

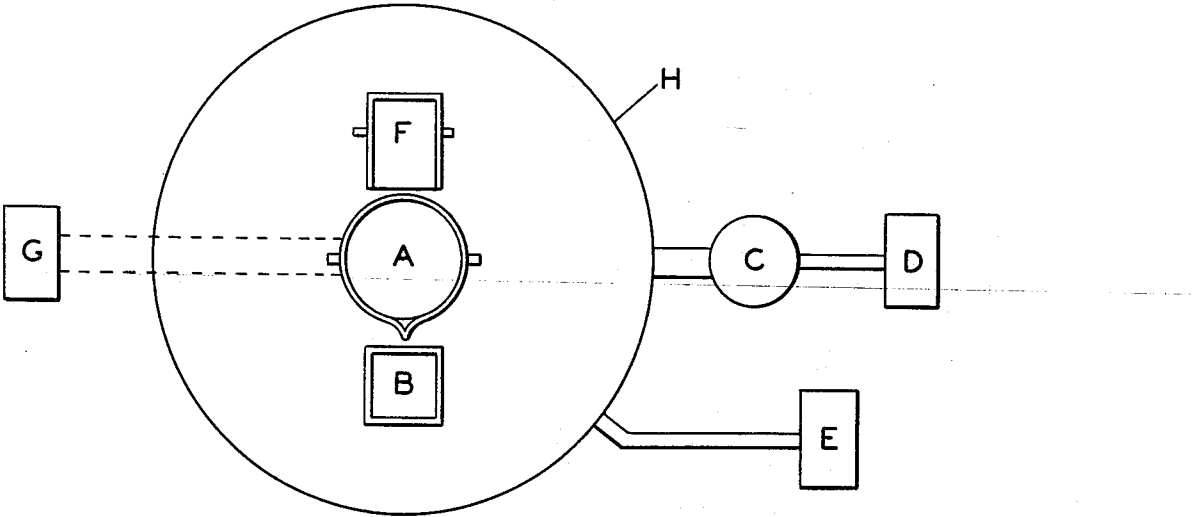
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METHOD OF ALLOYING GASEOUS MATERIALS WITH METALS

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METHOD OF ALLOYING GASEOUS MATERIALS
WITH METALS

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This invention relates to a novel and improved method for introducing alloying elements or compounds in gaseous form, such as nitrogen gas, into alloys, such as the steels, and particularly the austenitic steels.

In the commercial production of austenitic steels, it has been the prior practice to incorporate nitrogen into the molten steel in combined form, such as a nitride, a nitrogen-containing ferroalloy, nitrided iron powder, etc. This practice leaves much to be desired, for it is extremely difficult to obtain a steel containing more than about 0.3% nitrogen using this method. Also, these combined forms of nitrogen are comparatively expensive and their use adds considerably to the cost of the final product. Not only is it difficult to obtain an austenitic steel having more than 0.3% nitrogen, but when a nitrogen concentration in excess of this value is obtained using the customary procedure of melting the alloying metals under an atmosphere of air, it is difficult to cast sound and homogeneous ingots.

It is also known that the solubility of nitrogen in an alloy may be increased by adjusting the composition of the base alloy to increase the concentration of certain nitrogen-solubilizing elements, such as chromium and manganese. For example, the solubility of nitrogen in liquid iron containing only 16% chromium is 0.19% at 1600° C. and if 16% chromium and 10% nickel are present the nitrogen solubility is reduced to 0.16%. Liquid iron at this same temperature and which contains 16% chromium and 10% manganese will dissolve 0.25% nitrogen. However, the amount of nitrogen retained in steel which has solidified without porosity is usually less than the saturation concentrations in molten steels. Furthermore, even though the concentration of nitrogen-solubilizing elements in the basic alloy is substantially increased, only slight increases in nitrogen concentration are obtained. This technique is not a practical one since these nitrogen-solubilizing elements are also expensive and often scarce and higher concentrations of these elements may impart undesirable properties to the resulting alloy.

In spite of these difficulties, substantial benefits are obtained by increasing the nitrogen content of many alloys and a great deal of research effort has been directed to attempts to obtain higher nitrogen values. Previous efforts to solve the problem have not provided satisfactory results. Among the benefits resulting from the incorporation of nitrogen into alloys are those which may be obtained in the stainless steels. Nitrogen serves as an excellent replacement for nickel in austenitic stainless steels. Increases of a fraction of a percent in the nitrogen content will permit substantial reductions in the amount of nickel used in the alloy and yet provide an austenitic steel having comparable properties. This permits a substantial savings in the amount of the expensive and comparatively scarce nickel. In chromium grades of stainless steel nitrogen imparts fine and even grain structure, improved hardness, and greater strength and ductility at elevated temperatures. Nitrogen-bearing

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ing, 0.03% carbon, 18–8 stainless steel (18% chromium and 8% nickel) will provide stress rupture strengths in the 1200°–1500° F. temperature range which are comparable with those 18–8 type stainless steels which also contain columbium.

It is an object of the present invention to provide an efficient, reliable and economical process for introducing alloying elements or materials in gaseous form into alloys.

It is another object of this invention to efficiently, reliably and economically produce alloys, and particularly steels, such as the austenitic steels containing chromium and/or manganese, which shall contain a higher concentration of nitrogen than has heretofore been practical without incurring concomitant porosity or other undesirable characteristics.

It is an additional object to provide a cast alloy containing more than the normal saturated concentration of a gaseous alloying element homogeneously distributed throughout the casting without voids being present.

It is a further object of this invention to produce austenitic alloys more economically in which nitrogen is employed in place of some of the nickel as an austenitic-forming element.

Other objects and advantages of the invention will be apparent to those skilled in the art from the description which follows.

With these and other objects, features and advantages in view, the invention will be described in greater detail by reference to the accompanying figure of drawing which is a diagram of the melting furnace and appurtenant apparatus employed in the process.

As employed throughout this application and the discussion which follows, the term "alloying element" is intended to refer to the element per se, and to chemical compounds containing the element. Thus in the case of sulfur the element may be introduced into the alloy as an oxide of sulfur, such as the compound sulfur dioxide.

In the discussion which follows, the invention will be described primarily in connection with the employment of gaseous nitrogen as the gaseous alloying element or material. However, it will be readily understood that the process of the invention is applicable to other elements or materials in gaseous form. For example, sulfur may be introduced into an alloy in the form of a gaseous oxide of sulfur, such as sulfur dioxide, employing the process of this invention.

The process of this invention comprises a method for introducing economically, reproducibly and efficiently alloying materials in gaseous form, such as gaseous nitrogen, into alloys. In accordance with this process the gaseous material is introduced over the base alloy while the alloy is still in the molten state, or prior to melting the base alloy, and maintained over the alloy while it is cast. Maintenance of the gaseous alloying material over the alloy both while the latter is in the molten state and during casting and cooling constitutes an essential feature of this invention.

Preferably the atmosphere of air over the base alloy is removed as effectively as possible before the alloying gaseous element is added. This may be accomplished by vacuum melting techniques with which the art is familiar. Vacuum treatment removes most of the air and oxygen from the system and this assists in enhancing the solubility of nitrogen or other alloying element in the alloy. High vacuum treatment and refining of the alloy is preferred and pressures of about 10 microns of mercury or less are most satisfactory, although higher pressures, such as about 1 millimeter of mercury or higher, are also satisfactory. High vacuum treatment is preferred to higher pressures at this stage of the process since it permits more

rapid alloying of larger concentrations of the gaseous alloying element into the base alloy during the subsequent stages of the process.

After this vacuum refining of the base alloy, a nitrided alloy, such as nitrided ferro-chromium or nitrided manganese, is desirably added if the gaseous alloying element sought to be added is nitrogen. At about the time that the nitrided alloy is added, nitrogen gas is admitted into the evacuated system. Normally sufficient nitrogen, or other gaseous alloying element, is admitted to equalize atmospheric pressure (760 mm. mercury) although greater or lesser pressures are satisfactory. Preferably pressures in excess of 760 mm. of mercury are employed. Mixtures of gases containing nitrogen may be used but it is preferred to use substantially pure nitrogen since the solubility of the nitrogen in the alloy is somewhat dependent on the partial pressure of nitrogen in the system. The melting of the alloy is completed and any additional alloying materials added, after which the molten alloy is cast by pouring it into a mold and permitting it to cool and solidify. During the melting and casting operations the atmosphere of nitrogen is maintained. This process permits the incorporation of nitrogen in amounts in excess of the amount added in the form of the nitrided alloy and in excess of the amounts heretofore possible by prior art processes. The period during which the system is under an atmosphere of nitrogen gas may vary considerably, but short periods of from 6 to 35 minutes have proven satisfactory.

As an alternative to the above described embodiment, the atmosphere in the furnace over the cold, unmolten charge from which the base alloy is produced may be evacuated before melting the components of the base alloy. The gaseous alloying element or material is then admitted into the furnace until the pressure desirably reaches atmospheric pressure or higher and the heat is then melted, alloyed, cast and solidified under the atmosphere of the gaseous alloying element. Results similar to those of the previously described embodiment are obtained.

When alloying a base alloy with nitrogen gas, it is preferred, but not necessary, to supply part of the nitrogen in solid form, such as a nitrided alloy, as described hereinabove. Additions of the nitrided alloy along with gaseous nitrogen permit the alloying of larger concentrations of nitrogen into the base alloy more rapidly and efficiently.

In the practice of the process of the invention it is desirable to remove from the atmosphere above the molten alloy and solidifying casting as much as possible of the oxygen, hydrogen and water vapor which are normally present in the air. Although these gases may theoretically be considered as alloying elements, they generally impart undesirable properties to cast ferrous base alloys and it is therefore generally preferable to eliminate them from the system. By subjecting the system to high vacuum and then introducing the gaseous alloying element in relatively pure form, the elimination of the undesirable gases may be achieved.

The process of the invention may be further illustrated by referring to the diagram of the appended drawing. In the diagram, (H) is a standard vacuum furnace which houses a melting crucible (A) having a remote control pouring device, a tiltable tray or bin (F) to charge the crucible with nitrided alloy, and a mold (B) into which the molten alloy may be poured from the crucible and ingots cast. The heating of the crucible may be effected by means of a high frequency electric generator (G). The vacuum furnace is evacuated by means of a diffusion pump (C) in sequence with and augmenting a mechanical pump (D). The gas, such as nitrogen, is supplied by a tank (E) which is connected with the furnace by a suitable pipe or tube. The important feature of this vacuum furnace is that it permits retention of the nitrogen or

other gas over the alloy both while it is in the molten state and while it is being cast and cooled.

The process of the invention is applicable to ferrous and non-ferrous alloys of many types. Where the process is employed to introduce gaseous nitrogen as an alloying element, the invention is most advantageous for the production of the stainless steels, and particularly the austenitic stainless steels, such as those containing chromium, nickel and/or manganese, each of which may or may not contain nickel as an alloying element. The invention is applicable to the treatment of so-called 18-8 stainless steel, as well as straight chromium stainless steels.

It has been found that the nitrogen content which may be obtained in an alloy by practicing the process of this invention will vary somewhat depending upon several variables. The final concentration will be dependent upon the composition of the base alloy. Alloys containing a high total concentration of chromium and manganese tend to dissolve larger percentages of nitrogen. The process of the invention is particularly effective in increasing the nitrogen content of alloys having a high concentration of these elements and it has been possible to produce stainless steel ingots containing these metals which will contain about 0.6% to 0.7% nitrogen. The concentration of nitrogen is also somewhat dependent upon the degree of refinement of the molten metal and the amount of nitrogen introduced into the molten alloy in the form of nitrided master alloys. In general, the amount of nitrogen dissolved in the final alloy will increase when the nitrogen gas maintained over the alloy during melting and casting is maintained at higher pressures. The amount of nitrogen dissolved in the cast final alloy is also dependent upon the partial pressure of the nitrogen in the atmosphere over the alloy during melting and casting. The greater the differential between the partial pressure of the nitrogen in the metal and the nitrogen in the atmosphere above the metal, the greater is the tendency of the alloy to retain more nitrogen in solution. In most cases higher nitrogen contents are achieved when the melt is held under an atmosphere of nitrogen for longer periods of time. The amount of nitrogen dissolved will also depend upon the temperature of the molten alloy.

The successful results achieved by the process of this invention are believed to stem primarily from the fact that the gaseous alloying element, such as nitrogen, is held in solution during solidification, whereas in the processes of the prior art, which do not cast the alloy under an atmosphere of the gaseous alloying element, there is a marked decrease in solubility during solidification. For example, nitrogen is more soluble in the molten alloy than in the solid alloy. The nitrogen atmosphere provides not only a source of nitrogen to the alloy, but it assists in maintaining the nitrogen in solution because of the pressure of the nitrogen over the solidifying mass of metal. By means of the process of the invention it is possible to consistently provide alloys containing at least 0.3% of nitrogen. One of the important features of the invention is that it provides alloys containing more than the normal saturated concentrations of the gaseous element. Yet the gaseous alloying element introduced is homogeneously dissolved throughout the cast alloy or ingot rather than as a rind or surface concentration of the gas. This provides a highly homogeneous casting. When castings have been analyzed to determine the concentration of the gaseous element introduced during the process, it has been found that the concentration of the dissolved gas is substantially the same at all positions in the casting, whether the sample originated from the surface or the center of the casting. The castings are also substantially free of voids.

In order more clearly to disclose the nature of the present invention, specific examples illustrating the process will hereinafter be described. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the

invention nor limit the ambit of the appended claims. Unless otherwise stated, quantities of materials, including nitrogen and other alloying gases, are referred to throughout this application in terms of percent by weight.

Examples 1-10

Examples 1-10 describe the introduction of gaseous nitrogen into stainless steels in accordance with the process of this invention. Examples 1-7 describe the application of the process to molten steels containing chromium, nickel and manganese. Examples 8 and 9 describe the application to straight chromium stainless steels. Example 10 describes the treatment of a chromium-nickel stainless steel which also contains 1.2% aluminum. Each example is described in part by the table below. (The percentages of the elements contained in the molten base alloy and in the final cast alloy are given in the table. The difference between the total percentages of the elements given and 100% is made up of iron.)

TABLE I

Ex.	Percent Nitrogen Added as Nitrided Ferro-Chromium Alloy	Pressure of Nitrogen Atmosphere, mm.	Time Bath Under Nitrogen Pressure, min.	Carbon	Manganese	Silicon	Phosphorus	Sulfur	Chromium	Nickel	Molybdenum	Final Nitrogen Content
1.....	0.30	150	6	0.22	6.09	0.68	0.003	0.014	20.98	5.66	0.05	0.30
2.....	.45	680	20	.194	5.29	.67	.002	.012	20.68	5.46	.02	.44
3.....	.30	760	13	.194	5.29	.71	.003	.016	20.45	5.33	.03	.39
4.....	.45	+760	16	.224	5.26	.74	.004	.015	20.45	5.44	.02	.48
5.....	.45	+760	20	.248	6.30	.67	.005	.016	22.31	5.88	.02	.58
6.....	.45	+760	20	.192	5.85	.62	.005	.014	20.73	5.53	.01	.51
7.....	.45	+760	20	.238	9.99	.64	.004	.009	21.43	3.00	.02	.67
8.....	.13	740	12	.113	.72	.43	.003	.008	28.81	.05	-----	.37
9.....	.13	560	8	.153	.65	.51	.006	.017	28.77	.09	-----	.36
10.....	.40	+760	33	.21	1.28	.92	.007	.016	21.11	11.03	.02	.38
Aluminum...											2.12	

In each of these examples a base alloy containing iron and the other alloying elements listed in the above table (with the exception of nitrogen) were melted in the crucible of a vacuum furnace in accordance with the standard practice in the art. The vacuum furnace shown at (H) of the appended diagram was then evacuated by means of the diffusion pump (C) and mechanical pump (D) connected in series. The pressure was reduced to about 10 microns of mercury. In each example nitrided ferro-chromium alloy in sufficient quantity to introduce into the alloy the percentage of nitrogen found in the second vertical column of the table was introduced from the tiltable bin (F) into the melting crucible (A) which contained the molten base alloy. At about the same time, nitrogen gas was admitted into the vacuum furnace from (E) until the pressure of nitrogen was that listed in the table. The nitrogen atmosphere was maintained over the molten bath and the analyses of the alloys adjusted as needed and the molten alloys poured from the crucible into mold (B) and cooled. During the final melting and casting operations the nitrogen atmosphere in the vacuum furnace was maintained at substantially the same pressure. The time during which the bath was under nitrogen gas pressure in each example is stated in the table. The resulting ingots of the cast alloys were analyzed and found to contain the percentage of nitrogen stated in the column at the righthand side of each example in the table. As an indication of the excellent results obtained by the use of this process Example 7 in the table above should be noted. This cast alloy contained approximately 10% manganese and 21.43% chromium and had a final nitrogen content of 0.67%. The casting was perfectly sound without any indication of porosity.

Example 11

This example describes the introduction of sulfur in the form of sulfur dioxide into an alloy in accordance with the process of this invention.

A heat containing about 0.15% to 0.3% silicon, 0.013% sulfur, 0.15% to 0.3% chromium and the remainder iron was charged into a vacuum furnace. The furnace was evacuated to a pressure of less than 10 microns of mercury. The pressure was then increased to about 1 mm. of mercury by introducing sulfur dioxide gas. The charge was melted and maintained in this condition for about 2.3 hours. The pressure was then raised to about 600 mm. of mercury with helium gas and maintained at this pressure for about 0.15 hour. While under the combined atmosphere of helium and sulfur dioxide, final alloys of carbon and of manganese were added and the melt was then cast by pouring into a mold and cooling. During this casting operation the pressure in the furnace remained substantially the same. The final cast alloy was analyzed

and found to contain the following composition: 0.9% carbon, 1.6% manganese, 0.04% silicon, 0.004% phosphorus, 0.25% chromium, 0.02% nickel, less than 0.01% molybdenum, and the sulfur content was found to be 0.251% at the surface and 0.262% in the center of the cast ingot. The remainder of the alloy was iron.

The terms and expressions here employed are used as terms of description and not of limitation, and it is not intended, in the use of such terms and expressions, to exclude any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention.

What is claimed is:

1. A process for introducing a gaseous alloying material into an alloy, which comprises withdrawing the atmosphere surrounding the molten alloy, introducing the gaseous material over the molten alloy and then casting the molten alloy while in contact with the gaseous material.

2. A process as defined by claim 1, wherein the gaseous alloying material is sulfur dioxide.

3. A process for introducing a nitrogen gas into a steel, which comprises withdrawing the atmosphere surrounding the molten steel, introducing nitrogen gas over the molten steel and then casting the molten steel while in contact with the nitrogen.

4. A process as defined by claim 3, wherein the steel is a stainless steel.

5. A process as defined by claim 3, wherein the steel is austenitic steel.

6. A process as defined by claim 3, wherein a nitride is also introduced into the molten steel to provide an additional source of alloying nitrogen.

7. A process as defined by claim 3, wherein the gaseous nitrogen is introduced until a pressure of about 1 atmosphere of nitrogen is obtained.

8. A process as defined by claim 6, wherein the nitrogen content of the final cast alloy is at least 0.3%.

9. A process as defined by claim 1, wherein the surrounding atmosphere is withdrawn by evacuating the system to a pressure of less than about 1 mm. of mercury.

10. A process as defined by claim 1, wherein the sur- 10

rounding atmosphere is withdrawn by evacuating the system to a pressure of about 10 microns of mercury.

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