

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report

of

Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by George William Pearson for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

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May 6 1920

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Examination

This is to certify that we the undersigned, as a committee of the Graduate School, have given George William Pearson final oral examination for the degree of Master of Science . We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

May 28 1920.

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STUDIES ON THE PREPARATION
OF
MAGNESIUM-MANGANESE AND MAGNESIUM-CHROMIUM
ALLOYS

A THESIS
PRESENTED TO THE
FACULTY OF THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
BY
GEORGE WILLIAM PEARSON
WINTHROP MINNESOTA

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George W. Pearson.

I. REASON FOR INVESTIGATION.

1. Aluminum as a de-oxidizer of Steel: Aluminum is used to quite an extent in the manufacture of steel to affect the final de-oxidation. Aluminum is a vigorous and effective de-oxidizing agent but its high price and some technical difficulties make it impractical to use except for the final de-oxidation. It is, therefore, added to the steel after the manganese and the silicon have done their work. Ordinarily it is added to the metal as it is poured into the mold or ladle. Sometimes the aluminum is put into the mold and the metal poured on it. The aluminum added reduces the iron oxides present and in so doing produces considerable heat. The aluminum oxide ordinarily has time to leave the bath as a slag; if it does not, due to bad practise, it has an injurious effect on the steel. The effect of the metallic aluminum can be neglected, as generally there is very little present and what is present instead of having a harmful effect, of late is thought to be beneficial. Aluminum is in bad repute, partly because it can be used in such a way that increased production at the cost of quality, can be attained.

2. Magnesium as a De-oxidizer of Steel: Magnesium is used to only a very small extent in the manufacture of steel. It can not be used in the pure state as aluminum is, because magnesium is volatile far below the melting point of iron. The boiling point of magnesium at atmospheric pressure is about 1100° and the melting point of iron is 1530° and it is generally poured at a considerably higher temper-

ature. The attempts to use magnesium in a pure state have, therefore most often ended disastrously, metal being thrown out of the bath or the magnesium coming to the surface and oxidizing. It is used as an iron alloy(99-1) for de-oxidation to a limited extent.

3. Comparison of Magnesium and Aluminum: In comparing these two metals the following factors have been considered: a) specific gravity of metals, b) specific gravity of oxides, c) reacting agents, d) volumes, e) heats of formation, f) costs (occurrence of ore).

a). The specific gravity of magnesium is 1.74 as compared with 2.71 for aluminum. Any residual metal is, therefore, going to have a greater tendency to float out. Owing to the great differences in specific gravities between iron and magnesium there is not much chance of excess magnesium remaining in the iron to form undesirable alloys.

b). The specific gravities of the oxides are not so far apart. Magnesium oxide has a specific gravity of 3.43 while that of aluminum oxide is 3.75. This would seem to be an advantage for the magnesium but since we do not know that the magnesium oxide and the aluminum oxide particles formed have the same size, we can say nothing as to the rapidity with which they leave the bath.

c). From the formula it is evident that weight for weight, aluminum is more efficient than magnesium. Thus it takes 24.32 grams of magnesium to do the work of 18.1 grams of aluminum or one gram of aluminum does the work of 1.45 grams of magnesium. So, from a consideration of reacting weights aluminum is superior. If, however, magnesium can be added in such a way that very little is lost, it has other advantages over aluminum that might make its use more prac

ticable.

d). Magnesium, being more bulky than aluminum, would have more metal surface and therefore be a more efficient de-oxidizer.

e). One difference between the action of magnesium and aluminum as de-oxidizers is the amount of heat generated during the formation of the oxide. The molecular heat of formation of aluminum oxide (Al_2O_3) is 392,000 calories and that of magnesium oxide (MgO) is 144,000 calories. The heats for equivalent amounts of oxygen (8g.) are 72,000 and 65,000 calories for magnesium and aluminum respectively. This increased amount of heat per unit of oxygen consumed is going to result in greater fluidity. This in turn is going to permit oxides and gases to float out and will result in a lower amount of foreign inclusions and fewer blow-holes.

f). At the present time its high price is an objection to the use of magnesium. It costs about \$2.00 per pound now, although once it was quoted as low as \$1.75. Magnesium is about as abundant as aluminum and its process of manufacture is similar and need not involve a much greater expense. The magnesium ore used at the present time contains only 8% magnesium although deposits of 40% magnesium content exist in Canada. These, however, are rather inaccessible. Sea water contains one-eighth of one per cent magnesium and the waters of Salt Lake contain seven times as much. This means that a sixteen foot cube contains one ton of magnesium. If the demand for magnesium increases, methods will improve and it will become cheaper.

II. PURPOSE OF INVESTIGATION.

4. Since magnesium cannot be added as such to steel, it seems

feasible that it could be added as an alloy. In the form of an alloy of low magnesium content it would have a specific gravity more nearly approaching that of iron and would not float to the top of the melt immediately. It would probably not volatilize so readily either. Naturally it would be alloyed with some metal that is beneficial to steel or which in itself would help the process. Manganese is used in steel to reduce oxides and to remove sulphur as sulphide. Chromium is used more and more to give steel a greater hardness without affecting its ductility or tensile strength. An alloy of magnesium with manganese or chromium could therefore be used in steel to an advantage because it would be an excellent de-oxidizing agent and either the manganese or chromium remaining in the steel would give it desirable properties.

5. The purpose of this investigation was, therefore, to see if an alloy of the inter-metallic compound or solid solution type could be made using these metals. Mechanical mixtures are, of course, out of the question since the melting point of both manganese and chromium are above the boiling point of magnesium.

III. PROPERTIES OF MAGNESIUM.

6. Compounds of Magnesium: Magnesium will form oxides, carbides, nitrides and silicides quite readily. The oxide is formed most readily and the nitride is perhaps the most difficult of the four to prepare or retain. It is impossible to bring the magnesium very far above its melting point in air without igniting the metal. It was

found during this investigation that the carbide and nitride are readily formed at the temperatures to which it was necessary to bring the magnesium. Magnesium carbide is formed in air by heating magnesium with a bare gas flame. Acetylene is formed by the interaction of water and Magnesium-Carbide. Magnesium nitride is often formed in the atmosphere of the furnace. In water this decomposes to form ammonia and magnesium oxide. Magnesium attacks silica tubes, magnesium silicide and magnesium oxide being formed. In this case, the temperature of the melt makes a great difference; at 1000° silica is attacked quite rapidly and at 800° the action is slow. At the lower temperature, the same silica tube can sometimes be used for two melts.

7. Study of Fluxes: Owing to the low specific gravity of magnesium it floats on top of other metals and an intimate mixture is difficult to obtain. As yet a flux of lower specific gravity than magnesium has not been obtained. Potassium chloride and lithium chloride have a specific gravity of about two and these salts come closer to having the specific gravity of magnesium than any others which could be used as fluxes. A flux would be quite desirable because magnesium gets coated with a thin film of oxide in the air and this prevents it from coalescing when in the form of powder or chips. It is reasonable to suppose that this film of oxide is going to prevent intimate contact with other elements and, therefore, hinder alloying in some cases.

8. Effects of Gases on Magnesium: Because of the ease with which magnesium forms oxides it was necessary to exclude oxygen or air

from contact with molten magnesium. In this investigation it was not realized at first that an atmosphere of nitrogen would be harmful. Nitrides, however, were formed so this gas also had to be excluded. Hydrides do not form with magnesium so this gas and a vacuum were used successfully.

9. Melting and Boiling Point Considerations: The melting point of magnesium is 651° and the boiling point at a pressure of 760mm. is 1135° . The melting points of manganese and chromium 1260° and 1525° respectively. It is, therefore, evident that it ~~could be, and~~ is impossible (except perhaps at high pressures) to have molten magnesium in contact with molten manganese or chromium. To have an alloy formed it is necessary that, solid manganese or chromium dissolve in molten magnesium; or that, liquid (or solid) manganese or chromium take gaseous magnesium into solution.

10. Crucibles: Some difficulty was experienced in getting a crucible that would hold molten magnesium at a high temperature. The magnesium rapidly attacked porcelain and if the crucible lasted through the melting process it was generally broken when the metal solidified. Graphite crucibles contaminated the melt, magnesium carbide being formed. Fire-clay crucibles were also attacked and the melt contaminated. In this case, magnesium silicate and magnesium silicide were formed. Alundum (aluminum oxide) crucibles were found to be the most satisfactory. If the metal was heated up rapidly, the crucible ordinarily could not be used more than once. If some magnesium oxide was rubbed into the walls of the crucible and the crucible heated up slowly, it could be used repeatedly. Magnesium re-

duces aluminum oxide but the oxide of magnesium already in the wall and some that may have been formed there during the process seemed to have prevented further action.

IV. PREVIOUS WORK.

11. Work on Magnesium-Chromium Alloys: Parkinson¹ (1867) claims to have obtained an alloy of chromium and magnesium by heating magnesium with chromium oxide. He obtained a product which burned in air and which decomposed water. He also did some work on other alloys of magnesium. His work on chromium-magnesium was repeated. For details see page 15.

12. Work on Magnesium-Manganese Alloys: Terreil² (1874) claims to have obtained without much trouble an alloy of magnesium with manganese through the reduction of manganese proto-chloride. He does not describe his reaction or product. His work was repeated in air and in vacuum. For details of work in vacuum see page 15.

13. Work on Magnesium-Nickel Alloys: Gustav van Voss³ (1908) prepared a series of magnesium-nickel alloys by heating the two metals in contact. He did his work in an atmosphere of hydrogen in porcelain crucibles.

References:

(1)Guertler--p.415

(2)Guertler--p.415

(3)Z.anorg.Chem.57,61-67. (1908)

Since the melting point of nickel is 1492° , which is about 300° above the boiling point of magnesium, it might be possible to attack this problem in the same manner, i.e. by heating manganese or chromium in contact with magnesium it seemed probable that an alloy of magnesium-chromium or magnesium-manganese might be obtained.

V. STUDIES ON PREPARATION OF ALLOY:
HEATING THE METALS IN SEALED CRUCIBLES.

14. Preparation of Metals: The first attempts were made using large pieces of magnesium and manganese. Later the manganese was finely ground. It was unnecessary to use magnesium in a finely divided state since it melted at a comparatively low temperature. If magnesium filings were used it was found that magnesium oxide film formed on each particle prevented the mass from coalescing and they were found in the same shape before and after melting.

15. Crucible Linings and Seals: Different kinds of seals and linings were used. In the same crucible, the same kind of material was always used to seal up the crucible that was used to line it. The magnesium oxide lining that was used at first was made from rather coarse magnesite with hitempite binder. This, however, crumbled too readily. A more successful material was made by grinding magnesite down to 200 mesh and using that with hitempite as binder and some 50 mesh magnesite as body. This could be dried quite rapidly. If this material was cindered successfully it could be used a number of times without crumbling.

16. Tests: A number of different kinds of crucibles and linings were tried and the tests may be summarized under the following four groups: (The data in each group are the result of a number of tests)

a) The first crucible to be used was plumbage, lined with magnesium oxide. Because of the porous nature of the crucible, furnace gases penetrated it and the magnesium was all converted into nitride and carbide.

b) An alundum crucible, lined with magnesite, having a clay cover sealed on with hitempite was used. The results were the same as when the plumbage crucible was used so this must have been just as porous.

c) A porcelain crucible with a porcelain cover sealed on with hitempite was tried. The magnesium attacked the walls of the crucible and furnace gases entered. On solidifying the magnesium contracted faster than the porcelain and pulled with it the fluxed inner part of the wall and ruined the crucible.

d) A porcelain crucible was used as in the above case except that it was lined with magnesite. The crucible was not attacked in this case and there was not so much trouble with furnace gases. This was the only one with which any degree of success was obtained.

17. Results: In no case was the slightest tendency to alloy evident. In one case a hole was drilled into a piece of magnesium and this filled with manganese and heated. Later when the magnesium was sawed through, the manganese was found in the original shape and very nearly the same position. The film of ^{oxide} surrounding the magnesium ~~and~~ seemed to be very tenacious. In some instances where

the temperature had been brought well above the melting point of magnesium, sticks of this metal were inserted. ~~They were~~ about an inch high and just flattened out a little, On the whole, attempts that were made using sealed crucibles were not a success because gases would penetrate at the seal. This was always somewhat porous. There is one advantage in using sealed crucibles over using the vacuum furnace, namely, in the sealed crucibles the melt can be shaken ~~off~~ up so that the two metals come into closer contact. The non-all-oying properties of these metals is shown by the fact that the two metals were never made even to adhere by any of these methods.

VI. STUDIES ON PREPARATION OF ALLOY: THERMITE REACTIONS.

18. Theoretical Considerations: Aluminum alloys are frequently made by causing an excess of aluminum to react with the oxide of the element with which it is desired to form an alloy. By this means it is possible to produce alloys of a definite composition. Magnesium alloys can no doubt be made in the same way if the alloying elements are restricted to those that have a melting point below the boiling point of magnesium. There is more difficulty with those elements which have a melting point ~~above~~ that of the boiling point of magnesium as is the case in this investigation. Aluminum, having a boiling point of 1800° can be used with a greater number of oxides to form alloys. There are records, however, of aluminum alloys having been made by using aluminum with an oxide of a metal having a higher melting point than 1800° . Magnesium has a higher heat of formation than aluminum and will, therefore ~~be~~ reduce a greater number

of oxides. The following table contains those elements^{of} which alloys with magnesium have not been made or studied; the calories given are those liberated when the oxide is reduced with magnesium:

| Oxide | Oxide. | Cal. liberated per mole. of oxide. | Cal. liberated per at. wt. of metal. | Melting point of metal. °C. |
|-------|--------------------------------|------------------------------------|--------------------------------------|-----------------------------|
| | CoO | 86,400 | 86,400 | 1491 |
| | Co ₃ O ₄ | 382,200 | 127,400 | 1491 |
| | CrO ₃ | 291,700 | 291,700 | 1505 |
| | Cr ₂ O ₃ | 163,900 | 81,900 | 1505 |
| | FeO | 78,200 | 78,200 | 1505 |
| | Fe ₂ O ₃ | 234,000 | 117,000 | 1505 |
| | MnO | 53,100 | 53,100 | 1260 |
| | Mn ₂ O ₃ | 161,800 | 161,800 | 1260 |
| | MoO ₂ | 145,000 | 145,000 | 2535 |
| | MoO ₃ | 264,700 | 264,700 | 2535 |
| | PtO | 126,900 | 126,900 | 1755 |
| | TiO ₂ | 72,200 | 72,200 | 1800 |
| | V ₂ O ₅ | 409,000 | 204,500 | 1710 |
| | WO ₂ | 156,400 | 156,400 | 2974 |

An extensive tabulation showing the molecular and unit heats of formation of various oxides is included in the attached blue prints.

Heat of Formation

The values which are given were taken largely from Handbook of Chemistry and Physics, 7th ed. The Chemical Rubber Company. The heats of formation are in small calories for one gram molecule. The values under "Factor" are the conversion factors from the oxides to metals. When only three figures are given, they were calculated using a slide rule. The unit heat of formation represents the heat of formation per unit of oxygen (8 g.).

| Name | Molec. Wt. | For- mula | Factor | Phys. state | Heat of Formation. | |
|---------------------|------------|--------------------------------|--------|-------------|--------------------|--------|
| | | | | | Molecular | Unit |
| Alumina | 102.2 | Al ₂ O ₃ | .5303 | Solid | 392,600 | 65,430 |
| Antimony trioxide | 288.4 | Sb ₂ O ₃ | .8336 | Solid | 166,900 | 2,780 |
| Antimony pentoxide | 320.4 | Sb ₂ O ₅ | .7503 | Solid | 231,200 | 23,120 |
| Arsenic trioxide | 197.9 | As ₂ O ₃ | .7575 | Solid | 154,670 | 25,780 |
| Arsenic pentoxide | 229.9 | As ₂ O ₅ | .6520 | Solid | 219,380 | 21,940 |
| Barium oxide | 153.4 | BaO | .896 | Solid | 126,380 | 63,190 |
| Barium peroxide | 169.4 | BaO ₂ | .812 | Solid | 139,400 | 34,850 |
| Bismuth oxide (ous) | 464. | Bi ₂ O ₃ | .8965 | Solid | 137,800 | 22,980 |
| Boron oxide | 70 | B ₂ O ₃ | .3143 | Solid | 272,600 | 45,430 |
| Cadmium oxide | 128.4 | CdO | .8754 | Solid | 66,300 | 33,150 |
| Caesium monoxide | 281.6 | Cs ₂ O | .942 | Solid | 82,700 | 41,350 |
| Caesium dioxide | 297.6 | Cs ₂ O ₂ | .892 | Solid | 100,960 | 25,240 |
| Caesium trioxide | 313.6 | Cs ₂ O ₃ | .851 | Solid | 118,960 | 19,830 |
| Caesium tetraoxide | 462.4 | Cs ₃ O ₄ | .862 | Solid | 131,460 | 16,430 |
| Calcium oxide | 56.0 | CaO | .7146 | Solid | 151,900 | 75,950 |
| Calcium peroxide | 72.0 | CaO ₂ | .5556 | Solid | 156,010 | 39,000 |
| Carbon monoxide | 28.0 | CO | .4286 | Gas | 29,000 | 14,500 |
| Carbon dioxide | 44.0 | CO ₂ | .2728 | Gas | 97,000 | 24,250 |
| Cerium oxide | 172.3 | CeO ₂ | .813 | Solid | 224,600 | 56,150 |
| Chromium oxide (ic) | 152. | Cr ₂ O ₃ | .6842 | Cryst. | 267,800 | 44,630 |
| Chromium oxide | 152. | Cr ₂ O ₃ | .6842 | Amorph. | 243,800 | 40,630 |
| Chromium trioxide. | 100 | CrO ₃ | .5200 | Solid | 140,000 | 23,330 |
| Cobalt oxide (ous) | 75 | CoO | .7866 | Cryst. | 57,500 | 28,750 |
| Cobalt oxide (ous) | 75. | CoO | .7866 | Amorph. | 57,500 | 28,750 |

| Name | Molec. Wt. | For- mula | Factor | Phys. state | Heat of Formation | |
|-----------------------------|---------------|--------------------------------|--------|----------------|-------------------|---------|
| | | | | | Molecular | Unit |
| Cobalt oxide (ic) | 240.9 | Co ₃ O ₄ | .7343 | Solid | 193,400 | 24,180 |
| Copper oxide (ous) | 143.1 | Cu ₂ O | .8882 | Solid | 43,800 | 21,900 |
| Copper oxide (ic) | 79.6 | CuO | .7989 | Solid | 37,700 | 18,850 |
| Hydrogen oxide (water) | 18. | H ₂ O | .1119 | Liquid | 69,000 | 34,500 |
| Hydrogen oxide | 18. | H ₂ O | .1119 | Solid | 70,400 | 35,200 |
| Hydrogen peroxide | 34. | H ₂ O ₂ | .0588 | Liquid | 46,840 | 11,710 |
| Iron oxide (ous) | 71.8 | FeO | .7773 | Solid | 65,700 | 32,850 |
| Iron oxide (ic) | 159.7 | Fe ₂ O ₃ | .6994 | Solid | 197,700 | 32,950 |
| Iron oxide (ous,ic) | 231.5 | Fe ₃ O ₄ | .723 | Solid | 270,800 | 33,850 |
| Lanthanum oxide | 326. | La ₂ O ₃ | .853 | Solid | 447,300 | 74,550 |
| Lead monoxide | 223.2 | PbO | .9283 | Solid | 50,300 | 25,150 |
| Lead peroxide | 239.2 | PbO ₂ | .8662 | Solid | 62,400 | 15,600 |
| Lithium oxide | 29.9 | Li ₂ O | .4643 | Solid | 143,300 | 71,650 |
| Magnesium oxide | 40.32 | MgO | .6032 | Solid | 143,900 | 71,950 |
| Manganese oxide (ous) | 70.9 | MnO | .7744 | Solid | 90,800 | 45,400 |
| Manganese oxide (di) | 86.9 | MnO ₂ | .632 | Solid | 126,000 | 31,500 |
| Manganese oxide (ous,ic) | 228.8 | Mn ₃ O ₄ | .7203 | Solid | 324,900 | 40,610 |
| Mercury oxide (ous) | 417.2 | Hg ₂ O | .961 | Solid | 2,200 | 1,100 |
| Mercury oxide (ic) | 216.6 | HgO | .9261 | Solid | 21,500 | 10,750 |
| Molybdenum dioxide | 128. | MoO ₂ | .750 | Solid | 142,800 | 35,700 |
| Molybdenum trioxide | 144. | MoO ₃ | .6667 | Solid | 167,000 | 27,830 |
| Neodymium oxide | 336.6 | Nd ₂ O ₃ | .857 | Solid | 435,100 | 72,520 |
| Nickel oxide | 74.7 | NiO | .7858 | Solid | 57,900 | 28,950 |
| Nitrogen oxide (ic) | 30. | NO | .4667 | Gas | -21,600 | -10,800 |
| Phosphorus pentoxide | 142.1 | P ₂ O ₅ | .437 | Solid | 365,200 | 36,520 |
| Platinum oxide | 211.2 | PtO | .925 | Solid | 17,000 | 8,500 |
| Potassium oxide | 94.2 | K ₂ O | .8302 | Solid | 86,800 | 43,400 |
| Praseodymium trioxide | 329.8 | Pr ₂ O ₃ | .854 | Solid | 412,400 | 68,730 |
| Rubidium oxide. | 186.9 | Rb ₂ O | .914 | Solid | 83,500 | 41,750 |

| Name | Molec. Wt. | For- mula | Factor | Phys. state | Heat of Formation. | |
|----------------------------------|---------------|--------------------------------|--------|----------------|--------------------|--------|
| | | | | | Molecular | Unit |
| Selenium dioxide (Amorph. Se) | 111.2 | SeO ₂ | .712 | Solid | 57,080 | 14,270 |
| Silicon dioxide | 60.3 | SiO ₂ | .4693 | Solid | 191,000 | 47,750 |
| Silver oxide | 231.8 | Ag ₂ O | .9310 | Solid | 7,000 | 3,500 |
| Sodium oxide | 62. | Na ₂ O | .7419 | Solid | 100,700 | 50,350 |
| Sodium peroxide | 78. | Na ₂ O ₂ | .589 | Solid | 119,800 | 29,950 |
| Strontium oxide | 103.6 | SrO | .8456 | Solid | 131,200 | 65,600 |
| Strontium peroxide | 119.6 | SrO ₂ | .732 | Solid | 151,710 | 37,930 |
| Sulfur dioxide | 64.1 | SO ₂ | .500 | Gas | 69,260 | 17,320 |
| Sulfur trioxide | 80.1 | SO ₃ | .401 | Gas | 91,900 | 15,320 |
| Tantalum oxide | 443. | Ta ₂ O ₅ | .818 | Solid | 301,500 | 30,150 |
| Tellurium oxide | 159.5 | TeO ₂ | .798 | Solid | 78,300 | 19,580 |
| Thallium oxide (ous) | 424. | Tl ₂ O | .964 | Solid | 42,240 | 21,120 |
| Thorium oxide | 264.4 | ThO ₂ | .879 | Solid | 325,000 | 81,500 |
| Tin oxide (ous) | 134.7 | SnO | .8812 | Solid | 70,700 | 35,350 |
| Tin oxide (ic) | 150.7 | SnO ₂ | .7877 | Cryst. | 137,200 | 34,300 |
| Titanium oxide | 80.1 | TiO ₂ | .6008 | Amorph. | 215,600 | 53,900 |
| Titanium oxide | 80.1 | TiO ₂ | .6008 | Cryst. | 218,400 | 54,600 |
| Tungsten dioxide | 216. | WO ₂ | .8519 | Solid | 131,400 | 32,850 |
| Tungsten trioxide | 232 | WO ₃ | .7951 | Solid | 196,300 | 32,720 |
| Uranium dioxide | 270.2 | UO ₂ | .8816 | Solid | | |
| Uranium trioxide | 286.2 | UO ₃ | .833 | Solid | | |
| Uranium oxide (ous, ic) | 842.6 | U ₃ O ₈ | .8481 | Solid | | |
| Vanadium oxide | 182 | V ₂ O ₅ | .5604 | Solid | 310,500 | 31,050 |
| Zinc oxide | 81.4 | ZnO | .5339 | Solid | 84,800 | 42,400 |
| Zirconium oxide. | 122.6 | ZrO ₂ | .739 | Solid | 177,500 | 44,380 |

19. Reduction of Manganese Dioxide with Magnesium Filings: Some magnesium filings were mixed with a quantity of manganese dioxide in an iron crucible and a coil of aluminum wire put down into the mixture. A current was passed through the wire for an instant and the heat produced was sufficient to start the reaction between the aluminum and the oxide. The reaction was quite violent. The crucible became very hot and the ends of the copper leads were melted off. Some of the contents of the crucible were thrown out during the reaction. The material left in the crucible showed no traces of an alloy and since the reaction was of such violence, further experiment in air was discontinued.

20. Thermite Reactions in Vacuo: A number of holes were drilled in a piece of magnesium and these filled with manganese dioxide. This was heated in a vacuum furnace and a reaction was observed to take place. The manganese must have been reduced but it could not be determined that any of it entered into combination with the magnesium. Other trials were made with the thermite process using magnesium in different forms and arranging the two materials in different ways. In cases where it was possible, such weights of reacting materials were used as would give a 50-50 alloy after the reduction of the oxide. The reaction, however, always took place with such violence that most of the reacting materials were scattered through the furnace and the crucibles were often cracked. No trace of alloy was ever detected. The excess magnesium seems to have been volatilized by the heat generated in the reaction. Since no ^{favorable} results were obtained by this method, it was also discontinued.

VII. STUDIES ON PREPARATION OF ALLOY: EXPERIMENTS IN VACUO.

21. Heating in Evacuated Section of Iron Pipe: Since sealed crucibles did not give satisfactory results because of oxidation and since it is quite difficult to introduce a thermo-couple into the vacuum furnace, another method was tried before resorting to the vacuum furnace. An iron pipe 14 inches long, three inches inside diameter and provided with caps on both ends was obtained. One of the caps was provided with three openings, one for gas inlet (in case an inert gas would be used), one for outlet and one for thermo-couple. The sides were covered with fire-clay, hitempite being used for binder. The outlet was connected with a vacuum pump and the air exhausted. The pipe was then placed in a vertical position in a granular carbon resistance furnace, surrounded by the resistor to a height of eight inches and heated. Because of the thickness of the walls it was difficult to get the melt hot in the first trial. The outside of the apparatus got hot while the interior only went up to about 300° . In the final trial the outside of the pipe melted and the interior just went up to a scant 1000° . This apparatus was not satisfactory because the walls must of necessity be thick and it took too long for the heat to penetrate. The fire-clay became a conductor before the magnesium was melted. This arrangement might be a success in another kind of furnace but it would not be used in an electric resistance furnace.

22. Description of Vacuum Electric Furnace: An Arsen vacuum electric furnace was used. This furnace is the small furnace manufactur-

ed by the General Electric Company. It has a spiral carbon heating element with water cooled electrodes. The outside jacket is also water-cooled. The gas is exhausted by means of a two-stage centrifugal pump. This furnace may be used with an atmosphere of hydrogen by merely connecting a source of hydrogen to the vacuum line. The air is first exhausted and then the hydrogen admitted. The hydrogen should be removed before the furnace is opened again as explosions may follow if it is permitted to remain. One explosion which was more or less serious seems to have resulted from opening the furnace while certain parts were still hot; supposedly, air entered and formed an explosive mixture with the hydrogen.

23. Alundum crucibles were used in all the experiments in the vacuum electric furnace. They could be used a number of times if heated up carefully the first time. The various experiments can be considered from the following groups: (The data in each group are from a number of tests.)

a) In the first trial at producing an alloy in this furnace, plates of magnesium about one millimeter thick and one and one half centimeters square were placed in a crucible and powdered manganese ppt in between them. The temperature was kept at about 750° for 20 minutes. There was no sign of alloying. There was again the difficulty in getting the two metals even to adhere.

b) Pieces of manganese metal were ground down round and inserted in magnesium. The magnesium was raised to its boiling point and held there for a short time. The cooled melt was afterward ground down so as to expose a boundary between the two metals. No indica-

tion of alloying was found.

c) A piece of chromium was placed over magnesium in such a way that the magnesium in distilling would condense on the polished face of chromium. This piece of chromium was later polished in such a way that the boundary line between the two metals could be examined. It showed only an intermediate area of magnesium oxide.

d) A piece of chromium was examined under the microscope. This piece was then put in a crucible with some magnesium and the magnesium distilled off very slowly. The chromium showed very little change in structure and the observed change was no doubt due to the long anneal.

e) Parkinson's work (reducing chromium trioxide with excess magnesium) was repeated. (see page 7) In the experiment some green chromic oxide (Cr_2O_3) was obtained but the greater portion no doubt was reduced to metallic chromium. There was no alloy formed. Parkinson perhaps used carbon crucibles and so obtained something which would decompose water. The excess magnesium would cause the material to burn in air.

f) Terrell's work (reducing chloride manganous with magnesium) was repeated both in air and vacuum. (see page 7) If Terrell did the work in air, the manganese chloride being hygroscopic would absorb water and the magnesium would all be converted into magnesium oxide. The work was repeated in vacuum using a de-hydrated chloride. The manganese chloride was reduced but the excess magnesium did not combine with the manganese to form an alloy. If Terrell used silica or graphite crucibles he would get products (magnesium

carbide or magnesium silicide) that could be mistaken for alloys.

g) A piece of magnesium having one face as plane as it could be made by careful grinding and polishing was placed against a similar surface of manganese. The two were surrounded with magnesium filings and heated up in the vacuum furnace. When taken out of the furnace the two metals were found to adhere but careful polishing of the junction failed to show any alloying. A number of photographs were taken to prove that the two metals themselves had not alloyed. (see photographs #2 and #3)

h) Plane faces of magnesium and chromium were heated in contact as with manganese and with the same result. Under the microscope the metals showed straight edges and the microstructure of both metals was the same after, as before the experiment.

24. Conclusion: From the work it was evident that there was no alloy formed between the magnesium and manganese or magnesium and chromium. The edges of the two metals in contact were comparatively straight as shown by the photographs. No intermediate metallic material can be detected. The fact that the two metals adhered may be due to the fact that the magnesium reduces the oxide on the surface of the other metal.

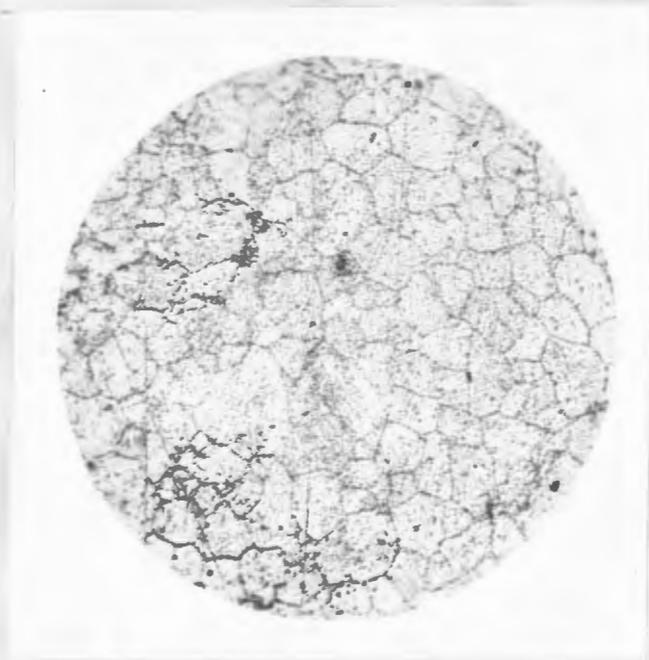


Fig.I. Pure Magnesium(x125) Etching Reagent, Ammonium Chloride.

This sample was used for comparison to detect any indication of alloying. Magnesium that had been used in any experiments with manganese or chromium was compared with this.

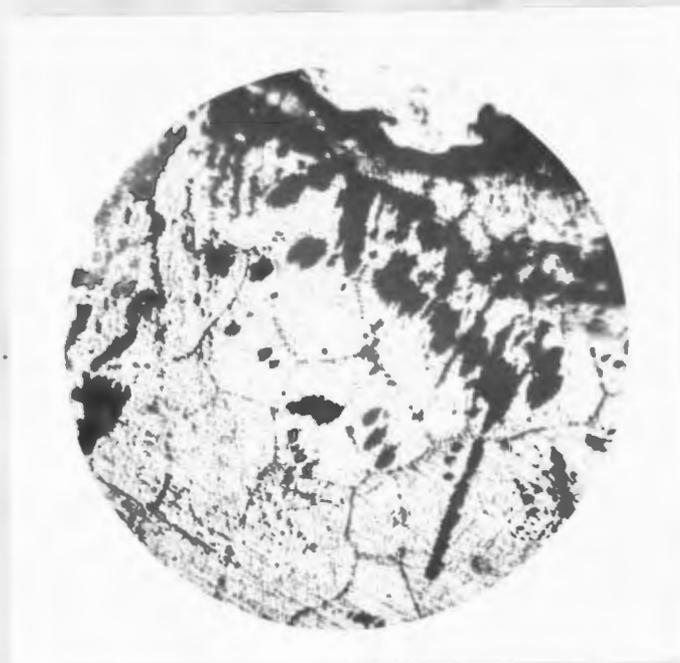


Fig.II. Section of Junction of Manganese and Magnesium.(x125).

Etching Reagent, Ammonium Chloride.

The small light area at the top is manganese metal. This photograph shows a structure which looks like an alloy more than any other obtained during this investigation. The magnesium had been molten while the manganese had not. The magnesium had perhaps reduced some oxide on the surface of the manganese or attacked some impurity in the manganese. The magnesium in the photograph shows essentially the same structure as pure magnesium.

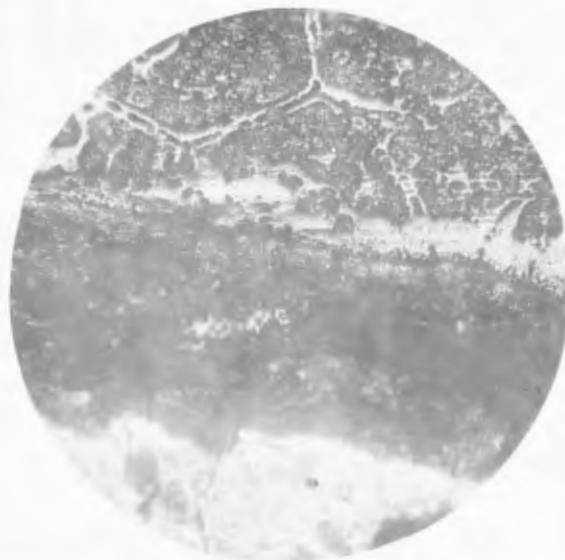


Fig.III. Section of the Junction of Magnesium and Manganese.(x200)

This shows a typical section of the junction of the two metals. The edge on the manganese is very nearly as straight as before it was put in the furnace. The intermediate material is perhaps oxide.

VIII. STUDIES ON PREPARATION OF ALLOY: MISCELLANEOUS TRIALS.

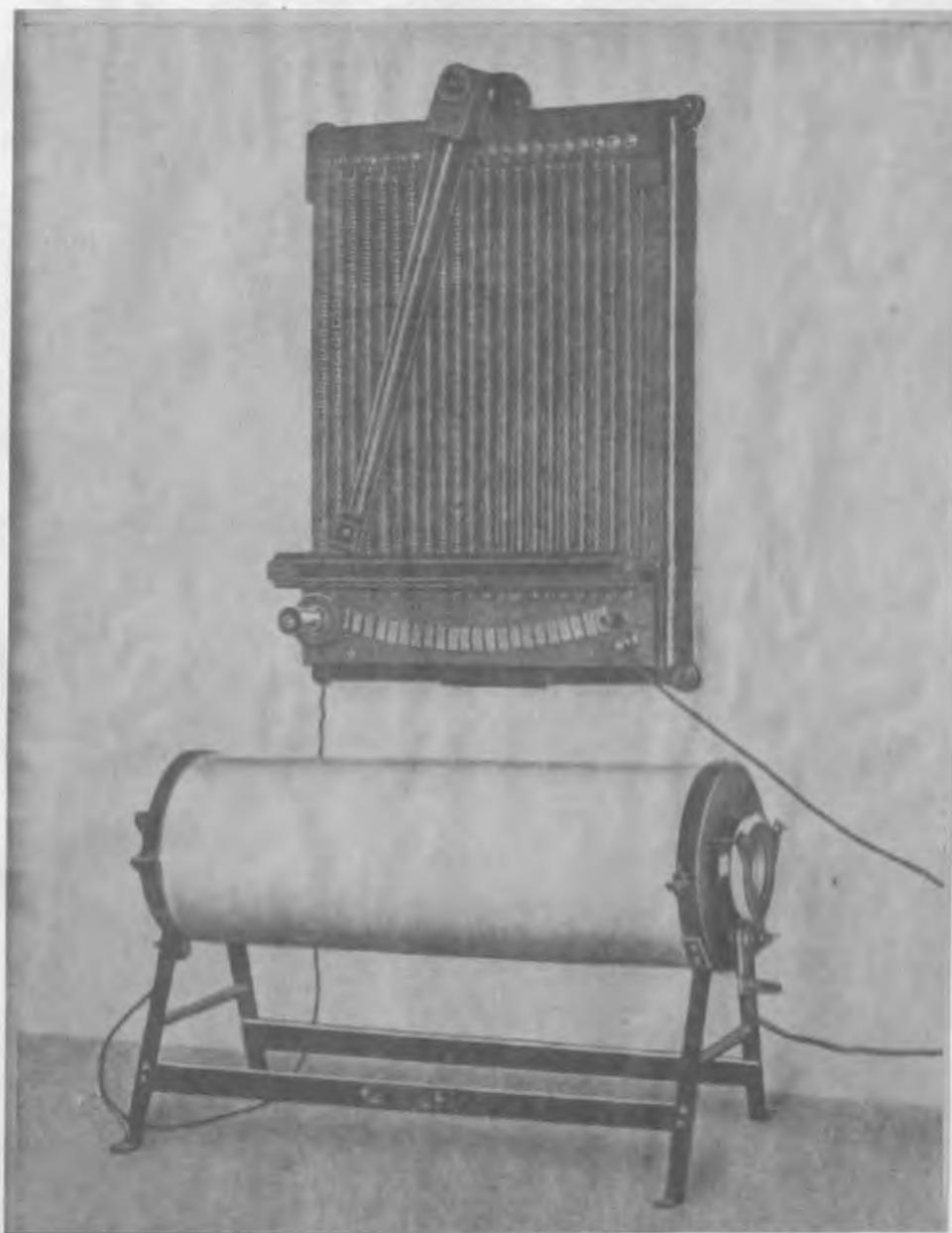
25. Heating in an Atmosphere of Hydrogen: Because of the difficulty of regulating the temperature and because magnesium boils at a much lower temperature ~~in a~~ vacuum, an attempt was made to have molten magnesium in contact with the other metals in an atmosphere of a neutral gas. A platinum wound furnace of the Rosenhain type with a usalite core was arranged in a vertical position so that hydrogen gas could be admitted at the top and escape at the bottom. The therm^{couple}~~ometer~~ was inserted so that it rested against the bottom of the crucible. The melt could be watched from above through a mica window. At first the hydrogen was generated by two Kipps but later a tank of hydrogen was used. This apparatus was at fault in that the usalite tube did not hold the hydrogen. A porcelain tube of different quality or a silica tube might keep the hydrogen from escaping.

26. Volatilization of Magnesium in Molten Manganese: It was thought that if magnesium vapors were forced up through a melt of manganese an alloy might be formed. A piece of gas-pipe about one-half inch, inside diameter and twenty inches long was stopped up about one inch from one end with magnesite. The inside and outside of this end were then covered with magnesite and allowed to dry. A hole about one inch long and one quarter inch in diameter was left. This was filled with magnesium filings and heated to about six hundred degrees. This was then plunged in some ferro-manganese which was well above its melting point, probably 1350°. There was a slight bubbling

on the outside of the pipe and the metal near the pipe became more liquid than the rest of the melt. The magnesite on the outside of the pipe scaled off and some of the pipe dissolved in the melt. Ferro-manganese was used in this case only to see if the method was possible and justified further study.

About 150 grams of manganese metal were brought to a temperature of 1350° in the electric furnace. Fluorspar was used as a cover to prevent oxidation. Magnesium was forced to volatilize up through this in the same manner as in the previous case. In this case an uncovered silica tube was used that was closed one inch from the end with asbestos fibre. This time the magnesium came up through the slag and oxidized in the air. The silica tube was attacked both on the inside and the outside so there must have been some silica dissolved in the melt as well as decomposed by the volatile magnesium.

On investigation, no difference could be found between the ferro-manganese that had been subjected to this treatment and other ferro-manganese. The manganese metal was carefully analyzed but no magnesium could be detected.



Rosenhain Electric Furnace.

IX. CONCLUSION.

27. Fluxes: In this work it was found that it is absolutely necessary to keep the molten metal out of contact with nitrogen as well as oxygen. A flux is necessary if the work is to be done in air. The flux should also remove the tenacious oxide film. Because of the low specific gravity of magnesium no satisfactory flux could be found.

28. Crucibles : Magnesium oxide crucibles would be the best for work with magnesium. The next best thing is a crucible in which a magnesium oxide lining can be placed and from which it will not scale off too easily. For ordinary work an alundum crucible will serve the purpose.

29. Thermite Reactions: Magnesium alloys with manganese or chromium cannot be produced with the same ease that aluminum alloys may be with the same metals by means of thermite reactions. No alloy was produced ^{by using} ~~having~~ magnesium ~~used~~ with an oxide of manganese or of chromium.

30. Alloys: If magnesium forms alloys with manganese or chromium it does so with extreme reluctance. Magnesium was found to alloy with nickel in a few minutes in the vacuum furnace while it was impossible to find a trace of manganese or chromium alloy after a prolonged heating. This work does not necessarily prove that alloys of magnesium with manganese or with chromium of the solid solution or inter-metallic compound type cannot be formed but that none of these metals could be formed by the methods tried in this investigation.

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