptible to temper embrittlement, and they concluded that carbon or nitrogen, or both are necessary for temper brittleness.

Nickel, Chromium, and Manganese

There was wide agreement that increasing amounts of any of these elements led to increased embrittlement; however, there was conflicting evidence as to whether plain nickel steels were susceptible [10,13,24].

Molybdenum

It was accepted that additions of up to 0.5 per cent either decreased or eliminated embrittlement [10,11], whereas larger amounts permitted embrittlement to occur [16].

*In the light of more recent developments which will be discussed later, this conclusion is no longer acceptable. What Buffum et al probably succeeded in doing was to make a steel which was pure enough that it did not contain sufficient levels of the specific impurities that lead to embrittlement.
Vanadium and Tungsten

The addition of 0.23 per cent vanadium to a chromium steel was reported to enhance embrittlement [11] and a 3.8 per cent tungsten steel with no chromium and low manganese was found to be susceptible [16].

Phosphorus

It was generally recognized that temper brittleness increased with phosphorus content, but it was also known that it could be observed at phosphorus levels as low as 0.008 per cent [11]. Virtually every published study of temper brittleness listed the phosphorus content in the composition tables.

Antimony and Arsenic

Although Jolivet and Vidal [11] showed that antimony produced severe embrittlement in a chromium steel, Woodfine, for some unknown reason, was unwilling to regard this as genuine temper embrittlement [2]. However, just after his review Austen et al [25] showed that both antimony and arsenic produced embrittlement in a nickel-chromium (Ni-Cr) steel, and that the effect of antimony was so strong that it could be detected in a low-temperature tension test.\(^\text{10}\)

The information available about other elements, such as oxygen, sulfur, silicon, nitrogen, aluminum, boron, titanium, and zirconium was sketchy; they did not appear to be strongly involved in temper embrittlement.

It should be reemphasized that the work reviewed up to this point had been carried out before the identity of the embrittling agents was documented. Hence, it is often not possible to know which elements were acting in each case, or whether differences in embrittling tendency attributed to various alloying elements were not sometimes due to different, but unmeasured, levels of the embrittling elements. Therefore, many of the conclusions up to this point about various alloying elements are open to question.

Effect of Microstructure

It was well known that an increase in the austenite grain size led to increasing severity of embrittlement. This is not surprising, since fracture of temper brittle steels occurs mainly along prior austenitic grain boundaries. There was ample evidence that pearlitic and bainitic steels could be embrittled in the same manner as tempered martensitic structures. The degree of embrittlement was thought to be less severe in these former cases, although quantitative evidence was lacking. Woodfine [14]

Unfortunately, their steels also contained 200 to 300-ppm phosphorus, and this effect must have been superimposed upon those of arsenic and antimony.
later compared the temper brittleness developed in all three microstructures in a 0.33 per cent carbon, 0.6 per cent manganese, 2.9 per cent nickel, 0.9 per cent chromium, 0.04 per cent phosphorus steel. The results are shown in Table 2; they indicate that embrittlement is most severe in tempered martensite and least severe in pearlite, when measured by the shift in transition temperature. (Note, however, that the embrittled-state transition temperatures are roughly equal for all three structures.)

**TABLE 2—Development of temper brittleness in different microstructures in a Ni-Cr steel (after Woodfine [14]).**

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Treatment</th>
<th>Transition Temperature, deg C</th>
<th>Embrittlement, deg C</th>
<th>Vickers Hardness, 50 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pearlite</td>
<td>austenize 900 C, transition 620 C temper at 650 C, $\frac{1}{2}$ h same plus embrittlement at 500 C, 32 h</td>
<td>+70</td>
<td>214</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+121</td>
<td>51</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>Bainite</td>
<td>austenize 900 C, transition 350 C temper at 650 C, $\frac{1}{2}$ h same plus embrittlement at 500 C, 32 h</td>
<td>+53</td>
<td>257</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+162</td>
<td>109</td>
<td>253</td>
<td></td>
</tr>
<tr>
<td>Martensite</td>
<td>austenize 900 C, oil quench, temper at 650 C, 1 h same plus embrittlement at 500 C, 32 h</td>
<td>−59</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+137</td>
<td>196</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>Martensite</td>
<td>austenize 900 C, oil quench temper at 650 C, 50 h same plus embrittlement at 500 C, 32 h</td>
<td>−52</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+56</td>
<td>108</td>
<td>220</td>
<td></td>
</tr>
</tbody>
</table>

**Effects of Prolonged Tempering Above Embrittling Range and of Double Tempering**

A significant result of two separate investigations was that prolonged tempering at high temperatures reduces the amount of embrittlement which subsequently occurs during tempering in the embrittling range. Woodfine [14] showed that an increase in tempering time at 650 C from 1 to 50 h decreased the embrittlement obtained at 500 C by almost one half. This is shown in Table 2. He also found that a double temper of 128 h at 575 C, then 2 h at 500 C, gave less embrittlement than observed after only 2 h at 500 C. This same type of effect was shown to occur in arsenical steels by Austen et al [25], and more recently by Keh in a phosphorus-containing 5140 steel. Woodfine [14] also showed that double tempering treatments of 8 h at 500 C, then 8 h at 550 C and
vice versa, gave degrees of embrittlement characteristic of the last treatment. (Both these sets of observations can be rationalized in terms of an equilibrium segregation of impurities to grain boundaries, which is reversible and which is inversely proportional to temperature. This will be discussed more fully later.)

Status of the Problem in 1959—Low's Review

The next review of the problem of temper brittleness was that of Low [3] in 1959; it concentrated mainly on the work reported since Woodfine's review. That work will be summarized in this section, with some differences in interpretation in the light of more recent work.

FIG. 5—Data of Steven and Balajiva [20] plotted in manner of Low [3] to show amount of embrittlement produced by various elements for an arbitrary embrittling treatment of 168 h at 450°C. Base steel was 0.2 to 0.3 per cent carbon, 3 per cent nickel, 0.8 per cent chromium.

Composition

Perhaps the most important single advance toward the understanding of temper brittleness came from the Mond Nickel Co. laboratories between 1956 and 1958. First, Balajiva et al [26] demonstrated that it was possible to make a steel consisting of 0.3 per cent carbon, 3.0 per cent nickel, and 0.75 per cent chromium under high-purity conditions that was not susceptible to temper brittleness, whereas a commercial steel of the same carbon, nickel, and chromium contents was susceptible. Later, Steven and Balajiva [20] determined the effects of specific elements added to the same high-purity alloy, one at a time. They found that the elements primarily responsible for temper brittleness are antimony, phosphorus, tin, and arsenic, and that manganese and silicon were also effective, but to a lesser degree. These results are summarized in
TABLE 3—Influence of minor elements on temper embrittlement according to Steven and Balajiva [20].

<table>
<thead>
<tr>
<th>Elements Which Can Cause Embrittlement</th>
<th>Elements Which Do Not Cause Embrittlement When Present Singly</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>Maximum Amount Added in Study, weight %</strong></td>
</tr>
<tr>
<td>Sb</td>
<td>0.05</td>
</tr>
<tr>
<td>P</td>
<td>0.04</td>
</tr>
<tr>
<td>Sn</td>
<td>0.11</td>
</tr>
<tr>
<td>As</td>
<td>0.23</td>
</tr>
<tr>
<td>Si</td>
<td>0.74</td>
</tr>
<tr>
<td>Mn</td>
<td>1.5</td>
</tr>
<tr>
<td>Bi</td>
<td>0.002</td>
</tr>
<tr>
<td>Co</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu</td>
<td>0.22</td>
</tr>
<tr>
<td>Ge</td>
<td>0.01</td>
</tr>
<tr>
<td>Ga</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>0.05</td>
</tr>
<tr>
<td>N</td>
<td>0.019</td>
</tr>
</tbody>
</table>

FIG. 6—Embrittlement data for Cr-C-P steels (solid points) and Mn-C-P steels (open points) showing enhancement of phosphorus effect by chromium and manganese from Preece and Carter [19] and Low et al [27]. All points for 0.1 per cent carbon except as indicated, and embrittlement for 670 h at 500 C except for those marked by * (670 h at 450 C) and † (step cooled).
Table 3. The relative effects of the embrittling elements are plotted in Fig. 5. It can be seen that the effects of manganese and silicon are of much lower magnitude than the other four elements. Indeed, it will be suggested later that these two should be discussed separately and that they might act in a different manner from the others.

With regard to the four main embrittling elements, it should be noted that the intensity of their effects might be significantly modified in steels of different compositions. In fact, recent work by Low et al [27] has shown that this is so. Also, much of the data of Fig. 5 is for very low concentrations where analytical techniques are perhaps susceptible to further improvement; thus, the exact shape of the curves shown should not be taken as the final word on the subject. In particular, the curve for tin seems a bit strange, and the intensity of the effect of antimony seems incredibly large.

Aside from the work of Steven and Balajiva [20], one of the few studies of temper brittleness carried out on high-purity steels (and thus amenable to unambiguous interpretation) was the work of Preece and Carter [19] which appeared in 1953. Their data enable one to get some understanding of the effects of alloying elements on the intensity of embrittlement by phosphorus. For example, Fig. 6 shows the effect of chromium; it can be seen that at low chromium contents (<0.6 per cent) even large amounts of phosphorus (about 0.1 per cent) are not too potent, whereas at higher chromium contents (>1.5 per cent) even small amounts of phosphorus (about 0.01 per cent) give large effects. What the effect of chromium is on the other three embrittling elements is not so clear; however, Preece and Carter did show that a 2.3 per cent chromium, 0.2 per cent carbon, 0.06 per cent arsenic steel had a $\Delta\theta$ of 64 C (where $\Delta\theta = \theta_E - \theta_{EB}$; $\theta_E$ is the transition temperature after embrittlement and $\theta_{EB}$ is that before). This would mean that, on a weight per cent basis, arsenic has about two thirds the embrittling strength of phosphorus, which agrees qualitatively with the findings of Steven and Balajiva [20] for a 3 per cent nickel, 0.8 per cent chromium steel. Finally, it is worth noting that Preece and Carter found that the Zephiran chloride etch indicated the presence of embrittlement only in steels which contained chromium.

Also shown on the plot in Fig. 6 are three points for plain manganese steels; they demonstrate that manganese is roughly twice as strong as chromium as an enhancer of the phosphorus effect. Some idea of the power of manganese can be seen from the fact that in a 2 per cent manganese, 0.2 per cent carbon steel with impurity contents of less than 0.001 per cent phosphorus, 0.02 per cent tin, 0.005 per cent antimony and 0.002 per cent arsenic, an embrittling treatment of 670 h at 500 C still produced a $\Delta\theta$ of 45 C. This can be compared with the 2.3 per cent chromium, 0.2 per cent carbon steel with less than 0.001 per cent phos-
phorus, 0.005 per cent antimony, and 0.002 per cent arsenic which showed a Δθ of only 20 C after the same treatment.

As noted earlier, there had been some controversy over whether a plain nickel steel will embrittle. The data in Table 4 show that it will, if both the phosphorus and nickel contents are high enough. It is obviously much less effective than chromium or manganese. It has been shown recently that plain nickel steels containing antimony, arsenic, and tin in the range 0.046 to 0.080 per cent are also susceptible [27].

Preece and Carter [19] also obtained some information on the effects

<table>
<thead>
<tr>
<th>Composition, weight %</th>
<th>Ni</th>
<th>Cr</th>
<th>Mn</th>
<th>Δθ</th>
<th>Embrittlement Treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni C P</td>
<td>4</td>
<td>0.20</td>
<td>&lt;0.001</td>
<td>0</td>
<td>670 h, 500 C</td>
<td>Preece and Carter [19]</td>
</tr>
<tr>
<td>1.7</td>
<td>0.17</td>
<td>0.048</td>
<td>0</td>
<td>144 h, 500 C</td>
<td>Preece and Carter [19]</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>0.19</td>
<td>0.119</td>
<td>51</td>
<td>670 h, 500 C</td>
<td>Preece and Carter [19]</td>
<td></td>
</tr>
<tr>
<td>2.94</td>
<td>0.27</td>
<td>0.134</td>
<td>84</td>
<td>24 h, 500 C</td>
<td>Woodfine [14]</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>0.35</td>
<td>0.054</td>
<td>41</td>
<td>step-cooled</td>
<td>Low et al [27]</td>
<td></td>
</tr>
</tbody>
</table>

* Also contained 0.1 per cent chromium—probably not significant.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ni</th>
<th>Cr</th>
<th>Mn</th>
<th>Δθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Cr Mn</td>
<td>0.1</td>
<td>2.3</td>
<td>1.0</td>
<td>228</td>
</tr>
<tr>
<td>3.0</td>
<td>1.6</td>
<td>166</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>0.1</td>
<td>132</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* After 670 h at 450 C.

TABLE 5—Some effects of nickel, chromium, manganese combinations in a 0.2 per cent carbon, 0.05 per cent phosphorus steel.

of combinations of alloying elements. This is given in Table 5, which shows that the combination of 1 per cent manganese and 2 per cent chromium is much worse than 1 per cent manganese plus 3 per cent nickel, which in turn is somewhat worse than 3 per cent nickel plus 2 per cent chromium. This is in line with the previous conclusion that the embrittlement-enhancing power decreases in the order: manganese, chromium, nickel.

With regard to the importance of carbon, Preece and Carter showed that lowering the carbon content to 0.014 per cent in a 1.4 per cent chromium, 0.04 per cent phosphorus steel decreased, but did not remove, the susceptibility to temper brittleness; the Δθ was still in excess of 35 C. They also decarburized some of their alloys to carbon levels of about 0.003 per cent. In all cases the "unembrittled" transition tem-
temperatures were raised by about 100 °C, probably due to the oxygen embrittlement which is common in low-carbon ferrite. The results of the "embrittling" treatments were erratic; in some cases the transition temperature increased as if embrittlement had occurred, and in other cases the transition temperature decreased, as if the aging treatment at 500 °C were enough to permit carbon to return to grain boundary sites to counteract the oxygen [28,29]. In any case, their conclusion that temper embrittlement could not occur without carbon was questionable; it has since been shown to be incorrect by Low et al [27]. Preece and Carter did confirm, however, the fact that plain carbon phosphorus-bearing (0.13 per cent carbon, 0.03 per cent phosphorus) steels are not susceptible to temper brittleness.

The work of Powers [30,31] in the mid-1950's affords the most extensive information on the effects of the strong carbide formers: molybdenum, tungsten, and vanadium. These results must be interpreted with

![Diagram](image-url)

FIG. 7—(a) Powers' plot showing effect of molybdenum on development of temper brittleness in 0.24 per cent carbon, 0.95 per cent chromium, 0.98 per cent manganese steel [30]. (b) Same plot modified to show actual transition temperatures.
great caution, however, since they contain no information on the levels of the embrittling elements: phosphorus, antimony, tin, and arsenic. Thus, some of the differences in $\Delta\theta$ attributed to variations in the alloy content may have arisen from differences in embrittling element content.

Powers [30] found that small amounts of both molybdenum and tungsten retard embrittlement produced by step cooling (see below), and that large amounts enhance it. Vanadium appears to enhance it in all amounts [31]. Molybdenum and tungsten seem to have roughly the same effectiveness on an atomic per cent basis, and the optimum addition appears to be three-fourths weight per cent molybdenum. There seems to be some benefit in adding combinations of molybdenum and tungsten or vanadium; however, these conclusions should be rechecked with high-purity steels.

In this regard one other point is worth mentioning. It is not settled whether such results should be evaluated as plotted in Fig. 7a, after Powers, or according to the slightly modified plot of Fig. 7b. That is, should one be most concerned with amount of embrittlement, that is, with $\Delta\theta$, or with the magnitude of the embrittled-state transition temperature? The point is that the lowering of unembrittled transition temperatures can more than compensate for an increase in $\Delta\theta$. The

---

**Figure 8**—Result of Hopkins and Tipler [32,33] showing fracture stress at 77 K of two low-carbon iron alloys water quenched from various temperatures (solid lines). Superimposed on these plots are data of Vidal [16] showing degree of embrittlement in a chromium steel in 24 h at different tempering temperatures.
probable reason for this is that some embrittlement by impurity segregation can occur during the standard tempering treatment in the 625 to 675°C range (that is, before the embrittlement treatment is carried out). This has been indicated by intergranular fractures and response to the Zephiran chloride etch for some steels in the unembrittled condition. Additions of molybdenum may decrease this effect, thus lowering the curves in Fig. 7 and producing the apparent paradox of high susceptibility and low (embrittled) transition temperature. It is probable that

![Graph](image)

**FIG. 9—Results of Powers [31] plotted according to Low [3] showing reversal of temper embrittlement by short time heating above the embrittling range for two different temperatures.**

the data shown in Figs. 7a and b could be better understood if one could know the impurity contents of each heat.

While on the subject of composition it would be well to clarify an ambiguity which has arisen in the literature. Hopkins [32] has suggested that the embrittlement phenomena observed by Hopkins and Tipler in low-carbon iron-nitrogen [33] and iron-phosphorus alloys [34] is an extreme manifestation of temper brittleness. There are several reasons to suspect that these observations have little to do with temper brittleness. First, the two types of embrittlement occur in two widely separated temperature regions, as shown by the superposition of curves in Fig. 8. Secondly, it is now well recognized that temper embrittlement does not occur in plain carbon steels, let alone high-purity irons. Thirdly, the results of Hopkins and Tipler, which were attributed to the grain bound-
ary segregation of nitrogen and phosphorus, can equally well be explained by the embrittling effect of trace amounts of oxygen in low-carbon irons, and by changes in the carbon-oxygen ratio at the grain boundaries brought about by the quenching treatments employed. In fact, their results are strikingly similar to those obtained with the same kinds of heat treatments on high-purity, low-carbon iron containing no appreciable amounts of nitrogen or phosphorus [29]. These latter observations were explained in terms of the grain boundary strengthening effects of segregated carbon.

Effect of Time and Temperature

The 'C-curve' nature of embrittlement behavior, best characterized by Jaffe and Buffum and co-workers (Fig. 4), and the "overaging" effects (Table 1) have already been discussed, as have the observations of retardation of embrittlement by long-time tempering at high temperatures.

Two important additional contributions by Powers should be noted. The first is his quantitative determination of the reversion of embrittlement when embrittled specimens are heated to temperatures above the embrittling range [31]. This is shown best by Fig. 9, taken from the report of Low [3]. Note that these steels had been embrittled by a step cooling treatment of about two weeks; the molybdenum-free steel could be almost completely de-embrittled by a 5-min treatment at 593 C, and that all of the steels could be reverted in 1 min at 677 C!

The second significant contribution [30] was the discovery that step cooling from around 590 C could produce as much embrittlement as much longer isothermal treatments at the maximum embrittling temperature. Powers rationalized this behavior on the basis of Fig. 4, which shows that initial embrittlement is most rapid at about 540 C, whereas maximum embrittlement can be achieved only at lower temperatures. The step-cooling treatment thus attempts to optimize the effects of the whole embrittling range.

Effects of Plastic Deformation

Low [3] reviewed a series of Russian papers which dealt with beneficial effects of plastic deformation both on steels in the austenitic condition (prior to quenching) and on steels which had been embrittled (prior to impact testing). In the former case it could not be determined whether the benefits were derived from the deformation, per se, or from simple austenitic grain refinement. Low pointed out that some of the results observed could be explained from the latter effects alone. Very

\[^{13}\text{Low [3]}\] reports that the step-cooling treatment now used to produce the same results is a shortened modification of Power's original method, as follows: hold 1 h at 593 C, furnace cool to 538 C, hold 15 h, cool to 524 C, hold 24 h, cool to 496 C, hold 48 h, cool to 468 C, hold 72 h.
definite improvement in toughness following a room temperature tensile deformation of 1.5 to 4 per cent of embrittled 0.10 per cent carbon, 0.97 per cent manganese, 0.96 per cent silicon, 0.36 per cent carbon, 1.10 per cent nickel steel was demonstrated by Stepanov [36].

Keh and Porr [35] studied the effects of cold work on 5140 steels of two different purities and found that if an embrittled steel was cold rolled and then reheated to the embrittling temperature, the degree of embrittlement was decreased. The amount of the decrease was proportional to the amount of cold work. If the steel was not reheated after cold work, the result was mainly a lowering of the impact energy in the ductile region and an obscuring of transition behavior. They attributed the effect of cold work plus annealing to a preferential segregation of impurities to dislocations, thus decreasing the concentration at grain boundaries.

Steeb and Rosenthal [64] found that a small strain in tension at 480°C lowered the subsequent susceptibility to embrittlement in 24 h at the same temperature. Recent work by Woodford [37] of the General Electric Co. on a nickel-chromium-molybdenum-vanadium (Ni-Cr-Mo-V) steel has shown that creep deformation in tension during the embrittling treatment succeeds only in delaying the development of embrittlement, but does not reduce the total embrittlement possible.

**Evidence for Structural and Chemical Change at Grain Boundaries**

The key to the understanding of temper brittleness lies in the microstructure and composition of prior austenitic grain boundaries. This fact has been realized for decades, but the examinations of these boundaries by numerous analytical techniques have yielded little in the way of understanding until quite recently.

Many hundreds of specimens have been etched with reagents based on picric acid, first used by Cohen et al [12]. The consensus is that these etchants produce grooving of prior austenitic grain boundaries of embrittled specimens containing phosphorus, but no precipitate is ever revealed. In severe cases, ferrite boundaries are also revealed. Examples

---

**TABLE 6—Etchants which reveal prior austenite grain boundaries in temper brittle steels.**

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethereal aqueous picric acid with Zephiran</td>
<td>Cohen, Hurlich, and Jacobson [12]</td>
</tr>
<tr>
<td>saturated chloride</td>
<td></td>
</tr>
<tr>
<td>Ethereal aqueous picric acid</td>
<td>McLean and Northcott [13]</td>
</tr>
<tr>
<td>Ethereal aqueous picric acid with cetyl-trimethyl ammonium bromide (CTAB)</td>
<td>McLean and Northcott [13]</td>
</tr>
<tr>
<td>Ethereal aqueous picric with aryl ether of polyethylene glycol (aryl EPG)</td>
<td>McLean and Northcott [13]</td>
</tr>
</tbody>
</table>
of some of the more effective etchants are given in Table 6. The response of embrittled chromium-free steels is negative-to-marginal for all except the last etchant in Table 6. The grain boundary grooving strongly suggests the segregation of impurities to grain boundaries, but of course does not prove it.

Evidence for the presence of a precipitate which would explain the embrittlement has been sought by many of the best electron microscopists without success. In 1959 it could be stated that: “In particular, no evidence has been found for any intergranular film or for any precipitation process in the grain boundary region” [3]. It will be shown later that this position should now be somewhat modified to take account of the carbide platelets which occur on prior austenite grain boundaries and which do play a significant role in the problem.

An important step forward was the work of Arkharov et al [38] which demonstrated that phosphorus segregated to prior austenite grain boundaries in embrittled Ni-Cr steels, and that this segregation was reduced by additions of molybdenum. His method consisted of etching the fracture surface of impact specimens with one drop of 1:1 nitric acid, then washing the surface with distilled water, and analyzing the resulting solution. Even with an embrittling treatment of only 3 h at 550°C, Arkharov found about 1.7 times the bulk phosphorus content on the intergranular fracture surfaces of steels containing 0.025 to 0.058 per cent phosphorus. When 0.18 to 0.80 per cent molybdenum was present, the results became somewhat erratic, but the excess averaged around 1.4 times the bulk content. Low [3] pointed out that Arkharov did not show that grain boundaries in unembrittled steels were free of excess phosphorus, since the fractures in these cases were fibrous.

Progress Since 1959

Most of the work done since Low’s review has been concerned with the effects of composition and microstructure and the study of grain boundary segregation. Throughout this period the consensus has been, and remains, that reversible segregation of impurities to grain boundaries is at the root of the problem.

Composition

The major investigation of this period dealing with compositional effects is the recently completed study by Low et al [27]. In the most exhaustive study since Steven and Balajiva [20], they examined the roles of chromium and nickel, together and separately, in conjunction with the four main embrittling impurities: antimony, tin, phosphorus, and arsenic. Their base steel contained 3.5 per cent nickel, 1.7 per cent chromium, and 0.4 per cent carbon, and it was shown to be essentially non-susceptible when high-purity melting practice was employed and with the
impurities absent. The heat treatments involved oil, then liquid nitrogen (N\textsubscript{2}), quenching from 870 C, tempering at 625 C for 1 h, and either quenching to give the unembrittled condition, or step cooling to give the embrittled condition. The criterion of embrittlement was the shift in transition temperature (\(\Delta\theta\)) as measured by a 50 per cent fibrous appearance.

Their findings on the interrelations between nickel and chromium and the embrittling elements are shown in Fig. 10. From this we can see the following:

1. The \(\Delta\theta\) for the high-purity base steel is 27 C, and is considered negligible. The fact that it is not zero is no doubt due to the 53 ppm (by weight) residual impurities.

2. Antimony has the largest effect in all cases, with tin, phosphorus, and arsenic following in that order.

3. The combination of nickel and chromium always leads to a greater \(\Delta\theta\) than either separately. The relative effects of nickel and chromium, when present individually, depend on the specific embrittler present, as shown.

FIG. 10—Results of Low et al [27] showing effects of alloying elements on temper embrittlement in steels containing 400 to 800-ppm (by weight) antimony, tin, phosphorus and arsenic.
4. Embrittlement is possible in the absence of carbon. Indeed, it is quite pronounced in the presence of 800-ppm antimony. It can be seen that the effect of removing the carbon (or carbides) is to reduce the $\Delta\theta$ by about 480 C.

FIG. 11—Results of Low et al [27] showing effect of antimony concentration on temper embrittlement of Ni-Cr steel, compared with results of Steven and Balajiva [20]. Small additions of other elements, as noted, had no apparent effect.

5. Embrittlement does not occur (with 800-ppm antimony) if alloying elements are not present. Thus, a true plain carbon steel (that is, with no manganese) is not susceptible.

Low et al point out that the combination of nickel and chromium should be avoided in steels to be used in situations where temper brittleness can be troublesome. (It was concluded earlier in this review that the combination of chromium and manganese is even worse.) They made the important point that the results that they obtained may reflect differe-
ences in rate of embrittlement rather than in maximum attainable embrittlement, since the same thermal cycle was used to evaluate all cases.

Other results pertaining to compositional effects stemming from this investigation can be summarized as follows:

1. Additions of up to 0.3 per cent zirconium to an impure steel (206-ppm total embrittlers) and to a steel containing antimony, yielded no beneficial effect.

2. Additions of up to 0.26 per cent rhenium and 0.04 per cent platinum to antimony bearing steels had no effect.

3. The addition of 0.3 per cent lanthanum to an impure steel appears to give some reduction in embrittlement, although the results are somewhat uncertain due to variations in the manganese content.

4. Investigation of the effect of sulfur showed that it is capable of producing or enhancing embrittlement. Addition of 200-ppm sulfur to the high-purity steel raised $\Delta \theta$ from 27 to 50°C.

This is in contrast to the results of Capus and Mayer [65] who reported that the addition of 0.01 per cent sulfur to a 0.3 per cent carbon, 0.08 per cent chromium, 3 per cent nickel, 0.11 per cent manganese steel produced no susceptibility to either temper embrittlement or 500°F embrittlement. The difference in manganese contents between the two steels may have been critical, since this element appears to have enormous capability of enhancing the embrittling effects of small amounts of the embrittling elements (see Fig. 6).
5. The increase in embrittlement with antimony content was measured and compared with the results of Steven and Balajiva (Fig. 11). It would seem possible that the values for antimony content given in the latter work in the low-antimony steel could have been in error.

It is worthwhile pointing out that the impure steels mentioned above were made under the same conditions as the pure steels, except that Armco iron was substituted for electrolytic iron. A comparison of typical impurity contents and $\Delta \theta$ values is shown herewith:

<table>
<thead>
<tr>
<th>ppm</th>
<th>Sb</th>
<th>Sn</th>
<th>P</th>
<th>As</th>
<th>$\Delta \theta$ (deg C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure steel</td>
<td>4</td>
<td>3</td>
<td>45</td>
<td>1</td>
<td>27</td>
</tr>
<tr>
<td>Impure steel</td>
<td>11</td>
<td>45</td>
<td>90</td>
<td>60</td>
<td>259</td>
</tr>
</tbody>
</table>

An interesting interaction between arsenic and phosphorus was reported by Kal'ner [39], who studied the effects of variation in arsenic content in steels containing two levels of phosphorus as follows:

<table>
<thead>
<tr>
<th>% C</th>
<th>% Mn</th>
<th>% Cr</th>
<th>% Ni</th>
<th>% Si</th>
<th>% S</th>
<th>% P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel A</td>
<td>0.42</td>
<td>0.65</td>
<td>1.03</td>
<td>0.08</td>
<td>0.31</td>
<td>0.010</td>
</tr>
<tr>
<td>Steel B</td>
<td>0.42</td>
<td>0.63</td>
<td>0.94</td>
<td>0.11</td>
<td>0.25</td>
<td>0.013</td>
</tr>
</tbody>
</table>

The effects of arsenic variation are shown in Fig. 12. It would appear that in the presence of phosphorus about 0.10 per cent arsenic can have some mitigating effect. This, of course, assumes that the levels of antimony and tin in these steels were negligible and constant. Since they appeared to be of essentially commercial quality, this may not have been true. In any event, Kal'ner attributed the effect to preferential segregation of arsenic to grain boundaries coupled with the fact that arsenic is a less severe embrittler than phosphorus. Even if real, the effect is too small to have any practical significance.

**Microstructure**

The investigation by Low et al [27] included an exhaustive search for a difference in appearance of prior austenite grain boundaries between embrittled and unembrittled steels. Their techniques included electron microscopic examination of both normal two-step and carbon extraction replicas of etched and unetched intergranular fractures, as well as transmission electron microscopy of grain boundary regions in thinned foils. No differences could be found, and it must be concluded that the embrittlement mechanism involves some form of atomic segregation not resolvable with current electron microscope techniques.
An investigation by Capus [40] produced some important information on the effect of prior austenitic grain size as well as on embrittlement at high tempering temperatures. He used the same type of high-purity steel as Steven and Balajiva [20]: 3 per cent nickel, 0.75 per cent chromium, 0.3 per cent carbon, and added either 0.023 per cent phosphorus or 0.074 per cent tin (that is, about 0.04 atm per cent of each). His thermal treatments involved oil hardening from 850°C, tempering at 600°C for 1 h, then either water quenching (giving the unembrittled state) or quenching and reheating for 168 h at 450°C to produce embrittlement. Austenitic grain size was varied by heating to higher temperatures before hardening, but the steels were always cooled to 850°C before quenching.

His most important results are shown in Fig. 13. First it should be noted that the $A_0$ for the pure steel is zero, and that a change in austenitic grain size has essentially no effect on transition temperature in either the tempered or embrittled conditions. The other results can be summarized as follows:

15 The only effect was that for the coarsest grain size (ASTM 0) the maximum impact energy was reduced from 145 to 115 ft lb. It was not apparent whether this could be explained in terms of a coarser ferrite-carbide aggregate in the steel.
1. The grain size effect in the phosphorus and tin steels is present in the unembrittled condition and is roughly the same magnitude as for the embrittled condition. The effect of tin is particularly strong. Thus, it appears that substantial embrittlement can occur at the 600 C tempering treatment used.

2. The actual Δθ measured was greater for phosphorus than for tin. This seems to be a reflection of the fact that a large part of the tin segregation had already occurred at 600 C.

3. Segregation of phosphorus could be detected by the aqueous picric acid etch, even for tempering temperatures of 650 C, but segregation of tin was not detectable in this manner.

4. The relative amount of intergranular fracture increased with increasing austenitic grain size in both the as-tempered and embrittled conditions.

The austenitic grain size effect can be attributed to two sources:

(a) For a given total amount of segregated solute (in austenite) the amount per unit boundary area can be greater for larger grain sizes.

(b) In cases of grain boundary fracture, a larger grain size allows the crack to propagate with fewer deflections as it passes through the structure.

Two recent studies have focused attention on an important factor in temper brittleness that had been overlooked. The first was that of Hill and Martin [41] who carried out a fractographic examination, via an extraction replica technique, on steels of the types used by Austin et al [25]. They were basically: 3 per cent nickel, 0.8 per cent chromium, 0.4 per cent carbon, with about 300-ppm phosphorus and 50 to 880-ppm antimony, with and without additions of molybdenum. They used an Izod test and found very large embrittlement in the high-antimony, low-molybdenum steel, with a tempering treatment of 620 C for 2 h and embrittling treatment of 525 C for 4 h.

The primary finding was that a great number of large platelets of cementite could be extracted from the intergranular fracture surfaces of embrittled steels. It was fairly definite that the fracture had taken place along the cementite-ferrite interface, rather than through the cementite itself, which indicated that this usually tenacious interface [42,43] had been weakened, presumably by the presence of antimony. They noted that as much as 75 per cent of the surface of prior austenite grain boundaries could be covered by this cementite.

They concluded that antimony segregates in austenite during austenitization, and they attributed the embrittling effect of antimony to a lowering of the ferrite-cementite interfacial energy which: (a) catalyzed the nucleation and growth of plate-like cementite in prior austenite grain boundaries, and (b) led to a large amount of low-fracture-energy interface. They did not report the appearance of grain boundaries in unembrittled steels.
In an investigation designed to examine the implications of Hill and Martin's work, the effect of antimony on the cohesive strength of ferritic interfaces was studied by Restaino and McMahon [44]. A vacuum melted ferrite containing 0.02 per cent carbon and 700 to 800-ppm antimony was heat treated to give a microstructure of large ferrite grains (about 0.1
mm diameter) with coarse cementite plates in the grain boundaries. This was done so that light microscopy could be used to study interface effects in a structure which was a coarse-scale analog of a tempered steel.

When such a material without antimony is tested in tension at low temperatures, carbides are found to crack [43], usually across their thickness, but occasionally along their length, as shown in Fig. 14.

FIG. 16—Carbon extraction replicas showing cementite platelets on austenitic grain boundary fracture facets of 3340 steel in the embrittled and unembrittled conditions (Ref 44).
They never crack along the interface; the tenacity of this interface has been recognized for many years [42].

In the antimony-bearing ferrite [44] it was found that the interfaces could be made to split open (Fig. 15) if the specimens were embrittled at 480 C for 24 h prior to testing, and they could be de-embrittled (that is, no interface splitting) if they were reheated for short times above 600 C. The de-embrittlement time-temperature curve looked much like that of Powers (Fig. 9) for reversal of temper brittleness; it is felt that they both represent the same phenomenon: the dispersion of segregated embrittling elements away from the interface, back into solution.

In order to carry these observations over to a steel, fractographic observations were carried out on a 3.5 per cent nickel, 1.6 per cent chromium, 0.4 per cent carbon heat with 620-ppm antimony (one of the steels used by Low et al [27]). It was found that carbide platelets could indeed be found on prior austenite grain boundaries in all three conditions: un-embrittled, embrittled, and de-embrittled (Fig. 16). (Intergranular fractures were obtained at low temperatures by using a very coarse austenitic grain size.) The appearance of these fractures was the same for all three cases; presumably the carbides formed during the initial 675 C tempering treatment. However, a striking difference was found when the antimony content on the fracture surface was determined by the one-drop etching technique of Arkharov [38]. Whereas the antimony content of the unembrittled and de-embrittled (650 C, ½ h) grain boundaries was below the limit of detectibility, the embrittled boundaries contained an average of 10 weight per cent antimony in the region within about 600Å of the fracture surface. (This was about 2½ times greater than the detectibility limit.) The conclusion drawn from this work was that antimony segregates in austenite during austenitization at high temperatures, but that it can segregate and de-segregate reversibly in ferrite at lower temperatures, thereby causing embrittlement and de-embrittlement. The carbides provide a path of easy fracture (along the weakened interfaces) and intensify the embrittlement. Low et al [27] showed that by elimination of the carbides from this alloy, the embrittlement could be reduced by about two thirds (Fig. 10).

**Evidence for Segregation**

The direct evidence that has been obtained so far includes the demonstrations of phosphorus segregation in steel by Arkharov [38], of antimony segregation in steel by Restaino and McMahon [44], and the phos-

---

16 Ferrite-ferrite interfaces were also embrittled, but to a much lesser degree.

17 It has been found [45] that brittle fractures of the as-hardened and quenched antimony-bearing steel discussed here are largely intergranular, especially for coarse grain sizes. This would indicate that segregation occurs during the austenti-
phorus segregation in iron by Inman and Tipler [46]. There have been several types of indirect evidence: the grain boundary grooving by picric acid etches in the presence of chromium and phosphorus, and the observation by Plateau et al [47] of striations (indicating surface rearrangements due to absorption) on parts of the intergranular fracture of an embrittled steel, and the recent demonstration by Low et al [27] that a slight difference in microhardness exists between grain interior and embrittled grain boundaries in carbon-free steel containing antimony. This latter technique had been used by Westbrook and Aust [48] in previous segregation studies.

Evidence of a negative sort is the fact that grain boundary precipitates cannot be found, whereas all indications point to either a precipitate or segregation as the cause of temper brittleness. Several attempts at using autoradiography have been made [31, 49] including the recent one by Low et al [27], but none with success. Stein [50] has discussed the limitations of this technique.

It would seem that the case for segregation is fairly well established; it now remains to work out the factors which control it.

Other Recent Work

There have been several other investigations during this period which are reported here for completeness, even though they do not materially alter the picture developed so far.

Banerjee [51] carried out a transmission and replication electron microscopic study of several steels tempered over a range of temperatures. He described the alteration of carbide type and morphology in detail, and concluded that both "500 F embrittlement" and temper brittleness were due to locking of dislocations by precipitates and to changes in dislocation density during tempering. These observations cannot hope to explain the classic characteristics of temper brittleness, such as reversibility, sensitivity to impurity content, and intergranular fracture mode, and therefore they will not be discussed further.

Various workers have made many other kinds of measurements in efforts to find correlated effects and to discover the nature of temper brittleness. They include magnetic coercivity and electrical resistivity [66], thermal emf [67] and internal friction [68-71], all without being very convincing. In particular, Kaddou and Rosenthal [68] compared internal friction peaks in embrittled and unembrittled 3310 steel and concluded that temper embrittlement was due to the pinning of dislocations by carbon and nitrogen, which occurred during the embrittling treatment. Keh and Swartz [72] later showed that such measurements could not differentiate between two 5140 steels with quite different embrittling susceptibilities, and Capus [73] detailed the arguments against the model,
which will not be repeated here. Later, Wert and Rosenthal [69] modified the position somewhat when they found that the internal friction measurements did not always correlate with embrittlement and that decarburization of a 3310 steel did not remove the susceptibility. They concluded that the primary cause of temper brittleness was the segregation of unspecified substitutional and interstitial elements to ferrite grain boundaries. However, they ignored the work of Steven and Balajiva [20] and did not say why the prior austenitic grain boundaries were preferred fracture sites.

Weiss and co-workers [74] have demonstrated that the impact transition temperature of heat treated steel is raised after coarsening of the ferrite plus carbide structure by prolonged heating at 600 to 700 C, as suggested earlier by Woodfine [2]. They also showed that this type of treatment had no additional effect on the temper embrittlement phenomenon. More recently, they found [75] that temper brittleness affects the fatigue properties of a 0.65 per cent carbon, 0.92 per cent manganese, 1.86 per cent silicon, 0.03 per cent phosphorus, 0.019 per cent sulfur, 0.40 per cent chromium steel by lowering the fatigue life at stresses above the fatigue limit. In notched specimens it was found that the fatigue cracks start earlier and propagate more rapidly in the steel after a temper embrittlement treatment.

Finally, it is worth noting that the presence of temper embrittlement can be detected by a hydrogen embrittlement type of experiment, that is, by cathodic charging of specimens statically loaded in tension. Cabral et al [76] have shown that in a 0.3 per cent carbon, 3 per cent nickel, 0.6 per cent chromium steel containing more than 1100-ppm phosphorus, arsenic, and tin, the endurance curve (stress-to-fracture versus loading time) was markedly lowered when the steel was tested in the embrittled condition (48 h at 500 C) as opposed to the unembrittled condition (quenched from 625 C). In the former case the hydrogen-induced fracture occurred along prior austenite grain boundaries, and in the latter it was transcrystalline. These tests were done with unnotched specimens. Since fractures of commercial purity heat treated steels caused by hydrogen embrittlement or stress corrosion cracking are often observed to be intergranular [59], there seems to be some justification for suspecting that impurities can enhance these embrittlement phenomena by producing weak interfaces along which H2 can be formed.

Theories of Temper Britteness

The mechanisms which had been suggested to explain temper brittleness up to 1959 have been reviewed by Woodfine [2] and Low [3]. They covered a wide spectrum and were usually rather simply stated propositions which did not attempt to rationalize the very complex set of mani-
festations which characterize the problem. It is appropriate at this point to summarize these characteristics in Table 7; the primary characteristics must all be accounted for by any general theory, while the secondary ones might wait for the development of later details of the theory. Of

**TABLE 7—Summary of characteristics of temper brittleness.**

**A. PRIMARY**

1. Embrittlement can occur in alloy steels having ferrite + carbide microstructures which are heated in or cooled slowly through the range \(~375\) to \(575\) C.

A time-temperature-embrittlement diagram exhibits a set of C-curves. Embrittlement can occur to a minor degree at temperatures above the nose, but appears to be diffusion-limited below the nose [1,17,18].

2. Embrittlement occurs only in the presence of specific impurities and increases in severity with the concentration of these impurities.

Antimony, phosphorus, tin and arsenic are the major embrittlers, listed in decreasing order of strength on a weight per cent basis. Manganese and silicon appear to be active in larger amounts, but this is less certain [20]. The increase in embrittlement with increasing concentration appears to saturate for As, P, and Sn.

3. Embrittlement is reversible.

Even severely embrittled steels can be de-embrittled in a matter of a few minutes when heated above the nose of the C-curve [37].

4. Embrittlement consists of a decrease in cohesion along prior austenitic grain boundaries.

The decohesion actually occurs in ferritic boundaries, but is restricted almost entirely to those which lie along surfaces of the prior austenite grains [1-3].

5. The degree and rate of embrittlement are profoundly affected by the alloy content.

Plain carbon steels (with \(< \sim 0.5\) per cent Mn) are not susceptible [2,27]. Susceptibility is enhanced greatly by chromium and manganese (Fig. 6) and less strongly by nickel (Table 4). Small amounts of molybdenum and tungsten are inhibitors but larger amounts are enhancers [31]. Decreases in carbon content can diminish, but not prevent, embrittlement [27].

6. The only metallographic indication of the embrittled state is the grooving of the embrittled grain boundaries by several specific etchants in steels containing phosphorus.

These etchants do not reveal a precipitate; neither is a precipitate to which embrittlement could be attributed observable by techniques of electron microscopy [3,14,27].

**B. SECONDARY**

1. In most cases a notched-bar impact test is required to show a significant difference in behavior between embrittled and unembrittled steels. (The shift in transition temperature is the usual criterion.)

In more severe cases low temperature tension tests can indicate embrittlement, but in general normal plasticity must be severely restricted (by high strain rates or low temperatures) to allow the intergranular weakness to manifest itself [3].

2. Prolonged heating at temperatures above the nose of the C-curve (but below \(A_1\)) causes a decrease in the rate of embrittlement at lower (normal embrittling) temperatures (Table 2; Refs 25 and 77).

3. When embrittled at temperatures somewhat above the nose of the C-curve, many steels exhibit an “overaging” type of response; that is, the degree of
TABLE 7—Concluded.

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>embrittlement goes through a maximum with increasing embrittling time (Table 1).</td>
</tr>
<tr>
<td></td>
<td>4. The shift in transition temperature ($\Delta \theta$) after embrittlement is greatest for steels of the tempered martensite microstructure and least for pearlitic steels, with bainitic steels falling in between (Table 2).</td>
</tr>
<tr>
<td></td>
<td>5. Increases in prior austenitic grain size result in proportionate increases in $\Delta \theta$, all other things being equal [40,52].</td>
</tr>
<tr>
<td></td>
<td>This is normal behavior for an intergranular mode of fracture. The effect is even more pronounced if the steel is equilibrated at a lower temperature in the austenite region prior to quenching [52].</td>
</tr>
<tr>
<td></td>
<td>6. Plastic deformation after embrittlement, but before impact testing, appears to lower the transition temperature [36]. Plastic deformation during embrittlement delays the development of embrittlement [37].</td>
</tr>
</tbody>
</table>

course, any general theory must at least be able to be developed to account for the secondary characteristics.

The suggested mechanisms which appear to have any connection with reality all involve the segregation of some element to ferritic grain boundaries, with or without precipitation or ordering. That this must be the case is inescapable, considering the characteristics listed in Table 7.

Many suggestions involved segregation of carbon or nitrogen or the precipitation of carbide or nitride films. These can now be ruled out with confidence, if only on the evidence that removal of carbon and nitrogen does not prevent embrittlement [27]. In addition, it has been shown that segregated carbon increases cohesion of ferritic boundaries [29]. Furthermore, it has been demonstrated that prior austenite grain boundaries in quenched and tempered steels susceptible to temper brittleness already contain cementite platelets [41,44]. Thus, it is extremely unlikely that any revertible carbide or nitride film would form in this location.

A Recently Proposed Model

Temper brittleness is a very involved metallurgical phenomenon whose complexities appear to multiply the more closely one examines it. It is obvious that no simple model will explain all of its manifestations. A model has been proposed recently [44], however, which is believed to offer promise for the further development of a complete theory. Most importantly, it raises some specific questions which should be experimentally answerable.

Concentrating initially on the four main embrittling elements antimony, phosphorus, tin, and arsenic, we note that their equilibrium diagrams with iron are all similar in that they exhibit restricted gamma loops [53]. That is, these elements tend to stabilize the alpha phase. Thus, they are expected to show a stronger tendency to segregate to interfaces in the gamma than in the alpha phase [54,44]. This means that appreciable segregation could occur in austenite at high temperatures, but that the
temperature range for strong segregation in ferrite could be much lower. The reasoning behind this proposition is that the forces which promote reduced solubility should be precisely those which promote segregation, for example, lattice strain, electron energy levels, etc. [54].

The proposal is that the embrittling elements segregate to austenite grain boundaries during austenitization and are retained there upon quenching. It is suggested that the tendency to segregate in ferrite is strong below about 550 C, but that the effect of entropy becomes too important above that range and the embritters tend to be “boiled off” the interfaces and driven back into solution (compare A-3, Table 7). When a steel is initially tempered above about 600 C, two things happen: first, the embritters are progressively dispersed away from the prior austenite boundaries, and, secondly, large carbide platelets form preferentially along these boundaries. When the steel is then held for long times at temperatures below about 550 C, the embritters tend to segregate back to interfaces. Since they are always in the general vicinity of prior austenite grain boundaries, the ferrite-ferrite and ferrite-carbide interfaces in these regions get a large dose of them (compare A-6, Table 7). It is postulated that these elements act to lower the cohesion of these interfaces (compare A-2, Table 7). This is especially damaging in the case of ferrite-carbide interfaces, since the lack of plasticity of the carbide tends to accentuate any tendency for interfacial weakness.

The prior austenite grain boundaries are thus the preferred site for fracture for two reasons: they are in the regions richest in embrittling element content, and they contain a large density of carbide platelets which, when poisoned by an embrittling element, provide a path of easy fracture (compare A-4, Table 7).

When a susceptible steel is heated below about 375 C after having been tempered at >600 C, the diffusivities of the embrittling elements are so low that they cannot get back to the interfaces in significant amounts in reasonable times, and embrittlement is not observed. The net result is an apparent C-curve behavior (compare A-1, Table 7).

It follows that the longer the tempering time at the high temperatures, the greater will be the dispersion of embritters. Hence, development of embrittlement at lower temperatures will occur more slowly (compare B-2, Table 7).

It is not at all unusual for an intercrystalline weakness to require a type of test which severely limits plasticity in order for the weakness to manifest itself. A good example is oxygen embrittlement of iron, which usually shows up best at low test temperatures or high strain rates. In

\[ \text{18 The reason for the preference for prior austenite boundaries is not known, but it appears to be rather general. Perhaps it is related to the segregation of some alloy or impurity elements. This matter should be given more attention in future research.} \]

\[ \text{19 This has already been demonstrated for the case of antimony [44].} \]
general, the less severe the embrittlement, the more extreme is the test necessary to manifest it. Thus, it is not of fundamental significance that most temper brittleness is only detected unambiguously in an impact test. (A notched-bar tension test at low temperatures would probably serve almost as well.)

The only important gap in the model, as it now stands, is that it says nothing about the roles of the alloying elements in temper brittleness. It is now clear that these elements act to either enhance or retard the action of the embrittling elements, or to modify the morphology or size of grain-boundary carbides. At this stage it is only possible to list

### TABLE 8—Possible roles of alloying elements in temper brittleness (speculative).

<table>
<thead>
<tr>
<th>Role</th>
<th>(speculative)</th>
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<tbody>
<tr>
<td>1. Enhancement of diffusivity of embrittling element thereby increasing rate of embrittlement</td>
<td>Mn increases diffusivity of P in Fe [55]</td>
</tr>
<tr>
<td>2. Reduction of diffusivity of embrittling element</td>
<td>...</td>
</tr>
<tr>
<td>3. Enhancement of segregation tendency of embrittling elements in austenite due to the segregation of the alloying element itself</td>
<td>(Cr?)</td>
</tr>
<tr>
<td>4. Enhancement of segregation of embrittling element in ferrite</td>
<td>...</td>
</tr>
<tr>
<td>5. Modification of carbide morphology</td>
<td>(Does Cr promote formation of carbides on prior austenite grain boundaries? Do Mo, W, and Cb inhibit this?)</td>
</tr>
<tr>
<td>6. Scavenging of embrittling elements</td>
<td>...</td>
</tr>
<tr>
<td>7. Solid solution hardening of ferrite so as to increase temperature and strain rate sensitivity of flow stress, thereby intensifying brittle tendencies</td>
<td>(Si?)</td>
</tr>
</tbody>
</table>

some of the more likely possibilities and to suggest in a few cases the roles that may be played by particular elements (Table 8).

It will obviously require further work to answer the questions that are raised here. In particular, we must have data on the diffusivities of the embrittling elements in iron and the effect that alloying elements have on these values. In addition, it will be necessary to determine the solubilities of the embrittling elements in iron and in the alloy steels. Virtually no information exists in this connection.

Finally, it has been shown in two cases (phosphorus in iron [56] and antimony in 3340 steel [44]) that the amounts of segregated impurity seem to be well in excess of the maximum amounts predicted by thermodynamic considerations. This raises the question of what is the state in which the segregated impurities exist. This question is completely open;
speculation would seem idle until we learn more about the solubility limits mentioned above, as well as the possible existence of metastable precipitation stages.

"500 F Embrittlement"

There exists another type of embrittlement which occurs during the tempering of low-alloy steels and which has been variously referred to as "500 F embrittlement" [57], "350 C embrittlement" [58], and "tempered martensite embrittlement" [59]. All three terms refer to the same phenomenon: the minimum in the notched-bar impact energy as a function of tempering temperature, as shown in Fig. 17. The impact test is usually performed at room temperature, although a temperature of -78 is sometimes used to distinguish mild cases [58]. It is important to note that the specimens are not tempered at some high temperature (as in the test for temper brittleness) before the tempering treatment to be studied.

There are some rather striking similarities between the two types of embrittlement, enough to make one wonder whether they are not really variations of the same phenomenon [59]. Accordingly, the characteristics of 500 F embrittlement will be briefly summarized, and some tenta-
tive suggestions will be made regarding its mechanism. These suggestions are made to indicate the connection which seems likely to exist between the two phenomena and to provoke discussion and investigation of the problem.

The characteristics of 500 F embrittlement are as follows:

1. It appears as an anomalously low room-temperature impact energy when a quenched steel is tested after tempering in the range about 250 to 400 C (about 430 to 690 F) [57].

2. It is revealed only by a notched-bar impact test or by a fracture toughness test at low temperatures [57,60].

3. It does not occur in high-purity steels with sufficiently low levels of antimony, phosphorus, tin, and arsenic; higher levels of manganese are also said to lead to embbrittlement [58].

4. The embrittlement appears to be connected with a lowering of cohesion along prior austenite grain boundaries; fractures of specimens tested between about 500 and 650 F (300 and 380 C) are largely intergranular [61,62].

5. Only martensitic steels are susceptible; bainitic steels are not [57].

6. The addition of silicon, which retards the third stage of tempering (low carbon martensite + epsilon carbide \(\rightarrow\) ferrite + Fe\(_3\)C), displaces the impact energy minimum to higher temperatures [63,58].

**Tentative Model**

It is important to emphasize the difference in testing procedures used to study the two phenomena. In the case of temper brittleness one measures a shift in transition temperature, as a function of tempering time and temperature, in specimens which had been previously tempered at a higher temperature; in the other case, room temperature impact energy is measured as a function of tempering temperature. This is probably the main reason why they are often taken to be two different phenomena. It might be pointed out that a maximum in transition temperature occurs at the same tempering temperature as the impact energy minimum [60].

It is suggested that the explanation of 500 F embrittlement lies along the following lines: the embrittling impurities, which have segregated to austenite grain boundaries prior to quenching, remain there during tempering at temperatures below about 600 C. They act to promote intergranular decohesion in untempered martensite. (This is demonstrated by the large amounts of intergranular fracture in as-quenched 3340 steel containing antimony [45].) When the steel is tempered below about 200 C, the softening which occurs tends to offset this factor, and the impact energy rises. The decrease in impact energy and general lowering of the impact curve at higher tempering temperatures is caused by the formation of carbides on prior austenite grain boundaries, which acts to intensify the action of the still-segregated embrittling elements. As the tempering
temperature is further increased, the impact values of a susceptible steel and a pure steel of the same basic composition should approach each other and should be about the same above 600 C, where dispersion of the embrittling elements has occurred. This effect can be seen in Fig. 17b.

If this model withstands future testing, there are still some questions which will need answering. For example, why does nitrogen [58] have such a strong enhancing effect in 500 F embrittlement? What role does it play in and around prior austenite grain boundaries? Also, is plain carbon steel really susceptible to 500 F embrittlement, as claimed [58], or is this just another case of the manganese content not being taken into account? Further research is necessary to clarify these issues.

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