manner, by Osmond (p. 31), and later by Charpy (p. 42) and by Benedicks (p. 159). The latter showed, with very simple reasoning from his experiments, the impossibility of attaining by means of cementation a definite maximum concentration of the carbon, corresponding to saturation of the iron, except by keeping the temperature rigorously constant during the whole of the cementation. Still more recent considerations and experiments (see pp. 160–167) have furnished direct proof and a clear theoretical explanation of the effects which even slight oscillations in the temperature produce on the apparent limit of saturation of the iron by the carbon in cementation experiments.

As to the cementation of the special steels, there is not much to add to what has been said in the preceding chapters. Caron (see p. 9) made the first investigations on the effects in cementation of foreign substances (such as manganese, silicon, etc.) alloyed with the iron. Guillet (see p. 52) studied essentially practical problems, such as the velocity of the cementation in various special steels, and the obtaining of zones of martensitic or polyhedral steel by cementing certain pearlitic steels.

The investigations of Charpy on the cementation of the special steels with carbon monoxide have been already noticed in the present chapter (see p. 191). We have also already reported the more precise data obtained in recent investigations on the distribution of the carbon in the cemented zones, and the exact definition of the conditions under which cements with carbon monoxide as base can be advantageously employed for the cementation of the various types of special steels (see p. 145).

A last group of investigations of great practical importance are the studies on the diffusion of the other elements than carbon into iron at a high temperature but still in the solid state. The experimental data published up to the present on this subject are few and not wholly reliable. We may mention here the experiments of Boussingault on the variations in the concentration of the sulphur contained in iron during cementation (see p. 23); those of Campbell and of Arnold and MacWilliam (see p. 34) on the diffusion of the sulphide and oxysulphide of iron into iron, and those of Arnold and MacWilliam on the diffusion of various metals into solid iron.

In connection with these last experiments, I must point out that recent investigations (to which we will refer in the second part of this book) do not confirm the division made by Arnold and MacWilliam (see p. 35) of the various elements into two classes, the first of which includes the elements capable of diffusing or "migrating" into the mass of the solid iron, while the elements belonging to the second class lack this power. The experiments to which I have just referred prove that the various elements classified by Arnold and MacWilliam in the second class can diffuse into solid iron, under suitable thermal treatment.

PART SECOND

INDUSTRIAL APPLICATIONS OF THE PROCESS OF CEMENTATION

INTRODUCTION

In the first part of this volume, we have tried to bring together all the data acquired up to the present on the process of cementation; it is only on the basis of these data that practical rules for operating processes of cementation can be derived.

In the second part of this volume we propose to consider the material means which modern technology uses for the practical application of these rules.

Since there are two essential objects for which the process of cementation is applied, we will therefore devote two separate chapters to the applications of cementation, on the one hand to the total transformation of wrought irons and soft steels into hard steels, and on the other to the superficial carburization of machine parts. In the second chapter I shall also refer briefly to some other processes which, while they cannot strictly be classified in either of the two preceding groups, present many characteristics in common with the processes of the second group, both as to the principles on which they are based and the objects at which they aim.

Although we are considering the subject of cementation, still it will be necessary also to deal briefly with the various complementary treatments of the cemented materials (such as tempering, annealing, etc.), especially since the effects of these treatments are closely connected with those of the cementation, and above all since they influence to a marked degree the results of the various methods used for the technical control of the cemented products.

We add also some data on the measurement of high temperatures, assuming a general knowledge of the same and limiting ourselves to the arrangements more especially adapted to the control of the temperatures in cementation.

Finally, I will add some data relative to the more important patents which deal with processes of cementation.

CHAPTER I

TOTAL CEMENTATION OF WROUGHT IRON AND SOFT STEEL

I have already pointed out on p. 4 that the cementation of steel began to assume a large industrial development in the first years of the seventeenth century, when from a simple process for the superficial hardening of objects of soft iron it became a true process for the manufacture of steel; when, that is, it was applied to the total transformation of pieces of soft iron or steel into hard steel intended for further heat treatment.

This manufacture of cement steel received a strong impetus in 1740 by the invention, by Benjamin Huntsman, of the process of crucible fusion of steel; so that, toward the end of the eighteenth century, the industry of the manufacture of cement steel destined for crucible fusion attained a great development.

Notwithstanding the subsequent decline of this industry in the nineteenth century, due to the marvellous development of other modern processes for the manufacture of steel, the technical importance of the processes of cementation, instead of diminishing, kept on rapidly increasing, for a reason inverse, so to speak, to that which had given it its great impetus at the beginning of the seventeenth century. In fact, while formerly the industrial development of these processes was due essentially to their application to the total transformation of soft iron or steel into hard steel, the further development of these same processes in the second half of the nineteenth century and in the first years of the twentieth is, on the contrary, due to their application to the superficial carburization of machine parts. This is explained by the recent great advances in the technology of mechanical construction.

The present causes of the slight importance of the older, original processes, at least as regards the quantity of the products manufactured by them, are above all of an economic nature, and are essentially the high price of the steel obtained by cementation as compared with the price of steels of corresponding quality obtained directly by other processes, such as, for example, the electric furnace. But besides these causes of an economic nature, others of a technical character serve to diminish their industrial importance. First among these is the increasing application of the special steels, whose properties render them for many uses far superior to the best carbon steels obtained by melting the purest cement steel in crucibles. The technology of the direct manufacture of the special steels by means of the so-called processes of "metallic cementation" is in its infancy, and has not yet given really practical results.

From what has been just said, it is seen that any one desiring to study the part which is still played to-day in siderurgy by the manufacture of cement

steel intended for fusion should attempt to seek the reasons of its survival rather than of its decline.

The industry is certainly gaining ground, for, according to the manufacturers of crucible-fused steel, the high-carbon product obtained by fusing wrought iron *first carburized by cementation* is far superior to that which is obtained by carburizing the steel during the fusion.

Still further, the product which is obtained by cementing best Bessemer or Siemens-Martin soft steels and *then* melting them in a crucible is considerably inferior in quality to that obtained by using as raw material good wrought iron and treating it, in other respects, in an identical manner.

No precise comparisons have been made of the qualities of the products of identical composition obtained by the various processes just mentioned, and it does not seem, in the present state of our knowledge, that a complete explanation can be given for the differences noted by practitioners in the qualities of these products. Some regard as an explanation the fact that the cementation of wrought irons permits of obtaining perfectly sound steels of very low manganese and silicon content, while it would not be possible with the other processes to reduce the percentages of these two elements to such low values without the steel becoming oxidized and brittle, as well when hot as when cold. On the other hand, it does not seem that there can be any reasonable doubt as to the reality and the constancy of these differences in quality, for there is no doubt that manufacturers would not hesitate to substitute the less expensive soft steel for wrought iron, if their experience had not proved the marked inferiority of the products obtained with soft steel.

I believe, therefore, that steels of high carbon content obtained by melting cemented best wrought iron in a crucible are uniformly of better quality than products of the same composition obtained either by carburizing fused soft steel or by fusing cemented soft steel. It is to this difference in quality that is due the survival and recent rejuvenation of the cementation industry for manufacturing high-carbon steels of superior quality.

The most important center of this industry to-day is Sheffield. But it is also practised in various other places, both in England and in France, the United States of America, Germany, Austria, Sweden, etc. In Italy, where it flourished in the seventeenth century (see p. iv), it still survives in Lombardy.

Using the expression in its widest sense, we must include in the processes of the manufacture of cement steel all those which are based on the carburization of the iron or steel by keeping it in contact with carburizing materials at a temperature not high enough to completely melt it.

These processes may be divided into two groups; to the first group belong those in which the operation of the carburization is effected simultaneously with that of the reduction of the iron ore, or at least directly on the iron such as it results from the reduction of the ore; to the second group, on the contrary, belong the processes in which there is subjected to carburization iron or steel which has already undergone a series of treatments for freeing it of the greater part of the foreign substances (scoriæ, etc.) and for fashioning it into definite sizes and shapes ("bars").

The processes of the first group have now only a historical interest; I limit myself, therefore, to referring briefly to some of them. Two English patents, granted in 1854 and 1856 to Samuel Lucas and to W. E. Newton, respectively, describe two processes, very similar to each other, consisting in heating for a long time in closed refractory vessels small fragments of iron ore mixed with an *excess* of pulverulent carbon (wood charcoal, animal charcoal, etc.); the product obtained ("sponge") must be crucible-fused. These processes, which various later experimenters attempted in vain to apply, present (besides many other defects) the serious disadvantage of never furnishing results which are uniform or which can be predicted on the basis of the composition and the proportions of the raw materials used.

Another process belonging to this same group is the Chenot process. This process, which on its appearance in 1857 gave rise to great hopes of success, presents over its predecessors the advantage that the carburization, while effected on the metallic sponge resulting directly from the reduction of the iron ore, is carried out separately from the reduction of the ore; this makes it possible to determine with some approximation the carbon in the final product. In the Chenot process the iron sponge was intimately mixed with powdered wood charcoal impregnated with tar or with fatty substances, and then heated in closed vessels; the cemented sponge was compressed into cakes and then fused in a crucible. According to Percy (treatise on Iron and Steel) the price of Chenot steel manufactured at Clichy was 1097 francs ($210) per ton.

The most serious disadvantage of the Chenot process lies, according to Percy, in the large volume occupied by the cemented sponge, even though strongly compressed; this does not permit of a good utilization of the space disposable in the crucibles in which this sponge must be melted, causing a very high cost for fusion.

Neither the Chenot process nor the other analogous ones which have followed it have justified the great hopes raised by their appearance, and today they may be considered as being abandoned.

The only processes of cementation at present in use for the manufacture of steels destined to undergo further working are those which we may call "processes of cementation of iron in bars." The importance and the diffusion of these processes are not great at present, not more than at or about the middle of the last century. Several inventions have been based on some supposed new process of cementation, but all such have quietly disappeared. I shall recall, as a single example, the "Bates process."

Francis Gordon Bates, of Philadelphia, obtained in the principal countries a series of patents between 1890 and 1893. According to the description of one of his first patents (German patent, Kl. 18, No. 57,729, May 20th, 1890), his process consists essentially in cementing iron by means of a mixture composed of 80 to 100 parts of carbon, 5 to 10 parts of cryolite, 10 to 20 parts of spent lime and 5 to 10 parts of rosin or soda. In another patent (German pat., Kl. 40, No. 63,404, of November 3rd, 1891), Bates describes a furnace with three hearths, designed for the carrying out of his process. In a third patent (German pat., Kl. 18, No. 83,093, of February 23rd, 1893), the inventor claims a further improvement of his cementation powder, consisting in adding to the ingredients already indicated in the preceding patents nickel oxide; according to Bates, this oxide is reduced during the cementation and the nickel alloys directly with the iron subjected to the treatment.

The Bates process was given wide publicity, and various technical reviews, especially English, dealt with it repeatedly, announcing it as destined to bring about a revolution in the manufacture of steels of superior quality. *Stahl und Eisen*, in March, 1893,[1] commenting on an article on the Bates process in the English journal *Iron* in which it was asserted that the new process had reduced to 7 pounds sterling per ton the price of steels identical in quality with so-called Mushet-steel, then sold in England at 140 pounds sterling per ton, says that if this process is merely an application of the patents obtained by Bates the manufacturers of fused steels of superior quality need in no wise fear the announced "revolution," and concludes by advising the author of the *Iron* article to test the steels manufactured in German steel works, either in convertors or in the Martin furnace, in order to convince himself that the Bates process is superfluous.

The making of cement-steel in bars is limited at present to the production of very pure steels of high carbon content and of superior quality for springs, files, etc.

The material which furnishes the best steel by cementation is wrought iron of the purest quality. This is partly explained by the purity of the wrought iron, which is in general superior to that of the fused soft steels, at least as regards the substances forming an integral part of the metal, such as substances in the state of solid solution (manganese, silicon, sulphur, etc.). The harmful influence of slag, always much more abundant in the wrought iron, does not make itself markedly felt in the cemented products, from which it is in great part eliminated by the subsequent treatments to which the cemented bars are always subjected, especially so when such treatments include crucible-fusion.

For many years the cement-steel manufacturers of Sheffield, the principal center of this industry, used almost exclusively as raw material the best qualities of iron imported from Sweden. Later, they also used materials

[1] Vol. XIII, pp. 217–218.

from other sources, and especially Russian wrought irons; but they always held and hold now that the use of fused soft steel in place of wrought iron furnishes a product far inferior in quality.

Another fact which almost all manufacturers of cement steel consider as certain, and on which is based one of the rules constantly followed by them, is the superiority of the product obtained by cementing *hammered* iron bars as compared with that furnished, under the same conditions, by *rolled* bars. Moreover in the industry with which we are now dealing, the greater part of the manufacturers strictly follow tradition and, in the absence of precise technical data, prefer to follow with minute accuracy the rules which the experience of centuries has shown to furnish good results, rather than to try the slightest innovations. Thus the various manufacturers have their preferences for irons of certain definite brands; but they do not take much care to find out just what the material furnished them under the preferred brand really is.

For this reason it seems to me superfluous to give detailed information as to the qualities of iron most widely used for the manufacture of cement steels. The number of the "brands" of cement iron which have stood and now stand in high repute is not small; such are the "Hoop L," "Double bullet," "CCND," "Little S," "OO" "W.W" brands, etc.

As an example we may cite the analysis of a Swedish iron, capable of furnishing, by cementation, a steel of the best quality:

Carbon	0.050 percent.
Silicon	0.045 percent.
Manganese	0.025 percent.
Sulphur	0.007 percent.
Phosphorus	0.010 percent.

As is seen, this is a material of high purity.

Thus, too, the iron obtained from the celebrated Denmark ores and placed on the market under the brand "Little S" is of marked purity, although somewhat rich in manganese; its composition, according to the analyses of Arnold, is as follows:

Carbon	0.050 percent.
Silicon	0.037 percent.
Sulphur	0.006 percent.
Phosphorus	0.012 percent.
Manganese	0.108 percent.
Copper	traces.
Arsenic	0.007 percent.

In many places (for example, in Westphalia, Germany, and in various English iron centers, etc.,) puddled iron is also used as raw material for the

manufacture of cement steel. I cite, as an example, the composition of an English puddling furnace wrought iron:

Carbon	0.16 per cent.
Silicon	0.00 per cent.
Manganese	0.09 per cent.
Phosphorus	0.09 per cent.
Sulphur	not determined.

As regards the carburizing substance, or "cement," many mixtures have been proposed with the object of accelerating the process, and of these I have already mentioned the mixture proposed by Bates.[1] But the number and the complexity of the carburizing materials proposed for total cementation remain far behind those reached by the "cementation powders" proposed for superficial cementation. The greater part of the manufacturers of cement steel have not abandoned the use of simple powdered wood charcoal, or have returned to it after unfortunate attempts to make use of more complex mixtures. This is probably due to the fact that the foreign substances in these mixtures, passing from the cement into the steel, impair its properties to a much greater degree in the processes of total cementation than in those of superficial cementation. This is because the quantity of the harmful substances which the steel absorbs in the processes of total cementation, in which the operation is protracted for a period ten to twenty times longer, is, all other conditions being equal, much greater than that which can diffuse into the metal in the processes of superficial cementation, and also because in the former processes much greater stress is laid on the high quality of the product. It follows that the foreign substances in the cementation powders used in case-hardening machine parts serve merely to give the manufacturer the illusion of employing an extraordinarily "perfected" agent. They cannot be tolerated in a cement intended to produce deep cementations, for in the latter case their harmful effects on the quality of the product make themselves felt to such a degree as to render impossible any doubt of the harm done.

The most "innocuous" cementation mixtures are those obtained by adding to the wood charcoal some proportion of alkalis or alkali carbonates or carbonates of the alkaline earth metals or animal charcoal, or by impregnating the wood charcoal with aqueous solutions of alkali carbonates, sodium chloride, etc. But among all the cements at present in use, the "surest," and not less efficient than many other more complex ones, is simple wood charcoal, and it is also the most widely used.

As to the quality of the wood charcoal best adapted to serve as cement, it seems certain that the cementation takes place more rapidly with charcoals

[1] Among the substances which have been proposed for total cementation, we may mention the cyanides, the ferrocyanides, borax, alum, vinegar, fats, blood, sugar, horn parings, marine algæ, etc., etc.

obtained from compact woods (oak, walnut, chestnut, etc.) than with those obtained from lighter woods (like the poplar, pine, larch, etc.), but the latter are also often used on account of their lower cost.

The wood charcoal designed to be used as cement is usually subjected to a simple crushing. Of the crushed charcoal, that portion is usually employed which passes through a sieve with square meshes 1 to 2 cm. on a side, and held by a sieve with about 4 meshes per sq. cm.

Experiment shows with certainty that carbon already used for cementing iron loses much of its efficacy. The probable causes of this phenomenon have been the subject of long discussions, especially between Margueritte and Caron, and later between Guillet and Ledebur. The supporters of the hypothesis of the preponderant action of gases in cementation attributed the "exhaustion" of the cements to the gradual elimination by the prolonged heating of the gases occluded in them. That the phenomenon really depends on this is proved by the fact (see p. 135) that the exhaustion does not occur in the slightest degree when care is taken to maintain in the cementation chambers an atmosphere of the gas most active as cement—carbon monoxide. I would add, however, without entering into details (this being a procedure whose technical application on a large scale is still being studied) that the use of "mixed cements" based on the specific action of carbon monoxide has given results beyond all expectations, even in the manufacture of fused steels, totally eliminating the phenomenon of "exhaustion." This confirms fully the hypothesis to which I have referred above.

In ordinary practice the effects of the exhaustion of the cement are remedied by using in each operation only a part of the carbon already used in the preceding operation, and completing the charge with carbon which has not yet been used. Usually, the cement is prepared by mixing one part (and sometimes as much as two parts) of the carbon already used with two parts of new carbon. It is said that expert operators can distinguish by the simple feel carbon already used from that which is new, and this by the fact that the particles of the former are more compact and heavier than those of the latter.

In many cases the carbon already used is subjected, before being used again, to washing, followed by drying, which removes from it the excess of ashes resulting from the combustion of part of the carbon in the preceding cementation.

The furnaces for the total cementation of iron which are still used to-day do not differ much, in their essential parts, from those used two centuries or so ago, when Réaumur published his classical researches on cementation. The slight importance of the changes introduced in more recent times is seen clearly from a comparison of the drawings of the furnaces described by Réaumur and those used a little later in England (see p. ix), with those of the more modern furnaces reproduced herewith.

Figs. 73 and 74 represent sections of a type of cementation furnace widely used to-day. The structure of the furnace is very simple. The two boxes *A*, *A*, designed to contain the bars of iron and the cement,[1] are made of re-

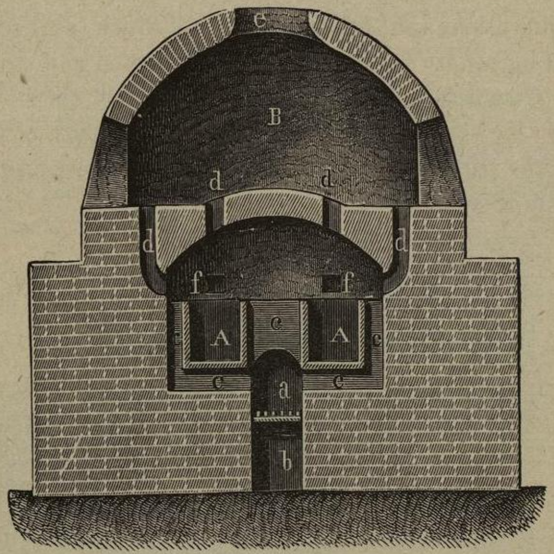

Fig. 73.—(*Ledebur.*)

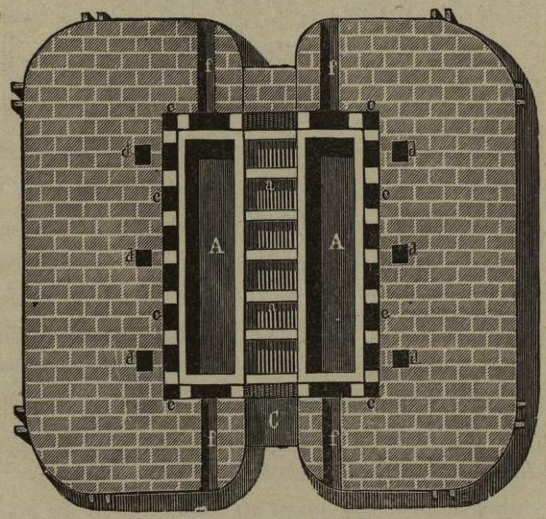

Fig. 74.—(*Ledebur.*)

fractory bricks and are placed on the rectangular base of an arched chamber, also of refractory bricks, with their long sides parallel to the long sides of the chamber; the free space at the bottom of the chamber is a hearth,

[1] Cementation furnaces with three boxes have also been constructed, but they have not given good results because they did not permit of obtaining a sufficiently uniform heating of the boxes.