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Ancient Carburization of Iron to Steel

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ABSTRACT The ideas that iron can be carburized simply by inserting it into a charcoal fire, and that it becomes carburized through repeated heating for forging, are untenable. To carburize iron, it must be enclosed with a source of carbon so as to exclude all or nearly all the products of combustion. Temperature above about 740°C is necessary for carburization to occur, and a temperature of more than 900°C is required to produce a useful thickness of carburized skin. Immersion of iron in a bath of molten cast iron held just above its melting point will carburize iron rapidly.

The advent of steel—carbon-containing iron that becomes extremely hard when quenched from a red heat into water—must have had a significant impact on human activities. The material could be made into excellent tools and edged weapons, but it was not easy to make intentionally. Initially, it occurred occasionally and unpredictably during the iron smelting operation which normally yielded tough, unhardenable wrought iron. Iron that could be hardened by quenching had an increased carbon content, which resulted primarily from an increase in the ratio of fuel to ore in the furnace charge. Since the charcoal fuel and ore reductant consisted mostly of carbon, and carbon can readily enter and leave iron at high temperature—facts not known in antiquity—it is not surprising that more than 2000 years, from the early fourth millennium to late in the second millennium B.C. (Waldbaum 1980), were needed to achieve a reasonably consistent production of steel.

Since steel was probably scarce and uncertain in supply during this period, it was extended by forge welding strips onto softer iron, a practice still known today as "steeling." The result was a duplex structure with a useful combination of hardness and toughness. Another way of creating quench-hardenable iron is to add carbon directly to the surface of the iron, by setting up conditions under which the carbon is available in a form soluble in iron and the iron can dissolve it. This process, called "carburization," is well understood and used today, but it could have been discovered in antiquity only through trial and error.

Two assumptions about carburization that are commonly made in archaeometallurgical literature have confused its proper study. The first is that a microstructural gradient of carbon concentration from the surface indicates intentional carburization of a soft iron. Identical carbon gradients can, however, occur in any wrought iron containing carbon, taken directly from the smelting furnace. The second is that iron can be easily carburized by inserting it into a charcoal fire in a forge. This latter assumption is questionable, and it will be shown here that more complicated procedures are necessary.

Carbon from organic matter, especially charcoal, has been the most common source of carbon for carburization, but at some time cast iron, which contains from two to over four percent carbon, came to be used also. Cast iron can impart carbon by transfer in the solid state at high temperature, as was done in early China, or by immersing solid soft iron in a bath of molten cast iron. The latter technique was practiced in Europe in the Renaissance, although there are few technical data on how it was done; its earlier history is unknown. New experimental evidence presented here shows that the process of using cast iron as a carburizing agent can be easily controlled by an experienced operator, without special equipment.

IRON AND CARBON

The difference between a soft malleable iron and a quench-hardenable steel is simply the presence of a small quantity of carbon, 0.2 to about 0.8 percent, dissolved in the iron. Carbon can enter iron either during the smelting of iron from ore, or during a subsequent heating of iron with carbon under the right circumstances.

When iron ore is reduced to metallic iron in a fuel-fired furnace, the combustion of the fuel supplies the necessary heat, and carbon monoxide (CO) gas in the products of combustion reduces the ore. If the ratio of carbon in the fuel to iron in the ore is above a certain value, the reduced iron dissolves carbon, in amounts increasing as the ratio increases. Thus, iron made in a furnace may contain from nearly zero to well over four percent carbon. When the carbon content is less than about two percent, the iron is constitutionally a steel, and is usually extracted from the furnace as a solid lump or bloom in which the carbon content is locally variable. Subsequent forging of the bloom at temperatures of 1100 to 1200°C is necessary to squeeze out molten slag and weld cavities shut. During this reheating, internal gradients in carbon content tend to level out by diffusion (Tylecote et al. 1971: 352).

When the fuel to ore ratio in the smelting furnace is high enough so that the carbon content of the reduced iron is more than about two percent, the iron starts to liquefy and then absorbs carbon from the fuel more rapidly. As a result, a pool of molten cast iron collects in the hearth of the furnace; it usually contains about four percent carbon and is free of slag which floats as a molten layer on the iron. Molten iron followed by slag can then be easily drawn from the furnace through a tap hole.

On reheating, pure solid iron can dissolve carbon in appreciable quantities only above a temperature of 727°C, but the impurities invariably present in iron ores, such as manganese, sulfur, and phosphorus, increase this "critical temperature" to about 740°C. The advantages of adding carbon to a low-carbon iron in the solid state are that the amount can be controlled more directly, and the location of increased carbon content can be predetermined by masking areas not to be carburized with a clay coating. The amount of carbon in iron desired for practical purposes is in the range of about 0.25 to 1.00 percent, which makes for a quench-hardenable steel that can become very hard and strong (Fig. 1).

The agent which transfers carbon into solid iron is usually carbon monoxide (CO) gas. Above about 740°C, its reaction with iron is given by:

$$3Fe + 2CO = Fe_3C + CO_2$$

with the Fe_3C (cementite) dissolving instantly in the iron. The reaction is temperature-dependent, so the amount of carbon in equilibrium solution in the iron is determined by the temperature and the ratio of CO to CO_2 in the gas (*Metals Handbook* 1964: 113). With continued holding at temperature, the carbon diffuses inward through the iron forming a concentration gradient fed from the surface. With extended holding, the amount of carbon at any given depth below the surface increases with the square root of holding time and exponentially with temperature of holding. For example, a "case" depth requiring two hours at 950°C will take seven hours at 850°C and 30 hours at 750°C; doubling case depth will require four times as long. It is therefore a relatively slow process; today, carburizing temperatures above about 850°C are used to obtain useful case depth in reasonable time.

Almost any form of carbon or organic matter can be the basic source of carbon, but CO or other carbonaceous gas is the transfer agent, except in molten systems. If iron is packed in a closed container with pulverized carbon and heated to above the critical temperature of about 740°C, it will become carburized. The mechanism is not one of direct transfer of carbon atoms, but a circulation of the oxygen in the air trapped in the container. CO is formed by reaction with carbon, the CO forms FeC_3 in the iron, and the released CO_2 then reforms with the external carbon which is always present in excess. These reactions are accelerated by the presence of small quantities of alkali carbonates in the carbon, which can occur in the ash or be intentionally added.

There are two physical conditions in iron that are created by carburization. In wrought iron, which was the basic iron of

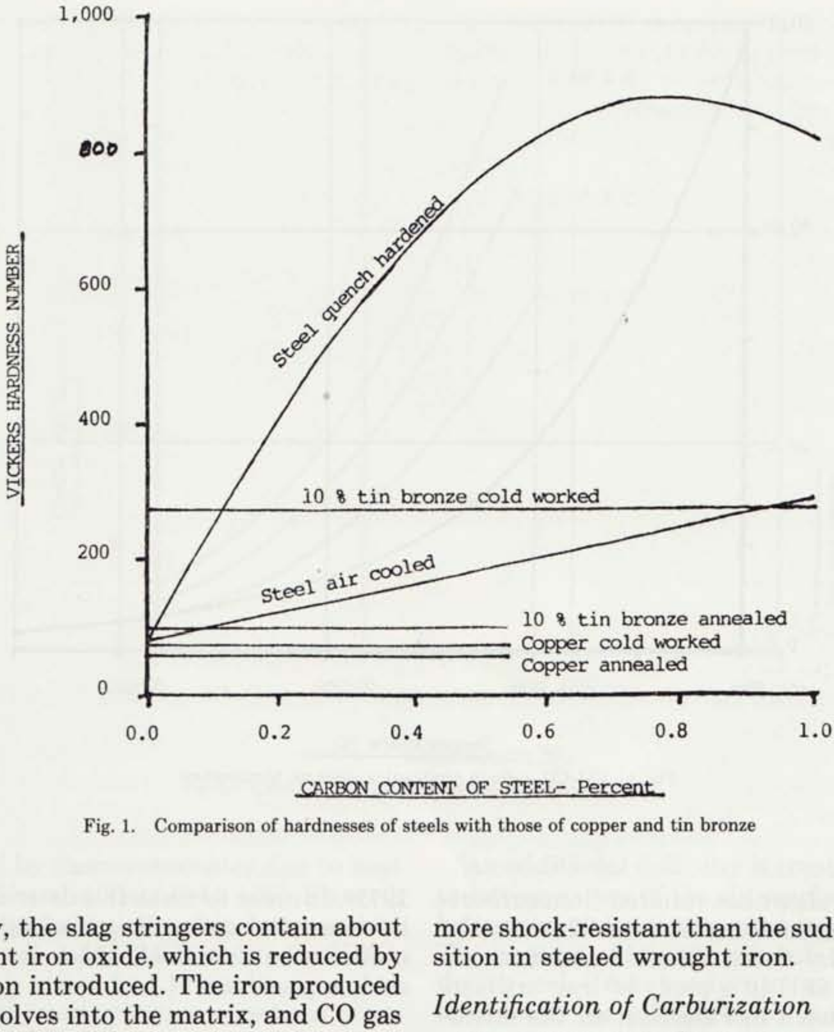

Fig. 1. Comparison of hardnesses of steels with those of copper and tin bronze

antiquity, the slag stringers contain about 80 percent iron oxide, which is reduced by the carbon introduced. The iron produced then dissolves into the matrix, and CO gas close to the surface escapes by diffusion. The result is a carburized skin which is low in slag. In the seventeenth and eighteenth centuries in Europe, when carburization to convert whole bars of wrought iron to steel was practiced intensively, the carbon monoxide formed could not all escape, so internal and external blisters were formed. These were welded shut by subsequent hot rolling, but the product was called "blister steel."

The other condition created by the carburization of iron is that the carbon gradient from the surface inward imparts graduated hardness and strength, so there is a smooth transition of mechanical properties in the duplex structure, which is much more shock-resistant than the sudden transition in steeled wrought iron.

Identification of Carburization

The principal evidence that an iron artifact has been carburized is the existence of a carbon concentration gradient. This can be detected and measured by microstructure, indentation hardness traverse, or layered chemical analysis. Even though a gradient can be discerned, there is no way of determining how it was formed, since gradients can occur in blooms of freshly smelted and forged iron, as well as in separately carburized iron. Variability in the amount and distribution of carbon in bloom iron is inherent in the smelting process, a fact often noted (e.g., McWilliams 1920; Tylecote 1976: 43; Smith as quoted in Pigott 1980: 432). It is therefore incorrect to assume that an observed carbon concen-

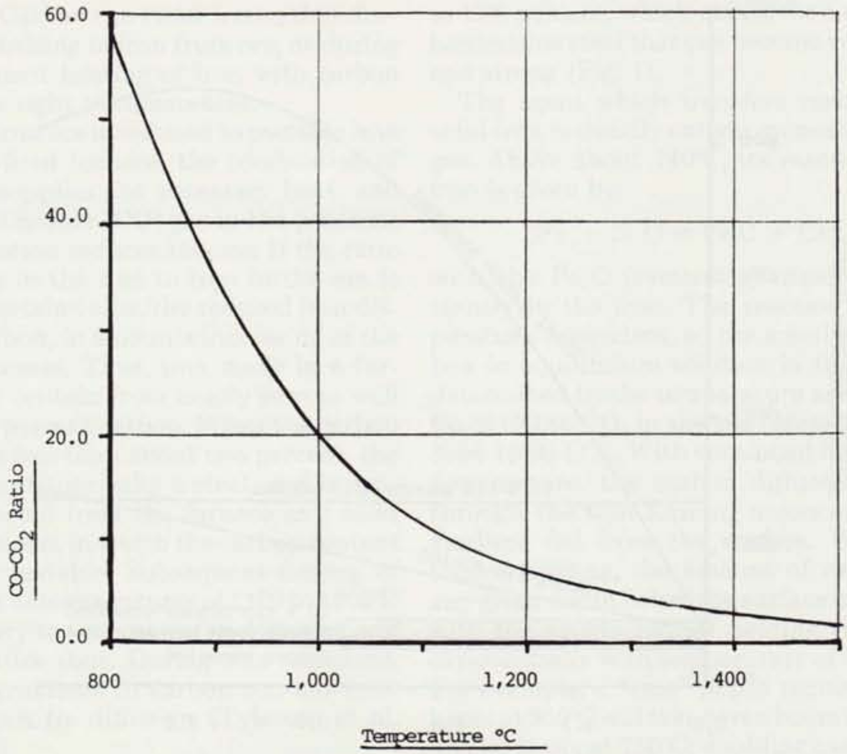

Fig. 2. CO–CO_2 ratio in combustion gases vs. temperature

tration gradient has resulted from carburization after smelting the iron. This mistake is made by Stech-Wheeler and her colleagues (1981) in a study of iron artifacts from Taanach in Palestine; all the microstructures illustrated could be found in freshly forged blooms.

Iron that has been steeled by welding on a piece of steel can often be identified by a very steep carbon concentration gradient and by the presence of aligned traces of slag or iron oxide inclusions marking the original weld face. Repeated forging with its repeated heatings can make the gradient more shallow, so that identification is difficult. In a sense, a steeled iron that has been reforged is self-carburized. In fact, any extensively forged artifacts have undergone the same changes.

One factor that may help distinguish the source of the carburization is the tendency to an irregular highest carbon line in iron carburized during smelting and a straighter line in iron carburized later (Piaskowski 1972). In order to make this determination, however, the entire length of an artifact needs to be examined, which is of course seldom possible.

CARBURIZATION IN A CHARCOAL FIRE

When a piece of iron is put into a bed of burning charcoal such as a forge fire, heat is transferred to it by radiation from hot lumps of charcoal and by hot gaseous products of combustion. For heat transfer to occur, the source must be at a higher temperature than the receiver, and for reasonably rapid transfer higher by 10 to 20 percent. Thus, in order to heat a bar of iron to 1200°C for forging, the fuel bed must be at a temperature of 1300 to 1400°C.

The temperature of combustion is a function of the percentage of CO_2 produced, so at high temperature the products of combustion have a low CO–CO_2 ratio and are very oxidizing. The actual temperatures created in a fuel bed are lower than those

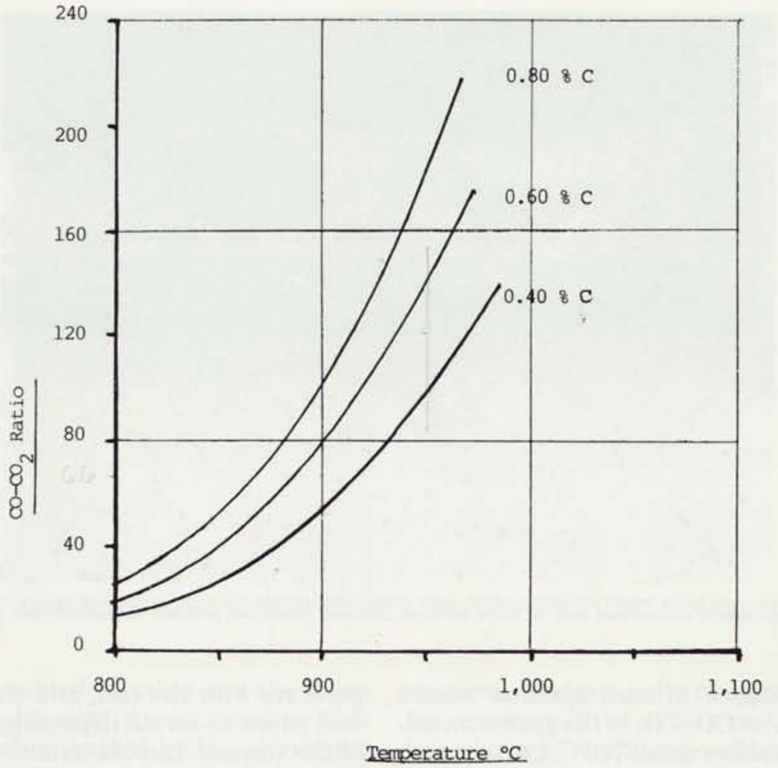

Fig. 3. CO–CO$_2$ ratio to carburize iron vs. temperature

predicted by thermochemistry due to heat losses (Hiles and Mott 1944: 155). Figure 2 shows a typical relationship between bed temperature and CO–CO$_2$ ratio; at 1350°C, the ratio is about four to one.

Using the carburization equations given above, the CO–CO$_2$ ratio necessary to carburize iron to a given surface carbon content at a given temperature can be determined (see Fig. 3 for data on three carbon contents which can give useful quenched hardness). When the iron has reached 1200°C, the CO–CO$_2$ necessary to carburize it is off the graph, at orders of size above the four to one available in the products of combustion. The iron will therefore not be carburized, any carbon already at the surface will be extracted, and some iron will be oxidized to scale. On the other hand, carburization is possible at an iron temperature of 800°C and a fuel bed temperature of 900°C, but at such low temperatures the diffusion of carbon is so slow that many hours would be required for the formation of even a thin carburized skin.

An additional difficulty is created by the pulsating nature of the air supply from the bellows or piston device used in antiquity. The increase and decrease in rate of air flow during each stroke produce an increase and decrease in the velocity of air leaving a tuyere nose; since the length and volume of the cone of combustion from a tuyere in a fuel bed are functions of air velocity, the position of any temperature level and gas composition moves back and forth from the nozzle of the tuyere. Under these circumstances, constant conditions cannot be maintained at a given location in a fuel bed for even part of a minute, let alone hours, and any thin layer of carburizaton that might be created at one moment will be oxidized away the next as the temperature and CO–CO$_2$ ratio shift. Therefore, the conclusion is that no useful degree of carburization can be achieved when iron is heated unprotected in a forge fire (contra, e.g., Snodgrass 1980: 366; Waldbaum 1978: 54; Wheeler and Maddin 1980: 116; all of these are expressions of opinion only).

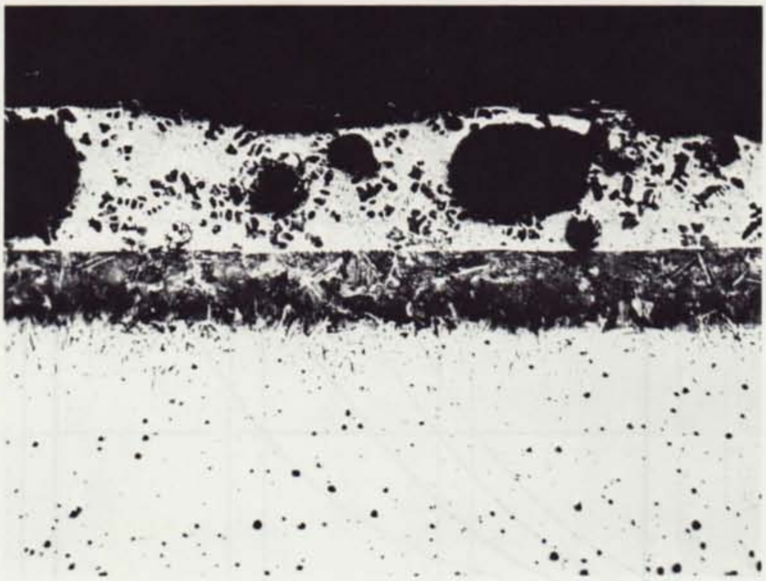

Fig. 4. Armco iron in molten cast iron for three minutes, adherent white cast iron and carburized case. ×50, Nital etch

Since absence of carburization results from a too low CO–CO_2 in the gas surrounding the iron above about 740°C, i.e., too much CO_2 in the combustion gases, the circumstances can be changed to carburizing by making a closed system of iron and a source of carbon. The closure can be a simple envelope of clay, and the package can be put into the hottest part of the fire to shorten the time necessary to create a useful case depth. The use of sealed clay boxes heated in pottery kilns would have been possible at a very early stage in the working of iron. Since clay coatings can be applied locally, carburization can be distributed as desired. When carburizing in a sealed box, a soft iron sword or knife can be carburized on the cutting edge, while a clay coating keeps the back of the blade soft and tough.

Carburization can be done in a charcoal fire, using a different type of enclosure. First, the forge fire must be blown to a relatively high temperature and the iron then buried in the fuel bed at the hottest point. The air supply must then be shut off, and the top of the fuel bed covered with some refractory material to exclude air and decrease the rate of heat loss by radiation. The CO–CO_2 ratio in the bed will rise to a high level, the iron will equalize in temperature with the bed, and the whole will cool down at a rate depending on the size of the furnace and the extent to which the refractories are heat-soaked. Carburization will be rapid at first and then decrease exponentially. If, for example, the iron reached 1100°C before starting to cool, and then took 15 minutes to cool to 740°C, the depth of carburization would be about one millimeter, which is a useful case depth. Although the procedure sounds simple to those who understand the action of carbon on steel, heat loss rates, and reaction times, it would probably have been impossible to conceptualize in antiquity.

CARBURIZATION BY CAST IRON

Directly smelted cast iron typically contains about four percent carbon, and if pulverized or fragmented to increase surface area, it can act as a source of carbon for carburization, provided that oxidizing gases such as the products of high temperature combustion are excluded. This was demonstrated experimentally by Whitaker and Williams (1969: 41), who wired together bundles of low-carbon iron sheets intercalated with pulverized cast iron, heated them to 950–1000°C in a closed box in a furnace, and then removed and forged the bundles.

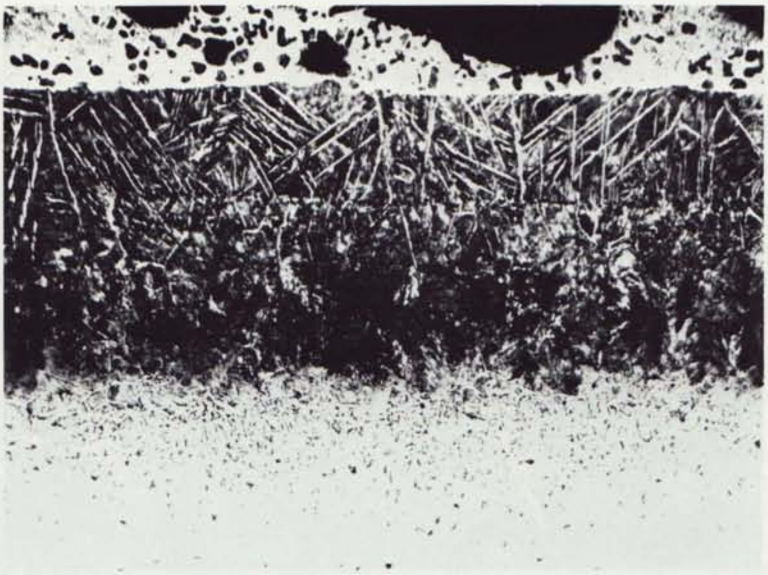

Fig. 5. Armco iron in molten cast iron for nine minutes; note steep carbon gradient under white iron. ×50, Nital etch

The sheets welded together and the interfaces showed under the microscope thin lines of pearlite created by the absorption of carbon from the cast iron. As the amount of cast iron was increased, the thickness of the pearlite (carburized) layer increased; holding at 900°C for eight hours caused the carbon to diffuse completely through the iron. The cast iron involved was decarburized by loss of carbon to the sheet, so it became part of the final steel product.

If, however, the cast iron is molten and held in a crucible or bath, it should in principle efficiently carburize wrought iron immersed and held in it. Furnace gases will not affect the process, since the transfer of carbon takes place below the surface of the bath. The difficulty of using this procedure is that low-carbon iron dissolves rapidly in the bath, and the rate of solution increases with both the temperature and carbon content of the cast iron (Guthrie and Stubbs 1973). The mechanism of solution is evidently one of rapid formation of a thin skin of carburized iron which is rapidly dissolved off because of associated lower melting temperatures; this precludes a useful retained degree of carburization in the solid iron.

In recent experiments, I have determined that iron can be rapidly carburized in molten cast iron. If the molten cast iron is held just above its melting point or within the liquidus-solidus temperature region, and low-carbon strip is immersed and held in the bath, formation of a carburized skin is more rapid than its rate of solution. Upon withdrawal of the iron strip from the bath, a thin layer of cast iron adheres to the surface in perfect weld. This layer protects the carburized iron from oxidation in air and further in reheating for subsequent forging. The lowest practical temperature of the cast iron bath that keeps it molten is essential to success; this can be determined empirically without temperature measurement by the "feel" or texture of the melt on moving the immersed iron. Once discovered, this procedure could be easily repeated many times.

The rate of carburization is very rapid, about five times that predicted by extrapolation to higher temperature of the equations that accurately predict carburization rate by CO gas or by pack carburizing in granulated carbon. Apparently a different mechanism of carbon transfer is involved. A carburized skin or case 0.8 mm. thick forms in eight to ten minutes immersion in a 4.0 percent carbon cast iron held just above

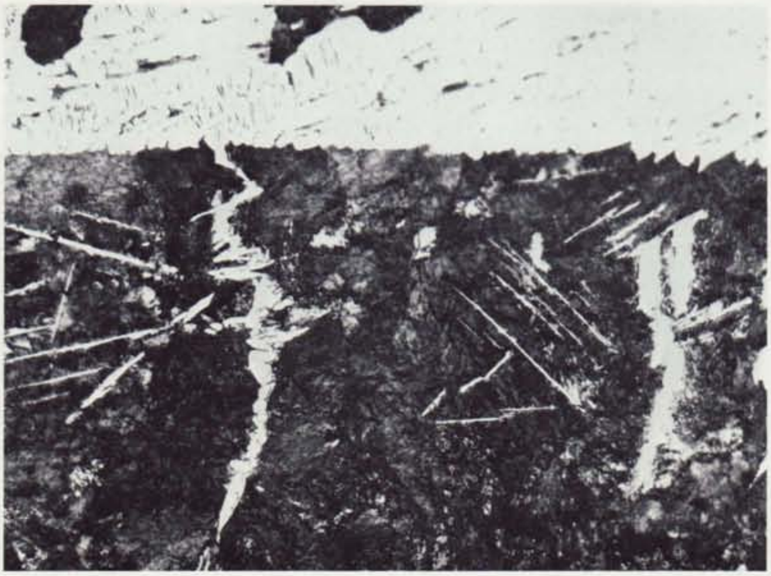

Fig. 6. Armco iron in molten cast iron for nine minutes; note sharp line of demarcation between white iron and carburized iron. ×500, Nital etch

its solidification temperature, a rate of increase in thickness of about 0.08 mm. per minute.

The microstructure of a carburized skin made in this way is idiosyncratic (Figs. 4–6). A thin white cast iron skin is welded perfectly to the iron being carburized, with a very sharp transition to the carburized layer itself. The abrupt decrease in carbon content from about three percent in the white iron to 1.6 to 1.8 percent in the carburized iron (estimated from the microstructures) is puzzling from a metallurgical point of view. From the interface the carbon content of the iron decreases rapidly to the nearly carbon-free interior.

Low-carbon iron can be given a useful thickness of carburized surface by immersion in molten cast iron if the lowest possible working temperature is used. It takes much less time than pack carburizing, but it does not require a bath of molten cast iron.

DESCRIPTIONS OF CARBURIZATION

The earliest Western description of carburization seems to be Theophilus' (ca. A.D. 1120; 1979: 94–95) comments on how to harden files:

> These are made from soft iron and you should harden them thus. When they have been cut with a hammer or a chisel or a small knife, smear them with old pig fat and wrap them around with leather strips cut from goat skin and bind them with linen thread. After this cover them individually with kneaded clay, leaving the tangs bare. When they are dried, put them into the fire, blow vigorously, and the goat skin will be burnt. Hastily extract them from the clay and quench them evenly in water.

This procedure will in fact produce a good file. The teeth are cut first; since it is only the teeth, and particularly the tips, which are effective in use, these alone need to be hardened. The teeth are short and thin, a fraction of a millimeter thick at the bases tapering to points at the tips. The file is then wrapped in fat and leather, and tied with a string to hold everything in place until it is covered with clay. Fat has a considerable carbon content, and leather and horn scraps were used as carburizing agents into the eighteenth century. The clay enclosure was necessary to exclude combustion gases which would oxidize carbon and prevent carburization. When put into the fire, the clay probably developed small cracks which would let the volatile matter from the decomposing fat and leather escape, but not admit much furnace gas. The fire was to be "blown vigorously" so temperatures of 900 to 1000°C or more were likely attained. At a temperature of 950°C, carburization would penetrate about 0.3 mm. in ten minutes, which would have satisfactorily carburized the thin file teeth, particularly their thin tips. The "hasty" extraction from the clay and water quench after firing would be essential to keep the thin teeth from decarburizing in air. In this procedure, the time at temperature is short and the depth of carburization small though effective, but the principle of heating soft iron with organic matter (carbon) in an enclosure to keep out furnace gases had clearly been established. It is possible that observation of a procedure like this led to the stories about iron being made hardenable simply by putting it into a forge fire, the details of the covering of organic material having been disregarded.

Barraclough (1984: 48) notes that the earliest clear reference to carburization by carbonaceous matter in a kiln or oven was published in Prague in 1574, while there is a detailed description that appeared in Nuremberg in 1601. Both of these establish the European origin of the process, and the fact that it must have been in use for many years. Intensive carburization of wrought iron came to be called "cementation"; it was done by embedding strips of iron in granulated carbonaceous matter, usually charcoal, in a box which was then sealed and heated with other packed boxes in large natural draft kilns. Holding at an orange heat for 24 or more hours caused carbon to diffuse uniformly through the iron to make "blister" steel (see above).

Carburization by Cast Iron

The earliest description of carburization of soft iron by cast iron derives from sixth-century A.D. China (Needham 1958, v. 1: 26, 28, 36). Pieces of cast iron and of wrought iron were tied together to form faggots, which were protected by clay, and then heated to a high temperature, apparently in a kiln. The whole was then forged, a process followed by repeated folding, reheating, and forging. The greater the number of folds and the number of reheatings and forgings, the better was the uniformity of carbon distribution in the steel and hence its quality. A sixteenth-century text mentions that the first heating of such a faggot was to a high enough temperature to melt the cast iron (Needham 1958, v. 2: 36), which not only distributed it through the bundle since it melts at a temperature several hundred degrees lower than does wrought iron, but also accelerated the diffusion of carbon. The temperature required was about 1160°C, easily reached in the ceramic kilns of the period.

Evidence for the direct use of molten cast iron to carburize is rare. The procedure presupposes the ability to make cast iron and to hold it in a bath. The Chinese were apparently the first to produce cast iron in quantity and to use it to carburize. The earliest intentional cast iron in the West was made at Lapphyttan in Sweden about A.D. 1250 (Gordon and Reynolds 1986: 110).

Biringuccio (ca. 1540; 1969: 69) has described what is taken to be the carburization of iron to steel in a bath of molten cast iron (see also Percy 1864: 807). A bowl-shaped furnace is filled with charcoal, ignited, and heated by combustion air from a tuyere which is directed from above at the center. Small pieces of "iron that has passed through the furnace" are added which sink through the charcoal to create a bath of molten iron. Then "three or four blooms . . . of the same iron" are put "while hot [from the forge hammer] into this bath of molten iron." The bath is kept molten and the blooms are stirred frequently for four to six hours. The blooms emerge as quench-hardenable steel.

The type of furnace is one used earlier for remelting copper and bronze, in which the mound of charcoal—burned by a downward-directed blast—acts as an insulating cover on the outside; the hottest burning charcoal rests directly on the material to be melted and transfers heat by direct radiation. When iron is being melted, it will absorb carbon from the charcoal at high temperature, increasing the carbon content of the iron to the three or four percent level of cast iron and decreasing the melting temperature from about 1530°C to 1180°C. This bath will carburize low-carbon or wrought iron as described above, provided the temperature control is good. The holding time of four to six hours was probably necessary because the iron was in lumps with a low ratio of surface area to volume. If the iron had been in the form of bars or strips, less time would have been required.

SUMMARY

The ideas that iron can be carburized simply by inserting it into a charcoal fire, or that it becomes carburized by repeated heating for forging, cannot be supported. Enclosure of the iron with a source of carbon, in such a way as to exclude all or nearly all products of the combustion which provide the necessary heat, is essential. A temperature above about 740°C is required for carburization to occur, and it must be 900°C or more to produce a useful thickness of carburized skin in a reasonable time. The mechanism of transfer of carbon is the formation of iron carbide by CO gas, and solution of the carbide in the iron. The enclosure would be of a material like clay which should leave archaeological traces.

There are few objective criteria which can be used to determine the source of carburization. A bar of iron direct from the smelter has a variable internal carbon content, and can possess microstructures which are difficult to distinguish from those in iron carburized separately. Caution is therefore necessary in discussing carburization.

Immersion of iron in a bath of molten cast iron held just above its melting point will carburize the iron rapidly, with the transfer mechanism being direct diffusion. Maintaining the proper temperature can be done without instruments.

The earliest literary evidence for carburization by cast iron is in sixth-century A.D. China, where a solid state procedure was practiced. The Chinese made cast iron long before that time, by the sixth century B.C., so theoretically they could have carburized by cast iron then. The earliest evidence for carburization by carbonaceous matter in an enclosure is that given by Theophilus.

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