

THE PRESENT POSITION AND FUTURE OF THE MANGANESE INDUSTRY WITH SPECIAL REFERENCE TO INDIAN RESOURCES

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Abstract

Statistics are quoted which show that manganese ore production is tied directly with world steel production, but fluctuations in steel output affect Indian ore production much more than production from other sources. A steady and increased demand for manganese is likely to result from research and development into:

1. Improvement of quality of the end product and concentration of the manganese metal content to reduce freight charges.

2. The technical advantages of manganese as an alloying constituent in steel and the replacement of the more expensive alloying constituents, such as nickel, by manganese in alloy steels.

3. The use of manganese in non-ferrous alloys with particular reference to alloying constituent which increase the stability of the ductile gamma-phase of manganese.

4. Manganese as a coating to provide corrosion and abrasion resistance to steel and non-ferrous metals, particularly in those fields in which zinc and nickel are at present used.

The formation of a research and development organization to promote the use of manganese is advocated.

Introduction

MANGANESE is estimated¹ to form about 0.1 per cent of the earth's crust and chromium about 0.04 per cent as compared with 0.02 per cent nickel, 0.0001 per cent copper, 0.00004 per cent zinc, 0.00002 per cent lead, and less than 1 part per million tin. The tonnage of ore mined annually is such that, in terms of metal contained in that ore, manganese is considerably less rare than magnesium and nickel and is, in fact, nearly comparable with aluminium and zinc. In the case of manganese about 1½ million tons of metal is contained in the ore which is mined. In terms of

value, however, manganese in the metallic form of standard ferro-manganese sells at a lower price than any other metal except iron.

The supply of manganese is essential to metallurgical industry. In the production of steel it fulfils vital functions of deoxidation, desulphurization and strengthening, and it cannot adequately be replaced by any other element or combination of elements. With the exception of the U.S.S.R. all the major industrial nations are dependent upon the importation of manganese ore for the bulk of their requirements. Outside the U.S.S.R. the largest deposits of high-grade manganese ore are in the African continent and the Indian sub-continent. Both these are geographically far removed from the principal steel-producing countries, the most important of which is the U.S.A., whose production runs at the extremely high annual level of about 80 million tons.

While the market for high-grade metallurgical manganese ore seems assured for many years to come, there are, nevertheless, trends in modern metallurgical thought towards conservation in the use of manganese and towards beneficiation processes for low-grade ores which may affect the long-term trading prospects for manganese ore. It is the object of this paper to review the present position from the point of view of the metallurgical use of manganese, particularly as it may affect the position of India in the world market for this commodity. The position will be discussed largely in terms of the situation existing, or likely to exist, in the U.S.A. There are two reasons which govern this choice: (1) America is the largest customer for Indian and for African ore; and

(2) fairly complete statistics of American consumption and uses for ore are available over a number of years.

The Use of Manganese Ore in Metallurgical Industry

About 96 per cent of the world's total production of manganese ore is used in the metallurgical industries, the remaining 4 per cent being used principally in dry batteries and in the chemical and paint industries. In metallurgical industry manganese is used predominantly as a refining agent in pig iron and steel production and as an alloying element in steel. Although manganese plays an important part in certain non-ferrous alloys, these uses, at the present time, account for only a very small proportion of the total utilization of manganese.

For use in steel-refining, manganese is normally used in the form of standard, high-carbon ferro-manganese. This alloy, which contains 78-80 per cent manganese, 6-7 per cent carbon and balance iron, is made in the blast furnace by reduction of manganese ore with coke. The material introduced into the blast furnace should contain at least 48 per cent manganese and in which the manganese to iron ratio should be about 9:1. Other ferrous alloys of manganese are produced in the blast furnace. These are spiegeleisen containing 18-22 per cent manganese, 4-6 per cent carbon and balance iron, and about 1-2 per cent silicon and manganiferous pig iron containing 5-10 per cent manganese. These latter alloys are made from relatively low-grade ores, ferruginous manganese ores containing 10-35 per cent manganese and manganiferous iron ores respectively. In addition to these ferrous alloys, silico-manganese, an alloy low in iron, containing silicon, 20; manganese, 65; and carbon 1.5 per cent max., can be made by treatment in an electric arc furnace of certain manganese ores mixed with flints and coke. For the correct treatment of steel ferro-manganese is much to be preferred to the alloys of lower manga-

nese content. It can be added to the ladle and consequently enables a much closer control of the steel-refining processes to be exercised.

The great preference for ferro-manganese can be judged from the fact that in 1949 in the U.S.A. 13.2 lb. of manganese were used for each short ton of steel which was produced. Of this amount, on an average, 11.8 lb. was in the form of ferro-manganese, 1.0 lb. as silico-manganese, and 0.3 lb. as spiegeleisen.

In addition to high-carbon ferro-manganese, there is a demand for special purposes, although on a much smaller scale, for low-carbon alloys of manganese. In steel production manganese is added to the metal, subsequent to the decarburization of molten pig iron, for the purposes of deoxidation (with silicon and/or aluminium) and desulphurization. Its presence improves the hot workability of the steel ingots and helps to produce sounder ingots. It also materially improves the mechanical properties of the steel and depresses the temperature at which steel shows a transition from ductile to brittle behaviour. Since it must be added to the steel, subsequent to decarburization, the use of high-carbon ferro-manganese can only be tolerated if the amount of carbon which its use entails is less than that required in the finished steel. This is true for structural steels, which account for the vast majority of steel production, but it is not true of special steels of high manganese content or of other special alloys. The production of some special steels and alloys demands the use of additional alloys of relatively low carbon content. Such alloys are medium-carbon ferro-manganese (containing approximately 1 per cent carbon), and low-carbon ferro-manganese (containing 0.5 per cent carbon or less). The most common process for the production of these special grades of ferro-manganese is by the electric arc furnace reduction of ore of a suitable grade with silico-manganese. Since this requires a two-stage smelting process, one to produce the

silico-manganese and one to reduce the ore, the cost of the product is appreciably higher than the cost of blast furnace production of standard ferro-manganese. In addition to these ferro-alloys, a low-carbon manganese metal may be produced by the arc furnace reduction of a low-iron manganese ore with a special grade of silico-manganese and by the aluminothermic reduction of a suitable ore or oxide. These metals are also relatively expensive to produce. They are usually of 97-98 per cent purity and contain small quantities of silicon and aluminium.

Finally a process has been developed in the U.S.A. for the production of high-grade manganese metal of 99-95 per cent purity by an electrolytic method, the electrolyte being obtained by leaching a suitable manganese ore.

The costs of some of these various products at present ruling in the U.S.A. are given in Table 1.

TABLE 1—CURRENT (AUGUST 1953) PRICES OF METALLURGICAL GRADE MANGANESE ORE AND MANGANESE ALLOYS AND MANGANESE IN THE U.S.A.

MATERIAL	PRICE PER LB. OF MN., cents
Metallurgical grade ore (48 per cent Mn)	3·17*
High-carbon ferro-manganese (78-80 per cent Mn)	13·15
Medium carbon ferro-manganese (80-85 per cent Mn, 1·25-1·50 per cent C)	21·35
Low-carbon ferro-manganese (85-90 per cent Mn, 0·07 per cent max. C)	30·00
Silico-manganese (65-68 per cent Mn, 18-20 per cent Si, 1·5 per cent max. C)	17·10
Manganese metal (96·5 per cent min. Mn, 0·2 per cent max. C, 1 per cent max. Si, 2·5 per cent max. Fe)	36·95
Electrolytic manganese	31·50*

*Additional premium of 1·50 cents for hydrogen removal and price does not include freight charge from Knoxville, Tenn., except east of Mississippi.

World Supplies of Manganese Ore

In general the demand for manganese ore has reflected the variation of output in the world's steel industry, high demands during rearmament and war periods being followed by decreasing demand during periods of trade recession. There are, however, noteworthy variations between ore-producing countries in the impact of trade recession. In this respect those producing countries furthest away from the consuming countries are more rapidly and substantially affected by a reduction in demand than are those producers which are geographically closer or whose mining interests are more closely linked to the economy of the consumers. This is clearly shown by the data plotted in Fig. 1 which shows the ore production over the years 1926-51 for India, the Union of South Africa, the Gold Coast and Brazil. The war of 1939-45 was naturally followed immediately by a sudden decrease in the demand for manganese ore, associated with the sudden and drastic curtailment of steel production and the adjustment to a peacetime economy. The decrease in demand was felt immediately and sharply by India and by the Union of South Africa whose production fell in 1945-46 to a very low level. Recovery of these industries has since been steady, following the recovery in steel production, but pre-war production in India was not regained until 1950-51. The manganese mining industry in the Gold Coast shows a striking contrast. Operations in this country are largely controlled by American capital and the distance from the Gold Coast to the American east and south coast ports is appreciably less than the distance from the U.S.A. to other manganese-producing countries outside the American continent. It is interesting to note that the ore production in the Gold Coast was relatively little affected by the post-war variation in steel output. The effect of the immediate post-war decrease in demands was also much less in the Brazilian manganese industry than in that of India

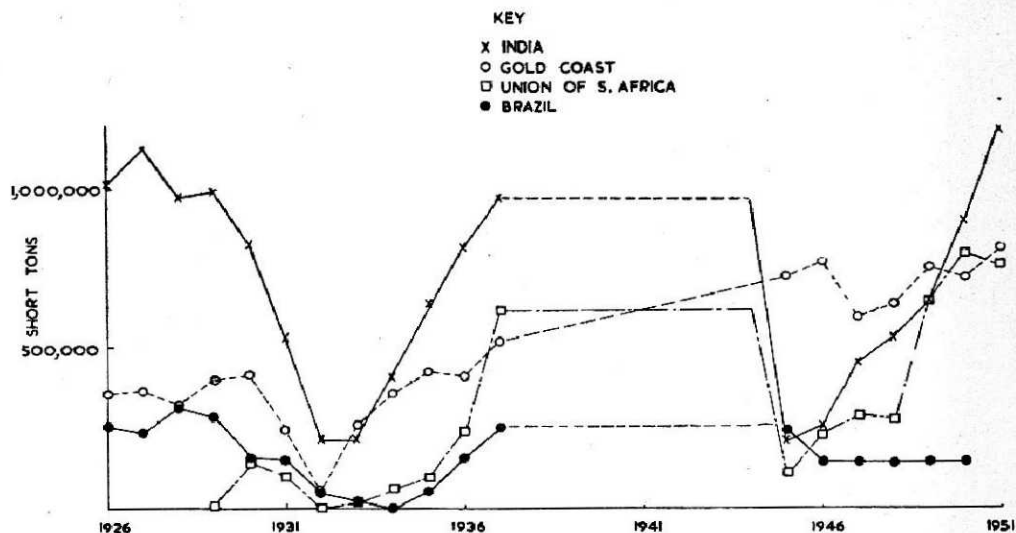


FIG. 1 — VARIATION OF OUTPUT OF MANGANESE ORE FROM 1926 TO 1951

and South Africa. This may also be accounted for by American financial interest in the mining industry and by relatively short shipping distances involved in transportation of the ore. It is clear that any decrease in the requirements of the U.S.A. for the importation of manganese ore will be felt first and most severely by Indian and South African producers.

This being so, it is relevant to consider the probable effects on these industries of the campaign which is being waged with increasing intensity in the U.S.A. aimed at the conservation of manganese and the utilization of low domestic grade ores of which America has large deposits.

Trends Towards Economy in the Use of Manganese and the Utilization of Low-Grade Ores

The U.S.A. has to import the overwhelming proportion of its manganese ore requirements, although it has very considerable domestic resources of relatively low-grade ore. The U.S. Government, being very conscious of the undesirable strategical consequences of too great a dependence on imports of such an important commodity, has

for many years fostered research on the beneficiation of low-grade manganese ore and the recovery of manganese from slags and other waste products of the steel industry. Capable surveys have also been made of current steel-making practice and the statistics made available by such surveys are of considerable value.

This stimulation of research and development has led to the establishment of a process for the production of electrolytic manganese on a commercial scale from an electrolyte produced by leaching manganese ore. This process could be used on relatively low-grade ores although at the present time production is based on high-grade imported ore. Production in the U.S.A. by this process is now at the rate of about 4000 tons a year and the price of the product, which is of over 99.9 per cent purity, is less than that of thermit and silicon-reduced manganese and compares with the price of low-carbon ferro-manganese (Table 1). While this is the first successful commercial exploitation to result from the intensive investigations at the U.S. Bureau of Mines and elsewhere on manganese, it will almost certainly not be the last. Several processes for the production of high-manganese concentrates from low-grade American

ore are being investigated on a pilot plant scale. One of these, the Nossen Nitric Acid Cycle, produces a sintered concentrate containing over 90 per cent $MnO_2 + MnO$ from a low-grade ore containing 10-13 per cent manganese, 25-40 per cent iron and 15-35 per cent silica. The economics of this process have been judged to be sufficiently promising to justify the erection of a pilot plant costing approximately £200,000 and its potential importance may be judged from the fact that there are estimated to be 275 million tons of ore suitable for treatment by this process in one region of Minnesota alone. Other processes for the beneficiation of manganese ore, for the reduction of manganese wastage in the steel industry and for the recovery of manganese in usable form from blast furnace and steel-making slags are under investigation. The American position in these developments has been well reviewed by S. L. Case and J. W. Clegg². In this respect the Americans lead the world and very little scientific effort appears to be directed elsewhere towards this end except in Germany, where during the 1939-45 war some interesting and potentially important processes for the recovery of manganese from slags and low-grade ores were pioneered.

Some of these processes have been described by R. Durrer and G. Volkert³.

It is still premature to predict what effects these efforts to conserve manganese and to utilize low-grade ores will have eventually on importations of manganese ore. It has yet to be established that some of the processes which have been proposed can be put on a sound economic basis. It is reasonable, however, to predict that such developments will, in due course, result in a decreasing demand in the U.S.A. for imported ore and increasing utilization of domestic supplies. Although the former has not yet been manifested, tendencies towards the latter can already be discerned. Fig. 2 shows the annual variation from 1926 to 1951 of the tonnage production of American domestic manganese ore (>35 per cent manganese). The increase in production stimulated from the 1939-45 war was not followed by a drop to pre-war levels. Production has continued at a rate of more than double that in 1939.

The position is thus reached that it may be reasonably argued that if present trends continue, the probable outcome will be a gradual but significant reduction of importation of manganese ore for use in the American steel industry, which is unlikely to be com-

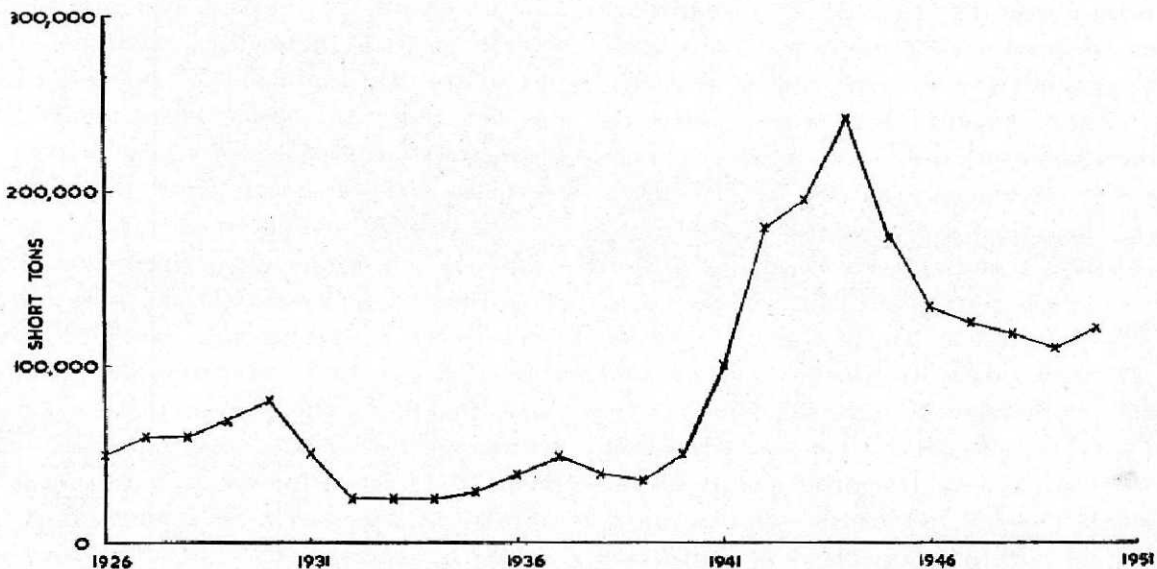


FIG. 2.— VARIATION OF OUTPUT OF DOMESTIC MANGANESE ORE IN U.S. FROM 1926 TO 1951

compensated for by an increase in steel production. The effect of this reduction in imports will be felt first and most markedly by Indian and South African mining operators. It is, therefore, relevant to consider what steps could be taken in these countries to safeguard the future of their manganese industry. At present very little is done beyond mining and shipping the ore. Two measures which would help to guard against future unfavourable trading conditions for ore may be considered:

- (1) the production in the mining countries of ferro-alloys and pure manganese; and
 - (2) stimulation of the use of manganese.
- These are considered more fully below.

The Production of Ferro-manganese and Pure Manganese

By far the largest use of manganese is as high-carbon ferro-manganese in steel production. High-carbon ferro-manganese is a blast furnace product and at first sight it seems that both India and South Africa would do well to undertake the production and exportation of ferro-manganese instead of ore, thereby increasing the profit margin and reducing the freight charges per unit of manganese. India already produces substantial quantities of ferro-manganese for consumption by its own steel industry. At present, however, there is no exportable surplus. Unfortunately, however, the blast furnace production of ferro-manganese in India is complicated by the fact that it is difficult to produce alloy of phosphorus content much less than 0.3 per cent from Indian ores and coke. The available supply of low-phosphorus (Giridih) coke is limited. It is also true that the average manganese : iron ratio of Indian ore is generally slightly below the 9 : 1 ratio required for the production of the highest grade (78-80 per cent) ferro-manganese and it is common practice in countries producing ferro-manganese to mix Indian ore with other ore of higher manganese : iron

ratio. These facts have been recognized for some time and as long ago as 1930 it was recommended by L. L. Fermor⁴ that, since India could never become a large producer of low-phosphorus ferro-manganese by blast furnace methods, the possibility of economic electric production deserved careful attention. This statement is equally true today and is lent point by Indian hydro-electric power development which creates a more favourable situation for electro-metallurgical processes. Arc furnace processes can be utilized successfully for the production of high-carbon and low-carbon ferro-manganese, silico-manganese and metallic manganese, the latter by the reduction of ores by silico-manganese. The possibility exists in a well-planned production unit of the economical treatment of high-phosphorus ores and of steel slags to produce high-grade ferro-manganese and manganese metal.

Moissan⁵ first produced essentially pure manganese metal by electrolysis into a mercury cathode and later by carbon reduction of Mn_3O_4 . Manganese metal for alloying with aluminium and in steel-making applications where low carbon contents are required is produced by aluminothermic or silicothermic reduction. Gayler⁶ produced relatively high purity metals by distillation, and established the existence of the three principal allotropic forms, alpha, beta and gamma. Only the latter modification is ductile and this cannot be retained at room temperature. Manganese is, therefore, essentially brittle and unsuitable as a structural material unless alloyed with other metals.

Grube⁷ in Germany and Allmand and Campbell⁸ in Britain have previously described the production of manganese by electrolysis, but a commercial process which now produces the purest form of manganese available today was developed by the Metallurgical Division of the U.S. Bureau of Mines, chiefly as a result of the work of R. S. Dean and his collaborators⁹. A review was first made of the occurrence of mining and metallurgy of manganese primarily to assess the

potentialities of the metal in the U.S.A. This was published in 1934 and the following year a major programme of investigation was undertaken on the preparation of pure manganese by electro-metallurgy. A pilot plant was set up and operated in 1936-37 and in 1938 the commercial Electro-Manganese Corporation was set up and commenced operations in 1939. This has led to a new and growing industry and makes possible the use of relatively low-grade ores. Essentially the manganese is leached from the ore with sulphuric acid. The impurities are removed and the liquor is fed to the cell which is a two-compartment diaphragm cell where insoluble anodes are used. The solution is then returned to leach fresh ore. The flow sheet of this process is shown in Fig. 3.

It is perhaps of interest to note here that the manganese is deposited initially in the gamma (ductile) form, but quickly reverts to the brittle alpha form.

This process is being worked in the U.S.A. by the Electro-Manganese Corporation and growth can be judged from the following figures:

1940	...	300 tons p.a.
1950	...	3000 tons p.a.
1952	...	4000 tons p.a.

Surprisingly some 60-75 per cent of the present production goes to steel-making. The metal with a purity of 99.98 per cent sells at 30 cents/pound and is about the same price as aluminothermic manganese.

But the production of pure manganese by electrolysis presupposes a cheap and ample supply of electrical energy. Not all countries are in this position and, in view of the developments that have recently taken place in extraction and refining of metals by distillation and in the light of certain observations in unpublished work at the Fulmer Research Institute, the time would seem opportune to re-examine the possibility of producing pure manganese by distillation.

Stimulation of the Use of Manganese

Any country or industrial concern which owns large manganese ore deposits must be interested in stimulating the demand for manganese in all its forms and it is curious how little effort has been made in this direction. All the other important non-ferrous metals are served by either national or international research and development organizations, for example, the Tin Research Institute, which is part of the International Tin Research and Development Council, and bodies like the Zinc Development Association, the Aluminium Development Association and the Copper Development Association in the United Kingdom. The formation of a similar body, preferably international in character to serve the interests of manganese producers, seems to be an obvious first step in extending the uses and demand for manganese.

In ore-producing countries such as India and South Africa the aim must be to devise processes of extraction and refining which will give a high quality product in a concentrated form, so that the effects of freight charges are less marked. Research and

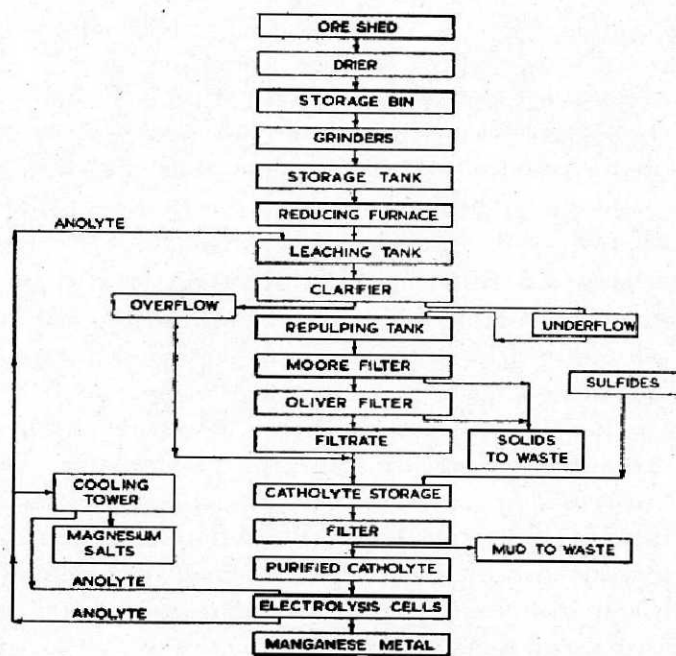


FIG. 3 — MANGANESE ORES ARE LEACHED BY A SULPHURIC ACID SOLUTION, AN ANOLYTE FROM THE ELECTROLYTIC CELLS

development to extend the use of manganese can be directed along the following lines.

1. *The Steel Industry* — The tendency towards conservation in the steel industry might be balanced by an increased use of manganese following a fuller appreciation of the advantages of manganese as an alloying constituent. In low-alloy structural steels it has recently been found that the transition temperature between brittleness and ductility in notched bar impact tests is depressed by an increase in the manganese: carbon ratio. This has an important bearing on the failure of welded structures such as ships and bridges at low atmospheric temperatures and may lead to a significant increase in the utilization of manganese since a large tonnage of steel is potentially involved.

A re-examination of the properties and potentialities of manganese-containing austenitic steels might be made with profit. In Germany during the 1939-45 war extensive use was made of manganese as a substitute for nickel in steels of this type and some steels with excellent strength properties at high temperatures such as Chromadur (Mn, 18; Cr, 12.5; V, 1.0 and C, <0.15 per cent) were developed. There appears to be scope for further research and development on steels of this general type and very little work is at present being undertaken in this field.

2. *Manganese in Non-ferrous Metals* — Pure manganese is never used in the fabricated form chiefly because the alpha and beta modifications are very brittle and the gamma form cannot be retained by quenching. Volume changes accompanying solidification make it virtually impossible to obtain a sound ingot. The stability of the gamma phase can, however, be extended by alloying as shown by the constitutional diagrams for Mn/Cu and Mn/Ni (Figs. 4 and 5). In these systems a most interesting series of alloys is obtained in the range 60-80 per cent manganese with high resistivity and low or negative temperature coefficients of resistivity. The

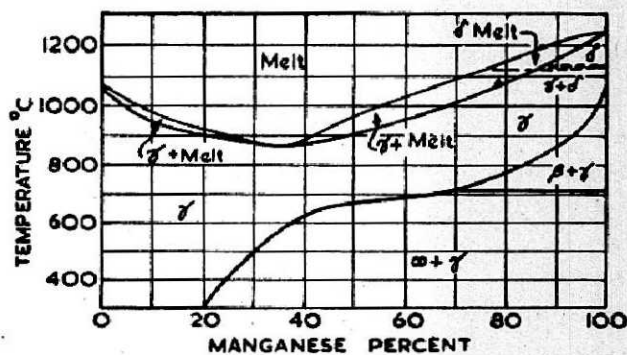


FIG. 4 — EQUILIBRIUM DIAGRAM OF THE COPPER-MANGANESE

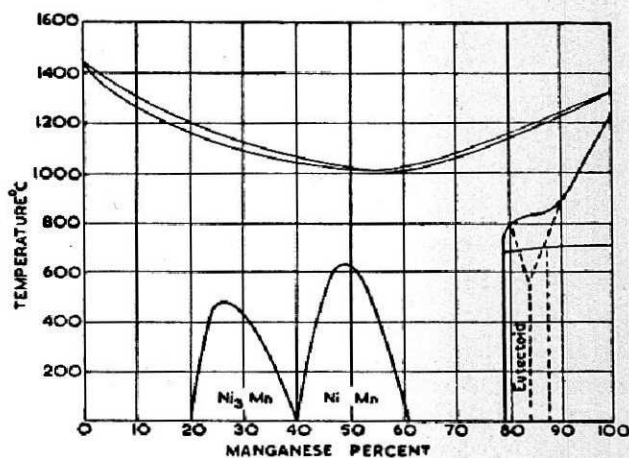


FIG. 5 — PROPOSED CONSTITUTIONAL DIAGRAM OF THE SYSTEM MANGANESE-NICKEL

manganese-copper alloys in this range also show remarkable maxima in coefficient of linear expansion and a very high damping capacity is shown by alloys containing about 82 per cent copper.

Mention must also be made of the ferromagnetic Heusler alloys containing 10-30 per cent Mn, 9-15 per cent Al and balance copper.

These applications are, however, highly specialized and are unlikely to consume an appreciable tonnage of metal. Somewhat larger quantities may be used in other non-ferrous metals produced in large quantities, for instance, Mn can partly replace zinc in alpha brass and the 70 per cent Cu, 10 per cent zinc and 20 per cent Mn alloy is white in colour. Its use in aluminium alloys in increasing strength without detriment to

corrosion resistance is well known. In magnesium-base alloys containing aluminium, manganese effects removal of iron and neutralizes its effect on corrosion resistance. It is also an important constituent in many of the copper-aluminium alloys or so-called aluminium bronzes. As a broad basis for further research on manganese metal, however, a promising line appears to be the investigation of alloying constituents which will increase the stability of the ductile gamma phase.

Corrosion and Abrasion Resistance

It is, however, in the field of protection against corrosion and abrasion that the biggest immediate new application may arise. Something over 40 per cent of the world's total output of zinc is used for protecting iron and steel against corrosion mainly in the form of galvanized coating. This represents an annual consumption of some three-quarters of a million tons of metal, equivalent to nearly half the present manganese output. Similarly, 20 per cent, representing about 25,000 tons of the nickel consumed, is in the form of anodes for electroplating, the principal use being as an undercoat to chromium plating on steel and brass. This use of nickel would undoubtedly grow but for the high price and current strategic shortage of the metal.

Manganese is moderately resistant to corrosion. The standard electrode potential of manganese is -1.134 volts compared with -0.762 for zinc and 0.44 for iron. This suggests that manganese may also find application as an anodic coating on iron and perhaps also on aluminium, and this possibility is currently under investigation.

The principal difficulties in the application of manganese as a protective coating are that pure manganese is brittle as normally deposited, tarnishes readily to an unattractive brown colour not unlike iron rust, and the higher melting point of pure manganese operates against the use of a simple hot-dip

coating which is so universally employed in hot-dip galvanizing. Even with zinc, however, the hot-dip process is facing competition with electro-galvanizing, and electro-deposition of manganese would seem a promising line of investigation. Bell¹⁰ has recently described a laboratory technique used for the preparation of manganese-coated steel and aluminium for corrosion testing. Other methods of coating with manganese worthy of study are metal spraying, using a powder pistol, vapour-phase impregnation and chemical replacement from a molten salt bath.

However, the two inherent disadvantages of brittleness and poor tarnish resistance remain and these can best be overcome by the production of an alloy coating, e.g. by co-electro-deposition, which enables the ductile gamma form to be retained and improves tarnish resistance preferably without affecting the anodic character of the coating.

Summary and Conclusion

Statistics are quoted which show that manganese ore production is tied directly with world steel production, but fluctuations in steel output affect Indian ore production much more than production from other sources. A steady and increased demand for manganese is likely to result from research and development into:

(1) Improvement of quality of the end product and concentration of the manganese metal content to reduce freight charges. These should include a study of methods of lowering the phosphorus content of ferromanganese produced from Indian ores and alternative methods of producing pure manganese, e.g. by distillation.

(2) The technical advantages of manganese as an alloying constituent in steel and the replacement of the more expensive alloying constituents such as nickel by manganese in alloy steels.

(3) The use of manganese in non-ferrous alloys with particular reference to alloying

constituent which increase the stability of the ductile gamma phase of manganese.

(4) Manganese as a coating to provide corrosion and abrasion resistance to steel and non-ferrous metals, particularly in those fields in which zinc and nickel are at present used.

The formation of a research and development organization to promote the use of manganese is advocated.

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