UNITED STATES PATENT OFFICE.

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IMPROVEMENT IN MANUFACTURE OF MANGANESE ALLOYS.

Specification forming part of Letters Patent No. **203,266**, dated May 7, 1878; application filed November 30, 1877.

To all whom it may concern:

Be it known that I, RICHARD HALE, of the town of Ledyard, in the county of Cayuga and State of New York, have invented certain new and useful Improvements in Metallurgy of Manganese Alloys; and I do hereby declare that the following is a full, clear, and exact description thereof, which will enable others skilled in the art to which it appertains to make and use the same.

The object of this invention is to form alloys of manganese with copper, tin, and nickel, either with or without the addition of other metals capable of alloying with these metals, so as to produce metals for use in the arts to take the place of brass, German silver, gun-metal, bronze, speculum-metal, bell-metal, white-metal, and similar compositions for forming articles by casting, stamping, and rolling, and as a base for articles to be gilded, silvered, or coated with other suitable metal.

The metal manganese, though easily reduced from its oxides, is only known as a chemical curiosity, on account of the facility with which it is reoxidized and its strong affinity for carbon and silicium. It has long been believed to possess properties which would give it value as an element to form alloys; but no practical method of dealing with the natural ores (which are generally contaminated by large admixtures of other metals) has been described, and its alloys are not known in the metal markets.

By my invention alloys of maganese with copper, tin, and nickel may be readily formed; and by varying the relative proportions of the manganese, or by the substitution for a portion of either metal of one, two, or more other metals, (such as cobalt, zinc, chromium, tin, lead, bismuth, silver, and the like,) the alloys may be changed in character, as hereinafter more fully specified.

The invention consists, substantially, in reducing manganese from its oxides, salts, or ores to the metallic state in the presence of copper, tin, or nickel, the substances from which the alloy is to be formed being in the relative proportions hereinafter specified, the manganese, as reduced, combining with nickel or falling into melted copper, tin, or alloy, and being dissolved thereby. If the operation be performed in a crucible, it is sufficient to introduce copper, tin, or nickel, together with the ore of manganese and its appropriate flux and reducing agent. The crucible must be efficiently protected, and exposed for several hours to a fair white heat. In a furnace, however, the hearth is covered with melted copper, tin, or alloy at the commencement of operations, and in continuous work there is left upon the hearth sufficient metal to protect it from slag and flux, and obviate the danger of chilling it by a sudden access of manganese, for the fusion-point of the alloy rises with the proportion of manganese.

By this method the ores of manganese are made as easy of reduction as those of iron, and skilled metallurgists need no further instructions to produce a great variety of useful alloys containing manganese.

Manganese has an extraordinary tendency to toughen and whiten copper. An alloy of eighty parts copper to twenty manganese appears white when casually inspected, though careful observation perceives a faint tinge of red. The formula Mn,Cu_3, equivalent to about twenty-two and one-half per cent. of manganese, seems to represent a true chemical combination, which has, when polished, a silvery luster. Another chemical combination is indicated by the formula Mn_2,Cu_5, containing about twenty-seven per cent. of manganese. As the proportion of manganese is increased beyond this percentage, the silvery white degrades toward steel-gray and the alloy becomes more liable to tarnish, yet it remains tough and malleable up to fifty per cent.

If the manganese is mingled with other metals, as is commonly the case with its ores, the alloy may become somewhat brittle at seventy per cent. copper and thirty per cent. of the mixed metals, and for all proportions of copper be more liable to rust; yet, with about seventy-five per cent. of copper, I have not failed to obtain a good white alloy from every specimen of commercial black oxide of manganese experimented upon, and the mechanical qualities of all alloys containing seventy-five per cent. or more of copper have been excellent. The specimens of black oxide which I have generally used contained cobalt, chromium, copper, iron, and nickel, some having but one and others having several such impurities. Iron proved the most injurious impurity, and cobalt the most useful, in the proportions in which they existed in the ores. An alloy of eighty per cent. copper, fifteen manganese, and five cobalt has superior mechanical qualities, and is white enough for plating upon as a white-metal.

All these alloys excel brass in toughness, and those of pure copper and pure manganese excel it in resistance to tarnish. With the addition of tin in proportions under fifteen per cent., they retain strength and malleability and acquire increased resistance to tarnish. I do not, however, limit the use of tin to fifteen per cent. Zinc hardens them. Nickel is capable of giving a very pure dead-white color; but, when the proportion of manganese is diminished and that of nickel increased, the color of the latter metal rapidly prevails. Lead in small quantities appears to have the same effect as in ordinary brass and bronze, while there is less occasion for its use. A rich yellow or golden color requires a larger proportion of zinc or of tin than of manganese, and in all ternary and quarternary alloys the proportion of manganese should be reduced in some measure as that of other white-metals is increased.

Definite alloys of manganese and copper are reached either by testing the forming alloy and drawing it off or stopping the furnace at the right time, or by securing an excess of manganese, to be afterward ascertained by analysis, and offset by adding the proper quantity of copper and remelting. The most valuable alloys, and especially the white alloy corresponding to Mn, Cu_3, in my opinion differ sufficiently from those containing either more or less manganese, to be distinguished by an experienced eye and by mechanical tests without quantitative analysis.

Having properly lined a crucible, I put into it pieces of copper small enough to lie upon the bottom. Then I introduce a small portion of ore mixed with its flux and reducing agent, and shake it until the spaces within and around the pieces of copper are filled. The remainder of the ore mixture is added in successive portions, and crowded down as compactly as possible until the crucible is nearly filled. A thin layer of carbon is put on top of the ore mixture, and the mouth of the crucible stuffed with paper, tow, or any other convenient carbonaceous material. The cover is then applied, and either luted or fitted to the mouth of the crucible. A little leakage around the edges of the cover is of no consequence so long as it retains its position. The cover has but a single hole for the escape of gases, which is made sufficiently large. I manage the fire in such a manner that the crucible and its contents shall gradually be raised to a low-red heat, but carried as rapidly as possible from a low-red up to a full-white heat, and so maintained for a time, approximately that which would be required for thoroughly fusing an equal bulk of copper in the same fire, generally about three hours. After the crucible has been removed and cooled the cover is taken off. The charred stuffing, the layer of charcoal, and any surplus that has floated upon the flux is poured out, and the slag and button of alloy dropped out by their own weight, aided, if need be, by blows upon the outside of the crucible. When a sufficient number of such buttons has been obtained, they are fused together, with whatever additions of copper or other metal may seem desirable, the weight of the buttons, compared with the known quantity of copper which they contain, furnishing the data for an estimate of their composition. Otherwise the buttons may be fused by themselves, and the result tested chemically or otherwise.

For reducing agent I prefer charcoal; but lamp-black, anthracite, and other forms of carbon may be employed.

I dislike the use of silicious and alkaline substances in the flux, and prefer fluorides; yet the composition of a flux must depend, more or less, upon considerations of economy and upon the minerals which are associated with the ore used.

For an ore carrying thirty per cent. of minerals containing silica, alumina, and baryta, I use one part of fluor-spar to six parts ore, and one part charcoal to seven parts ore. For pyrolusite, containing but ten per cent. silica and alumina, and only traces of other impurities, I use one part charcoal and one part of the slag from the above-mentioned ore to six parts pyrolusite. For pure black oxide manganese, I use one part charcoal and one part cryolite to six parts oxide, and the slag thus obtained takes the place of cryolite in subsequent operations. The excess of carbon which is recovered from the crucibles may generally be used over again.

The ore, flux, and carbon should be powdered and mixed with ordinary care; but fine powders and very intimate mixtures are not essential. I do not, indeed, restrict myself to any single detail of process herein mentioned. The copper, for instance, may be placed on top of the ore, and the proportions of carbon and flux much diminished, and the fire managed quite differently, yet the ultimate result be the same.

The principal difference between crucible and furnace work is in the use of copper or alloy to protect the hearth from the action of slag. I calculate, in continuous work, to preserve a body of melted metal, which floats the slag upon its surface between certain limits of altitude, so that only a predetermined portion of the furnace can be attached by its erosive action. At the commencement of work this protective office is preferably performed by copper, afterward by the alloy. A mixture of ore, flux, and carbon is added from time to time. The slag is run off when it reaches its upper limit, and the alloy is drawn down to its lower limit and replaced by copper whenever it attains the desired richness in manganese.

Tin is employed in crucibles or furnaces in precisely the same manner as copper. The alloy thus obtained may be used for mangan-bronze. There is no appreciable loss of tin.

Nickel is used in crucibles, either in the same manner as described above for copper, or by disseminating it through the ore mixture. It combines readily with the reduced manganese, and forms a fusible alloy, having a strong affinity for carbon.

I am aware that alloys of iron and manganese have been formed in large quantities for use in making steel, and also that traces of manganese may be found from accidental association with the ores of other metals.

I am also aware that it has been proposed to heat together in a crucible, in the presence of copper, a mixture of peroxide of manganese, four pounds; nickel, one-half pound; crushed charcoal, two pounds, and cyanide of potassium, one-half pound, with coal-tar enough to moisten the same and cause adherence; and also that it has been proposed to subject a mixture of copper, or metals similar thereto, and oxide of manganese to the action of the reducing-gases of a Siemens furnace. Neither method, however, contemplates an open-furnace process. The latter method employs neither carbon nor flux. The former method employs an excess of carbonaceous and reducing agents, while the proportions of carbon and flux used by me are such that nearly all the carbon is consumed by combination with the oxygen of the ore, and the surplus floats upon the top of the slag or flux through which the metallic manganese falls down.

Having thus described my invention, what I claim, and desire to secure by Letters Patent, is—

1. The process of producing alloys of manganese with copper and other metals, as described, which consists in reducing manganese from its oxides, salts, or ore by means of reducing agents and fluxes, in the proportions as specified, in the presence of the metal to be alloyed, the proportion referred to being about one-sixth part of carbon and cryolite to one part of black oxide of manganese, when these materials are used, and, in general, such that nearly all the carbon is consumed in the operation, and the remainder floats upon the top of the flux, as set forth.

2. In the art of making manganese alloys, the process which consists in maintaining, in a furnace, a suitable body of melted metal to float the slag, to protect the hearth, and to prevent chilling, and in adding from time to time a mixture of manganese ore, oxide or salt, flux, and carbon, as described.

3. The continuous process for making alloys of manganese with the described metals, which consists in maintaining a suitable body of melted metal and adding thereto proper quantities of the mixture of manganese ore, carbon, and flux, and of the metal to be alloyed with manganese, as described, and drawing off from time to time the slag from the top and the alloy from beneath without reducing the body of metal below the point necessary to protect the furnace-hearth and prevent chilling, as specified.

In testimony that I claim the foregoing as my own I affix my signature in presence of two witnesses.

RICHARD HALE.

Witnesses:
E. P. Clark, Jr.,
Frederick Crane.