TEMPER-BRITTLENESS: PART II — ALLOY STEELS

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Abstract

In the case of alloy steels the *modus operandi* of minor elements and of phases such as nitrides, carbides, etc., in causing temper-brittleness has been experimented upon, discussed and speculated over probably more than any other alloy steels subject. The most interesting problem in this field is the suppression of temper-brittleness in nickel-chromium steels by means of molybdenum. The underlying phenomena still remain largely unresolved and no clear picture has been developed by what other elements act in the same way as molybdenum. From the discussion it emerges that temper-brittleness must be considered in terms of brittle transition temperatures. The effects of aluminium and molybdenum, in lowering the ductile to brittle fracture range in alloy steels, have been outlined. It has been shown that the susceptibility ratio depends on grain size and an etchant based on solution of picric acid in ether can furnish metallographic evidence of temper-brittleness. Hypotheses put forward to explain temper-brittleness are stated and suggestions made for further research.

Introduction

IT is well known that after a martensitic quench, toughness of most nickel-chrome medium alloy steels is adversely affected both by tempering in a certain temperature zone and by slow cooling after tempering treatment. This phenomenon of embrittlement is universally known as 'temper-brittleness'. It has been recognized that nickel-chrome steels are brittle if cooled slowly from tempering temperature. This brittle behaviour is shown only in notched-bar impact tests and is not reflected in other physical properties as discussed later on.

In this paper the effects of chemical composition, grain size and microstructure on temper-brittleness will be briefly discussed and no attempt will be made to present a complete review on the subject. The kinetics of embrittling treatment has not been touched and the controversial theories have been indicated.

On cooling at different rates after tempering at 600°C. results obtained by the authors[1] with 0·40 per cent C, 0·71 per cent Mn, 3·33 per cent Ni and 0·87 per cent Cr coarse-grained steel after initial oil-quenching from 850°C., are given in Table 1. The rate of cooling is, therefore, the decisive factor for toughness.

TABLE 1 — EFFECT OF RATE OF COOLING ON TEMPER-EMBRITTLEMENT

TEMPERED AT 600°C. FOLLOWED BY	IZOD IMPACT VALUE, ft.-lb.
Slow cooling at the rate of 1·5°C./min.	6
Slowly cooled	10
Air-cooled	16
Oil-quenched	47
Water-quenched	46
Specimen annealed at 900°C., cooled to 600°C., water-quenched, reheated to 600°C., water-quenched	44

Fig. 1 illustrates the effect of tempering nickel-chrome steel at different temperatures followed by either slow cooling or rapid cooling on impact toughness. The lowering of toughness begins to take place when tempering is conducted at 200°C., and between 300° and 400°C. minimum toughness results. From above 400°C. the time of heating and the rate of cooling exercise marked influence
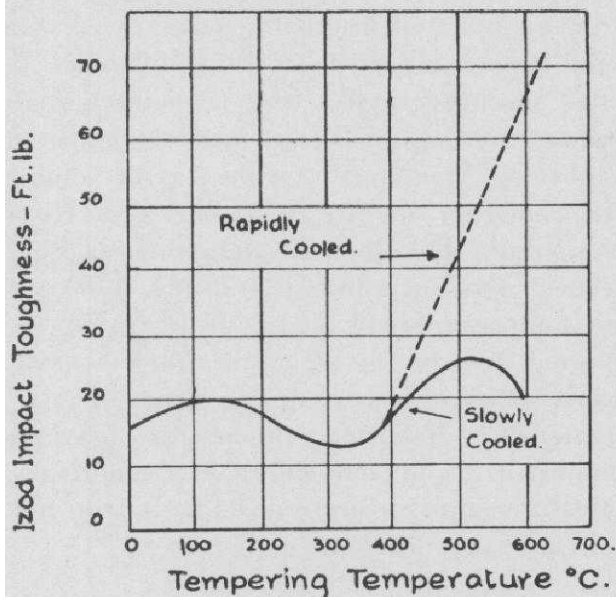
FIG. 1 — EFFECT OF TEMPERING Ni-Cr STEEL AT DIFFERENT TEMPERATURES AND RATE OF COOLING ON IMPACT TOUGHNESS

TABLE 2 — CHANGE WITH DECREASE IN TEMPERATURE IN NOTCHED-BAR IMPACT RESISTANCE OF COMMERCIALLY PURE ANNEALED 1-INCH DIAMETER WROUGHT ALUMINIUM, COPPER, IRON AND NICKEL RODS

TEMPERATURE, °C.	IZOD IMPACT VALUE (FT.-LB.)			
	Aluminium	Copper	Iron (Armco)	Nickel
Room	19	43	78	89
−40	19	45	—	91
−74	—	—	4	
−80	20	44	—	92
−120	21	45	—	93
−180	27	50	1·5	99

Chemical Composition

Si	0·054	C	0·035	Si	0·230
Fe	0·070	Mn	0·020	Co	0·140
		Si	trace	Fe	0·100
		S	0·016	Mg	0·260
		P	0·003	S	0·005
Al 99·876	Cu 99·985	Fe 99·926	Ni 99·700

on the toughness as depicted in Fig. 1. The rate of cooling from tempering temperature should be sufficiently fast to ensure optimum toughness of the steel. But such rates may not be feasible in commercial practice without introducing distortion and quenching stresses. The phenomenon of temper-brittleness and its supression have been discussed and speculated upon probably more than any other single alloy steel subject. The work on the subject has been critically reviewed by Hollomon[2] and by Woodfine[3].

The susceptibility to temper-embrittlement in alloy steels is designated by the ratio of notched impact values after tempering at 650°C. followed by water-quenching and furnace-cooling respectively. Previously the impact tests were conducted at room temperatures only. It is known, however, that all steels and most of the metals having body-centered cubic lattice structure behave as brittle materials at lower temperatures as shown in Table 2.

The drop in the value of energy absorbed during fracture, therefore, depends on the temperature. The temperature at which the fracture changes from tough (transgranular) to brittle or cleavage is called the ' Brittle transition temperature '. Jolivet and Vidal[4] indicated that susceptibility ratio at a particular temperature level did not give a correct picture of the phenomenon of temper-brittleness which uplifted transition temperature ranges in alloy steels. This is schematically shown in Fig. 2 which reveals that the magnitude of the susceptibility ratio greatly depends upon the relation of testing temperature with respect to the transition temperature. The low temperature brittleness of structural steels has received much attention particularly after the catastrophic failure of Liberty welded ships during World War II.
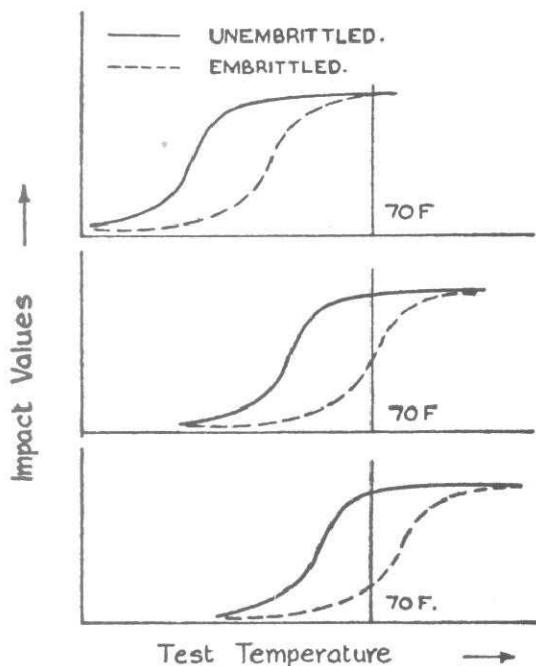
FIG. 2 — DEPENDENCE OF SUSCEPTIBILITY RATIO ON THE POSITION OF IMPACT TEMPERATURE CURVES

Effect of Temper-brittleness on Mechanical and Physical Properties

While the temper-brittleness is readily detected by impact tests at different temperatures, it does not affect the other mechanical properties like hardness, yield stress, ultimate tensile strength or fatigue[5]. Chapman and Jominy[6] subjected SAE 5140 to different heat treatments which gave the same hardness but markedly different impact values. Determination of endurance limit of these steels at room temperature and −35°F. revealed no conspicuous difference. In severely embrittled steels, a ' star ' type fracture[2] was observed instead of normal ' cup and cone ' in the tensile test. The thermal analyses of non-embrittled and embrittled specimens failed to show any regular change in the range of 300°-600°C., although Grenet[7] reported that by using differential dilatometer, Chevnard noticed differences in thermal expansion; these may, however, be due to relief of internal stresses[3]. Greaves and Jones[8] reported that the difference in the specific gravity was negligibly small while Andrew and Dickie[9] in steels tempered above Ae_1 mentioned that the specific volume depended on the rate of cooling. Electrical resistivity[8] and magnetic and electrical properties[7] were not affected on being subjected to temper-embrittlement, but Riedrich[10] reported that slightly higher electric resistivity occurred on slow cooling. X-ray investigations[11,12] reported differences between embrittled and non-embrittled conditions. Measurements of electrode potential do not disclose any difference.

Effect of Composition on Temper-brittleness

Although many factors contribute to temper-brittleness, the chief is chemical composition. The effects of change of microstructure, hardenability and grain size due to an element should be considered.

Carbon in Alloy Steels — The phenomenon of temper-brittleness in plain carbon steels is dealt separately by one of the authors (Dr. Nijhawan). Though Hollomon[2] reported that plain carbon steels are not susceptible (FIG. 3), Libsch *et al.*[14] and Zaffe and Buffum[15] mentioned that plain carbon steels are very susceptible to temper-brittleness.
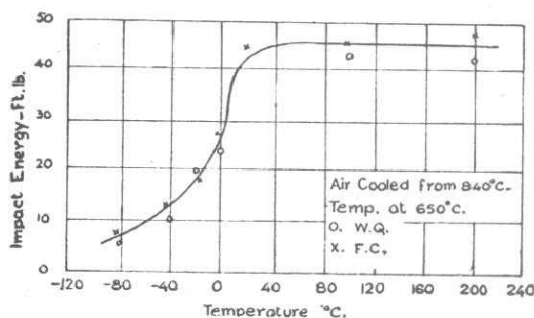

FIG. 3 — TEMPER-BRITTLENESS TESTS ON SAE 1035 STEEL (AFTER HOLLOMON)

The effect of the variation of carbon on a susceptible alloy steel has not been properly investigated. Jolivet and Vidal[4] showed that on lowering the carbon from 0·22 to 0·073 per cent, the susceptibility was reduced. Buffum, Zaffe and Clancy[16] reported that an alloy containing 1·5 per cent Ni, 0·6 per cent Cr with only 0·003 per cent C was free from temper-embrittlement. Working with high-purity alloys, Preece and Carter[17] mentioned that in Fe-Cr alloy susceptibility to temper-brittleness disappeared on reducing the carbon to about 0·003 per cent. It is fairly clear that in steels susceptible to temper-embrittlement carbon plays an important role and lowering its amount reduces the susceptibility towards temper-embrittlement.

Manganese, Chromium and Nickel — Any two of these elements introduce temper-brittleness. Hollomon[2] noticed that manganese-vanadium (FIG. 4) and manganese-molybdenum (FIG. 5) steels containing moderate amounts of Mn and V or Mo are not very susceptible to temper-brittleness. In plain nickel steels containing 3 or 3·5 per cent Ni, with 0·15 and 0·24 per cent Cr respectively, Jones[18] noticed lower impact values in quenched steels tempered and reheated to 400°C. Greaves and Jones[18] indicated that nickel was less effective than manganese in increasing the susceptibility. Recently Woodfine[19] showed that nickel alone did not contribute to temper-brittleness. In plain Cr and Mn steels amounts greater than
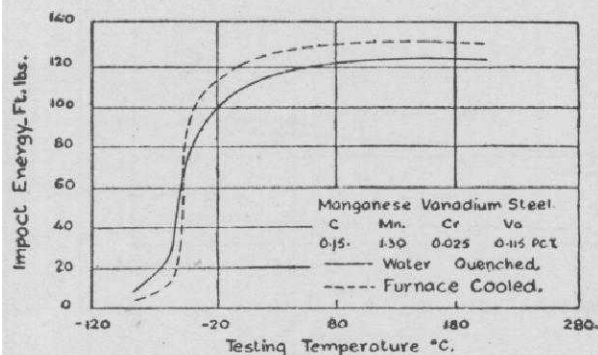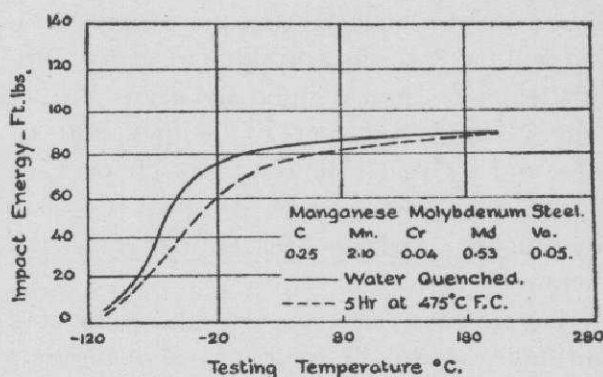

FIG. 5 — TEMPER-BRITTLENESS TESTS ON MANGANESE-MOLYBDENUM STEEL (AFTER HOLLOMON)

0·60 per cent enhance the susceptibility to temper-brittleness[20]. Manganese has greater effect than nickel and chromium. Hollomon[2] mentioned that steels having the same hardenability due to Ni, Cr or Mn will have approximately same susceptibility. In alloys made from high-purity materials, Hultgren and Chang[21] have reported that chromium in the absence of phosphorus does not lead to embrittlement.

Vanadium and Tungsten — Jolivet and Vidal[4] reported that addition of 0·23 per cent V to Cr steel increased the susceptibility, and Vidal[20] showed that 3·8 per cent W steel free from Cr was also susceptible to temper-embrittlement.

Phosphorus — Jolivet and Vidal[4], Baertz et al.[22,23], and Harris and Elsea[24] showed that increase in phosphorus increases the susceptibility to temper-embrittlement for chromium, manganese and Mn-Cr steels. Phosphorus raises the transition temperature[23,24]. But chromium steels[4] containing only 0·008 per cent P were also not immune to temper-brittleness. The addition of 0·1 per cent P to 3 per cent Ni steel raised the transition temperature[19] from —34° to 12°C. Preece and Carter[17] mentioned that phosphorus increased the susceptibility, though its presence was not essential for temper-embrittlement.

Nitrogen — The effect of nitrogen on temper-brittleness has not been fully studied.

FIG. 4 — TEMPER-BRITTLENESS TESTS ON MANGANESE-VANADIUM STEEL (AFTER HOLLOMON)

It is, however, believed that increase in nitrogen will increase susceptibility to temper-embrittlement. Jones[8] indicated that 3·0 per cent N - 0·33 per cent C - 0·8 per cent Cr steel and Jacquet[25] showed that 3·25 per cent N - 0·3 per cent C - 1·65 per cent Cr steel are highly sensitive to temper-embrittlement.

Arsenic and Antimony — Both arsenic and antimony are usually present in small amounts in commercial alloy steels. These elements belong to the same group as phosphorus in the periodic table. Houdremont, Bennek and Newmeister[26] showed that arsenic raises the transition temperature of plain carbon steel. Jolivet and Vidal[4] reported that antimony exercises considerable effect on the embrittlement characteristics of 1·5 per cent Cr steels. Jones and Morgan[27] stated that plain carbon steels are embrittled by antimony. Austin, Entwisle and Smith[28] studied the effects of

antimony and arsenic on En 24 steels with or without molybdenum and their results are summarized in Fig. 6. While arsenic raises the transition temperatures of both embrittled and unembrittled conditions moderately, antimony increases the susceptibility to temper-brittleness markedly. Carr[29] showed that addition of 0·09 per cent and 0·08 per cent of antimony raised the transition temperature from —25° to 100°C. and 30° to 150°C. respectively after embrittling treatment of 24 hr. at 520°C. These examples show that antimony exerts overwhelming influence in bringing about temper-brittleness.

Molybdenum — The effect of molybdenum is rather complex as by itself it produces temper-brittleness[30] while its presence in Cr, Ni-Cr and Ni-Mn steels prevents it. By the addition of 0·15 per cent Mo to 0·98 per cent Cr steel and 0·27 per cent Mo to nickel-
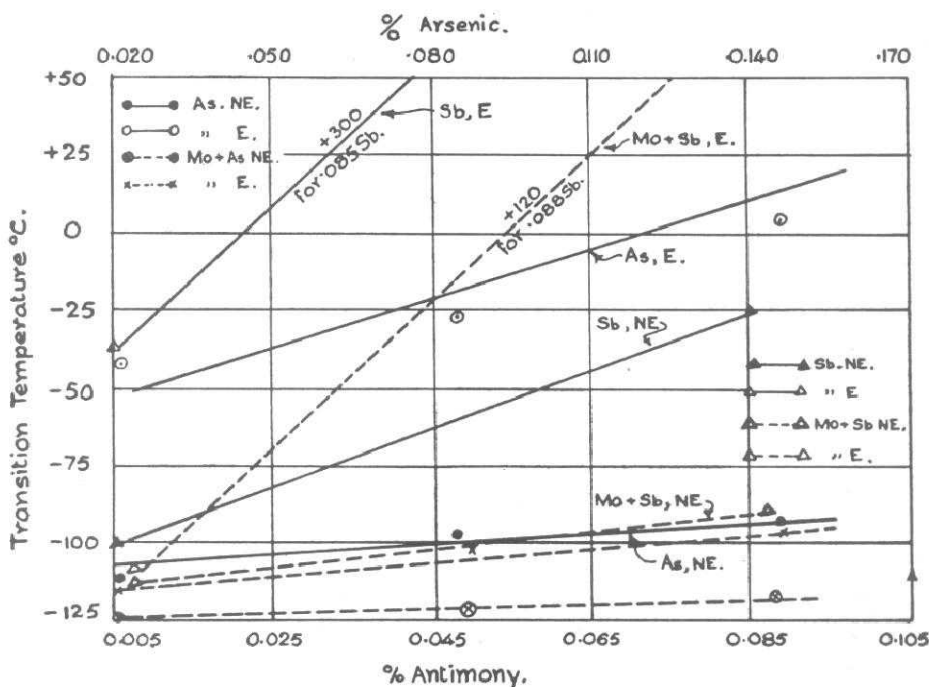

FIG. 6 — EFFECTS OF ARSENIC AND ANTIMONY ON THE TRANSITION TEMPERATURE OF En 23 STEEL, WITH OR WITHOUT MOLYBDENUM (AFTER AUSTIN, ENTWISLE AND SMITH)

chrome steel, the susceptibility to temper-embrittlement disappears as shown in Figs. 7 and 8 respectively. Nijhawan[31] observed that slow cooling after tempering of Ni-Cr-Mo bullet-proof armour plate gives relatively lower impact values.
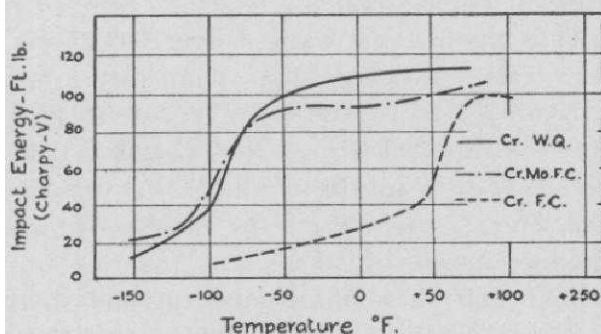
FIG. 7 — EFFECT OF MOLYBDENUM ON THE IMPACT-TEMPERATURE CURVE OF A CHROMIUM STEEL (AFTER ARCHER, BRIGGS AND LOEB)
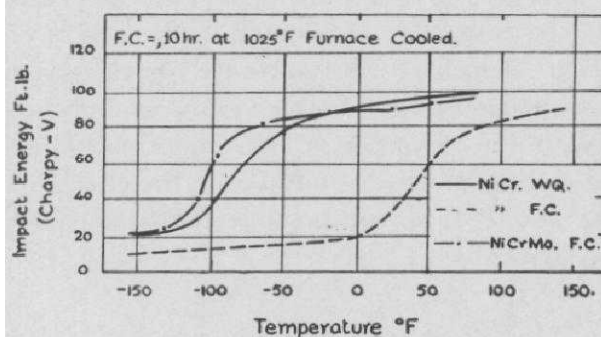
FIG. 8 — EFFECT OF MOLYBDENUM ON IMPACT-TEMPERATURE RELATIONSHIP OF A NICKEL-CHROMIUM STEEL (AFTER ARCHER, BRIGGS AND LOEB)

Aluminium, Titanium and Zirconium — The indirect effect of the addition of aluminium in so far as it relates to deoxidation and refinement of grain size is dealt with later on. The effect of larger amounts of the aluminium in excess of quantity required for deoxidation has received attention only recently. Jolivet and Vidal[4] mentioned that the presence of 0·5 per cent Al in a chromium steel did not alter the susceptibility to temper-brittleness. In 3 per cent Ni - 1 per cent Cr steel, Wood-

fine[19] mentioned that the addition of 0·95 per cent aluminium did not prevent temper-embrittlement. But Crafts and Offenhauer[32] showed that high acid soluble aluminium lowers the transition temperatures of both plain carbon and chromium-copper-nickel steels. Geil, Carwile and Digges[33] showed that aluminium can lower the transition temperature of 0·30 per cent C steels with nitrogen contents varying from 0·004 to 0·032 due to the stabilization of nitrogen as aluminium nitride. Since excess of aluminium over the optimum required for grain refinement (0·02-0·05 per cent[34]) causes grain-coarsening, the effect is truly due to its function as alloying element.

It is, therefore, felt that the influence of increasing additions of aluminium in other alloy steels and particularly nickel-chrome steel on temper-brittleness be investigated to ascertain its beneficial effects, if any. It may also be worthwhile to study the effectiveness of aluminium in the presence of rare earth elements.

The addition of titanium (in presence of aluminium) did not affect temper-brittleness[19]. Herres and Lorfig[35] mentioned that Ti and Zr did not prevent temper-embrittlement. These elements can form stable nitrides, but as they do not alter the embrittlement characteristics, the theory based on the precipitation of nitride from a solution in ferrite appears untenable.

Boron, Oxygen, etc.— Herres and Lorig[35] reported that boron steels were susceptible. As boron can replace nickel in contributing hardenability, its effect on temper-embrittlement has received much attention[46] and is shown in Fig. 9. It may be observed that addition of usual amount of boron will not create any difficulty by increasing the susceptibility to temper-brittleness. The effect of oxygen has not been properly investigated.

Vanadium and Tungsten — Jolivet and Vidal[4] showed that the presence of 0·23 per cent V in chromium steel increased the

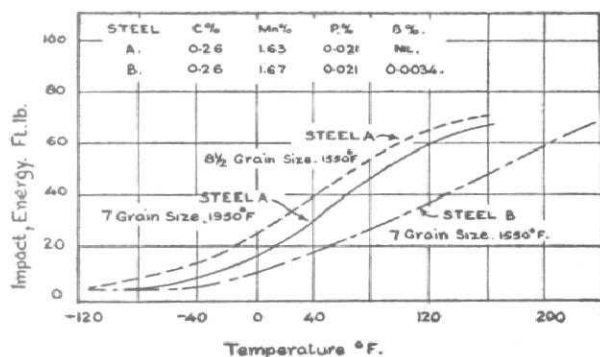| STEEL	C%	Mn%	P%	B%.
A.	0·26	1.63	0·021	Nil.
B.	0·26	1.67	0·021	0·0034.

FIG. 9 — IMPACT TOUGHNESS AND TRANSITION CURVE FOR TEMPER-EMBRITTLED (900°F. FOR 100 HR.) STEELS (AFTER POWERS AND CARLSON)

susceptibility while Vidal[30] showed that 3·8 per cent W in low manganese steel caused embrittlement.

It is, therefore, observed that the chemical composition of steel largely determines the susceptibility to temper-brittleness. Summarizing the effects of chemical composition on temper-embrittlement it may be mentioned that it occurs when more than 0·003 per cent C is present in steels containing manganese or chromium or molybdenum. The elements manganese and phosphorus exercise marked influence in promoting temper-brittleness. In sensitive steels, the susceptibility is increased in the presence of antimony, arsenic and nickel and reduced by molybdenum or tungsten. The elements like boron, vanadium, aluminium and titanium appear to have negligible effect.

The elements nickel, arsenic and antimony do not confer temper-embrittlement. It has been reported that chromium by itself does not lead to temper-embrittlement and phosphorus in Fe-C-Cr alloys renders to susceptibility[21]. The influence of different elements on the notch toughness at various temperatures of pearlitic steels with base composition of 0·30 per cent C, 1·0 per cent Mn and 0·3 per cent Si has been investigated by Rinebolt and Harris[36]. It was reported

that carbon, molybdenum and phosphorus raise the transition temperature. Chromium and boron do not affect and nickel lowers the transition temperature. Titanium and vanadium up to about 0·2 per cent initially increase and then decrease the transition temperature, while the effect of aluminium appears to be small.

It is known that oxygen over 0·0025 per cent raises the transition temperature remarkably. It is, therefore, apparent that the elements which raise the transition temperature also adversely affect the temper-brittleness. Considering the elements which produce temper-brittleness, it may be observed that these form substitutional solid solution with iron and also form carbides; while nickel, antimony, arsenic and phosphorus, though form substitutional solid solution with iron, do not form carbides. Some of the elements which are soluble in γ-iron give a closed austenite loop and cannot be easily accommodated in the γ-lattice. Such elements will segregate during part tempering costing to the grain boundaries (with the exception of Mn and C) leading to embrittlement. Considering the effects of As and P it is not possible to explain the mechanism[2,19].

Effect of Grain Size on Temper-brittleness

Numerous instances[37-39] can be cited to prove that finer the grain size, lower is the transition temperature and the susceptibility ratio. The effect of actual grain size on the transition temperature is illustrated in Fig. 10. The authors[1] obtained the results shown in Table 3, the impact tests were conducted at room temperature (20°C.).

In arsenic-bearing steels differing in austenitic grain sizes, Austin et al.[28] concluded that the effect of grain size on temper-brittleness was more pronounced than that of arsenic itself.

TABLE 3 — EFFECT OF GRAIN SIZE ON SUSCEPTIBILITY RATIO

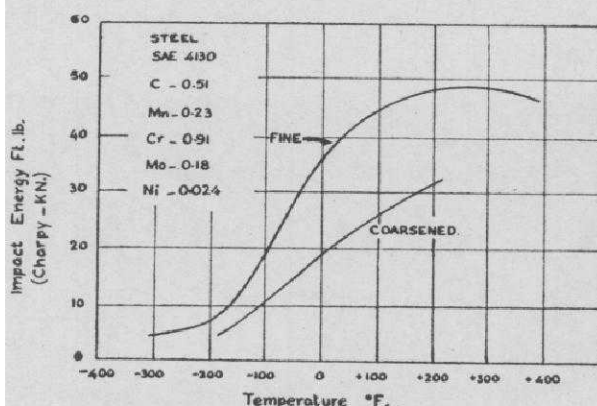| REF. NO. OF STEEL	COMPOSITION OF THE STEEL	McQUAID-EHN GRAIN SIZE	IMPACT VALUES, FT.-LB. AFTER O.Q. 850°C., TEMP. 600°C.		V.P.H. No.		SUSCEPTI-BILITY RATIO (20°C.)
			Furnace-cooled A	Oil-quenched B	A	B	
1	C 0·40% Mn 0·71% Ni 3·33% Cr 0·87% Al nil	3-4	10	47	278	290	4·7
2	C 0·400% Mn 0·710% Ni 3·300% Cr 0·860% Al 0·029%	7-8	17	55	287	295	3·2

FIG. 10 — EFFECT OF ACTUAL GRAIN SIZE ON TRANSITION TEMPERATURE (AFTER GILLET AND McGUIRE)

Effect of Microstructure on Temper-brittleness

As the steels after oil-quenching and tempering generally possess tempered martensite structure, the effects of the various microstructures on temper-embrittlement have not been clearly indicated. Pellini and Quenean[40] subjected the specimens to isothermal treatments to develop various microstructures and reported that susceptibility in pearlitic structure was less than in martensitic structure. The presence of pearlite or bainite with tempered martensite due to faulty hardening treatment raises the transition temperature[41], as illustrated in Fig. 11. Woodfine[19] concluded that the transition temperature was lowest in martensite, intermediate in bainite and highest in pearlite
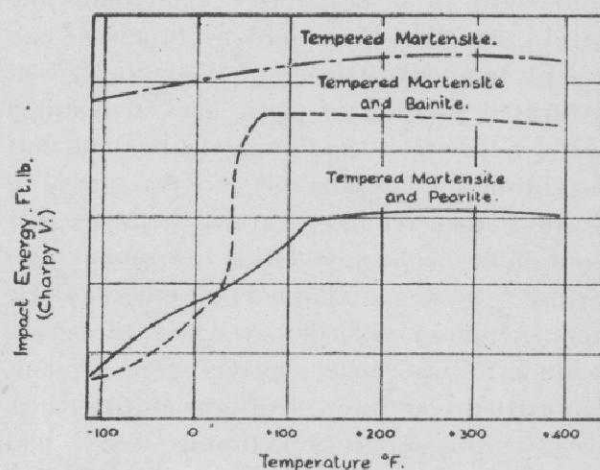

FIG. 11 — EFFECT OF MICROSTRUCTURE ON IMPACT VALUES AT VARIOUS TEMPERATURES OF A NICKEL-CHROME-MOLYBDENUM STEEL (AFTER ARCHER, BRIGGS AND LOEB)

structure. Amongst embrittled and unembrittled nickel-chrome steels the extent of embrittlement was more in tempered martensitic structure. Notch effects of micro-constituents can be avoided by proper distribution of carbide in the microstructure. It should be recognized that such structural alteration is reflected not only on impact toughness but also on tensile ductility, which is not affected by temper-embrittlement.

Metallographic Examination of Temper-brittleness

Considerable attention has been devoted to detect temper-brittleness in a steel by the use of a suitable etchant. It was noticed that normal reagents like nital, picral, alkaline, sodium picrate, Murakamis reagent did not distinguish between embrittled and unembrittled specimens. Cohen, Hurlich and Jacobson[42] demonstrated that temper-brittleness can be detected by etching in a solution of picric acid in ethyl ether to which Zephiran chloride (alkyl-dimethyl-benzyl aluminium chloride) was added. McLean and Northcott[13] showed that even in the absence of Zephiran chloride, etchants based on picric acid with a surface-active compound like cetyl trimethyl ammonium bromide can reveal temper-brittleness. Woodfine[19] used saturated solution of picric acid in distilled water. In steels containing manganese but no chromium, considerable care is required to produce the etching effect with the reagent containing Zephiran chloride. Spretnak and Speiser[43], however, claimed that etheral picric acid Zephiran chloride attacked the grain boundaries of nickel-chrome steel in non-embrittled condition. Authors during their investigation on nickel-chrome steels[1] had noticed Cohen, Hurlich and Jacobson's[42] work, but as Zephiran chloride was not readily available, they tried a few alternative etchants based on etheral solution (250 cc.) of picric acid (25 gm.) to which dilute ammonia (1 drop in 25 cc. of above solution) and ammonium chloride (2 drops of 10 per cent solution to 25 cc.) were added. The embrittled and unembrittled specimens were mounted side by side and after usual polishing were etched in aforesaid reagent. Etching and polishing lightly a number of times clearly distinguished between embrittled and unembrittled conditions of coarse and fine-grained steels as shown in Figs. 12(i)-(iv). Fig. 13 shows continuous network around the grains of embrittled steel. As the etching attack at the grain boundaries persisted on lightly abraiding the specimen followed by polishing which destroyed the structure inside the grains, it is presumed that the grain boundary attack of the etchant produced grooves and not ridges which is in confirmation with observations made from electron micrographs[3,44].
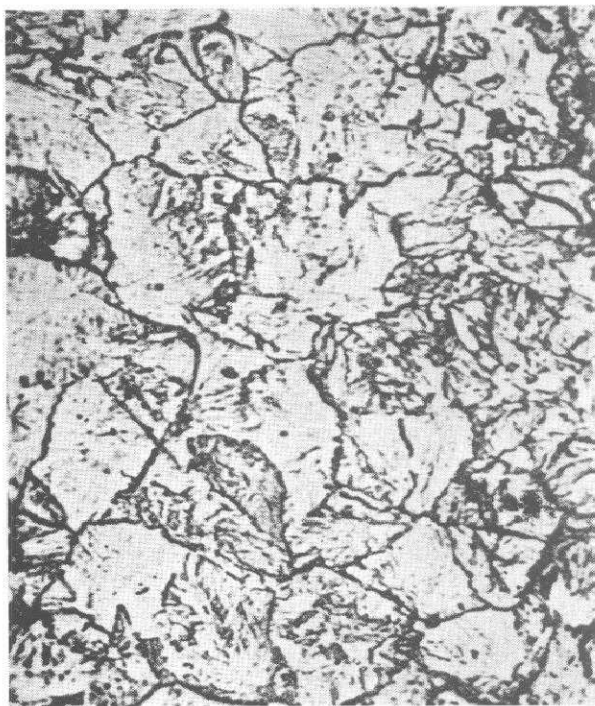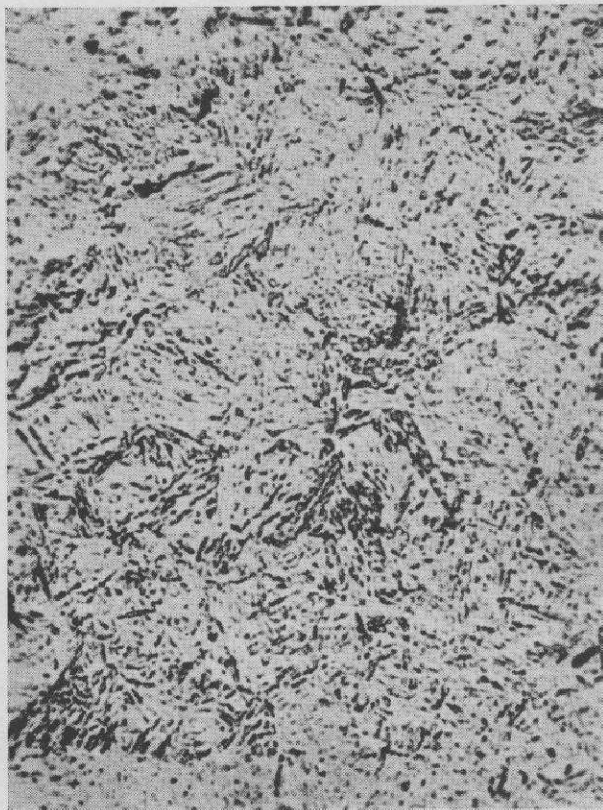

FIG. 12(i)

Fig. 12(ii)

Fig. 12(iv)

Fig. 12(iii)

Theories of Temper-brittleness

It is not intended to give a detailed critical examination of the various theories proposed to account for the complex phenomenon of temper-brittleness. Apart from the effect of the chemical composition, grain size and microstructure of the steel, steel-making practice, austenitizing temperature and time-temperature relation during the tempering treatment affect the susceptibility to temper-embrittlement. It is known that embrittled specimens behave normally after retempering and quick cooling indicating reversibility of the process. The mechanism should also take into account that other physical properties are not affected by embrittling treatment.

Jolivet and Chouteau[45] summarized that the hypothesis on the phenomenon had attributed it to (i) transformation in the existing phases, viz. allotropic change of iron, change in the molecular arrangement of
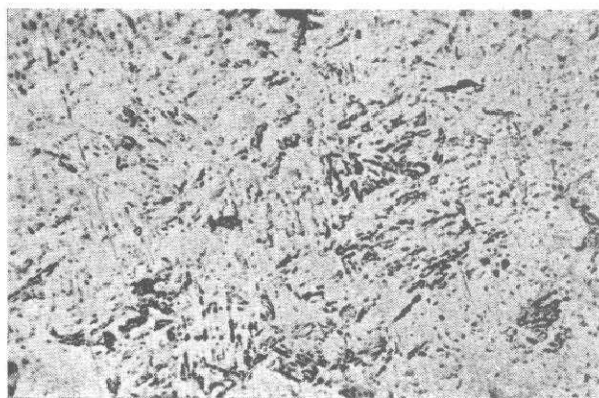
FIG. 13(i)

FIG. 13(ii)

atoms, alteration of the carbides, (ii) trans-formation of retained austenite to martensite, and (iii) precipitation of a new phase at the grain boundaries like cementite, carbide, chromium oxide, nitride or phosphide. McLean and Northcott[13] have proposed segre-gation of various elements to grain bound-aries. Zaffe[47] proposed segregation at the ferrite grain boundaries and Maloof[12] suggest-ed distribution of carbides to account for the phenomenon. Woodfine[19] modified McLean and Northcott's[13] theory by suggesting that solute atoms of Cr, Mn, Mo and W segregate to the austenite grain boundaries and C atoms segregate at the ferrite grain bound-aries. Russel[48] while discussing Woodfine's[19] paper suggested two theories, firstly, that regions of high tensile strength can be set up by unequal contraction of the pre-existing austenite zones during slow cooling. His second hypothesis is based on orderly distri-bution of otherwise randomly distributed atoms of responsible elements on or within α-lattice during slow cooling, the random distribution being retained on faster cooling. This depletion of alloying elements causes weakening at the grain boundaries. McLean[44] mentioned that electron micrographs of tem-per-embrittled steel showing absence of coalescence of the precipitate after prolonged embrittling treatment at the grain boundary

(FIG. 14) decided in favour of segregation theory amongst the two rival ones, the pre-cipitation theory and the segregation theory. From etching characteristics Preece and Carter[17] were, however, in favour of the theory on precipitation of carbides, although no pre-cipitate has been detected or identified even under the electron microscope. Segregation of solute atoms is known to occur. In case of substitutional solid solution, the segregation is the same in austenite and ferrite. Intersti-tial atoms occupying large space in austenite segregate markedly in ferrite. Substitu-tional atoms of antimony, having 30 per cent more atomic diameter than iron, would segregate markedly resulting in highly em-brittled condition. But as the phenomenon mainly occurs in ferritic condition, segrega-tion of interstitial atoms is the probable cause[44]. Sage[49] suggested that segregation of atoms to austenite grain boundaries during heat treatment followed by segregation of carbon atoms to ferrite grain boundaries led to temper-brittleness. When ferrite and aus-tenite boundaries are common, the carbon atoms are anchored by carbide-forming elements, thus constituting a continuous brittle envelope on the grain.

It has been observed that an acceptable theory on the mechanism of temper-brittle-ness must explain (i) the increase in suscep-
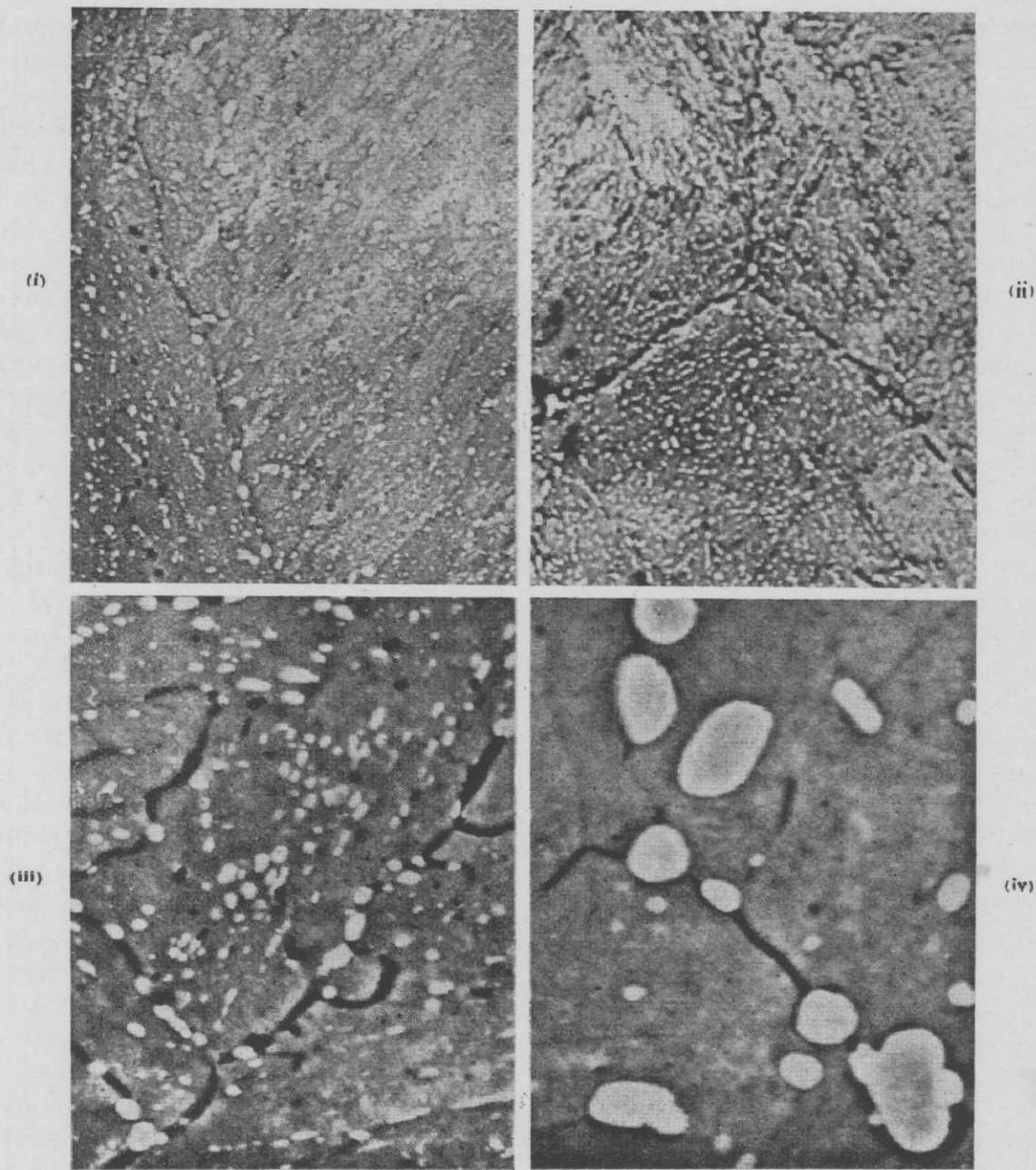
FIG. 14 — ELECTRON MICROGRAPHS OF Ni-Cr STEEL. (i) QUENCHED AFTER TEMPERING AT 635°C; TOUGH CONDITION, IZOD VALUE 68 FT.-LB. (ii) AND (iii) AS (i), HELD 24 HR. AT 500°C. (WITHIN THE EMBRITTLING RANGE) AFTER TEMPERING AT 635°C.; BRITTLE CONDITION, IZOD VALUE 14 FT.-LB.; THE BLACK BOUNDARIES (GROOVES IN THE ETCHED METAL SURFACE) ARE ASSOCIATED WITH BRITTLENESS. (iv) AS (i), HELD FOR 2400 HR. AT 500°C., MUCH GROWTH OF CARBIDE PARTICLES, BUT NO DETECTABLE SPHEROIDIZATION OF BOUNDARIES. (i) AND (ii) 5000, (iii) AND (iv) 20,000. (AFTER MCLEAN)

tibility due to high austenitizing temperature, (ii) the effect of various elements on embrittlement, (iii) the occurrence of brittleness primarily at the prior austenite grain boundaries, (iv) kinetics of the embrittling reaction, and (v) the reversibility of the phenomenon. Spretnak and Speiser[43] proposed a mechanism based on the depletion of carbon atoms with the conversion of retained austenite to martensite during slow cooling after

tempering. The theory, however, has not gained much support. Considering the absence of any convincing evidence of coalescence after prolonged embrittling treatment [Fig. 14 (iv)] in the excellent electron micrographs given by Woodfine[19] and McLean[44] [Fig. 14(i)-(iv)] it is felt that the segregation theory is more probable, although it may not explain the effects due to arsenic and antimony.

An attempt will now be made to explain the complex behaviour of molybdenum.

Based on the hypothesis that precipitation of carbides or nitrides contributes to temper-brittleness, Hollomon[2] considered that molybdenum decreases the amount of precipitate by retarding the rate of precipitation and thereby ameliorates the embrittlement.

On the assumption that tendency to segregation is greater for molybdenum in comparison with chromium, Sage[48] mentioned that the grain boundaries will have higher concentration of it, but as carbon atoms will be kept anchored by chromium because of its higher affinity for carbon, they will not be able to reach the grain boundaries to form a brittle layer and consequently will not be embrittled. Molybdenum appears to affect temper-brittleness by its influence on other elements.

Summary

The occurrence of temper-brittleness in certain alloy steels has received considerable attention both from theoretical aspects and practical applications. While the production metallurgist is satisfied with the removal of the susceptibility by the addition of molybdenum, considerable work has been conducted to ascertain the fundamental aspects. It has been recognized that the chemical composition of steels determines the susceptibility to temper-embrittlement. Chromium and manganese in amounts greater than 0·6 and tungsten enhance the susceptibility to temper-brittleness. Nickel has much less influence on the susceptibility which increases in presence of phosphorus. Molybdenum by itself produces the embrittlement and also satisfactorily immunizes sensitive steels like the nickel-chrome steel to make them suitable for commercial applications. Phosphorus and presumably nitrogen make the steel markedly susceptible. Aluminium lowers the transition temperature, but its effect is not thoroughly investigated. Vanadium, titanium and boron exercise minor effects, if any. Arsenic and antimony pronouncedly increase the susceptibility in temper-brittle steels. Increase in the grain size and incomplete hardening raise the transition temperature. Embrittlement is shown by a deterioration of toughness only, as other mechanical properties like tensile strength, endurance limit, hardness, and physical properties like dilatation, electrode potential, electrical resistance are not affected.

Temper-brittleness can be lowered by adding molybdenum or tungsten to the steel. It is reduced by limiting the addition of alloying elements which form substitutional solid solution and also form carbides for requisite hardenability, refining the grain size and by proper hardening treatment so as to get tempered martensitic structure.

Metallographic evidence of temper-embrittlement was readily obtained by etching in a reagent based on a solution of picric acid in ether to which ammonia, ammonium chloride and alcohol were added and the results were comparable to reagents based on etheral picric acid with either Zephiran chloride or CTAB.

Regarding the theories on temper-brittleness, the electron micrographs of specimens of non-embrittled and embrittled for prolonged periods indicated in favour of the segregation theory which puts forward the mechanism that atoms of Cr, Mn, Mo and W segregate towards austenite grain boundaries during austenitizing followed by segregation of carbon to ferrite grain boundaries, which produces a network of brittle material along the original austenitic grain boundaries,

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