Manganese Alloys in Open-Hearth Steel Practice*

How Much of this Element, and in What Form, Represents the Best Usage?

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BROADLY speaking, the purpose of the manganese investigation was to consider the most suitable means of utilizing domestic manganese, thus relieving to the greatest extent possible our shipping of the burden of importing manganese ores. It was not held that any decided shortage of manganese was imminent, but rather that every legitimate means should be utilized for making our ship tonnage available for European service. Although this country has considerable deposits of manganese, it occurs largely as a low-grade mixture with either iron or silicon or with both, consequently the open-hearth investigations were made to determine the extent to which domestic or low-grade alloys could properly be substituted for high-grade alloys without materially impairing the steel production either as to quality or quantity. Moreover, it was held that such an extensive investigation of this important step in the manufacture of steel would undoubtedly yield valuable results to the steel industry as well as contribute, in no small way, toward directing future investigations in the same field.

The evolution of the details of a definite experimental program from the statement of the general problem, considering the time element and the many and varied factors involved, was not lightly undertaken nor finally reached without due consideration of competent metallurgical advice. After making a preliminary survey, it seemed important to determine (a) the conditions in open-hearth practice that would lead to a conservation of manganese, both during the working of the heat and in making the final additions; (b) the most satisfactory metallurgical conditions for the use of manganese in the form of low-grade or special alloys; and (c) the effect on the finished steel, both as to quality and "condition," of the various methods and processes studied.

It was decided to determine slag and metal compositions during the refining of the heat and to observe the temperature each time a sample was taken, the latter to determine, if possible, the temperature effect. The "recovery" of manganese was to be determined from the residual and final manganese contents and the weight of the metal. To this end a sample of the finished steel was taken during teeming. By taking three such samples, one at the beginning, one toward the middle, and one at the end of teeming, tests for uniformity were possible. This practice was generally observed throughout the investigation. The data obtained were also supplemented by the plant records covering given heats as well as by personal observation during refining, pouring, and teeming.

When it came to planning steps that should be taken to determine the quality and "condition" of the steel, it was found that no definite and well-proved method, which could be adopted, was available. It is quite true that the open-hearth melter knows whether his heat is in proper condition but what was needed was a quantitative estimate of "condition." Without attempting to enter upon a discussion of the physical chemistry of a heat of molten steel, it may be said that the condition of a heat of steel must depend, aside from the temperature, upon the composition of the steel in those substances that affect the "condition." Of these there are two kinds: (1) Those that promote "openness," or the gases, which again may be classified as (a) gases that are products of chemical reactions, being in so far as we know, CO and possibly CO₂, and (b) gases that are absorbed from the furnace gases such as H, N, CO and CO₂; and (2) those that promote "soundness," such as the reducing and solidifying agents, C, Mn, Si, and Al.

In general it is held that Mn, Si, and Al inhibit the chemical reactions producing CO by reducing (or partly reducing) FeO, the principal constituent that produced the reactions. In this statement only the metal bath is considered and the FeO, and not Fe₂O₃, is held to be in solution in the steel. According to this idea, reducing action on a slag containing Fe₂O₃ would produce FeO, part of which would enter the steel to react later with C, Mn, and other reducing agents present. The reduction of FeO, then, is the principal means of "settling up" the liquid steel and it is for this reason that Mn is added in the finals. It is also held that Si and Al produce solidity in the finished steel, aside from reducing FeO and CO, either by keeping the gases H, N, etc., in solid solution, or by preventing the dissociation of the compounds of these elements and iron.

The obvious procedure to get a quantitative estimate of the "condition" of the steel, considering both the behavior of the molten metal and the character of the ingot, would be to determine the amounts of the constituents in each of these two groups and to weigh one set against the other. Even this procedure would not, at present, lead to results that could be interpreted with entire confidence, even though there were no uncertainties in the analytical methods, inasmuch as we do not know the quantitative effect of each constituent, either by itself or when associated with other constituents in varying amounts. In view of this lack of fundamental data, it was decided to make the analyses and use the results in a qualitative way, at least, to compare the different practices investigated.

THE FUNCTIONS OF MANGANESE.

During such a critical period as that now passed, the question might be raised as to the possibility of eliminating manganese from steel making. This point was duly considered but it was at once held that the use of manganese is not merely an expedient, one for which some substitute might readily be used, but rather, one of the basic requirements of successful practice in working steel. It is quite true that in many cases the actual amount of manganese used in a heat of steel is greater than purely metallurgical considerations demand and any excess could well be considered as so much wasted.

It may be well to review briefly the important functions of manganese as they bear directly on both of the points mentioned above. The first function of manganese, broadly considered, is to refine and "settle up" the molten bath of steel. The aim here is to put the metal in a proper condition for pouring, and to produce ingots (or castings) of the desired quality and texture. While manganese is not the most efficient of the elements that can be used for this purpose, calculated from the heat of combustion of the element to its oxide, it is without doubt the most satisfactory element for the purpose on account of the excellent condition (freedom from objectionable foreign inclusions) in which it leaves the bath.

The proportion of manganese theoretically required for this operation might possibly be calculated from the amount of oxygen converted from the active form, FeO, to the inactive form, MnO. Assuming an oxygen content of 0.075 per cent. in the unsettled steel and of 0.015 per cent. in the finished steel (oxygen by the Ledebur method), the amount of manganese used in this way would be 0.2 per cent. The writer is informed by the Bureau of Standards that such a calculation is premature, owing to our lack of knowledge on the subject of "deoxidation" and the faultiness of the Ledebur determinations. However it would seem to the writer, from the work done at the Bureau of Standards, that the amount of oxygen determined is the amount present as FeO (active form), subject possibly to an error due to partial reduction of CO during the determination. At any rate, the above is advanced as at least the first approximation of the amount of manganese required simply for destroying the ferrous oxide present in the bath. The amount of manganese required naturally would vary with the condition of the bath and, in order to insure efficient "deoxidation," would be somewhat in excess of the calculated amount. A well-made heat of steel would probably not require more than 0.35 per cent. Mn.

Manganese is also desirable in steel to improve the rolling properties, in which capacity it appears to serve a dual purpose. First of all, manganese deoxidizes and refines the molten steel in such a way as to give ingots of the desired texture without robbing the steel of its hot-working properties. Thus, ingots may be rolled into finished shape without the formation, in excessive amount, of fissures or of surface defects. Other reducing agents, such as Al, and Si, are prone to leave the metal in a poor condition for rolling and forging. While they eliminate one cause of hot shortness—iron oxide—they fail to convert the sulphur into a harmless form, as manganese does, and leave behind their highly refractory oxides, both of which tend to produce poor rolling qualities. Secondly, manganese, by retarding the rate of coalescence or grain growth, renders steel less sensitive to the effects of the high temperatures used in ordinary steels, at rolling temperatures. Silicon and aluminum, on the other hand, increase, rather than decrease, the grain size of steel. The proportion of manganese required in this

capacity probably does not exceed 0.35 per cent. in well-made steel.

Finally, manganese is desired in the finished steel to produce certain physical or mechanical properties or to make the steel more amenable to subsequent heat treatment.

The foregoing discussion indicates that manganese is an important factor in the steel industry. Of course, material such as "American Ingot Iron" can be successfully rolled, even though no manganese be added, but requires greater time and care.

It is interesting to note that manganese, coming in the periodic system between iron and the strengthening elements on one side and the hardening elements on the other, has the dual function of strengthening and hardening steel, which is not possessed by any other element.

Manganese conservation would best be obtained by eliminating the manganese specification except in case the amount of manganese present in the finished steel has some definite bearing on the properties of heat treatment of the steel. In other words, whenever only casting and rolling-mill practice (plant problems) are involved, the steel man should be allowed to exercise his own judgment as to the amount of manganese which should be used to give the most satisfactory and economical practice, and the finish and quality of the product should be controlled by adequate inspection. On the basis of Ellieott's figures¹ by reducing the manganese requirements by 0.2 per cent. in making plates and shapes and other low-carbon steel (estimated production, 21,350,000 tons), 54,000 tons of 80 per cent. ferromanganese could be saved.

The investigation here reported indicated that three practices for utilizing our domestic alloys in open-hearth steel practice seem to commend themselves above the others. These are as follows (but not in the order of their importance): 1. The use of a "molten spiegel mixture" for deoxidation and recarburization. 2. The practice of melting and refining the steel bath so as to insure a comparatively high residual manganese content, say 0.3 per cent. Mn. 3. The use of manganese alloys containing silicon. In selecting plants for investigating these practices, two points were kept in mind. The plant should have either "ordinary" practice, for the sake of comparison, or else one of the three just mentioned, and the product or kind of steel made should be representative of the larger tonnages such as shell steel, plates, or sections.

"MOLTEN SPIEGEL MIXTURE" PRACTICE.

The practice has been adopted at a few plants of combining in one operation both recarburization and deoxidation by using a mixture of pig iron and spiegel that has been premelted in a cupola. This "molten spiegel mixture" contains 5 to 11 per cent. Mn, 4 per cent. C, and the desired amount of Si, and is added to the ladle during the tapping time in such a way as to cause a thorough and uniform mixture of the two streams.

The principal advantages of interest here, not considering questions of plant and operating economy, are as follows: 1. A low-grade or domestic alloy can be used in the preparation of the "mixture." 2. The deoxidation is accomplished by means of a dilute solution with a consequent increase (on theoretical grounds) of the efficiency of the deoxidizer. This point will receive further consideration. 3. The deoxidizer is added in the molten state, insuring certain attendant advantages, which will also be considered at greater length. 4. A special advantage, if a large steel output is desired, is that the amount of the recarburizer is comparatively large and the capacity of the plant is materially (and economically) increased thereby. There is some question as to the propriety of including this advantage as peculiar to this particular practice. The use of pig iron as a recarburizer may be accomplished in other ways with the same economy and increase in plant capacity. 5. Another advantage would seem to the writer to be as follows: As compared with the results in the usual practice of adding carbon and manganese, there should be less likelihood of missing a heat.

This practice, at least at the plant visited, and it is understood to be the

¹Ellieott, C. R. Manganese conservation in steel making. *Iron Age*, vol. 101, June 6, 1918, pp. 1484-1485.

*War Minerals Investigations Series, No. 11.

with 0.20 per cent. carbon would require the working of the carbon until the content was about 0.10 per cent., and the molten mixture added would have to contain about 20 per cent. manganese (spiegel). The amount of the addition would be reduced from 13,000 pounds to about 4,000 pounds, which would mean that some of the advantages just enumerated would be lessened, and, with the increased loss of manganese the practice would probably not be commercially feasible. On second thought, however, when the other alternative, the use of ferromanganese, either solid or liquids is considered, the practice of premelting spiegel in the cupola would seem to commend itself, on grounds to be considered later. In case of undue shortage of high-grade ferromanganese there can be no doubt that the practice would offer a ready solution of the problem of using domestic alloys in making steel for shapes, plates, etc. Against the increased cost of production, as compared with the cost of cold ferromanganese practice, there would be greater uniformity of product and more uniform practice as an offset.

HIGH RESIDUAL MANGANESE PRACTICE.

At certain plants the practice of preferential oxidation and elimination of carbon and phosphorus has been developed, the residual manganese being kept at a comparatively high value, say, 0.25 to 0.30 per cent., as compared with 0.10 per cent. manganese for a final carbon content of 0.10 per cent. This is accomplished, broadly speaking (a) by rapidly removing the phosphorus and retaining it as stable calcium phosphate during the earlier and colder period of melting; (b) by maintaining a high finishing temperature and working the charge with a high manganese content so that the slag contains about 8 per cent. manganese; and (c) by increasing the lime content of the slag to about 47 per cent. as a minimum.

This process possesses undoubted advantages but they are such that they are probably best appreciated by plants in which it has been developed and where it is now in operation on a sound commercial basis. First of all it may be stated that the practice, correctly applied, leads to the production of high-grade and uniform steel, which in itself means increased rolling-mill output, fewer rejections, and a more ready market. This is largely due to the fact that the steel is made—where it should be made—in the furnace.

A second advantage derived from the high MnO and CaO contents of the slag, is that the manganese finals can be added to the furnace with a recovery comparing favorably with that of ladle additions. A third advantage is that the same pig iron used for the charge, and containing appreciably more manganese than ordinary basic iron does, can be used to recarburize and partly deoxidize the bath. The remainder of the manganese is added as ferromanganese. At a steel plant which operates in conjunction with a blast-furnace plant, a harmonious and economical cycle of plant operations is made possible. At the same time the open-hearth slag can be resmelted in the blast furnace for the recovery of the iron and manganese and the utilization of the lime.

This line of practice is largely dependent upon the amount of phosphorus in the slag, for, obviously, it would not be worth while to recover the manganese at the expense of unduly increasing the phosphorus content of the pig iron. In this country we are fortunately situated in this respect, inasmuch as there is still a large amount of rather low phosphorus ore available. No definite figure can be given at this time as to the maximum allowable phosphorus content of the pig iron, but it is the opinion of at least one steel man who uses this process that 0.6 per cent. phosphorus would not be prohibitive. Under the conditions prevailing during the past year, this practice possessed the additional advantages that the high-manganese pig iron could be procured by smelting domestic manganiferous iron ore and that the manganese alloy added to the furnace at the end of the heat could as well be spiegel as ferromanganese, assuming that the finished steel contains more than about 0.10 per cent. carbon. There would also be certain disadvantages, particularly that the carbon content of the bath would have to be worked to a lower figure than in present practice. On account of the high cost of spiegel and the greater time required, it is doubtful whether the steel plants would substitute spiegel for ferromanganese. Another interesting point, in connection with the possibility of utilizing domestic manganiferous iron ore, is that low-silica ore could be added to the slag as a source of manganese oxide.

The high manganese content of the charge is generally obtained by using a "high-manganese" pig iron, 2 to 3 per cent. manganese, but may also be obtained by adding manganese ore to the slag, or manganese alloys to the bath, or by a combination of these methods. This point would be determined by plant economy but

it seems doubtful whether the practice would be worth while unless a high-manganese pig iron were available. The writer is informed by one blast-furnace superintendent that running the manganese up to 2 per cent. does not materially affect the production, so that lowering of pig iron production would not be held as a disadvantage in this practice. The loss of manganese by oxidation and transference to the slag is considerable. This loss may be kept at a minimum by increasing the basicity of the slag in CaO and FeO, which, combined with the MnO which also acts as a base, exert the desired effect upon the manganese of the bath.

As the working of the charge progresses, its temperature rises until finally with the high CaC, and, particularly the high MnO content of the slag, the carbon is eliminated more rapidly than the manganese, with the result already stated, namely, the manganese can be held to about 0.3 per cent. at the end of the heat. Present data indicate, unfortunately, that no material increase in the recovery of manganese in the additions may be expected, so that the advantages are derived not from a decreased consumption but from the form in which it can be added.

Data for one such heat showed that a total of 3,728 pounds of manganese was used in one form or another to produce 1,272 pounds of manganese in the finished steel, or, in other words, that 3.54 pounds of manganese was used to produce 1 pound of manganese in the finished steel. The manganese added in the recarburizer and as ferromanganese amounted to 1,068 pounds of which, assuming the manganese loss to come from these two sources, 838 pounds was recovered in the finished steel, a recovery of 78.4 per cent. In this heat the ferromanganese was added to the furnace. Another more or less comparable heat selected at random, but more representative of "standard" practice, used 2,190 pounds of manganese to produce 1,200 pounds of manganese or 1.82 pounds of manganese (as compared to 3.54 pounds to produce 1 pound of manganese in the finished steel).

USE OF MANGANESE-SILICON ALLOYS.

The high silica content of most of our domestic manganese and manganiferous iron ores made it advisable to consider the possible use of manganese-silicon alloys in steel making, in both acid and basic practice. For the purposes of the present discussion, these alloys will be divided roughly into two classes—high-grade silico-manganese containing about 50 per cent. Mn and 25 per cent. Si, and low-grade silico-spiegel with about 15 to 20 per cent. Si and 30 to 35 per cent. Mn with 50 per cent. Fe. The manganese-silicon ratio of the first alloy is about 2 and of the second alloy 2 1/3 to 1 1/2. Each of these alloys would be made from the silicious manganese ores of California and Montana, and the low-grade alloys from the silicious manganiferous iron ores of Minnesota.

While there is nothing new about the practice of using manganese-silicon alloys in steel making, it may be well to review some of the points connected therewith in the light of present requirements.

Silicon is always an efficient reducing or settling agent when used in the customary small amounts. It is understood that "silicomanganese" has been used fairly extensively in Europe, and in this country it was used at certain plants as standard practice until the supply was cut off by the war. Silicon is always an efficient reducing or settling agent when used in the customary small amounts, but it may or may not be desirable in the finished steel. On this account, the possibility of using manganese-silicon alloys depends upon the amount of silicon that can be tolerated in the finished steel in the ingot form. In certain grades of steel, particularly in steel that must be welded, silicon should be low or practically absent. In steel for sheets and plates, which must give a good finished surface, the most efficient rolling-mill practice requires that the silicon be kept tolerably low, but it is believed that 0.10 to 0.15 per cent. could be used, provided the manganese content were not too high. In forging steel, high-carbon steels, and castings, where the aim is to produce sound steel, more silicon can be used, or between 0.20 and 0.35 per cent. Of these three fields, the latter is the one in which manganese-silicon alloys will find their first application. In the second field, it seems quite probable that conditions (to be discussed later) will many times permit their use; but from the very nature of things manganese-silicon alloys cannot be used to make steels of the first group—those that must be welded.

MANGANESE-SILICON ALLOYS IN ACID PRACTICE.

It is with considerable hesitation that the discussion of manganese-silicon alloys in open-hearth practice is approached, particularly as the controversial character of many of the points is so clearly recognized. Consequently, it may be well, at the outset, to state

briefly the manner in which the writer first became interested in the possibilities of their use. A number of years ago the writer was conducting a series of experiments on the occurrence and identification of foreign inclusions in acid open-hearth steel, principally ordnance steel. In this work ferromanganese, ferro-silicon, and a mixture of ferromanganese and ferro-silicon were added to a steel sample taken shortly after "oreing," that is, to "wild" steel, in an attempt to produce an excess of the constituent, or constituents, supposed to form as a result of the addition.

It seemed fairly clear as a result of this work that the use of silicon was apt to be dangerous, not on account of any harmful effect of the residual metallic silicon but because it produced a constituent (assumed to be SiO₂, or at least a highly refractory silicate) that was likely to remain in the ingot and produce hot shortness. Hence the idea was suggested that a manganese-silicon alloy might and probably would, form a manganese silicate containing some ferrous oxide (a true slag) which would be fluid and more readily coalesce into larger particles than SiO₂, would, and therefore free itself more readily from the steel. By using such an alloy it would then be possible to take full advantage of the use of silicon as a deoxidizer without suffering the usual attendant disadvantages of its use. None of the manganese-silicon alloy was available at the time so a parallel experiment could not be conducted.

As binary alloys are known to be generally more active, or powerful, than the weighted sum of the two constituents would indicate, it was also assumed that, aside from the possibility of obtaining a better separation of the insoluble products of the deoxidation process, the alloy of manganese and silicon would prove to be a more powerful reducing agent than ferromanganese and ferrosilicon used separately. On reflection, the thought occurs that manganese and silicon, reacting separately with FeO, would produce the oxides MnO and FeO or a silicate of iron. Manganese and silicon reacting as an alloy with FeO would produce a silicate of manganese, which may or may not form a double silicate with FeO. In either case we would expect to find the advantage in favor of the manganese-silicon alloy.

The relative weights of the silico-manganese and of the mixture of the ferromanganese and ferrosilicon will be considered at another place.

Another point of great technical importance is the percentage recovery of manganese when added as silico-manganese and as ferromanganese along with ferrosilicon. First of all let it be stated that a 100 per cent. recovery, based on the present theory of "deoxidation," is hardly possible, and if possible would not be desirable. Such recovery would mean a retention of the products of the deoxidation, to be determined later as metallic manganese and silicon. A method of addition that would lead to a satisfactory deoxidation and yet would eliminate the loss due to admixture with the slag, volatilization, etc., and could be accomplished with the minimum amount of manganese, would be very desirable because it would lead to both conservation of manganese and uniformity of composition of the steel. Conservation of manganese would be given by the actual value of the percentage recovery of the manganese, and uniformity of composition would be assumed by the constancy of the percentage recovery.

Fortunately the writer was able to examine records of heats made with silicomanganese covering a period of several years, from which some fairly satisfactory conclusions may be drawn bearing on these points. During this time when silico-manganese was being used there were periods when the alloy was not available and the mixture of ferromanganese and ferrosilicon had to be substituted. Thus, a direct comparison of these two methods of deoxidation was afforded.

It can hardly be claimed for the figures obtained, or for the three years' records which they represent with reasonable accuracy, that they furnish a truly scientific basis of comparison of the two alternate practices, but they do show rather convincingly that the same results (Mn and Si contents of the finished steel), by using silico-manganese can be obtained with consistently smaller amounts of both manganese and silicon, as compared with the combination of ferromanganese and ferrosilicon. In addition there is the advantage of having a more uniform practice, which in itself would warrant smaller additions. The weights of the additions favor the silicomanganese in some cases by as much as 460 pounds against 385 pounds and 615 pounds against 510 pounds. The low carbon content of the silicomanganese may or may not be a material advantage but at any rate it is in favor of the single-alloy addition because the carbon need not be worked as low and there seems to be less danger of missing the carbon.