United States Patent Office 3,218,156 Patented Nov. 16, 1965

3,218,156

PROCESS FOR VACUUM DEOXIDATION OF ALLOYS

Jay L. Vander Sluis, Grand Haven, and Frank G. Vihtelic, Whitehall, Mich., assignors to Howe Sound Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Oct. 16, 1963, Ser. No. 316,513
8 Claims. (Cl. 75—49)

This is a continuation-in-part of our copending application Serial No. 296,078, filed July 18, 1963, and entitled "De-Oxidation of Alloys," and now abandoned.

This invention relates to a process for de-oxidizing metal alloys. The invention is particularly directed for use in the production of alloys which are prepared by means of vacuum melting techniques.

It is well-known that certain impurities in metal tend to closely affect the physical and mechanical properties of such metals. This is particularly true in the case of oxygen and many varied techniques have been devised for effecting de-oxidation of alloys containing detrimental amounts of oxygen.

In many instances, the use of vacuum melting techniques has been effective to reduce oxygen levels whereby the resulting alloys were suitable for certain applications. However, where maximum physical and mechanical properties are desired, vacuum melting alone has been found to be unsuitable for the preparation of the alloys. In such instances, de-oxidizing agents have been added to the melt whereby oxygen compounds could be formed which were less detrimental insofar as the properties of the resulting alloy were concerned. Elements commonly used as de-oxidizing agents include aluminum, titanium and zirconium. These elements form an oxide which has greater stability than the compounds normally included in the melt, and they also have a lower solubility whereby removal of some of the oxides is facilitated.

Known techniques employing de-oxidizers in the manner described above have, however, been unsuitable since in the case of vacuum melting, the oxides formed possess extremely low dissociation pressures. For this reason, a significant amount of the oxides cannot be removed from the melt by any practical method.

It is an object of this invention to provide an improved method whereby alloys having an extremely low oxygen content can be produced in an economical and efficient manner.

It is a more specific object of this invention to provide an improved technique for the production of alloys substantially free of oxygen wherein the processing is carried out in combination with vacuum melting operations.

These and other objects of this invention will appear hereinafter and it will be understood that the specific examples set forth herein are provided solely for purposes of illustration and not by way of limitation.

The method of this invention comprises a system for de-oxidizing alloys wherein the alloy is reduced to a molten state and subjected to a vacuum. As recognized by the prior art, this technique provides for removal of a substantial amount of the impurities within the metal. To provide for more effective purification of the melt, the present invention contemplates the addition of a small percentage of cerium which is adapted to preferentially combine with the oxygen contained in the melt. After the addition of cerium, a relatively high vacuum is effected whereby the cerium oxide and excess cerium will vaporize and dissociate from the melt.

In accordance with this invention, the amount of cerium added is between 0.01 and 0.5 percent by weight of the melt while amounts between 0.1 and 0.3 percent

are preferred. The application of vacuum over the melt is controlled whereby the initial melting operation is undertaken with a vacuum of greater than 100 microns of mercury whereby dissociation of a substantial amount of the impurities in the melt can be effectively undertaken. The cerium is added to the melt in the desired amounts after the pressure over the melt is increased to about 200 microns of mercury. The cerium is added at this time, and combination of the cerium with the oxygen is effected under these relatively high pressure conditions. Finally, the melt is subjected to a vacuum in the order of about 10 microns of mercury after the cerium has had an opportunity to go into solution and combine in the desired manner. By employing the low pressure above noted, the cerium oxide and excess cerium will dissociate from the melt to leave an extremely pure alloy.

With reference to the initial stages of the process, it is to be noted that the vacuum conditions prevailing can be maintained during the entire melting operation. On the other hand, it is contemplated that a melt be subjected to a vacuum for initial removal of impurities irrespective of the manner in which the initial molten state is achieved. Insofar as the other vacuum values above listed are concerned, it will be appreciated that variations thereof are contemplated. Thus, the initial vacuum is preferably high enough to remove a substantial amount of impurities; however, a previously purified melt may not require any extensive initial period. The cerium is to be added while employing a relatively low vacuum since it is necessary to maintain conditions whereby the cerium will go into solution and combine with the oxygen. The final vacuum stage, on the other hand, must be conducted at a sufficiently high vacuum whereby dissociation of the cerium and cerium oxide will be possible.

As noted, the cerium additions are undertaken at a pressure which permits the cerium to go into solution and combine with the oxygen. Introduction of an inert atmosphere is preferably effected to achieve an increase in pressure and the melt can be maintained under this atmosphere until after the cerium has gone into solution and the desired oxides formed. The final vacuum of 10 microns or less can then be effected in the same manner as described above. Addition of the cerium as pure cerium, in the form of rare earth alloys, or any other conventional manner is contemplated.

The instant invention has particular application to the casting of large heats of vacuum cast metal which will subsequently be used as remelt stock in producing vacuum investment castings. However, the invention also has application with respect to other vacuum melting practices where a reduction of oxygen in solution and dissolution of oxides in solution is desirable to improve the alloy properties both with respect to castability and with respect to physical and mechanical properties in the as-cast state. In the preparation of certain alloys, for example the so-called iron, nickel and cobalt base super alloys, long vacuum refining cycles have heretofore been common. The present invention provides for substantial reductions in such cycles since the reduction of the oxygen level depends on the reaction of cerium and oxygen and not on the slow process of out gassing the melt.

The following comprise specific examples of alloys which can be effectively prepared in accordance with the techniques of this invention. As previously indicated, the instant invention is particularly applicable to iron, nickel and cobalt base alloys which are used under conditions requiring high strength as well as substantial resistance to heat and corrosive atmospheres. In order to achieve the desired properties in such alloys, removal of oxygen has been a prime requirement. It will be understood, however, that in addition to the following types of alloys,

other alloys wherein oxygen presents a problem can be treated in accordance with the principles of this invention.

Example I

	Percent
Ni	70
Cr	12
W	5
Al	5
Mo	3.5
Ti, Nb, Ta	2.5
Fe	Balance

Example II

		Percent
C		.35–.45
Mn	max.	1.0
Si	max.	1.0
Cr		18.5–20.5
Ni		19.0–21.0
Co		42.0–44.0
Mo		3.5–4.0
W		3.5–4.0
Nb		3.5–4.0
Fe		Remainder

Example III

	Percent
C	0.5
Si	1.25
Cr	14.0
Ni	16.0
W	3.5
Fe	Balance

Example IV

	Percent
Co	60.0
Cr	20.0
W	10.0
Nb	2.0
Ni	1.0
Fe, C, Mn, Si	Balance

In a typical procedure for treatment of any of the above alloys, the constituents thereof can be first melted down using standard melting techniques and standard vacuum practices. The time necessary for initially refining the metal will vary with the individual melt practice, type of alloy, amount and nature of revert material used in the charge, condition of the melting plant, and on other obvious factors. The factors which are primarily considered when determining the length of the refining cycle are the vacuum pressure in the melting chamber and the melt temperature. Alloys are usually refined until a final vacuum pressure of about 15 microms of mercury is achieved with a reasonably low leak rate. A typical 1000 to 2000 pound melt will have a melt-down and initial refining cycle in the range of seven to 12 hours. It will be understood, however, that the initial refining cycle does not constitute a novel aspect of this invention.

A partial pressure of inert gas can then be introduced into the vacuum chamber to achieve a vacuum of about 200 microns or less. Cerium in amounts between 0.01 and 0.5 percent by weight of the melt and preferably in an amount between 0.1 and 0.3 percent is then added by introducing pure cerium or rare earth metal alloys into the melt. While maintaining the pressure at the last mentioned level, the cerium will go into solution and will combine with the oxygen whereby the cerium oxides are formed. A calculation regarding the amount of oxygen should be made whereby the quantity of cerium introduced will be at least sufficient to combine with this amount of oxygen. The time necessary for this reaction will usually be about 5 to 10 minutes.

Since the vapor pressure of cerium at 2600° F. is about 100 microns, the additions of cerium must be undertaken at a lower vacuum while the dissociation of cerium oxides and excess cerium must be conducted at a higher vacuum. As suggested by the above discussion, a pressure well above 100 microns is preferably maintained during the addition of cerium in order to insure that the cerium goes into solution and combines with the oxygen. On the other hand, a pressure in the order of about 10 microns of mercury is preferably maintained during the phase of the operation providing for dissociation of cerium oxide and excess cerium from the melt. When the desired removal of cerium oxide and cerium is completed, the metal will be ready for casting into ingot molds.

The time necessary for the dissociation of the cerium oxide can only be estimated since this time will vary, depending on the particular melt practice and facilities available. However, the cerium content of the melt can be analyzed during the melt cycle and the values obtained can be compared with the oxygen content of the initially refined metal. Since cerium additions will be controlled within the above ranges in accordance with the oxygen content of the initially refined metal, the progress of the formation of cerium oxide can be determined, and the time necessary for this phase of the operation can be, thus, accurately estimated. An average cycle on a 1000 pound melt will take from 25 minutes to two hours. The temperature of the melt will have a significant effect on the dissociation rate and the practice of the individual melt shop will, therefore, effect the exact time.

The system of the instant invention has been found to provide significant improvements in the physical properties of the alloys treated. The stress rupture life, impact properties, tensile properties, thermal shock properties, and corrosion resistance are all positively effected by the de-oxidation technique herein described.

The noted improvements are believed to result by reason of the reduction of deleterious oxides which has caused changes in the micro-structure of the treated alloys. By dissociating the metallic oxides from the melt in the manner described, the metal originally forming the deleterious oxides will go back into solution to serve its intended role as a solid solution strengthener, to enhance oxidation resistance, or for whatever other purpose it was added.

In the above description, reference has been made to the use of cerium; however, it will be understood that the addition of cerium can be effected in any conventional way, for example through the use of cerium alloys or other combinations. The use of Misch metal is cited as a particular mechanism for providing the necessary amounts of metal capable of reacting in the desired fashion. Other equivalents of cerium are also obviously contemplated. As used herein and in the aforementioned copending application, the term "equivalents of cerium" is meant to include the rare earth metals mainly, cerium, lanthanum, praseodymium, neodymium, illinium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, yttrium, ytterbium, scandium, lutecium. Excellent results are secured when yttrium is employed instead of cerium in the examples heretofore described and in corresponding amounts. The others of the rare earth metals can also be substituted for cerium in equivalent amounts.

It will be understood that various changes and modifications may be made in the above described procedures which provide the characteristics of this invention without departing from the spirit thereof particularly as defined in the following claims.

We claim:

1. A method for de-oxidizing an alloy comprising the steps of melting the alloy while maintained under a vacuum below 100 microns of mercury to thereby remove a substantial amount of the impurities therein, increasing the pressure over the melt above 100 microns of mercury, adding from about 0.01 to about 0.5 percent by weight rare earth metal to the melt whereby the rare earth metal will go into solution and combine with the oxygen therein, and reinstituting a vaccum below 10

microns of mercury whereby rare earth metal oxide and excess rare earth metal will vaporize and dissociate from the melt.

2. A method for de-oxidizing an alloy comprising the steps of melting the alloy while maintained under a vacuum below 100 microns of mercury to thereby remove a substantial amount of the impurities therein, increasing the pressure over the melt to about 200 microns of mercury, adding from about 0.01 to about 0.5 percent by weight rare earth metal to the melt whereby the rare earth metal will go into solution and combine with the oxygen therein, and reinstituting a vacuum in the order of about 10 microns of mercury whereby rare earth metal oxide and excess rare earth metal will vaporize and dissociate from the melt.

3. A method for de-oxidizing an alloy comprising the steps of melting the alloy while maintained under a vacuum below 100 microns of mercury to thereby remove a substantial amount of the impurities therein, increasing the pressure over the melt above 100 microns of mercury by introducing inert gas into the vacuum chamber, adding from about 0.01 to about 0.5 percent by weight yttrium to the melt whereby the yttrium will go into solution and combine with the oxygen therein, and reinstituting a vacuum below 10 microns of mercury whereby yttrium oxide and excess yttrium will vaporize and dissociate from the melt.

4. A method for de-oxidizing an alloy comprising the steps of melting the alloy while maintained under a vacuum below 100 microns of mercury to thereby remove a substantial amount of the impurities therein, increasing the pressure over the melt to about 200 microns of mercury, adding from about 0.01 to about 0.5 percent by weight cerium to the melt whereby the cerium will go into solution and combine with the oxygen therein, and reinstituting a vacuum in the order of about 10 microns of mercury whereby cerium oxide and excess cerium will vaporize and dissociate from the melt.

5. A method in accordance with claim 4 wherein the amount of cerium added is between 0.01 and 0.3 percent by weight of said melt.

6. A method for de-oxidizing an alloy comprising the steps of melting the alloy while maintained under a vacuum below 100 microns of mercury to thereby remove a substantial amount of the impurities therein, increasing the pressure over the melt above 100 microns of mercury by introducing inert gas into the vacuum chamber, adding from about 0.01 to about 0.5 percent by weight cerium to the melt whereby the cerium will go into solution and combine with the oxygen therein, and reinstituting a vacuum below 10 microns of mercury whereby cerium oxide and excess cerium will vaporize and dissociate from the melt.

7. A method for de-oxidizing an alloy comprising the steps of melting the alloy while maintained under a vacuum below 100 microns of mercury to thereby remove a substantial amount of the impurities therein, increasing the pressure over the melt to about 200 microns of mercury, adding from about 0.01 to about 0.5 percent by weight yttrium to the melt whereby the yttrium will go into solution and combine with the oxygen therein, and reinstituting a vacuum in the order of about 10 microns of mercury whereby yttrium oxide and excess yttrium will vaporize and dissociate from the melt.

8. A method in accordance with claim 7 wherein the amount of yttrium added is between 0.01 and 0.3 percent by weight of said melt.

References Cited by the Examiner

UNITED STATES PATENTS

2,144,200	1/1939	Rohn	75—49 XR
2,360,717	10/1944	Phelps	75—58

FOREIGN PATENTS

870,162	6/1961	Great Britain.

OTHER REFERENCES

Vacuum Metallurgy, Papers presented at the Vacuum Metallurgy Symposium of the Electrothermics and Metallurgy Division of the Electrochemical Society, October 6 and 7, 1954, Boston, Massachusetts, pages 100–105.

ASM Metals Handbook, 8th edition, vol. 1, published by American Society for Metals, Novelty, Ohio, 1961, pages 1227, 1230 and 1231.

BENJAMIN HENKIN, *Primary Examiner.*

WINSTON A. DOUGLAS, *Examiner.*