

Experimental Research on Super-Heating of Molten Cast Iron

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Experimental Research on Super-Heating of Molten Cast Iron*

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Synopsis

The experiments were performed by melting cast iron in non-oxidizing atmosphere of Tammann furnace at temperatures between 1250 and 2000°C. With the rise of melting temperature, the graphite structure of the specimens became fine and such changes are analogous to those of the structure changes due to reducing slags such as CaC_2 , deoxidizing metallic elements such as Ca, Mg or vacuum melting. At low melting temperature, the structure was apt to be varied by specimens, even if their chemical compositions were equal, but at the temperature of super-heated melting, fine granular graphite structure appeared regardless of the chemical composition of specimens.

I. Introduction

These experiments were performed to prove that with the decrease of oxygen dissolved in the melt, the deoxidation process by means of vacuum melting, reducing slag treatment⁽¹⁾ such as CaC_2 and deoxidizing metallic elements such as Ca, Mg, and the process of melting temperature change and treatment time change in super-heated melting are the same especially that by vacuum melting, reducing slag treatment and deoxidizing metallic elements and also by super-heated melting, fine graphite structure, further super-cooled white cast iron with tempered carbon can be obtained.

II. Apparatus and method

1. Apparatus for experiments

A Tammann furnace was used for melting. Fig. 1 shows its structure. Both ends of the carbon tube (A) are shut tight by lids of graphite (B) and (C) with a crucible containing the specimen at the center. In the case of super-heated melting, the fire-proof material is a matter of importance. A crucible should not contain a large quantity of SiO_2 or other compounds to be deoxidized by carbon. Ideal ones are alumina, magnesia, thoria, zirconia, etc. of high purity. Alumina must shape itself into the crucible to use a binder of aluminium silicate compound and to be heated to high temperatures. As for magnesia, MgCl_2 can be shaped into the crucible without any help from others, but it is difficult to change a chloride completely into an oxide by calcination. For these reasons we used

* The 964th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of Japan Institute of Metals, 17 (1953), 375.

(1) M. Homma, J. Japan Inst Metals, 16 (1952), 486; 457; 607; 666.

alumina or magnesia, without shaping it into crucible form. We crammed pure alumina for chemical use which had been calcined at 1000°C into a graphite crucible (D) manufactured with electrode carbon, with the specimen to be melted

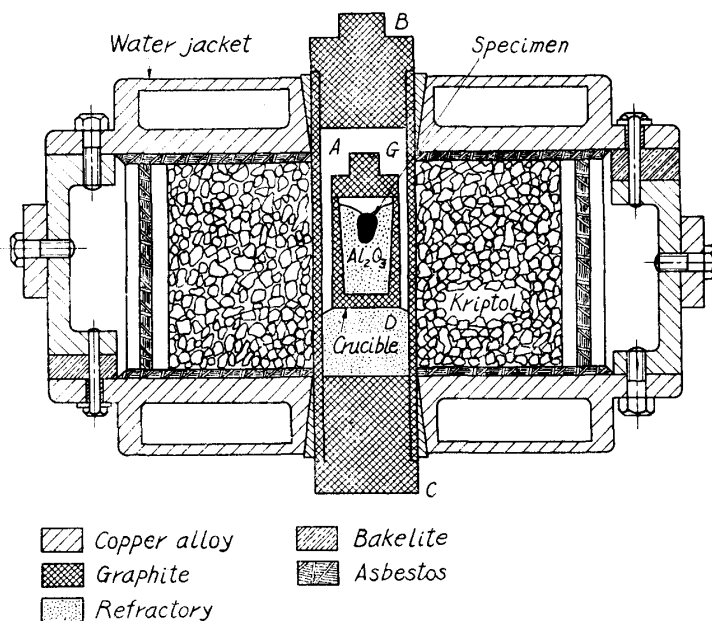


Fig. 1. Super-heating furnace.

in the center of the crucible, sufficiently far from its walls. So long as the specimen does not touch the side-walls the effect is eventually the same when a crucible of pure alumina is used. This is applicable not only to alumina but to magnesia and others. But as a Tammann furnace of ordinary size can contain only a few grams of melt at a time, we put pure alumina into the furnace without using a graphite crucible, when we need a little more amount of specimen for analysis, and bury specimen in this alumina. About 30 grams can be melted by this method. The atmosphere of experiments may be taken to be non-oxidizing.

2. Method of experiment

Chemical compositions of cast iron specimens used are shown in Table 1.

Table 1. Chemical Analysis of Specimens.

Nos. of Specimens	Chemical Compositions					
	T.C.	Si	Mn	P	S	
1	3.51	1.68	0.53	0.44	0.08	Commercial Cast Iron
2	3.84	1.91	0.004	0.005	0.017	Fe-Si-C Alloy
3	3.44	2.71	tr.	0.0038	0.011	„

After heating the Tammann furnace up to a fixed temperature, we placed in it a graphite crucible containing a specimen and then put the lid (G) on the top of the furnace to close it. After a certain interval of time, the current was turned off to cool the furnace. Treatment time is measured from the time when the specimen was put in the crucible to the time when the current was switched off.

The cooling velocity was 100°C/min on the average between 1200~1100°C (the range of freezing). Temperatures below 1450°C were measured by Pt-Pt-Rh thermocouple, after putting it in a protecting tube from furnace gas, inserted from the bottom of the furnace, while higher temperature was measured by means of an optical pyrometer. In this case thermometry was carried out with the current in the furnace kept constant, and after the temperature in the furnace had become stable, the crucible was placed in the furnace. After this, only the regulation of current was conducted without measuring the temperature lest air should be introduced while the lid of the furnace was taken off. Of course the fluctuation of temperature was experimentally examined. It remained in the range about $\pm 10^\circ\text{C}$. In this paper we dealt with the three kinds of specimens which were treated by the above method for half an hour and for an hour at temperature between 1200~2000°C.

III. Results of experiments

1. Changes in chemical composition according to temperature

Figs. 2, 3 and 4 show the changes in chemical composition when ordinary cast iron No. 1 and synthetic cast iron (Fe-S-C alloy) No. 2 and No. 3 were treated for 30 minutes at different temperatures.

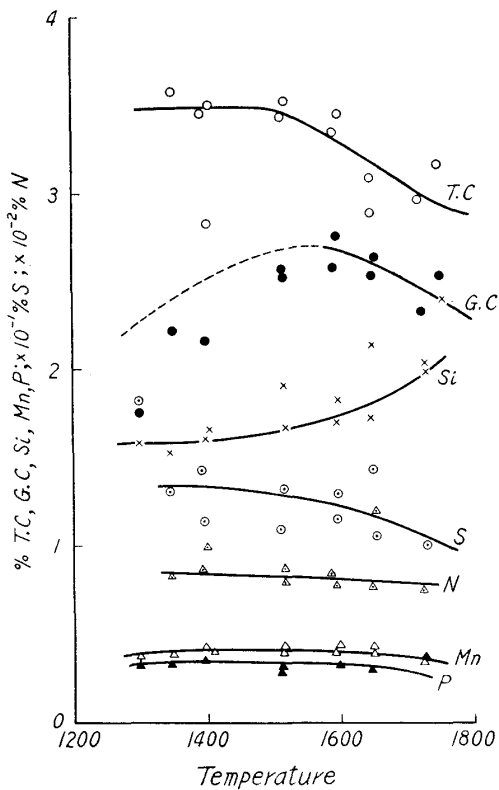


Fig. 2. Chemical composition change of No. 1 specimen.

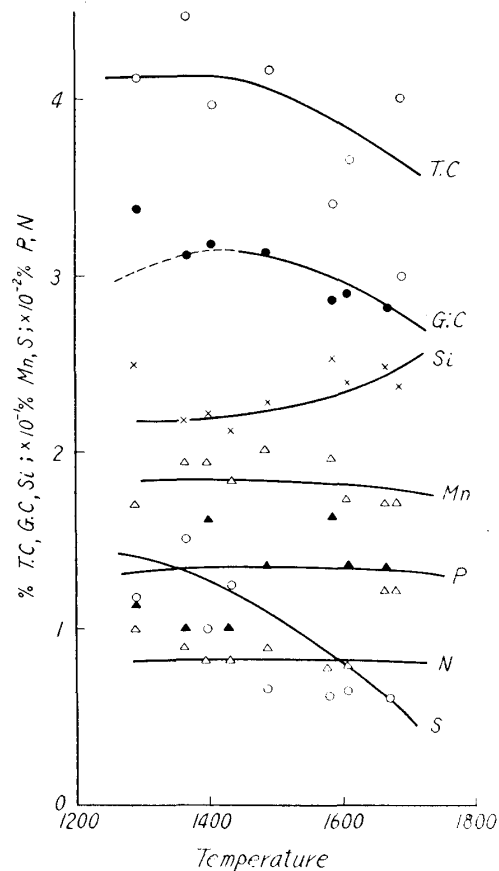


Fig. 3. Chemical composition change of No. 2 specimen.

(i) Carbon

In the temperature range below 1500°C the amount of carbon changes very little, if any. But above 1500°C the amount of carbon gradually decreases. This tells that at the super-heated temperature the reduction of carbon is active and it, after reducing the oxygen and oxide in the melt, escapes in the gas phase. From the G. C. curve it is clear that the G. C. decreases according as whether the total amount of carbon decreases at the super-heated temperature, but we cannot be sure of the range in G. C. amount at low melting temperature, due to the fluctuation in the analytical values. Piwowarsky's⁽²⁾ relation in the change between melting temperature and combined carbon was not found in this experiment. When heated too excessively, Al_2O_3 in the refractory material is also reduced and Al will be alloyed with the melt, but Al, like Si, has no relation with the refining of graphite structure and the inclination of white cast iron.

(ii) Silicon

Contrary to the case of carbon, silicon increases in amount when heated up to about 1500°C. This is because SiO_2 in the refractory material is reduced by carbon and joins the melt. Even if SiO_2 cannot be separated from the melt, it remains in it as an intervening substance. This SiO_2 is considered to have come into it from outside, because the Si value obtained by analysis is that of all the Si there, including Si in SiO_2 . The SiO_2 contained in the alumina chemically pure which we used in this experiment was about 0.5 per cent. We took this into consideration and used 0.046 per cent SiO_2 in our experiment with No. 3 specimen. The so-called turning temperature (see the previous paper II-1, Fig. 2) in these experiments was 1450~1500°C in the analytic values of C and Si.

(iii) Manganese, phosphorus and nitrogen

No conspicuous change was observed, especially in N_2 which did not change at all. This suggests that there is little correlation between N_2 and structural change, and too, between N_2 and the phenomenon of heredity.

(iv) Sulfur

With the rise of treatment temperature, desulfurization grew, but not so con-

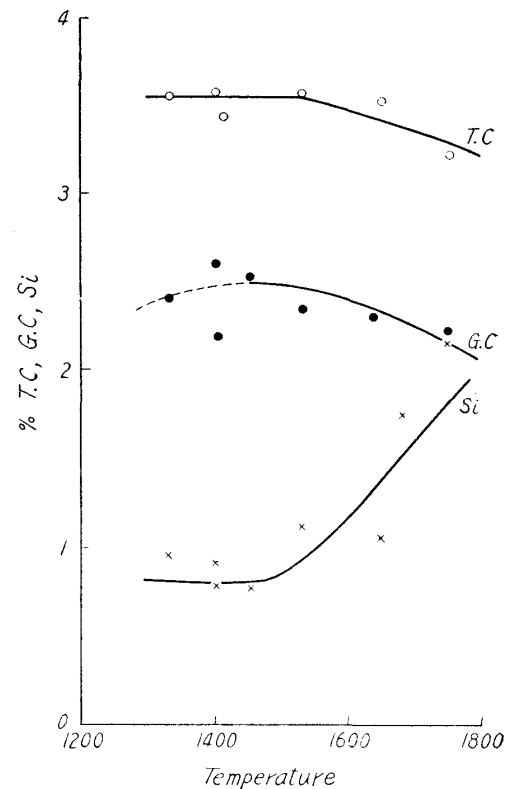


Fig. 4. Chemical composition change of No. 3 specimen.

(2) E. Piwowarsky, *Stahl u. Eisen*, **45** (1925), 1455; Hochwertig Grauguss, (1929).

(3) F. Richardson and J. Jeffes, *Iron and Steel*, **25** (1952), 597.

spicuous. This desulfurization is considered to be due to carbon and silicon present⁽³⁾.

As stated above, changes in constituent elements caused by treatment were clearly observed, but it was considered that these changes did not give rise to the micro-structural changes such as will be stated below.

2. Relation between treatment temperature and structure

In the previous paper⁽¹⁾ we treated in detail the changes in cast iron structure caused by the changes in oxygen content. We made it by means of the vacuum melting and by the treatment of reducing and oxidizing slags (e.g. FeO, Fe₂O₃ etc. and CaO). And as a verification of this treatment we stated that the treatment time and thermal change in the super-heated melting also gave the same results. Now in order to give a concrete explanation we are to describe the experimental result of the latter. Fig. 5 is the graphical representation of the

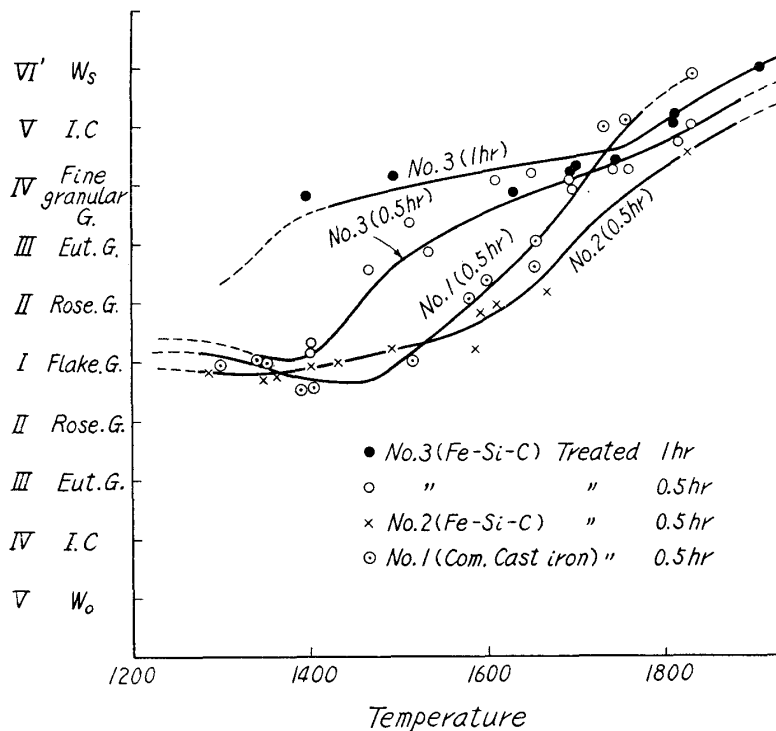


Fig. 5. Relation between micro-structure change and melting temperature.

relation between treatment temperature and structure in each of the several specimens mentioned above. We ascertained by the experiment on the change of oxygen content by vacuum melting and then by using reducing slags. According to the decrease in oxygen content, the structure changes in this order upwards from the lower part of the ordinate axis⁽⁴⁾. This method, as already mentioned, is far more reliable than determination by a questionable analysis of oxygen. The curves in Fig. 5 all concave upward at temperatures higher than super-heating temperature (about 1500°C). In other words, the process of structural change accompanying the rise of treatment temperature in the case of super-heated melt-

(4) M. Homma, J. Japan Inst. Metals, 17 (1953), 371.

ing is the same as that accompanying the extension of treatment time by the method of vacuum melting and using reducing slags—in both cases the change take place through the same steps and can be said to be a structural change accompanying deoxidation. A remarkable point in structural change is that the fine graphite structure which appears accompanying super-heating is due to the super-cooling caused by the decrease of oxygen content. (This is the reason why this structure has no relation to Si content.) And in the fine structure, too, the eutectic graphite structure (Photo. 1) grows into the fine granular graphite structure (Photos. 2 and 3) as the degree of super-heating advances. With further

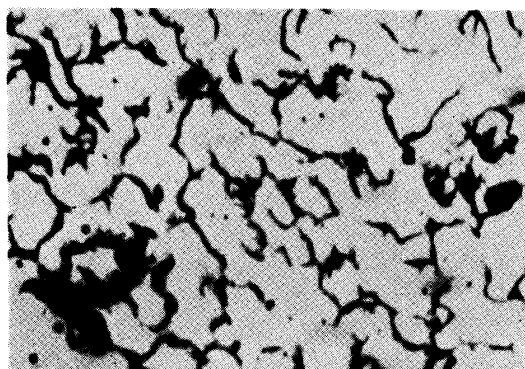


Photo. 1. Eutectic graphite structure III'. $\times 300$

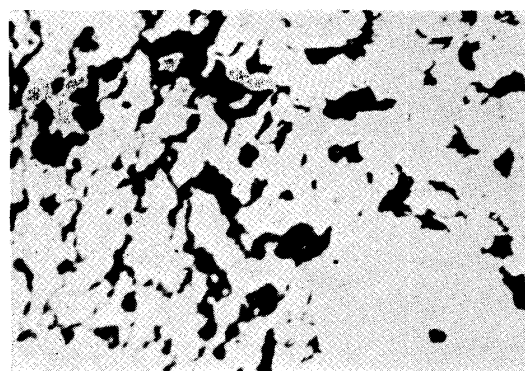


Photo. 2. Fine granular graphite structure IV'. $\times 300$

advance of super-heating, the structure produces white cast iron (Ws) (Photo. 4), and with the advance of super-cooling, the tempered graphite of a spheroidal form segregates in the course of cooling after solidification. In Fig. 5 the following two points are to be noted. First, the curve has a tendency to fall at near 1450°C , which means an increase in oxygen amount. This may seem to coincide with the fact that at about this temperature there is a peak (where dissolved oxygen arrives at its maximum amount) in the qualitative theoretical curve of the melt (cf. the previous paper Fig. 2), but a definite conclusion cannot be given as the degree of change—change in oxygen amount—in both cases is slight as is seen. In Piwowarsky's "melting temperature—combined carbon content" changing curve, this relation (i. e. the increase of carbide carbon by the increase of oxygen amount) is shown (though he interprets this otherwise), but this does not appear

in Figs. 2, 3 and 4 as analytical values of graphite carbon. It is considered to be within the limit of analytical errors. Second, according to different specimens

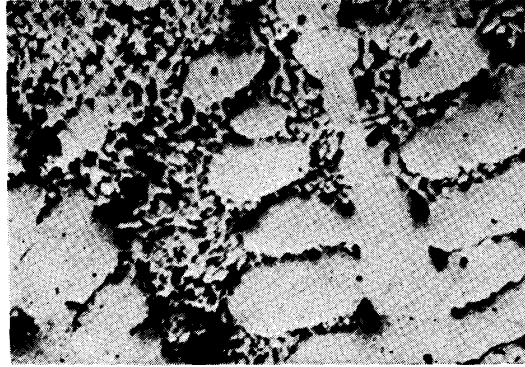


Photo. 3. Fine granular graphite structure IV'. $\times 100$

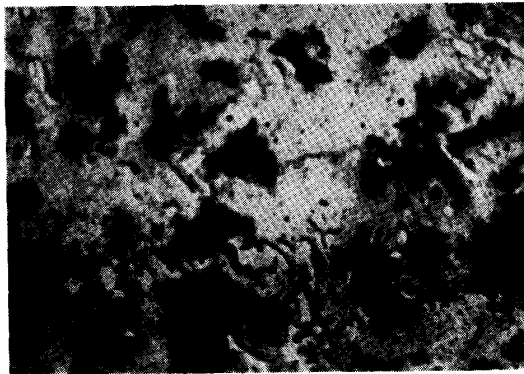


Photo. 4. Super-cooled white cast iron and tempered graphite structures VI'. $\times 100$

(especially, No. 2 and No. 3 of like chemical composition) there are discrepancies in positions between their curves within the range of melting temperature not exceedingly high and the curves (especially, No. 1, and No. 2, No. 3 which are of different chemical composition) drawn at the same position as super-heating temperature goes up. In the former case, the chief cause, in our interpretation, lies in the difference in the original amount of oxygen and that in the form of dissolved oxygen, according to different specimens, while in the latter, specimens are deoxidized by super-heating and the oxygen amount becomes nearly the same, irrespective of their chemical composition. This fact tells of the phenomenon of heredity that qualities of iron castings depend upon the difference in raw material iron. Generally speaking, in the former case (first point), the degree to which the melt is oxidized and reduced is nearly constant in the same type of furnace, and in the latter case (second point), it shows that all raw materials not of the same kind approach the same structure. In other words, they have the same properties, only if they are super-heated or fully reduced and refined.

IV. Relation between super-heated melting and heredity

Super-heated melting and heredity are inseparably related to each other.

Pfannenschmidt⁽⁵⁾ says in *Giesserei* that the question of heredity has been settled unartificially with its cause undiscovered since the method of super-heated melting was adopted recently. His words indicate that the cause of heredity and the essential significance of super-heated melting are the same—both a phenomenon in which oxygen (deoxidation) takes part. The molten cast iron is deoxidized when super-heated. The heredity of the melt, whatever kind it may be, is erased by reduction and refining. Ordinary cast iron of flake graphite structure changes itself first into roes graphite, next into eutectic graphite, then into fine granular graphite super-heated structure, as deoxidation goes on. And up to this structural stage, deoxidation is comparatively easily worked, but as to nodular graphite structure in which rather extreme deoxidation is required, it is supposed that the presence of a certain impure third element (e.g. As, Sb, Sn, etc.) works as a preventive to deoxidation.

Summary

- (1) In super-heated melting the tendency is for carbon to decrease and for silicon to increase. This change has no direct relation to the structural change. Mn, P and N₂ do not change in their amount. S gradually decreases.
- (2) Super-heated melting shows its effect in making graphite, first, fine and then into super-cooled white cast iron with spheroidal tempered graphite. Deoxidizing forces of Al and Si are not strong enough to make graphite fine.
- (3) At ordinary melting temperature, heredity—the properties of cast iron are different according to the difference in the amount of oxygen which raw material contains—is observed even if their chemical composition is similar. But as the reduction by super-heating goes further, this hereditary phenomenon disappears and fine graphite structure arrives irrespective of their chemical composition.

Thanks must be offered to Honorary Professor Keizō Iwase, Tōhoku University, who gave us his valuable and cordial assistance all the time during our studies.

(5) C. Pfannenschmidt, *Giesserei*, 37 (1950), 105 ; 38(1951), 276.