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MEMORANDUM REPORT

NO. WAL 322/2

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TEMPER-BRITTLENESS IN A MANGANESE-NICKEL-CHROMIUM-MOLYBDENUM ARMOR STEEL.

BY

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JOHN H. HOLLOMON
Captain, Ordnance Department

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Watertown Arsenal Laboratory
Memorandum Report WAL 322/2.
Problem Number H-1.4

1 July 1944

SUBJECT

TEMPER-BRITTLENESS IN A MANGANESE-NICKEL-CHROMIUM-MOLYBDENUM ARMOR STEEL.

ABSTRACT

It was observed by the Armor Section of the Laboratory that one manufacturer of rolled armor using a manganese-nickel-chromium-molybdenum steel for two and one half inch to four-inch plates was obtaining mottled (partly fibrous and partly crystalline) fractures, possibly indicative of low toughness, when the heats contained high percentages of manganese and chromium, but were fibrous when the percentages were low. The purpose of the experiments discussed in this report was to determine the cause of this anomalous behavior. Small specimens taken from one heat of this type of steel were variously heat-treated, machined into Charpy specimens and tested at -40° F. Examination of the impact results indicates that this steel is susceptible to temper-brittleness. The results are in complete agreement with the early fundamental work of Greaves and his collaborators

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as to the nature of this phenomenon. If tempered above about 1100° F., armor made from this steel must be quenched from the tempering temperature to avoid embrittlement. If it is to be used for sections above about six inches, even water-quenching from the temper is not likely to be severe enough to prevent the embrittlement. At lower tempering temperatures (hardness above about 330 Brinell), no practical method of avoiding the embrittlement has yet been proposed for other than very thin sections.

INTRODUCTION

In examining the properties of steels made by one of the rolled-armor manufacturers, it was found that when the manganese and chromium contents were on the high side of the aim analysis, mottled or speckled* fractures were observed in the fracture test. The cause of this behavior was not understood and the Physical Metallurgy Section of the Laboratory was requested by the Armor Section to investigate the properties of specimens taken from a plate of this type of analysis.

It was believed that there were only two phenomena

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*Designated Fc type of fracture in the Watertown Arsenal Laboratory system of classification. See Table II.

which could cause nonfibrous fractures (lowered notched-bar-impact energies) when the analyses were on the high side, while fibrous fractures were being obtained with lower alloy heats. Increases in alloying elements, particularly manganese and chromium, will depress the martensite transformation range and may result in the retention of austenite at room temperature. This retained austenite may transform upon tempering to some isothermal product, the exact nature of which will be governed by the tempering cycle employed and the transformation characteristics of the steel. For example, if this retained austenite transforms to pearlite upon tempering, it is expected that the notched-bar-impact energy will be less than that obtained if the structure were entirely tempered martensite. Whether or not retention of austenite occurs and has an effect can easily be determined experimentally by cooling specimens to a low temperature following quenching and then tempering, and comparing the impact energies with specimens quenched only to room temperature (and tempered).

Temper-brittleness could also cause lowered impact energy with increasing alloy content. Much experimental work was performed and many papers written concerning this phenomenon just after the last war. The fundamental references are those of Greaves and his collaborators[1, 2, 3, 4], based on experiments performed at Woolwich Arsenal on steels which were presumably used for guns. Some attention was given to this phenomenon between the two wars, but primarily by Japanese[5, 6, 7], and German[8, 9], and Russian[10] investigators. Recently Lorig and co-workers[11] in an N. D. R. C. report described results of experiments with several armor steels. These results are in essential agreement with the early work of Greaves and his co-workers. The general nature of temper-brittleness is fairly well understood, primarily as a result of the fundamental work of Greaves. Carpenter and Robertson[12] have summarized this information in their general discussion on the classification of steels.

In general, the relation of the impact energy of steels with tempering temperature (or hardness) can be of three types. Firstly, there is the behavior of non-temper-brittle steels, the impact energy of which increases continuously with tempering temperature*. This relation is illustrated as Curve A in Figure 1. The second type of relation is characterized by temper-brittle steels which are cooled rapidly from the tempering temperature (Curve B, Figure 1). As the tem-

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*This discussion is concerned with steels quenched to martensite before tempering.

pering temperature is increased, the impact energy first rises slightly, then decreases, then rises again. If, however, a temper-brittle steel is slowly cooled following tempering, the third relation between impact energy and tempering temperature results. This relation is illustrated as Curve C in Figure 1. Below about 800° F., the impact energy is independent of the rate of cooling from the tempering temperature. Above about 800° F., the impact energy rises with cooling rate, the slower the cooling from the temper, the lower the impact energy. The higher the tempering temperature, the greater is the difference between the impact energies of rapidly and slowly cooled specimens. The magnitude of the valley between about 400° F. and 800° F. and the magnitude of the effect of slow cooling from the tempering temperature will depend upon the composition of the steel. Greaves and Jones[4] pointed out that any steel showing a difference in impact energy between rapidly and slowly cooled specimens following tempering at a high temperature will be characterized by a relation between impact energy and tempering temperature as illustrated by Curve B of Figure 1 when quenched from the temper. These same two investigators concluded that manganese, nickel, chromium, and vanadium had a potent effect in increasing the susceptibility to temper-brittleness. However, they also found that molybdenum would cure the malady in nickel-chromium steels containing low percentages of manganese, but only reduce the susceptibility in high manganese steels. Generally speaking, it appears that the higher the over-all hardenability (unless it is obtained with increasing carbon content), the less likely is molybdenum to cure the difficulty. As will be pointed out in a subsequent report[13], if the hardenability of a manganese-nickel, chromium steel is sufficient to develop martensite on quenching in sections thicker than about three inches, molybdenum will not completely eliminate the susceptibility to this type of brittleness. Early investigations also indicate that steelmaking practice affects this susceptibility. The interpretation of the temper-brittleness phenomenon is that, in susceptible steels, there is some constituent present, the solubility of which increases with increasing temperature. In the temperature range between 400° F. and 800° F., the solubility is low enough and the diffusion rate is sufficient to cause precipitation from the supersaturated solution and embrittlement. Above about 800° to 1000° F., the solubility is so great that precipitation can not occur at temperature, but will occur (in the range 400° to 800° F.), on slow cooling from the temper. Below

400° F., on the other hand, diffusion is too slow for appreciable precipitation to occur in the usual tempering times. The precipitating constituent has not been identified.

In order to determine whether the undesired fracture of the plate in question was caused by temper embrittlement or by the retention of austenite, the experiments reported herein were performed.

MATERIALS

The steel was made by the Basic-Open Hearth process and cross-rolled to four-inch plate. A fracture test specimen from a plate indicated that the steel was of exceptionally high quality*, but the fracture was found to be mottled (partially fibrous and partially crystalline). The analysis of the steel was as follows:

	C	Mn	Si	S	P	Ni	Cr	Mo	Cu	B	Al	Ti
Ladle	.26	1.50	.26	.023	.018	.74	1.07	.47	.10	-	-	-
Check at W.A.	.28	1.57	.32	.027	.017	.63	1.06	.49	.09	.0012	.04	.04

The heat-treatment used by the manufacturer is listed below:

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* "B" steel quality fracture rating.

Heat to 1650° F. - 6½ hrs. rise, 3 1/6 hr. hold, W.Q.
Heat to 1195° F. - 6 3/4 hrs. rise, 6 hrs. hold, A.C.
Brinell Hardness - - - - - - - - 255/269.

Small specimens (approximately 5/8" square) were machined parallel to the principal rolling direction from one half of the fracture-test specimen. These specimens were heat-treated, two .01 inch radius V-notch Charpy bars were cut from each and were tested at -40° F.

RESULTS

Before proceeding with the impact tests on the small specimens, the martensite transformation starting temperature was determined by thermal arrest measurements and the martensite finish temperature dilatometrically. The procedure used for these measurements will be described in a subsequent report[14]. The cooling rate (at 1300° F.) for these determinations was approximately 80° F./sec. The martensite start was found to be at 645° F. and the finish at 440° F. From these data, it might be deduced that there probably will be little or no retained austenite present after water-quenching of the four-inch plate. However, the more slowly a specimen is cooled through the martensite range, the more likely the retention of austenite becomes. Furthermore, the transformation of the austenite may continue until some small percentage of austenite remains instead of going continuously to completion as a specimen is cooled. Thus, the dilatometric technique could indicate an end to the martensite transformation even though some small percentage of austenite had not transformed.

The small specimens were heat-treated according to the schedule given in Table I. The results of the "V"-notch Charpy tests performed at -40° F. are also listed in this table, as well as the Rockwell "C" hardnesses of the specimens. In order to determine the effect of retained austenite on the impact properties, the results of the tests on specimens 21 and 32 should be compared. Specimen 21 was cooled only to room temperature before tempering and specimen 32 was cooled to -190° C. This low-temperature treatment had little effect*, and it may be considered that there is little if any effect of retained austenite, or that there is little if any retained on quenching to room temperature.

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*The difference in hardness must be considered. This is probably due to the fact that the tempering at 1000° F. of the two specimens was carried out in different furnaces.

The effect of tempering temperature and variation of cooling from the tempering temperature for this steel is illustrated in Figures 2 and 3. In Figure 2, the results of the impact tests are plotted as a function of hardness (for various times and temperatures of tempering). All of the specimens which were air-cooled and water-quenched from the temper, except those tempered for ten minutes at 1000° F., fall on a smooth curve. Below about 37 Rockwell C, the impact energy of the furnace-cooled* specimens first rises, and then falls precipitously. Greaves and his co-workers have shown that the brittleness of specimens tempered in the range of from 400° to 800° F. may be avoided by tempering for a short time at a high temperature, if the tempering is followed by rapid cooling. Such treatment will avoid precipitation in the lower temperature range, simply because at higher temperature, the solubility is sufficient to prevent precipitation. Specimens given such a short-time treatment must of necessity be small and must be cooled rapidly from the temper to avoid the precipitation. This improvement brought about by short-time

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*The rate of cooling was not measured but is estimated to be about 1/10° F. per minute at 1300° F.

tempering is illustrated by the results of specimens tempered for a short time at 1000° F. (Numbers 41 and 42). In Figure 3, the impact energies (at -40° F.) are plotted as a function of tempering temperature for five hours at temperature. It is to be noted that this figure is in agreement with Curves B and C of Figure 1. A sharp rise in impact energy occurs between 1000° and 1100° F. irrespective of the rate of cooling from the temper. At higher temperatures, the impact energies of the furnace-cooled specimens are less than those of the corresponding rapidly cooled specimens.

In all cases, the fracture ratings (See Table I and Table II) are consistent with the impact energies, particularly in that specimens tempered at 1200° F. (about 250 BHN) show a mottled (Fc) type of fracture, after slow cooling from the temper.

DISCUSSION

The results indicate that this manganese-nickel-chromium-molybdenum steel is fairly susceptible to temper-brittleness, although it will probably not contain retained austenite if properly quenched (i. e., if the bainite formation is avoided*). The consequences of this

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*See Troiano[15] for effect of the formation of some bainite on the retention of austenite.

temper-brittleness will be a lowering of the impact energy following slow cooling from the tempering temperature (for tempering temperature in excess of about 1100° F.). Because of the thickness of the armor for which this steel is used, even air-cooling from the tempering temperature will probably result in some temper-embrittlement. Further, this steel cannot be heat-treated to above about 330 Brinell (33 Rockwell C) without a precipitous decrease in impact energy. This decrease occurs independent of the cooling treatment after tempering and can only be avoided by a short-time tempering at a high temperature which is not practicable, except for very small specimens.

On the basis of the experimental data of this report and the data of the metallurgical literature, it may be concluded that certain precautions must be taken in the heat-treatment of temper-brittle steel. If nonfibrous fractures are obtained at hardnesses below about 300 BHN, when the analysis is sufficient for obtaining martensite on quenching, the steel should be retempered and quenched from the temper, (if the original tempering was followed by slow cooling). If the total alloy content or carbon content is very high, the nonfibrous fractures may be due to the retention of austenite, in which case retempering will probably have no effect. A solution for this latter difficulty other than refrigeration will be presented in a subsequent report[13]. For sections thicker than about six inches, it is doubtful whether water-quenching is severe enough to eliminate the temper-embrittlement. If, on the other hand, nonfibrous fractures occur at hardnesses, between about 320 to 400 Brinell (for carbon content in the range .25 to .35 per cent), rapid cooling following tempering will be of no avail in improving the fracture if martensite was obtained on quenching. In this case, the only hope is to choose a new analysis which does not exhibit temper-embrittlement. For low hardenability steel, additions of molybdenum may be of some help. For high hardenability steels, experimentation with various analyses is necessary and there may be no solution to the problem, at the present time.

Further, if it is necessary to quench from the temper, stresses will certainly be introduced which might affect fabrication. Stress-relieving can not be considered at temperatures in the range of about 650° to 900° F., for embrittlement will result. Stress-relieving from higher temperatures (after welding for example) must, of course, be followed by cooling sufficiently rapidly to avoid embrittlement. Such treatments will relieve local stresses even though additional stresses of a different distribution will be introduced in the rapid cooling following tempering.

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Private D. C. Buffum and Mr. L. D. Jaffe assisted materially in obtaining and assembling the data discussed in this report.

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Captain, Ordnance Department

Concurred in:

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APPROVED:

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TABLE I

HEAT-TREATMENTS, IMPACT RESULTS (-40° F.) FROM SMALL SPECIMENS TAKEN FROM FOUR-INCH, MANGANESE-NICKEL-CHROMIUM-MOLYBDENUM ROLLED ARMOR PLATE*

BAR NUMBER	TEMPERING TEMP.	TEMPERING TIME	COOLING FROM TEMPER	INDIVIDUAL CHARPY ENERGIES (FT.-LBS.)		AVERAGE CHARPY ENERGIES (FT.-LBS.)	FRACTURE	AVERAGE**** ROCKWELL "C" HARDNESS
11	300	5 hr.	A.C.	27.3	28.2	27.8	F	47.7
12	400	"	"	29.5	26.7	28.1	F	46.5
13	500	"	"	13.6	18.1	15.9	Cdf	45.2
14	600	"	"	16.8	18.1	17.5	Cdf	44.7
15	700	"	"	12.9	16.9	14.9	Cdf	42.8
16	800	"	"	17.0	16.8	16.9	Cdf	41.4
17	900	"	"	18.1	15.7	16.9	Cdf	39.6
21	1000	"	"	25.0	23.3	24.2	Cdf	36.3
22	1100	"	"	67.9	65.6	66.8	F	30.5
23	1200	"	"	77.1	72.3	74.7	F	25.3
24	1275	"	"	74.8	69.6	72.2	Cdf	20.4
25	As quenched			15.6	13.8	14.7	Cd	51.8
26	150	5 hr.	A.C.	19.4	8.3	13.9	Cd	51.0
27	1000	"	W.Q.	27.6	33.4	30.5	Cdf	35.7
31	1000	"	F.C.	26.6	20.6	23.6	Cdf	34.4
32**	1000	"	A.C.	26.5	31.1	28.8	Cdf	34.8
33**	1000	"	F.C.	28.0	22.9	25.5	Cdf	34.3
34**	1000	"	W.Q.	30.3	31.4	30.9	Cdf	34.7
35	400 & 1000***	"	A.C.	20.5	19.4	20.0	Cdf	35.3
36	"	"	[redacted]. → [redacted]. F.C.	15.5	16.4	16.0	Cd	35.8
37	"	"	[redacted]. → [redacted] C.Q.	23.6	20.5	22.1	Cdf	36.0
41	1000	10 m.	A.C.	23.6	26.4	25.0	Cdf	37.9
42	1000	10 m.	W.Q.	28.2	23.7	26.0	Cdf	38.7
44	1000	1 hr.	A.C.	22.4	22.7	22.6	Cdf	35.8
45	1000	1 hr.	F.C.	16.4	21.2	18.6	Cd	36.5
46	1000	"	W.Q.	20.8	29.7	25.3	Cdf	36.0
47	1000	24 hr.	A.C.	67.9	61.5	64.7	F	28.3
51	1000	"	F.C.	51.0	53.8	52.4	Fc	29.4
52	1000	"	W.Q.	58.6	69.0	63.8	F	29.4
53	1125	10 m.	A.C.	58.2	51.2	54.7	Fc	33.7
54	1125	"	W.Q.	61.9	58.2	60.1	F	33.7
55	1025	1 hr.	A.C.	25.0	25.8	25.4	Cdf	34.4
56	1025	"	F.C.	22.2	22.2	22.2	Cdf	35.4
57	1025	"	W.Q.	28.2	35.0	31.6	Cdf	34.9
61	950	24 hr.	A.C.	18.2	18.7	18.5	Cdf	36.7
62	950	"	F.C.	15.5	15.6	15.6	Cd	36.0
63	950	"	W.Q.	16.6	17.4	17.0	Cdf	37.3
71	1100	5 hr.	F.C.	60.0	54.2	57.1	Fc	30.5
72	1100	"	W.Q.	65.6	70.7	68.2	F	30.2
73	1200	4½ hr.	F.C.	42.4	44.1	43.3	Cdf	22.3
74	1200	4½ hr.	W.Q.	74.9	71.3	71.3	F	23.4

*All specimens quenched after three hours at 1650° F.

**Cooled to -300° F. before tempering.

***Tempered at 400° F. for five hours, followed by 1000° F. for five hours.

****Average of six readings.

TABLE II

STANDARD TYPES OF NOTCHED-BAR-IMPACT FRACTURES.

SYMBOL	DESCRIPTION
F	Fibrous
S	Silky (generally encountered with steels of high hardness)
Fc	Fibrous matrix with spots of crystallinity
Cdf	Dull crystalline patch surrounded by fibrous border
Cbf	Bright crystalline patch surrounded by fibrous border
Cd	Dull crystalline (complete)
Cb	Bright crystalline (complete)

Note 1: Additional terms such as: dendritic, conchoidal, etc., used to describe the fractures, should be written out in full following the fracture type symbol.

Note 2: If it is desired to estimate the relative amounts of fibrous and crystalline surface areas, a fraction will be placed following the fracture symbol. This fraction will refer to the estimated surface area which is crystalline.

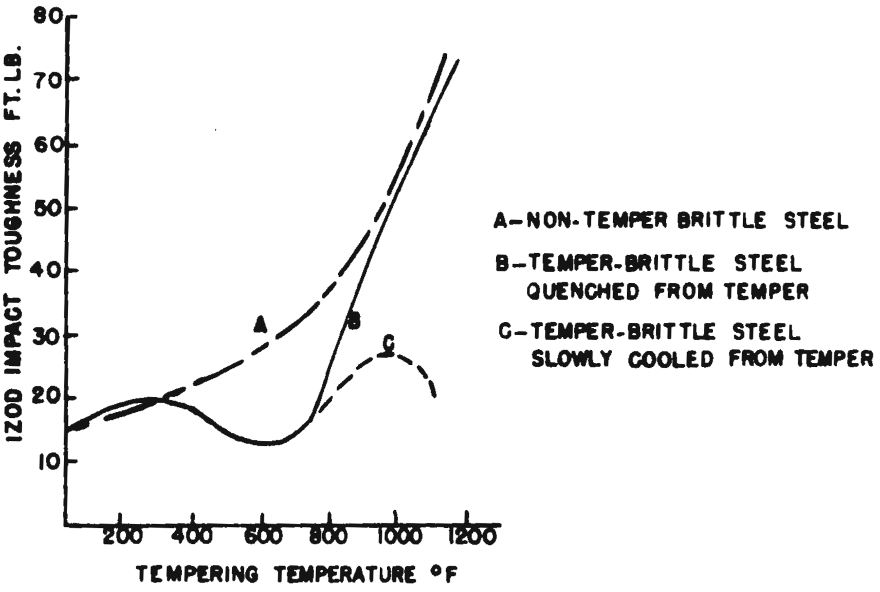

FIGURE I

EFFECT OF TEMPERING ON IMPACT TOUGHNESS

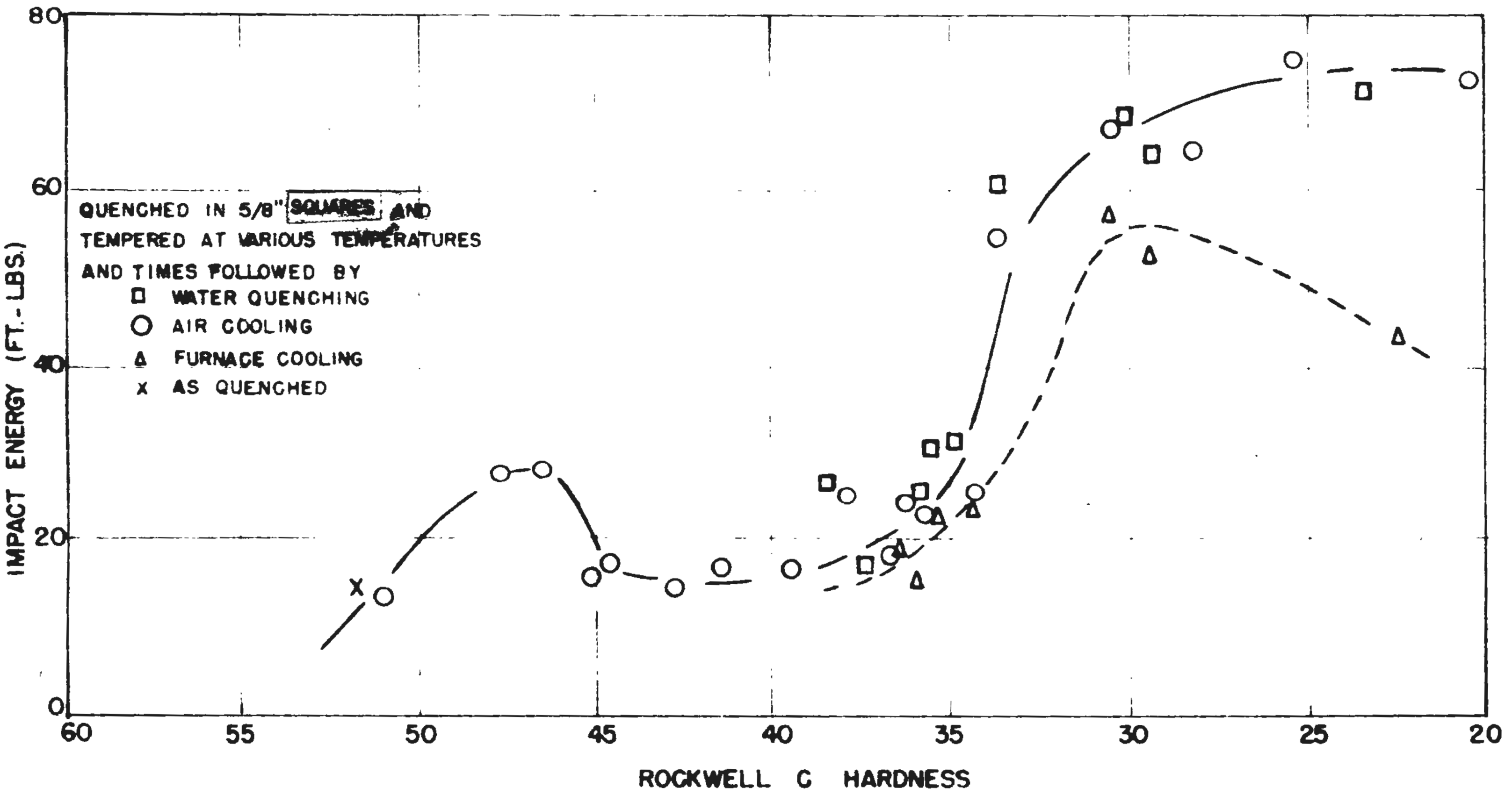

FIGURE 2

EFFECT OF HARDNESS AND VARIATION OF COOLING FOLLOWING TEMPERING ON CHARPY IMPACT ENERGY. (Mn-Ni-Cr-Mo STEEL)

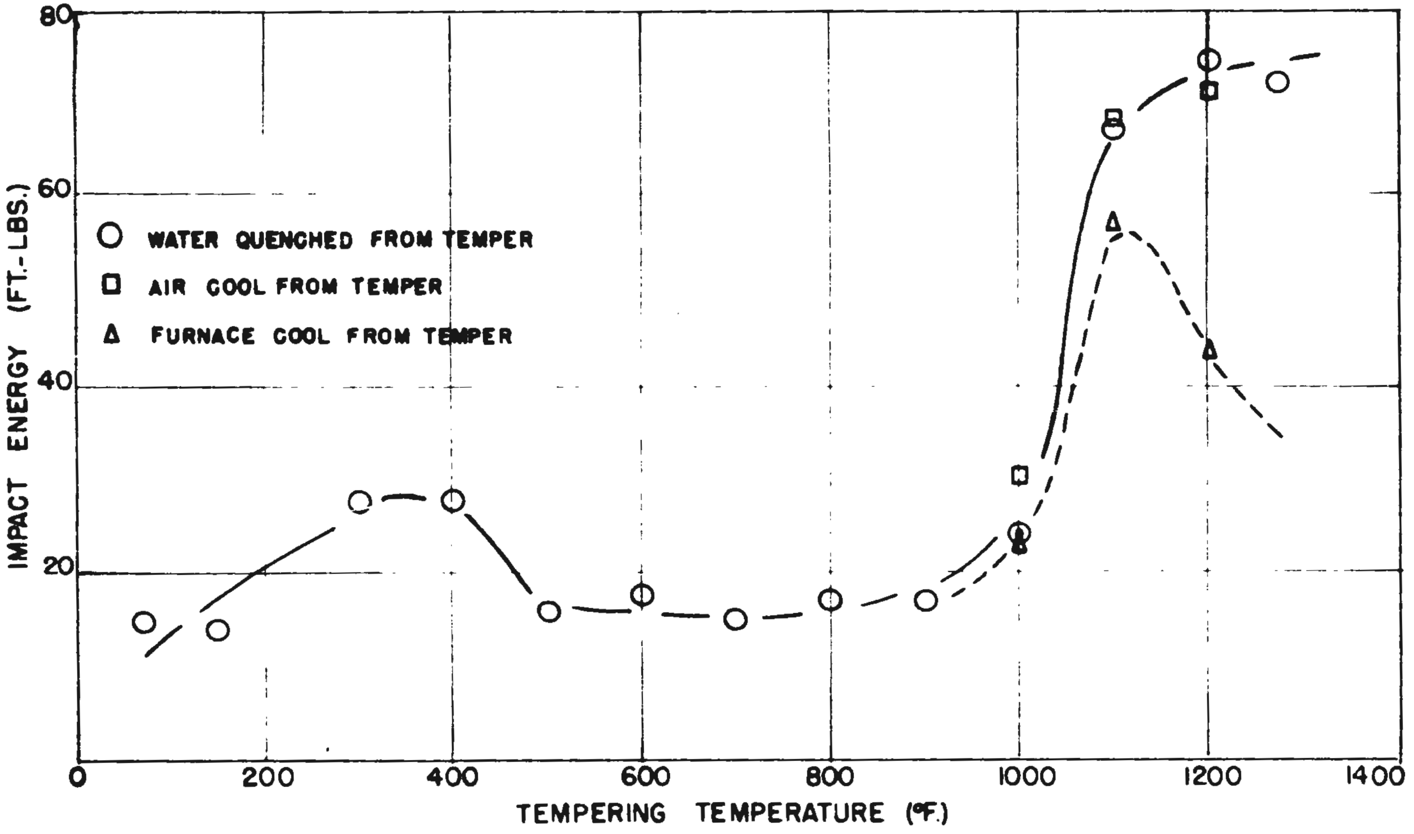

FIGURE 3

EFFECT OF TEMPERING TEMPERATURE AND VARIATION OF COOLING FOLLOWING TEMPERING ON CHARPY IMPACT ENERGY (Mn-Ni-Cr-Mo STEEL) (5 HOURS AT TEMPERATURE)

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