

Effect of Arsenic, Copper, Tin and Molybdenum on Impact Properties of Steels

By

Hiroshi SAWAMURA and Toshisada MORI

Department of Metallurgy

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I Introduction

The present investigation was carried out for the purpose of determining the effects of arsenic, copper, tin and molybdenum on impact properties of steels. Among the various influences of arsenic and tin on the mechanical properties of steel, the decrease in toughness of steel is most serious. When a steel containing arsenic or tin is heated to a high temperature in an oxidizing atmosphere, contamination of these elements occurs on the surface layer of steel¹⁾²⁾³⁾ and the steel becomes liable to produce surface cracks. Copper has a similar tendency of promoting the embrittlement of steel by contaminating on the surface layer. Since this tendency of embrittling is a common property of these three elements, the influence of these elements on the impact properties of steel was investigated in the range of from room temperature to 900°C. About 0.3 per cent of molybdenum was added to some of the specimens used in this investigation and its effect was also investigated. The allowable limits of arsenic, copper, and tin that give effect on deformability of several kinds of carbon steel and dead soft steel were estimated from these results.

II Preparation of specimens

Swedish carbon steel and dead soft steel were used as raw materials and the charge weighing 80 or 100 kg was melted by a high frequency electric furnace of 100 KVA capacity. Kenjiho white pig, ferro-silicon and metallic manganese were added to the charge as required in order to keep the content of carbon, silicon and manganese as constant as possible. In addition, metallic arsenic, electrolytic copper, metallic tin and ferro-molybdenum were added to the molten metal and after the melt was deoxidized by an aluminum wire, it was cast into an ingot as shown in Fig. 1. The weight of each ingot is 12 kg of which 3.8 kg is the weight of the head and the balance is that of the body. Forty-eight kinds of specimens were manufactured by

Table 1. Chemical Composition

Specimen	%													Total O	Total N
	C	Si	Mn	P	S	As	Cu	Sn	Mo	Ni	Cr	Al			
A0	0.06	0.25	0.42	0.006	0.028	0.018	0.025	—	—	—	—	0.017	0.0075	—	
A1	0.05	0.25	0.40	0.006	0.027	0.35	0.025	—	—	—	—	0.028	—	—	
A2	0.06	0.25	0.41	0.008	0.027	0.61	0.023	—	—	—	—	0.024	—	—	
A3	0.06	0.23	0.38	0.008	0.025	0.85	0.022	—	—	—	—	0.058	—	—	
A4	0.06	0.21	0.37	0.008	0.026	1.07	0.040	—	—	—	—	0.015	—	—	
B0	0.28	0.04	0.25	0.029	0.021	0.011	0.036	—	—	—	—	—	0.0047	—	
B2	0.26	0.06	0.25	0.028	0.022	0.59	0.018	—	—	—	—	—	—	—	
B3	0.24	0.04	0.26	0.029	0.020	0.79	0.024	—	—	—	—	—	—	—	
B4	0.23	0.05	0.25	0.032	0.022	1.01	0.022	—	—	—	—	—	—	—	
D0	0.57	0.26	0.37	0.028	0.020	0.018	0.018	—	—	—	—	—	0.0039	—	
D1	0.56	0.43	0.39	0.028	0.022	0.34	0.017	—	—	—	—	—	—	—	
D2	0.59	0.22	0.38	0.026	0.018	0.54	0.015	—	—	—	—	—	—	—	
D3	0.54	0.21	0.38	0.028	0.018	0.87	0.018	—	—	—	—	—	—	—	
D4	0.55	0.23	0.38	0.029	0.017	1.04	0.020	—	—	—	—	—	—	—	
E0	0.85	0.30	0.43	0.024	0.015	0.014	0.014	—	—	—	—	—	0.0036	—	
E1	0.84	0.25	0.43	0.024	0.017	0.34	0.014	—	—	—	—	—	—	—	
E2	0.85	0.26	0.43	0.025	0.014	0.54	0.014	—	—	—	—	—	—	—	
E3	0.85	0.27	0.42	0.025	0.015	0.80	0.015	—	—	—	—	—	—	—	
E4	0.83	0.27	0.43	0.025	0.015	0.98	0.015	—	—	—	—	—	—	—	
F0	0.04	0.23	0.40	0.008	0.017	0.002	0.07	tr.	tr.	0.03	0.08	0.017	0.0073	0.0189	
F1	0.04	0.21	0.40	0.008	0.016	0.004	0.18	tr.	tr.	0.03	0.08	0.040	—	—	
F2	0.03	0.21	0.40	0.008	0.017	0.004	0.18	0.06	tr.	0.04	0.08	0.055	—	—	
F3	0.04	0.19	0.41	0.012	0.014	0.11	0.18	0.05	tr.	0.03	0.08	0.051	0.0062	—	
F4	0.04	0.19	0.40	0.011	0.015	0.25	0.18	0.06	tr.	0.03	0.08	0.041	—	—	
F5	0.04	0.21	0.38	0.013	0.017	0.43	0.17	0.05	tr.	0.03	0.08	0.060	—	—	
F6	0.05	0.23	0.37	0.012	0.014	0.44	0.19	0.04	0.26	0.03	0.08	0.019	—	—	
G0	0.04	0.18	0.43	0.008	0.014	0.008	0.07	tr.	tr.	0.03	0.07	0.017	0.0066	—	
G1	0.04	0.23	0.46	0.009	0.017	0.007	0.07	0.14	tr.	0.03	0.08	0.036	—	—	
G2	0.04	0.21	0.43	0.009	0.016	0.007	0.15	0.15	tr.	0.03	0.08	0.030	—	—	
G3	0.03	0.20	0.44	0.011	0.016	0.11	0.17	0.10	tr.	0.02	0.07	0.028	0.0055	—	
G4	0.03	0.18	0.41	0.011	0.017	0.26	0.19	0.11	tr.	0.03	0.09	0.028	—	—	
G5	0.03	0.17	0.39	0.012	0.016	0.43	0.17	0.09	tr.	0.02	0.07	0.047	—	—	
G6	0.03	0.15	0.34	0.013	0.016	0.42	0.18	0.11	0.31	0.03	0.08	0.037	—	—	
H0	0.03	0.17	0.33	0.008	0.017	0.005	0.07	tr.	tr.	0.01	0.06	0.008	0.0115	0.0173	
H1	0.03	0.16	0.39	0.009	0.015	0.007	0.35	tr.	tr.	0.03	0.08	0.023	—	—	
H2	0.04	0.17	0.38	0.011	0.017	0.005	0.34	0.14	tr.	0.03	0.07	0.038	—	—	
H3	0.03	0.18	0.35	0.011	0.014	0.10	0.33	0.11	tr.	0.03	0.07	0.022	0.0036	—	
H4	0.03	0.18	0.36	0.010	0.015	0.26	0.37	0.11	tr.	0.02	0.07	0.020	—	—	
H5	0.03	0.18	0.30	0.011	0.015	0.43	0.34	0.10	tr.	0.03	0.08	0.024	—	0.0155	
H6	0.03	0.15	0.27	0.012	0.016	0.45	0.33	0.08	0.28	0.03	0.07	0.015	—	—	
J0	0.04	0.21	0.35	0.009	0.016	0.007	0.07	tr.	tr.	0.03	0.07	0.009	0.0145	—	
J1	0.04	0.23	0.39	0.011	0.016	0.005	0.07	0.05	tr.	0.03	0.07	0.045	—	—	
J2	0.04	0.23	0.39	0.010	0.015	0.007	0.35	0.04	tr.	0.03	0.07	0.045	—	—	
J3	0.04	0.21	0.39	0.011	0.017	0.11	0.36	0.06	tr.	0.03	0.07	0.041	0.0087	—	
J4	0.04	0.21	0.37	0.011	0.016	0.26	0.34	0.06	tr.	0.03	0.07	0.038	—	—	
J5	0.04	0.21	0.35	0.012	0.016	0.46	0.35	0.05	tr.	0.04	0.08	0.048	—	—	
J6	0.04	0.18	0.31	0.012	0.014	0.46	0.35	0.05	0.30	0.02	0.07	0.020	—	—	

Note. —: not determined.

eight heats, but one of them blew up after it was cast into the mould because of deficiency of deoxidation. The total number of specimens used for the present experiments, therefore, were forty-seven.

As shown in Table 1, A-, F-, G-, H- and J-series are dead soft steels, B-series is 0.25 per cent carbon steel, D-series is 0.55 per cent carbon steel and E-series is eutectoid steel. Up to 1 per cent of arsenic was added to A-, B-, D- and E-series; and up to 0.35 per cent of copper, up to 0.1 per cent of tin, up to 0.5 per cent of arsenic and 0.3 per cent of molybdenum were added either individually or simultaneously to F-, G-, H-, and J-series.

The head of the ingot was cut off by sawing and after the surface skin of the ingot was machined off, the ingot body was heated in a gas furnace and then was forged into 20 mm square rod by a pneumatic hammer. The forging was done within the temperature range of from 1100 to 750°C. No difficulties were experienced in the process of forging the ingots and the square rod specimens were perfect without any recognizable cracks and defects. The rods were then cut to 113 mm long and annealed in a molten lead bath.

The following two methods of annealing processes were employed.

Annealing process (I):

The annealing process (I) is as shown schematically in Fig. 2. When the temperature of a lead bath reached 700°C, the specimens were charged into it and heated to the annealing temperature (T°C). After keeping the specimens for 1 hr at that temperature, they were furnace cooled to about 600°C (T'°C) and then air cooled from that temperature. The values of T and T' are shown in Table 2.

In case of A-, B-, D- and E-series, the annealing temperatures were changed⁴⁾ corresponding to the contents of arsenic, but in case of F-, G-, H- and J-series the temperature was set constant at 920°C because the change of A₃ transformation temperature was unknown as arsenic, copper, tin and molybdenum were contained together in these specimens. The air cooling temperatures of the specimens of A-, B-, D- and E-series taken out from the lead bath were not kept constant, but since it was discovered afterwards that it was desirable to keep the air cooling temperature constant, the temperature was kept constant at 600°C in case of the specimens of F-, G-, H- and J-series.

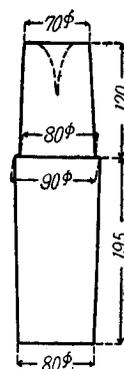


Fig. 1.

Dimensions of the ingot

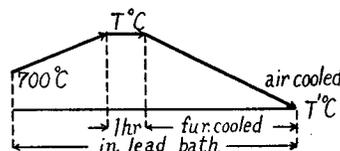


Fig. 2. Annealing process (I)

Annealing process (II):

The annealing process (II) is as shown schematically in Fig. 3. This annealing process was employed for the specimens for measuring transition temperature. In this process the specimens were furnace cooled to room temperature ($\sim 50^\circ\text{C}$), reheated to 370°C , and then they were air cooled from that temperature.

After the annealing, the specimens were machined to Charpy impact test pieces (10 mm square and 55 mm long with 2 mm deep U-notch) specified by JIS B7703 No. 3.

III Experiment methods

High temperature impact test was performed as follows: A test piece was inserted into a nichrome electric furnace which, being composed of upper and lower parts, easily opened or closed on a horizontal sectional plane. It was so arranged that the hot junction of a thermo-couple would touch the test piece at the lower center. After heating it to the testing temperature, the piece was taken out of the furnace, fixed to a Charpy

impact testing machine, and was struck with the blowing hammer as fast as possible. Caution must be taken at stage to (1) the temperature fall of the heated test piece after it was taken out of the furnace and (2) the surface oxidation of the piece while being heated in the furnace: but, since it was known that the latter would have no serious effect⁵⁾ if the maximum heating temperature would be lower than 900°C and the heating time comparatively short, we employed the method for heating them in

Table 2. Annealing and air cooling temperatures of annealing process (I)

Specimen	Annealing temp. $T^\circ\text{C}$	Air cooling temp. $T' ^\circ\text{C}$
A0	920 (920)*	620
A1	935 (920)*	610
A2	950 (920)*	650
A3	970 (920)*	630
A4	990 (920)*	640
B0	865	650
B2	895	630
B3	915	620
B4	930	580
D0	790 (795)*	600
D1	800 (795)*	570
D2	810	600
D3	820	650
D4	830	600
E0	760 (765)*	610
E1	765	630
E2	765	600
E3	765 (770)*	640
E4	765 (770)*	620
F0	920	600
}	}	}
F6	"	"
G0	"	"
}	}	}
G6	"	"
H0	"	"
}	}	}
H6	"	"
J0	"	"
}	}	}
J6	"	"

* Annealing temperature of process (II)

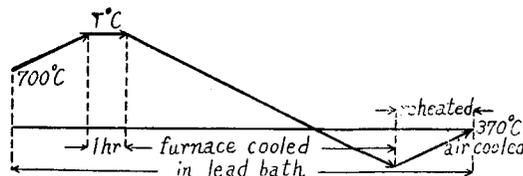


Fig. 3. Annealing process (II)

air atmosphere. To measure the temperature fall of a test piece, we prepared two test pieces shown in Fig. 4; on one of which was drilled at the center of the section (A) and on the other was drilled along the lower part 1.5 mm above the bottom (B). Each of these hole was 1 mm in diameter and 27.5 mm deep and the Pt.-Pt. Rh thermo-couple of 0.1 mm diameter was inserted into these holes and they were stuffed with asbestos at the mouth so as to prevent them from slipping off. When the furnace was heated to the testing temperature, a test piece was put into it and the time required to attain the same temperature between the furnace and the inner portion of the test piece was measured and the time required for heating the test piece was determined. It was found that from 10 to 15 minutes was adequate for heating the test piece. After the temperature of the inner part of the test piece became equal to the furnace temperature and being kept in the furnace for about another 3 minutes, the furnace was opened, the piece was pinched by a small tongs, set to the Charpy testing machine, and was blown by the hammer. As soon as the test piece was caught by the tongs to be removed, the temperature of the test piece was recorded every 2 seconds by counting the time interval by a metronome. These temperature measurements on both of the test pieces A and B were performed more than twice for each temperature and it was found that (1) the initial time lag at the beginning of recording temperature of the test piece seriously affected the reading temperature of the specimen, and (2) the cooling rate of the test piece was very so high outside of the furnace that the temperature difference between the pieces A and B could hardly be discerned. Averaging the results obtained of the test on A and B pieces, the curves of time versus temperature fall for the correction of impact temperature of the test piece were drawn as shown in Fig. 4.

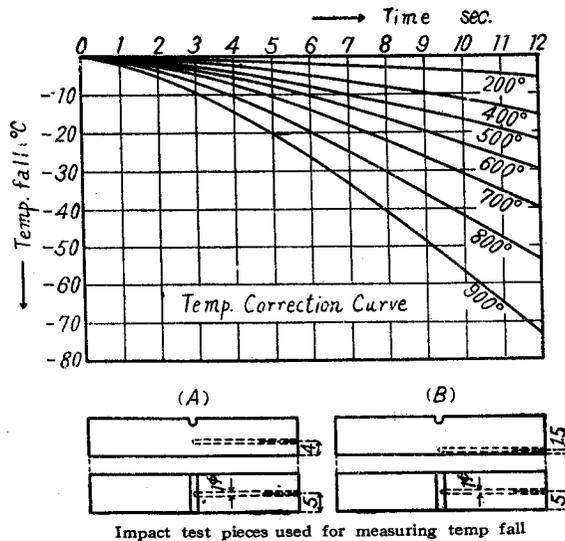


Fig. 4. Temperature correction curves and impact test pieces used for measuring temperature fall.

The time required for a test piece to be taken out of the heating furnace and be blown by the hammer was from 5 to 8 seconds (in most cases 5 seconds). The number of testings at each test temperature below 700°C were three on the average

and in the range higher than 750°C, two or more testings were handled.

Besides these impact tests, austenite and ferrite grain sizes, and hardness in annealed condition were measured and the microscopic structures were examined to investigate the effects of these factors on the impact properties.

IV Experimental results and consideration

1. Impact Test

The relations between impact values* and impact test temperatures are shown in Figs. 5~51. The symbols used are categorized as follows:

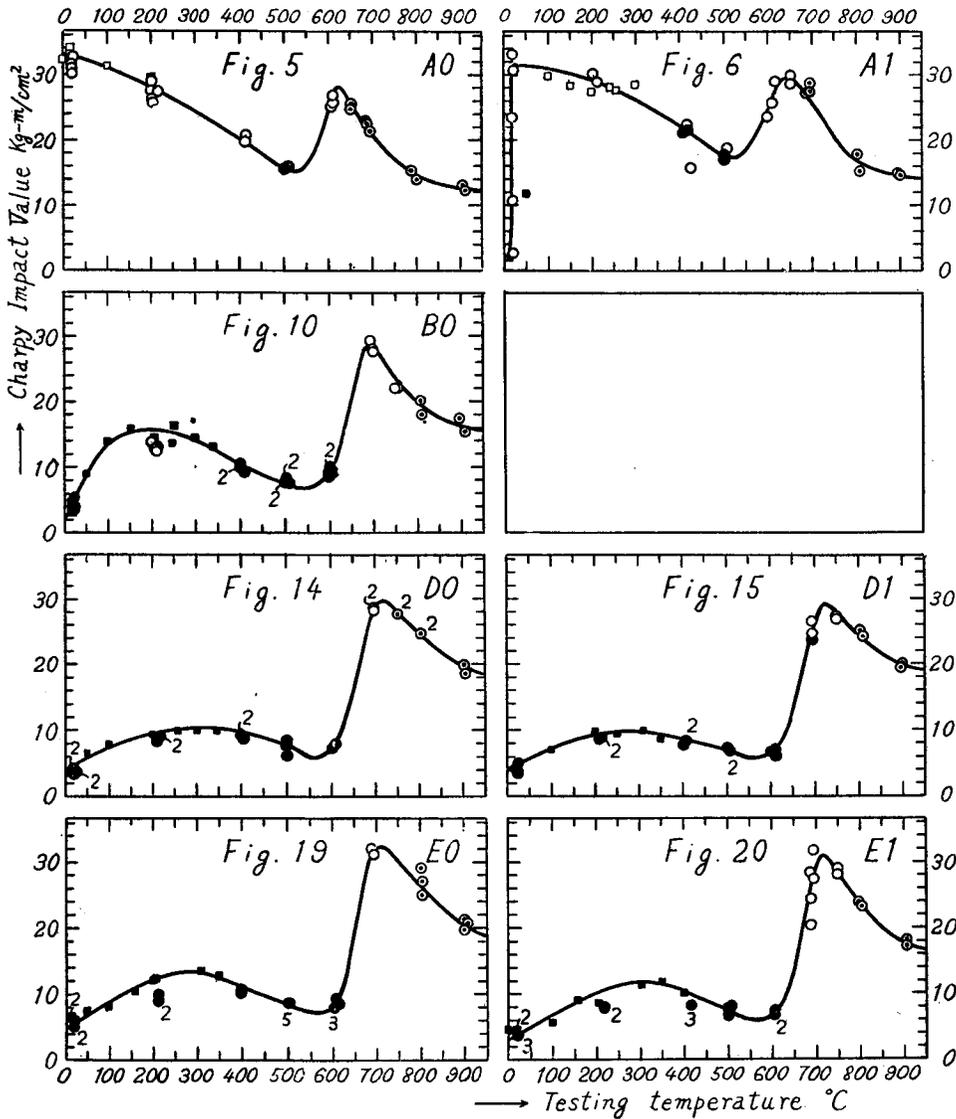
Symbol	Definition
⊙	The test piece which was annealed by the process (I), bent by impact testing, and no cracks was observed.
○	The test piece which was annealed by the process (I), bent by impact testing, and cracks were observed.
●	The test piece which was annealed by the process (I) and was broken into two pieces by impact testing.
□	The test piece which was annealed by the process (II), bent by impact testing, and cracks were observed.
■	The test piece which was annealed by the process (II) and was broken into two pieces by impact testing.

Numerals written in these figures signify the number of the test pieces which gave the same impact value.

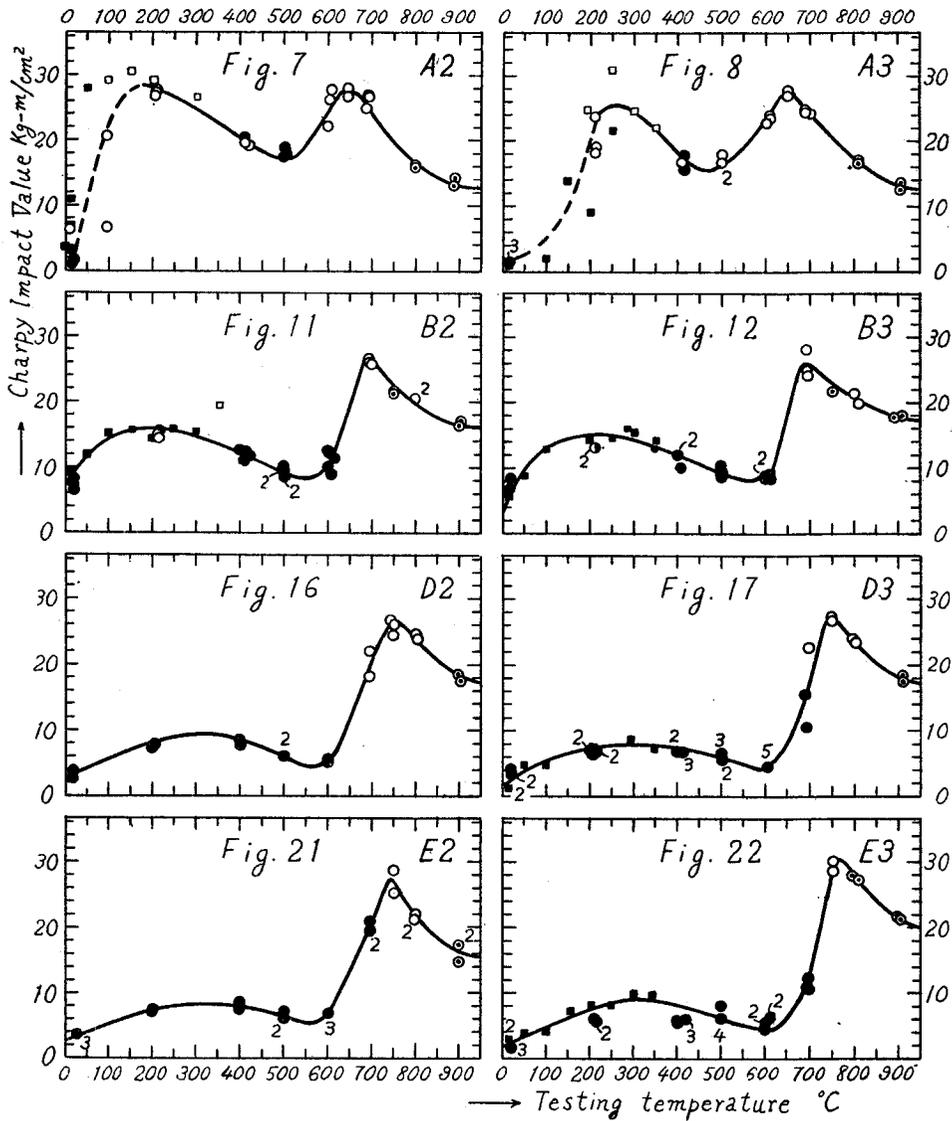
As shown in these figures, the specimens annealed by the process (II) show nearly equal or somewhat higher impact values at each temperature compared with those of the specimens annealed by the process (I).

(a) A-series: In A-series, i.e. in the case of dead soft steel whose carbon content is 0.05 to 0.06 per cent, the impact value of the specimen AO containing no arsenic is very high at room temperature and the impact value decreases markedly as the quantity of arsenic content increases and it decreases to 2~3 kg-m/cm² when the arsenic contained becomes more than 0.6 per cent. The annealing temperature of the specimens in the annealing process (I) was changed, as shown in Table 2, in correspondence with the content of arsenic because the A3 transformation point rises⁴⁾ considerably as the content of arsenic increases. Grain coarsening of ferrite was observed in these annealed specimens and the impact values decreased. To make sure of the cause of grain coarsening whether it was due to the high annealing temperature or to the

* The term "impact value" is used in this treatise in a broad sense including impact resistance when the specimen does not break off.

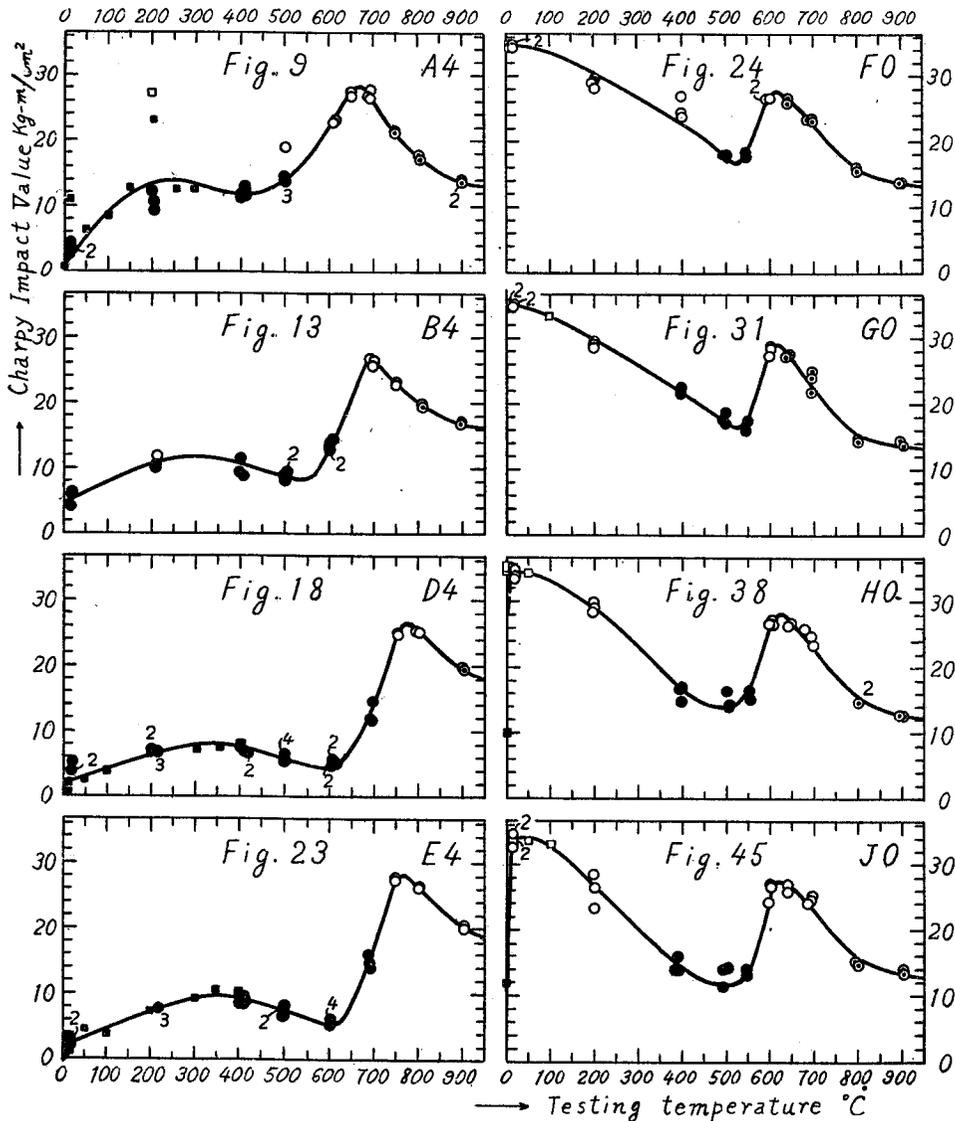


increase in the content of arsenic, the specimens AO, A1, A2, A3 and A4 were put together in the lead bath, heated to 920°C, slowly cooled after being kept at that temperature for an hour, and the sizes of ferrite grain were examined. It was found from this experiment that, in this heat treatment also, ferrite grain coarsening is observable when the content of arsenic increases. In addition, cementite, developed thin and long at the boundaries of the coarsened ferrite grains was recognized. These long cementite is conceivable to be the primary cause of the decrease in impact value as referred to later. As for the transition temperature of the specimens, arsenic

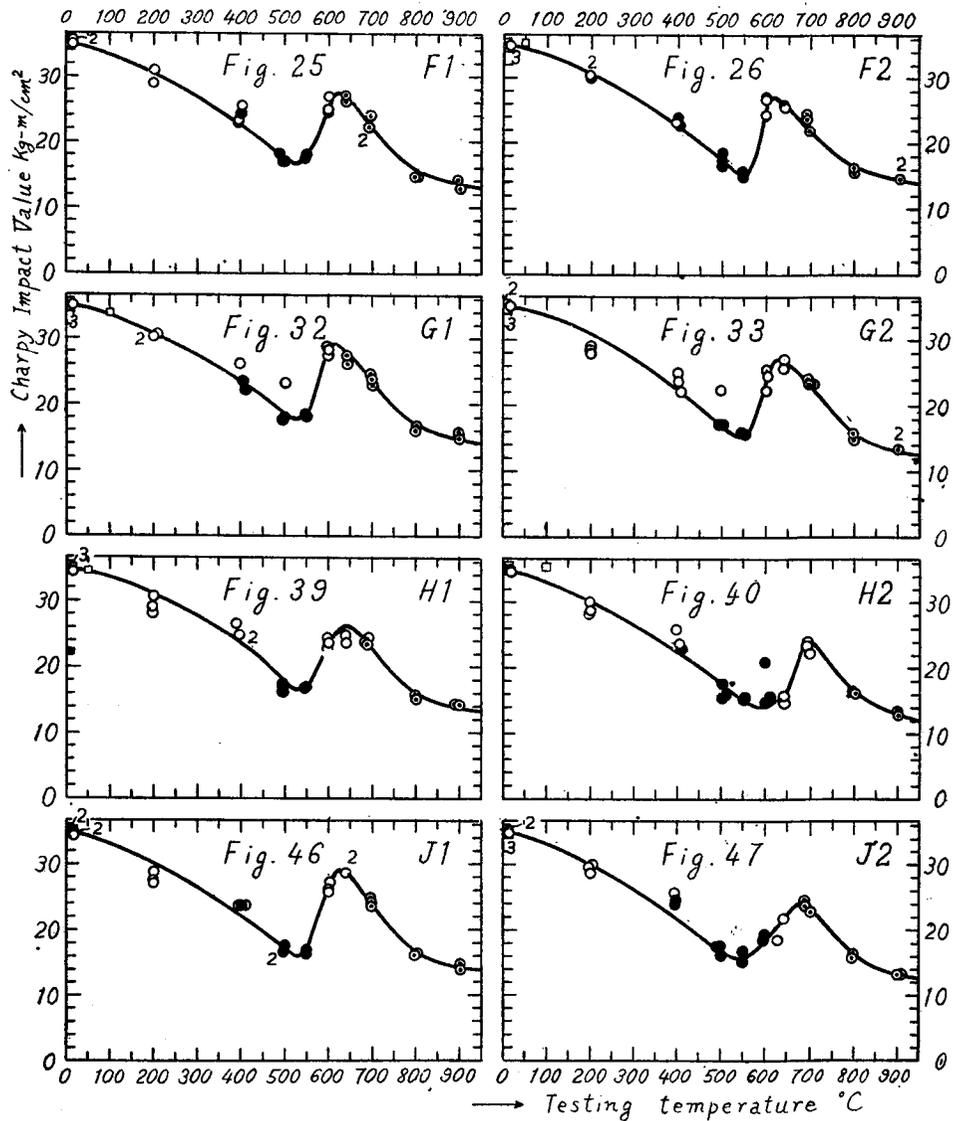


raises transition temperature of the specimens by decreasing the impact value at room temperature. The influence of arsenic is remarkable in the range lower than 500°C in A-series, but its influence can hardly be recognized in the range from 500 to 900°C. Judging from these results, dead soft steel becomes very brittle in cold deformation when it contains more than 0.3 per cent of arsenic but when the content is less than 0.1 per cent, arsenic seems to have no influence.

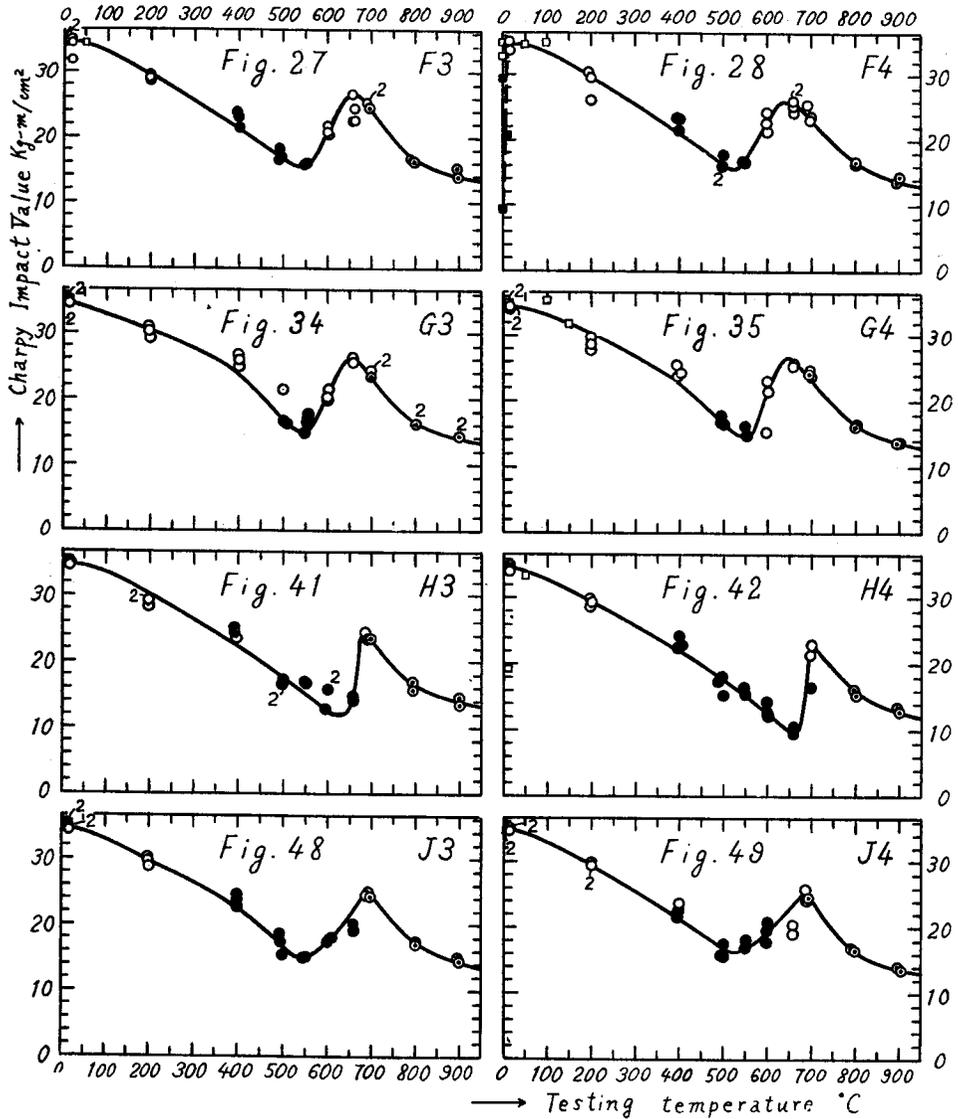
(b) B-series: Considerable influence of arsenic is recognized in B-series, i.e. in the case of low carbon steel containing 0.23 to 0.28 per cent carbon, and the impact value



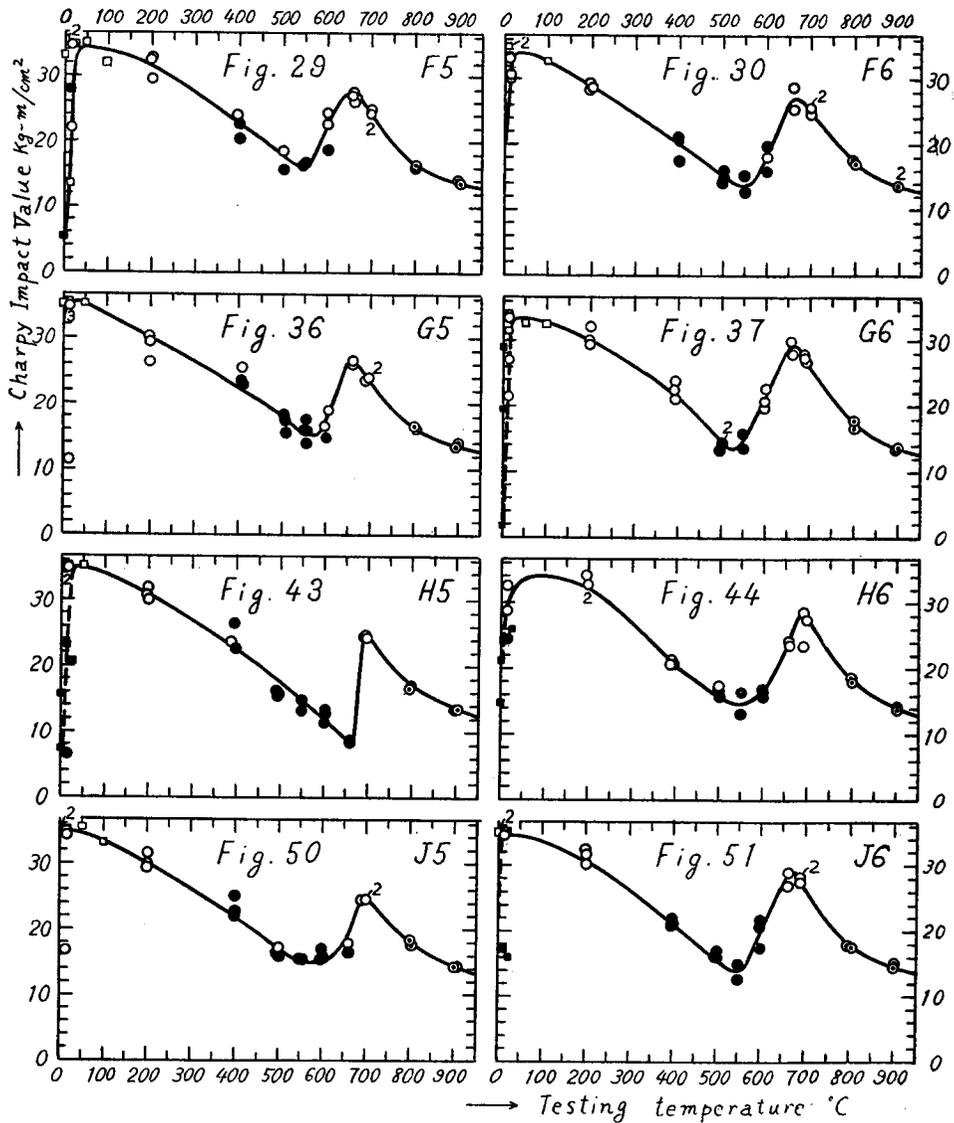
decreases as the content of arsenic increases, but the decrease of impact value caused by the effect of carbon is so great that the influence of arsenic is not so remarkable as in case of dead soft steel. The fact that the impact value in BO at 500°C or below is lower compared with that of B2 and B3 specimens seems to be due to deficiency of deoxidation. B-series was melted at first and the preliminary experiment for deoxidation of molten metal was not conducted, and; therefore, aluminium addition was insufficient in BO and gases blew up before solidification in the ingot B1 completed. The amount of aluminum addition was increased up to 0.04 per cent in the



ingot B2, B3 and B4, but it was 0.02 per cent in the ingot B0. The content of oxygen in the latter, therefore, may be higher and that of aluminum, lower than in the others of B-series. The decrease of impact value at room temperature in B0 specimen is due either to the insufficient deoxidation referred to before or a little higher contents of carbon as compared with those of others. The effects of gases and aluminium on transition temperature of steel is omitted here and is discussed later in the authors' succeeding report. Since the contents of carbon in B-series were decreased successively one after another, the influence of arsenic would have been more distinctly



recognized than it was shown in Figs. 10~13 if the carbon contents were the same. (c) D-series: In D-series, i.e. in the medium carbon steel which contains 0.54 to 0.59 per cent of carbon, the impact value tends to decrease a little as the content of arsenic increases, but the tendency is not so severe as in A- and B-series. However, in the range from 500 to 900 $^{\circ}\text{C}$, the blue shortness region moves gradually toward the higher temperature range as the content of arsenic increases. The temperatures of the minimum and maximum impact values of the specimen DO which contains almost no arsenic are observed at the vicinity of 550 $^{\circ}$ and 710 $^{\circ}\text{C}$ respectively,



but in the specimen D4 containing 1.04 per cent of arsenic these temperatures are at the vicinity of 600 and 780°C which are about 60°C higher than those of DO. Judging from this result, there may be some danger of causing cracks at the end of the forging period in case of the steel containing high percentage of arsenic unless the finishing temperature of forging is kept sufficiently high.

(d) E-series: A similar tendency as in D-series was noticed in E-series, i.e. eutectoid steel containing 0.83 to 0.85 per cent of carbon. The blue shortness range is moved toward the high temperature range as the content of arsenic increases and,

in case of E4 containing 0.98 per cent of arsenic, the brittle range is raised about 50° to 60°C higher than in eutectoid steel containing no arsenic.

(e) Dead soft steel: When arsenic is contained in carbon steel, the influence of arsenic is decidedly noticeable especially in low carbon steel as mentioned in the preceding section. Since dead soft steel containing more than 0.3 per cent arsenic showed a marked brittleness at room temperature, in case of F-, G-, H- and J-series, the amount of arsenic addition was fixed to be less than 0.5 per cent and, moreover, copper and tin, which give similar effect to steel, were added alone or together. The quantities of copper and tin added were fixed to be less than 0.35 and 0.1 per cent respectively. The influences of these elements on the impact properties of dead soft steel was examined at each temperature: 0.3 per cent of molybdenum was further added to some of the specimens and the effect of molybdenum upon steel was also studied.

Silicon and manganese additions were made to the specimens FO, GO, HO, and JO and efforts were given to make the contents of these elements as equal as possible among these specimens, therefore, it is desirable that the impact value versus temperature curves of these four specimens at each temperature be approximately the same. However, as shown in Figs. 24, 31, 38 and 45, these curves nearly coincide to each other in the range higher than 600°C but the curves show a considerable difference in the range from 300 to 550°C, that is to say, the impact values of FO and GO are higher than that of HO and JO. The content of total aluminum in FO and GO is higher than that of HO and JO, and the content of oxygen in the former is lower than that in the latter. The total amount of nitrogen seems to be nearly equal in these four specimens and, therefore, nitrogen seems to be present in the form of aluminum-nitride (AlN) in FO and GO, but in HO and JO there may be some silicon-nitride (Si_3N_4) together with aluminum-nitride.⁶⁵ In case of insufficiency of deoxidation, it is conceivable that alumina (Al_2O_3), ferrous oxide (FeO), aluminum-nitride and silicon-nitride, etc, are present in steel, but which of these are the main cause of the decrease of impact value cannot be determined at the present state.

Inclusion content of these specimens were determined by the method of Science Promotion Society⁷⁾ and the results are shown in Table 3.

Oxide-type (B-type) non metallic inclusions are more frequently found in HO and JO than in FO and GO as predicted from the analytical results. Whether the quantity of the oxide-type nonmetallic inclusion affects directly the impact value of steel or the difference in the quantity and size of nitrides causes the decrease in toughness is not yet clear and is the problem to be further investigated.

When the curves of F1, G1, H1 and J1 are compared to each other in the above mentioned temperature range, no such difference as was recognized in FO, GO, HO and JO is found among them. All the specimens having the numerals from 1 to 6

Table 3. Inclusion content.

Specimen	Inclusion	F0	G0	H0	J0
1	A*	0	0	0	0
	B**	2.9*** 3 μ †	4.9 3 μ	5.9 3 μ	5.9 3 μ
2	A	0	0	0	0
	B	5.5 3 μ	3.7 3 μ	6.4 3 μ	6.1 3 μ
Average value	A	0	0	0	0
	B	4.2 3 μ	4.3 3 μ	6.2 3 μ	6.0 3 μ

* Sulphides and silicates inclusions ** Oxides inclusions

*** Numerical designation † average thickness

in the symbol were deoxidized by aluminum in a graphite crucible ladle, and the quantity of its addition was 0.05 per cent each. But the specimens having the numerals of 0 in the symbol were deoxidized not in the ladle but in the furnace and, therefore, the deoxidizing condition in the former may be more uniform than in the latter.

(f) F-series: In F-series the impact values of each specimen at each temperature are nearly equivalent and no noticeable differences is recognized among them. However, there is an exception which will be discussed later.

(g) G-series: In G-series, the trend is very similar to that in F-series.

(h) H-Series: The content of arsenic, copper and tin are maximum in H-series. The minimum and maximum impact temperatures of the impact value versus temperature curve in H2 containing 0.34 per cent copper are raised by around 100° and 70°C to higher temperature range and when arsenic is added more than 0.25 per cent to the steel, the minimum impact value shows a further decrease.

(i) J-series: Concerning J-series, the maximum impact temperature at the vicinity of 630°C is raised to higher temperature range in the specimen J2 which contains 0.35 per cent copper, 0.05 per cent tin and no arsenic. Further, when arsenic is added to J2, the same trend of decreasing minimum impact value was observed as in case of H-series though in a small degree.

(j) Brittle specimens at room temperature: Considerably low impact values were noticed at room temperature in the impact test in the following eight kinds of specimens indicating that transition temperature was raised by arsenic:

Specimen	Arsenic %	Copper %	Tin %
F5	0.43	0.17	0.05
F6	0.44	0.19	0.04
G5	0.43	0.17	0.09
G6	0.42	0.18	0.11

Specimen	Arsenic %	Copper %	Tin %
H5	0.43	0.34	0.10
H6	0.45	0.33	0.08
J5	0.46	0.35	0.05
J6	0.46	0.35	0.05

(k) Effect of copper: The effect of copper was examined by comparing the results of FO, HO, F1 and H1, and copper was found to have no effect at all if the content of copper is less than 0.18 per cent and in case of copper content of 0.35 per cent no other effect was observed but a slight decrease of maximum impact value.

(l) Effect of tin: The effect of tin was examined by comparing the results of GO, JO, J1 and G1, and no effect of tin was observed upon the impact value of steel if the content of tin is less than 0.1 per cent.

(m) Effect of co-existence of copper and tin: The effect of the co-existence of copper and tin was examined by comparing both results of FO, GO, HO and JO, and those of F2, G2, H2 and J2, and no effect was observed in the ranges lower than 550°C and higher than 700°C and higher than 700°C. In case of steels containing less than 0.18 per cent copper and less than 0.1 per cent tin, no influence was observed either in the range from 550 to 700°C, but in case of the steel J2 containing 0.34 per cent copper and 0.05 per cent tin, the temperature of maximum impact value is raised to higher temperature range and in case of steel H2 containing 0.34 per cent copper and 0.14 per cent tin, the temperature of minimum impact value is raised to higher temperature range with a slight decrease in the maximum impact value.

(n) Effect of co-existence of arsenic, copper and tin: There is a tendency to decrease the impact value at room temperature, in other words, to raise the transition temperature, in a steel containing more than 0.45 per cent arsenic, when arsenic, copper and tin are contained simultaneously in steel. It is mainly due to the effect of arsenic that raises the transition temperature; however, the influence of these elements on the transition temperature of steel shall be discussed in particulars in the next report. The most noticeable effect of co-existence of arsenic, copper and tin in steel is the trend to decrease the minimum impact value at the blue shortness range but no other effect was observed except at the blue shortness range and at room temperature.

(o) Effect of molybdenum: The effect of molybdenum was examined by the addition of 0.3 per cent of molybdenum to steels containing arsenic, copper and tin. The impact values of these steels decreased at room temperature as shown in the curves of F6 to J6 (Fig. 30, 37, 44 and 51). If the influence of molybdenum on the transition temperature is estimated by the definition that the transition temperature is decided on the base of temperature at which the impact value begins to decrease, molybdenum has a tendency to raise transition temperature of steel and this is in agreement with the report of J. A. Rinebolt and W. J. Harris, Jr.⁸⁾ There is little or no influence of molybdenum on the maximum impact value of the specimen F6, but molybdenum has

the tendency to raise the maximum impact value in the specimens G6, H6 and J6. In case of the specimen H6, molybdenum inhibits the decrease of the minimum impact value caused by co-existence of arsenic, copper and tin, and moreover prevents the rise of temperature of the minimum impact value thus contributing for prevention of embrittlement. Estimating from these results, molybdenum has no useful effect on steel, if the contents of arsenic, copper and tin are low; but has somewhat useful effect in the blue shortness range if the contents of these elements are as high as in G6, H6 or J6. However, the steel becomes hard and brittle at room temperature as the content of molybdenum increases.

(p) Comparison of A-, F-, G-, H- and J-series: The difference between the influence of arsenic alone and that of co-existence of arsenic, copper and tin can be seen from the results of A-, F-, G-, H- and J-series when these are compared to each other. There are some differences of the contents of carbon and sulphur among them, but no serious effect is considered to be caused by such slight differences on the impact properties of these steels. Therefore, it is assumed that there would be no serious error even if the influence of arsenic, copper and tin is judged by comparing these results. In case arsenic alone is contained, the ferrite grains of the steel become coarse, the boundary cementite becomes large and long as the content of arsenic increases, and the impact value shows a marked decrease at room temperature; but when arsenic, copper and tin are contained together in a steel, the ferrite grains are fine and copper and tin seem to lessen the bad influence of arsenic. In other words, in F-, G-, H- and J-series, ferrite grain coarsening could hardly be recognized and boundary cementite was much smaller and shorter than in A-series. However, further investigations are yet to be conducted to determine whether copper and tin inhibited the growth of ferrite grain or the difference of the content of aluminum, oxygen, etc. affected the grain sizes. A decided decrease of impact values in the blue shortness range was found in the specimens H4 and H5, but there was no noticeable difference among these five series in the range above 700°C.

2. Austenite, ferrite grain sizes and microstructures

Austenite grain size was measured by the method of Science Promotion Society,⁹⁾ and ferrite grain was also determined by using the same austenite grain size chart. According to the results shown in Table 4, the ferrite grain sizes are all very fine except A- and B-series and the grain size number are greater than 7. Ferrite grain coarsening is remarkable in A-series as the content of arsenic increases. Since the annealing temperatures of A-series were made very high in accordance with the content of arsenic in the steel it seemed to favour grain growth, the ferrite grain size was measured on the specimens AO, A1, A2, A3, and A4 which were annealed at 920°C, maintained at that temperature for 1 hr, and air cooled from 600°C.

As shown in Table 4, ferrite grain coarsening is found also in these specimens

Table 4. Ferrite and austenite grain sizes.

Specimen	No. of grain size		specimen	No. of grain size		Specimen	No. of grain size	
	Ferrite	Austenite		Ferrite	Austenite		Ferrite	Austenite
A0	6.5(7.0)*	6.7	F0	8.0	7.5	H0	7.5	6.5
A1	2.3(4.7)*	5.7	F1	8.0	7.0	H1	8.0	7.0
A2	2.2(2.2)*	6.0	F2	8.5	8.0	H2	8.5	7.5
A3	2.2(2.0)*	6.0	F3	7.0	8.0	H3	8.0	7.5
A4	5.8(2.5)*	5.7	F4	8.0	7.5	H4	7.0	8.0
B0	6.6	4.7	F5	8.0	7.5	H5	8.0	7.5
B2	7.1	6.7	F6	8.0	7.5	H6	8.0	7.0
B3	5.4	6.7						
B4	5.4	5.7						
D0	9.9	7.7	G0	8.0	8.0	J0	7.0	6.5
D1	9.9	6.9	G1	8.5	8.5	J1	7.5	8.0
D2	10.2	7.7	G2	8.0	7.5	J2	8.0	8.0
D3	9.1	7.0	G3	8.0	7.0	J3	7.5	8.5
D4	9.8	7.2	G4	8.5	7.5	J4	7.5	7.5
E0	—	7.7	G5	8.0	7.5	J5	7.5	7.0
E1	—	6.7	G6	8.0	7.5	J6	7.5	8.0
E2	—	6.6						
E3	—	6.7						
E4	—	5.7						

* Annealed at 920°C for 1hr. and air cooled from 600°C.

Table 5. Ferrite and austenite grain sizes of brittle specimens.

Specimen	No. of grain size			Specimen	No. of grain size		
	Ferrite		Austenite		Ferrite		Austenite
	Outer portion	Inner portion			Outer portion	Inner portion	
F5	8.0	6.0	6.5	G6	6.5	6.5	8.0
G5	7.0	4.5	7.0	J5	5.5	6.5	7.0
H5	6.5	4.5	7.0				

annealed at 920°C, the grain size numbers of these specimens are written in parentheses in the same table. No such coarsening effect was found in F-, G-, H- and J-series, but the ferrite grain sizes are somewhat larger than the others in those specimens which showed brittle fractures at room temperature impact testings as shown in Table 5. Austenite grains were all fine and no remarkable effect of arsenic, copper and tin was recognized.

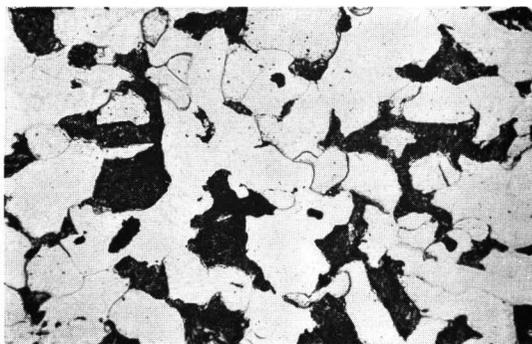
The intergranular parts of the fractures of these brittle specimens just mentioned correspond generally to the portion of coarse ferrite grains, and, therefore, brittle

fracture seems to show the ferrite grain boundaries which is in agreement with the report of B. C. Woodfine.¹⁰⁾

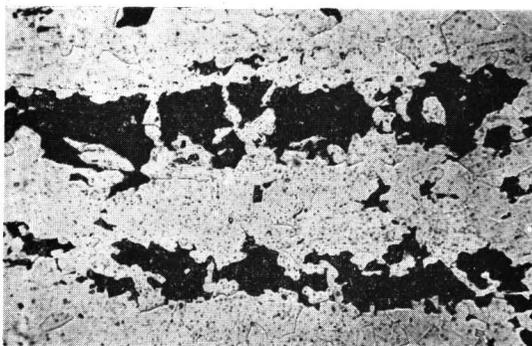
When the content of arsenic in a steel increases, a tendency to develop microscopic banded structure of ferrite and pearlite is found in the section parallel to the forging direction. Microphotograph No. 1 shows a normal structure which is found in a specimen containing no arsenic and No. 2 shows an example of the banded structure.

The cementite formed at the ferrite boundary in dead soft steel has a tendency of growing large and long as the content of arsenic increases and in the specimen A3 containing 0.85 per cent arsenic, for example, the length of boundary cementite is about three times as long as in the specimen AO containing 0.018 per cent arsenic. In the brittle specimens of F-, G-, H- and J-series, also, boundary cementite is larger than in other tough specimens. There is no special micro-structures grown in the range of composition used in this investigation even if the content of arsenic, copper and tin increases. The impact values of HO and JO in the range from 400° to 500°C were considerably lower than those of FO and GO as has been discussed previously. Therefore, microstructures and ferrite grain sizes of these specimens were examined but no difference was found concerning these factors. Consequently, the difference of impact values seems to be due to the difference of the content of aluminum, nitrogen, oxygen, etc.

Sorbite and lamellar pearlites are found in a mixed state in the specimen E4 and the other specimens of E-series had lamellar pearlite structure. It may be due to this difference in microstructure that the specimen E4 had a little higher impact



Microphotograph No. 1 ×100
0.28%C, 0.011% As
Normal structure after annealing.
Picral etch.



Microphotograph No. 2 ×100
0.24%C, 0.79% As
Banded structure after annealing.
Picral etch.

values than the specimen E3 at low temperature range.

3. Hardness

Hardness measured by Rockwell B scale of each specimen after annealing is as shown in Table 6.

Table 6. Hardness of annealed specimens (Rockwell B Scale).

Specimen	Hardness No.	Specimen	Hardness No.	Specimen	Hardness No.
A0	54.8	F0	59.1	H0	61.1
A1	55.5	F1	60.5	H1	58.3
A2	58.6	F2	61.3	H2	61.5
A3	64.3	F3	65.3	H3	63.6
A4	67.0	F4	65.5	H4	63.7
B0	63.6	F5	68.1	H5	66.7
B2	70.4	F6	70.9	H6	73.1
B3	71.1				
B4	73.5				
D0	80.8	G0	56.9	J0	64.0
D1	83.9	G1	60.7	J1	60.1
D2	86.3	G2	62.8	J2	63.5
D3	87.9	G3	63.2	J3	64.1
D4	89.0	G4	64.0	J4	66.6
E0	84.1	G5	68.8	J5	67.3
E1	86.6	G6	70.0	J6	71.2
E2	89.6				
E3	92.1				
E4	93.0				

Hardness of the specimens increases as the content of arsenic, copper, tin and molybdenum increases. That the hardness of HO and JO is a little higher than that in the others shows the fact that these two specimens are under slightly different conditions as has already been discussed. The smaller the content of carbon, the greater becomes the rate of increase in hardness of annealed specimens.

4. Workability

Generally speaking, iron and steel with high impact values have a good toughness and are fit for forged or cold work; consequently, we can estimate the feasibility of work on the materials by studying their impact value and impact fractures. Judging from the results obtained in this experiment, the hot deformation of dead soft steel is not influenced by arsenic, copper and tin if the content thereof is within the range examined in this investigation. As for the cold deformation we cannot discuss about general case unless the degree of deformation is determined, but esti-

mating from the obtained impact values and appearances of cracks in each test piece, it is conceivable that the composition range shown in Table 7 will ensure good cold deformation.

Table 7. Allowable limit of arsenic, copper and tin for hot- and cold-deformation of dead soft steel.

	One of these is contained.			All of these are contained.		
	As%	Cu%	Sn%	As%	Cu%	Sn%
Hot deformation	+1.0	+0.35	+0.10	+0.45	+0.35	+0.10
Cold deformation	<0.3	+0.35	+0.10	<0.25	<0.35	<0.10

The symbol "+" signifies that the allowable limit is higher than the value shown here.

These values are applicable to killed steels which have no conspicuous segregation. But arsenic, copper and tin are all apt to segregate and the degree of segregation depends upon the mass and shape of ingots. The degree of segregation in 1 to 3 tons ingots, estimated from several references,¹¹⁾⁻¹⁶⁾ is as follows:

	Arsenic	Copper	Tin
Per cent of segregation in { killed ingot	+40	+10	+50
{ rimmed ingot	+70	+30	+80.

The symbol "+" signifies positive segregation, i. e., the higher concentration than that of average value.

The allowable limit of the contained elements must be changed to the values shown in Table 8 if the segregation is taken into account.

Table 8. Allowable limit of arsenic, copper and tin for hot- and cold-deformation where the segregation is taken into account.

		One of these is contained.			All of these are contained.		
		As%	Cu%	Sn%	As%	Cu%	Sn%
Killed steel	Hot deformation	+0.71	+0.32	+0.067	+0.32	+0.32	+0.067
	Cold deformation	<0.21	+0.32	+0.067	<0.18	<0.32	<0.067
Rimmed steel	Hot deformation	+0.59	+0.27	+0.056	+0.26	+0.27	+0.056
	Cold deformation	<0.18	+0.27	+0.056	<0.15	<0.27	<0.056

The symbol "+" signifies that the allowable limit is higher than the value shown here.

In case of rimmed steel, more severe limitations may be imposed on these allowable limits because the influence of contained gases cannot be ignored.

If the steel containing arsenic, copper and tin is heated for a long time at high temperature in an oxidizing atmosphere such as in a soaking pit or in an annealing furnace, the contamination of these elements occurs in the surface layer of steel and

causes to crack on the surface of steel during hot or cold working¹⁾²⁾³⁾¹⁶⁾¹⁷⁾ and, therefore, the above mentioned limit must be the limit of the concentration on the contaminated surface layer of steel. In other words, we have to determine the allowable limit of these elements in correspondence with the heating temperature and the duration of heating operation. If we have to anneal during the process of cold working, the concentration of these elements on the surface layer of steel must not exceed the limits shown in Table 8.

Suppose, for example, the steel is heated to 1200°C and kept for about 3 to 4 hrs at that temperature, the degree of contamination of arsenic, copper and tin on the surface is approximately as follows:³⁾¹⁷⁾¹⁸⁾

Arsenic Copper Tin

Contamination per cent in 1 mm layer of steel surface 50 10 70.

This contaminated layer may not be removed completely by hot working and, therefore, if cold working is continued, the allowable limit of arsenic, copper and

Table 9. Allowable limit of arsenic, copper and tin where the contamination of surface layer is taken into account.

	One of these is contained.						All of these are contained.					
	(a) With segregation			(b) With no segregation			(a) With segregation			(b) With no segregation		
	As%	Cu%	Sn%	As%	Cu%	Sn%	As%	Cu%	Sn%	As%	Cu%	Sn%
Killed steel	<0.14	+0.29	+0.039	<0.20	+0.32	+0.059	<0.12	<0.29	<0.039	<0.17	<0.32	<0.059
Rimmed steel	<0.12	+0.25	+0.033	"	"	"	<0.10	<0.25	<0.033	"	"	"

The symbol "+" signifies that the allowable limit is higher than the value shown here.

tin may have the values such as shown in Table 9. Provided, if we assume that we need not consider the effect of segregation because the positive segregation of arsenic, copper and tin generally occurs in the inner portion of the ingot, the allowable content in (b) column of the same table may be sufficient as allowable limit values.

V Summary

To investigate the influence of arsenic on the workability of carbon steels and also to know the influence of arsenic, copper, tin and molybdenum on the workability of dead soft steel, 47 kinds of specimens were melted and forged to square bars and after full annealing, Charpy impact testing was performed at various temperature to about 900°C.

Ferrite and austenite grain sizes, hardness after annealing were measured and microscopic structures were also examined. Results obtained are as follows:

(1) When a steel contains less than 0.3 per cent carbon, the impact value decreases as the content of arsenic increases in the range of temperature lower than 500°C,

but the influence of arsenic is scarcely observed in the range higher than 500°C.

(2) When a steel contains carbon ranging from 0.5 per cent to eutectoid composition, the impact value decreases as the content of arsenic increases in the range of temperature lower than 500°C but the degree is slight; the temperature of minimum and maximum impact value is raised to higher temperature range and when the steel contains about 1 per cent of arsenic these temperatures become 50 to 60°C higher than those of the steel containing no arsenic.

(3) The influence of arsenic is most severe in dead soft steel and when it contains more than 0.3 per cent of arsenic, the impact value at room temperature decreases and causes the decrease in cold deformability.

If a steel contains arsenic, copper and tin together, a marked decrease in impact value is observed at room temperature as the content of arsenic increases. The limit within which no influence is observed on the decrease of impact value is as follows:

	Arsenic	Copper	Tin
per cent:	<0.25	<0.35	<0.1.

(4) In the range of composition applied in this experiment, no influence of copper or tin was observed on the impact value of steel, when one of these elements is contained alone in steel.

(5) When a steel contains both copper and tin together, no influence is found in the range lower than 550°C and higher than 700°C, but in the range from 550 to 700°C, the temperatures of the minimum and maximum impact values are raised to high temperature range.

(6) When a dead soft steel contains arsenic, copper and tin together, the temperatures of the minimum and maximum impact values are raised to higher temperature range and the minimum impact value decreases as the contents of these elements increase.

(7) When 0.3 per cent of molybdenum is added to a dead soft steel containing arsenic, copper and tin, the impact value at room temperature is decreased, but it protects decrease of the minimum impact value at the blue shortness range, and inhibits the temperature of the minimum impact value to be raised to higher temperature range.

(8) Even if a steel contains arsenic, copper and tin together, these elements have practically no influence on the austenite grain size of the steel if they are within the range of composition examined in this investigation.

(9) When a steel contains arsenic, it has practically no effect on ferrite grain size except in the case of dead soft steel.

(10) Ferrite grain grows in dead soft steel as the content of arsenic increases, and

the portion of the brittle fracture corresponds generally to that of coarsened grains.

(11) The tendency to form banded structure of ferrite and pearlite becomes noticeable as the content of arsenic increases.

(12) Cementite of ferrite grain boundary in dead soft steel becomes long as the content of arsenic increases and this is the main cause of embrittlement of steel by arsenic.

(13) Hardness of steel after annealing increases as the content of arsenic, copper, tin and molybdenum increases.

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