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METHOD OF IMPROVING THE PHYSICAL AND MECHANICAL PROPERTIES OF ALLOYS

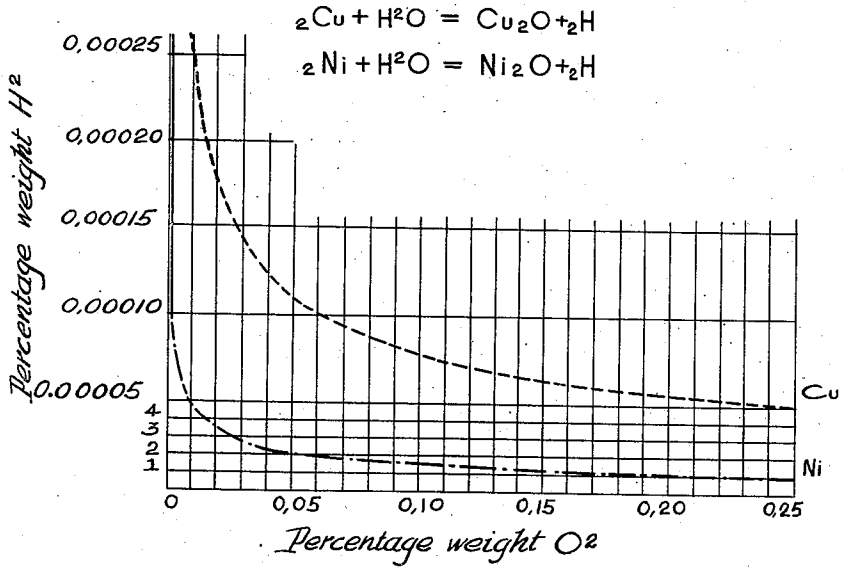
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Equilibrium between Hydrogen and Oxygen in Cu and Ni

according to the reversible reactions

$$_2Cu + H^2O = Cu_2O + _2H$$

$$_2Ni + H^2O = Ni_2O + _2H$$



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METHOD OF IMPROVING THE PHYSICAL AND MECHANICAL PROPERTIES OF ALLOYS

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It is known that gases absorbed during melting of metals and alloys adversely affect the physical properties thereof.

The most harmful gases are: H, SO_2, CO, and, to a certain degree, may be mentioned also the cyanide compounds, (CN), nitrogen, and CO_2.

These gases are dissolved in the metal because they are present in the flames during melting and because the bath possesses at the melting temperature a great dissolving power.

Absorption of the gases is not only due to the direct action in furnaces with naked flames, but also to a large extent in pot furnaces, because the walls of these pots, for example of graphite, can be traversed by large quantities of gas, which effects at high temperature a great diffusion thereof within the crucibles.

Absorption of the gases by the bath consequently modifies the quality of the metals obtained, which results generally in a decrease of breaking stress and of elongation.

In general, the absorbing power decreases very sharply on cooling, when the metal is in the solid state. The gases partly become free and form inter-crystalline cavities and, in numerous cases, serious pipes which give a non-homogeneous structure.

Various methods have been tried for eliminating the gases dissolved in the metal in melting and in foundries a large number of methods for the purification of the metals has been recommended. Thus, it has been attempted to remove the gas from the baths by using neutral gases, for example nitrogen, this nitrogen being passed through the bath in the form of a gaseous current.

In lieu of nitrogen, chlorine has also been employed which apart from the physical effect of entraining the gases present also performs a chemical action, since the formation of the chloride with the impurities present in the bath gives off volatile chlorides which escape from the bath.

Also, methods of oxidation used in known manner may provide sufficient removal of gases. In this case, the oxygen introduced into the bath containing reducing gases such as hydrogen, the solubility of which in copper is very great, forms water vapour which is hardly soluble in the bath, and permits sufficient purification.

In general, there is used an oxidizing agent in excess in order that, according to the law of action of the masses (Guldberg & Waage) elimination of the dissolved gases is effected with certainty. For example, in the case of copper refining, the bath is first oxidized, and even superoxidized, and finally receives a reducing treatment (poling for example) which eliminates the excess oxygen.

It is also known that in the case of "poling" in excess, new gases are introduced into the copper which can only again be eliminated by further oxidation.

The principles of purification by oxidation reside thus principally in this that an excess of oxygen must be employed in order to be sure of eliminating completely the impurities, and that this excess must be compensated for by a reducing medium. The sequence of purifying operations must thus be effected first by an oxidation, or even a superoxidation, and then by a reduction.

The object of the present invention is the purification rendered possible by a new, simpler and more exact process of degasifying molten metal baths by means of an oxidizing action.

It has recently been recognized that by observing exactly certain conditions the gaseous impurities in the bath could be completely eliminated by employing a quantity of oxygen substantially equal to that theoretically required to oxidize the gases present in the molten metal, which renders superfluous a subsequent reduction. There is thus obtained a notable improvement of the mechanical properties of the metal or alloy.

The present invention consists in a method of improving the breaking stress and elongation of metals, for example, copper, nickel, and their alloys, and particularly those which are produced by the melting of scrap metal, characterized by this that after melting, neutral or preferably slightly reducing conditions are first created in the furnace chamber above the molten metal due to a neutral or slightly reducing atmosphere, the flame in the furnace is then rendered oxidizing and there is added to the melted metal an oxidizing agent or agents not dissociated solely by heat at the temperature of the metal and in a quantity proportioned to the quantity of gaseous impurities present in the metal in such manner as to effect a selective oxidation of the said impurities, this oxidation taking place in the presence of a slag containing for example one or more compounds of barium and in the presence of a metal or metals less noble than the principal metal in the molten alloy.

By selective oxidation must be understood that

at the end of the treatment the impurities, including arsenic and antimony, will have been oxidized in the order of their affinities for oxygen under the temperature conditions existing at the time, the added base or less noble metal probably being the last to be oxidized; the quantity of oxide added being at least sufficient to carry out the necessary reactions, leaving the molten metal or alloy free from its gaseous impurities for all practical purposes and substantially free from oxygen.

The invention does not include the use of oxidizing agents which are practically or nearly completely thermally dissociated at the temperature of fusion of the metal or the alloys in question, as for example, chlorates, perchlorates, etc.

The method of carrying out the process employed is as follows:

The metals are first melted in a neutral or very slightly reducing atmosphere. Only in the cases where the charge already contains a large quantity of oxide, should melting be effected under highly reducing conditions. Quite different is the case where the charge contains a large quantity of reducing impurities. It happens, for example, with brass waste or special bronze that aluminium scrap is found mixed therewith. In such cases it is necessary, at the moment of melting, to work under oxidizing conditions and take precautions to cover the bath with a slag having a low melting point, in order that these impurities, at the moment of melting, are entrained in the slag. It should be observed that to come within the conditions of the method of the invention it is always necessary at the beginning of the said claimed method to work in a neutral or slightly reducing atmosphere.

It is absolutely essential to have in the bath during the subsequent selective oxidation a constituent which is less noble than the principal metal in the bath. This element will act as reducing agent. It will reduce any slight quantity of metallic oxide formed during fusion of the metal or of the alloy in the presence of the oxygen of the surrounding atmosphere and will serve as transporter of oxygen during reduction of the oxidizing substances added to the bath.

It is particularly advantageous, but not absolutely essential, that this less noble constituent should have a vapour pressure at the temperature of the bath. For example, in the case of nickel and nickel alloys the presence of manganese and of iron is found sufficient.

The metal which is most suitable is zinc, which, by the addition of an oxidizing agent, is oxidized into ZnO and which in this form acts on the hydrogen present.

In most of the ordinary alloys, as for example brasses and bronzes, zinc is already one of the constituents of the alloy and is contained in sufficiently large quantity in the bath. In other cases, as for example in pure tin bronzes, a small quantity should be added. It is sufficient in this case to make a small addition of a few tenths per cent in order to obtain equilibrium in the direction of complete elimination of the gases. After oxidation in the latter case the zinc is eliminated almost completely from the alloy.

Nevertheless, in the case where for technical reasons a content of zinc or of iron is not permissible, other substances should be used as additions, for example phosphorus, manganese, sodium or cadmium.

Before or during melting, the bath must be covered with materials intended to form the slag, which contain a barium compound. The selection of a barium compound has special advantages because on the one hand it serves to slag traces of sulphur existing in the bath, and also because the compounds of barium form particularly stable compounds with the existing impurities, so that these compounds which are most often of the third order (containing three elements) are completely absorbed by the slag, without any traces remaining in the bath.

These impurities are generally Sb—P—As—Zn, etc. and oxides thereof which react with barium to form antimonates, arsenates, phosphates, etc. hard to reduce but readily absorbed by the slag, as previously stated in the case of aluminum.

Of these compounds of barium, the carbonates come mainly into consideration, but fluorides, chlorides, nitrides can also be used, and finally the oxides and peroxides of barium may also be used. Nevertheless, most of these compounds having a high melting point do not permit of ensuring that the bath is completely covered. Therefore it is necessary to supplement them by other substance suitably chosen for the alloy treated, which substances lower the melting point.

To lower the melting point the addition of soda and potash has been found very favourable, since it forms with barium carbonate double carbonates which are not very stable and which permit the barium to react.

In lieu of soda, other fluxes, such as borax, or sodium fluoride, potassium fluoride, calcium fluoride, and so on may be used.

In lieu of barium compounds, strontium compounds may also be employed.

Calcium compounds which have often been recommended for this reaction are not found suitable for this purpose.

The bath should be subjected to a preliminary treatment, independent of the method claimed, in circumstances where, apart from the elimination of gaseous impurities, there is also present a large quantity of other impurities. This may happen for example when it is desired to eliminate a large quantity of aluminium by means of cryolite or other fluorides.

Sulphur plays a very special part, and it is part of the invention that, before the addition of slag described above, elimination of the sulphur should be effected, if the metal does not have as constituent tin, zinc or other desulphurizing media. This is the case in melting copper and cupronickel alloys. In this case SO_2 is increased by oxidation and the latter is soluble in the bath in such manner that complete degasification is not obtained. Elimination of the sulphur takes place only if, before the addition of the slag described above, there is added a mixture of compounds of barium, preferably barium carbonates, sodium carbonates, or other carbonates, with wood charcoal, maintaining a reducing atmosphere.

According to the present method, and while maintained reducing conditions, the sulphur is combined in the state of barium sulphide; this combination is so stable that it is possible by the linking of the reversible reaction.

$$BaO + MeS \rightleftarrows MeO + BaS$$

with reduction of the metallic oxide to eliminate all the sulphur of the bath. The bath must then be carefully skimmed in order that no trace of the barium sulphide remains in the slag during the succeeding oxidation operation, which gives

an inverse reaction and would carry the sulphur again into the bath.

In the copper alloys containing zinc and tin, the sulphur on the contrary combines to a large extent, from the start, in the form of tin sulphide or zinc sulphide. It then escapes as ZnS or it becomes SnS; in basic slag, stannate.

With neutral flames, the S combines partly into sulphide, partly into sulphite ($BaSO_3$).

In an oxidizing atmosphere, which is recommended according to the nature of the alloy, the sulphur is first transformed into $BaSO_3$ and then, by oxidation, into $BaSO_4$, and passes into the fluid slag or into an oxidizing atmosphere; it is particularly stable.

BaO_2 is specially suitable for this "precipitation" which oxidizes the $BaSO_3$ and transforms it into $BaSO_4$.

When the molten metal is in the desired condition for treatment by selective oxidation, an oxidizing agent or agents mixed with the slag is or are then added. The oxygen introduced with the oxidizing agent will be suitably proportioned to the quantity of impurities; for example hydrogen must be oxidized to the form of steam. This proportioning must be carefully effected, so that it will be certain, according to thermodynamic conditions of equilibrium to be fulfilled, to form water vapor and that no harmful quantity of hydrogen remains in the molten metal.

The process is carried out in the same way for other dissolved impurities, such as CO, cyanides, nitrides, carbonyls, and the like. The quantity of oxygen necessary should be calculated on the basis of the conditions of thermal equilibrium. In the accompanying diagram there is indicated an example giving the temperature of 1235° C. for copper, and 1465° C. for nickel, the quantities of hydrogen and oxygen in equilibrium in these metals. In the diagram the ordinates indicate the percentage of H_2 by weight in relation to the quantity of pure metal, and the abscissae the percentage of O_2 under the same conditions. It is easy to estimate on these curves the quantity of oxygen theoretically necessary to reduce the amount of hydrogen present in the metal to a negligible value. That is to say, by reference to the diagram the approximate quantity of oxygen initially present is determined by the intersection of the curve with the ordinate corresponding to the abscissa determined by analysis for the impurity. The quantity necessary to lower the impurity to a given percentage is now directly read from the curve on the corresponding ordinate. The difference in the quantities of oxygen thus determined represents the approximate amount which should be added at the beginning of the operation to lower the impurity to the desired percentage.

A matter of great importance in the process is that the quantity of oxygen necessary from the thermodynamic point of view should become available at the requisite temperature. It is not sufficient for example, as has been recommended by others, to employ a compound thermally dissociating at the temperature of fusion of the metals, liberating oxygen, but it is necessary that the oxygen should become available at the requisite temperature. It is necessary that the oxygen should react chemically with the reducing elements and the gaseous impurities present in the molten metal. For this purpose the products which act best are the metallic oxides such as CuO, ZnO, MnO_2, and so on, according to the alloy to be treated and its melting point.

If the quantity of oxygen for reaction is suitably chosen in the proportion which the concentration of impurities requires, there is obtained a selective oxidation which acts only on the gaseous impurities, without leaving a harmful excess of oxygen in the molten metal and without leaving an appreciable quantity of gaseous impurities.

These precautions depend on the equilibrium curves between hydrogen and oxygen in copper, nickel and their alloys. In other words, and for a given metal at a given temperature, the behavior of the corresponding curve indicates a minimum amount of oxide necessary to obtain an effective degasification.

In order to obtain the desired results great precautions should be taken, so that after melting the atmosphere may be neutral or slightly reducing.

After the oxidizing agent to which is added slag, for example $BaCO_3+Na_2CO_3$, has been introduced into the bath, the flame must be regulated, and maintained oxidizing to reduce the hydrogen formation by thermo-dissociation of water vapor. Further, by maintaining an excess of O_2 in the furnace atmosphere, the dissociation of H_2O which would liberate H is avoided.

In practice, it may be difficult to ascertain exactly the quantity of hydrogen, of CO and the like contained in the bath, which prevents exact determination of the quantity of oxidizing agent to be added. Empirical methods may be employed, since generally there is known the absorption of the quantity of gas, in melting, by a certain type of furnace, when the conditions of the flame, the time of fusion, the dimensions and quality of the charge are known, the quantity of absorbed gases remaining under these conditions almost constant.

Furthermore, as stated previously, the process is performed in practice with a quantity of oxidizing agents strictly necessary for eliminating gases, a fact herein disclosed in the case of copper at .05% oxygen for the elimination of hydrogen (or .25% CuO). This percentage is necessary for the removal of hydrogen but, in practice, it may happen that baths are encountered which are quite impure and include a large quantity of turnings, oil, etc., or the flame used for melting was of reducing nature. As a result, the percentage of occluded reducing gases (CO— hydrocarbons and eventually carbides, nitrides etc) in the bath is rather high and an addition of .05% O_2 or even .1% is not sufficient for a complete degasifying. Then, to save the bath, it is permissible to increase the addition of oxidizing agents to reach the required result; the process must be carefully watched, however, and test-pieces frequently taken to observe, by the break, the gaseous condition thereof. As known, the criterion is the segregation of tin in bronze, so that when a test-piece reveals traces of gas it is necessary to again add CuO (up to .2% for instance) whereas if the test-piece is homogeneous degasification may be considered complete.

For any charge, the composition of which is not exactly known, the optimum quantity of oxidizing agent can be ascertained by taking tests before or during melting. While these tests could obviously consist of a preliminary analysis of the charge to be treated from the point of view of its constituents and its impurities, for a sufficiently experienced practitioner these tests could be reduced to the removal of a test from the bath and an examination of its fracture.

The conditions during melting, that is to say, the admission of the gas or oil of combustion, the composition of the slag and the regulation of the flame during oxidation should be so selected that they cause no disturbing effect on the action of the oxidizing agent, and above all, no uncontrolled modification in the action of the oxygen introduced in exactly determined quantity.

Bronzes can contain as impurities H, CO in very small quantities, as also P, As, Sb. The quantity of oxidizing agent necessary to purify the bath of a bronze of this character will be calculated as follows:

(1) As regards hydrogen, the equilibrium curves of the kind annexed to this application, indicate that in order to reduce the concentration of hydrogen to a negligible quantity, it is necessary to have present in the bath a certain quantity of oxygen; for copper infusion at a temperature 1235° C. with a .1% of oxygen, that is to say, 0.5% of oxide of copper, the remaining percentage of hydrogen would be 0.000015% and would be considered as insignificant. Naturally the behaviour or appearance of the curves will vary according to the temperature of the bath used.

(2) Oxide of carbon is very little soluble in bronzes. It is admitted that this oxide of carbon is at its maximum of solubility and tests have demonstrated that a quantity equal to 0.1% of oxide of copper will suffice to remove this impurity with certainty from the bath.

(3) The quantity of oxygen and consequently of oxidizing agent required to eliminate the phosphorus, arsenic, antimony, are calculated from the following equations:

$$P_2+O_5 \rightarrow P_2O_5$$
$$As_2+O_3 \rightarrow As_2O_3$$
$$Sb_2+O_3 \rightarrow Sb_2O_3$$

a preliminary analysis having determined the quantities of these three elements which are present in the samples. The slag is chosen in view of the fact that it must be very fluid at the temperature of the bath so as to be easily capable of scorifying the non-volatile products of destruction of the impurities.

Naturally, the maintenance of a favourable casting temperature, the observation of details known by foundry experts, and the ordinary precautions are necessary to obtain the desired qualities in the metal.

In proportioning of the oxidizing agent, it should equally be observed if the waste already contains oxidizable components, such as for example As, Sb, it is necessary to make a corresponding addition of a supplementary quantity of oxidizing agent corresponding to the quantity of arsenic and antimony present in order to have sufficient oxygen available to effect selective oxidation of the gaseous impurities.

In following the above processes, there is obtained for different sorts of bronze, the undernoted values:

Quality of the alloy	Strength	Elongation
		Percent
Bronzes R. G. 10	30-37	25-50 (70)
Standard R. G. 9	28-32	20-50 (62)
German R. G. 5	25-30	20-40 (47)
G. B. 10	30-37	25-50 (65)
G. B. 13	28-36	8-20

The numbers in brackets are the maximum values which have been obtained.

These values are obtained, as should be pointed out on test pieces, untempered, cast horizontally in moist or dry sand; and these values have never been hitherto obtained.

The best qualities obtained result from the waste itself.

The special advantage of the process resides mainly in this that it is possible to obtain the values given by the use of charges containing 100% waste and shavings. The lower limit obtained is due solely to the presence of other impurities which it is not necessary to remove completely although it may be possible to do so by increasing slightly the duration of the reactions. Beneath are given several examples of the results obtained by the process:

(1) About 100 kg. bronze waste of the following composition:

	Per cent
Cu	85
Sn	8.7
Zn	5
Pb	1
Sb	0.1
Fe	0.2

were melted in a neutral or reducing atmosphere in a graphite crucible furnace.

When the charge is molten, the bath is covered with a mixture of about 1 kg. of barium and sodium carbonates. This mixture has substantially the same effects as known slags.

After having reached the casting temperature say about 1170° C. the flame is given an oxidizing character and the following oxidizing mixture added:

	Kilograms
Barium and sodium carbonates in the proportion of 1/1	0.5
CuO	0.5
BaO_2	0.15
MnO_2	0.15

This mixture melts in the bath and reacts on the impurities molten in the metal. As soon as the reaction is complete, i. e. after about 5 to 10 minutes, the metal is cast.

The test samples give according to the place from which they are taken:

25–30 kgs. breaking stress 20–33% elongation about 60 of Brinell hardness.

(2) 100 kgs. of bronze waste of the following composition:

Cu	89.6
Sn	9.8
Pb	0.4
Fe	0.2

is melted in a crucible furnace heated with oil. The flame is regulated to be either neutral or reducing.

Melting is obtained after about one hour and, at this moment, the bath is covered with about 1 kilo. of a mixture of barium and sodium carbonates in the proportion of 4–6.

As soon as the temperature of casting, say 1200°, is reached, an addition of 0.2 kg. Zn is made. The latter serves to introduce into the bath an element of less noble character. The flame is at the same time rendered oxidizing and the following oxidizing mixture is introduced:

	Kilograms
Mixture of barium and sodium carbonates in the proportion of 1/1	0.5
CuO	0.5

After several minutes, as soon as the reaction is complete, the metal is cast when there is carefully added 0.03 kg. phosphorus to compensate for the new introduction of oxygen into the bath when the metal is cast. The test samples taken give the following characteristic:

28/35 kg. breaking stress, 15/30% elongation, about 60 Brinell hardness.

(3) 100 kgs. copper waste, without special impurities was cast in a crucible furnace heated by oil in a neutral or reducing atmosphere.

There is added about 2 kgs. of a mixture of barium and sodium carbonates in the proportion of 1/1 and 0.4 kg. of pulverized wood charcoal, serving to cover the bath.

As soon as the casting temperature is reached, the bath is skimmed, the flame is rendered oxidizing and there is added 0.05 kg. phosphorus which serves, like the zinc in the preceding case, to give reducing conditions to the bath.

The addition of phosphorus in the copper is more favourable since the lowering of the conductivity is not so great as with the addition of zinc; at this moment the bath is at once covered by the mixture of:

	Kilograms
Barium and sodium carbonates in the proportions of 1/1	1
CuO	0.3

As soon as the reaction is complete and there have been added again 0.03 kg. phosphorus to compensate the oxidizing absorption during casting, the metal is cast. The test samples give a conductivity of 67%.

(4) 100 kgs. of waste of a Cu-Ni alloy with about:

Cu	80%
Ni	20%
Fe	traces
S	0.1

are melted in the same manner in a crucible furnace heated by oil with a neutral or reducing atmosphere. The bath is covered with 2 kg. of a mixture of barium and sodium carbonates in the proportion of 6–4 and of 0.3 kg. of pulverized wood charcoal. Immediately a large part of the sulphur is eliminated.

In order to eliminate the remainder, the bath is covered with the same mixture of barium and sodium carbonates and wood charcoal. This slag is then carefully skimmed.

The temperature of the bath has, in the meantime, reached the casting temperature, say about 1240°, the flame is rendered oxidizing and about 0.3 kg. manganese is added. This manganese serves, like the zinc and the phosphorus above, to introduce into the bath a component of a less noble character.

In connection therewith, the bath is covered with the following oxidizing agent:

	Kilograms
Barium and sodium carbonates in the proportion of 1/1	1
CuO with NiO	0.5

After the conclusion of the reaction which takes place in a few minutes, there is added a new addition of 0.3 kg. of manganese. This addition is effected in order to introduce into the alloy, as constituent, a little manganese, since the presence of this product in Cu—Ni alloys has been found very favourable for the subsequent treatment thereof. Moreover, there is also added 0.06 kg. Mg. and 0.003 kg. P which also serve to compensate for the introduction of new oxygen by the casting gate.

Although in all the present examples it has been indicated that the melting was effected in a crucible furnace, this melting process could be used with advantage in other types of furnace.

In these cases, the addition of oxygen should alone be regulated, since the absorption of gas during melting is varied.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed I declare that what I claim is:

1. Process for improving the physical and mechanical properties of non-ferrous metals and alloys, including those resulting from the remelting of old metals, said metals and alloys consisting of copper, nickel, and their alloys including bronzes, said alloys containing at least one impurity in the group consisting of H, CO, CO_2, N, and CN, which comprises melting the metals or alloys in a non-oxidizing atmosphere and under an alkaline slag consisting of alkaline substances selected from the group consisting of barium compounds, strontium compounds, and alkali metal compounds, adding to the molten bath while at least hot enough to flow an oxidation-preventing agent comprising at least one element less noble than the least noble dominant element in the molten bath unless such less noble element is already present, said less noble element selected being free from properties which would lower the physical and mechanical properties of the refined metal or alloy, thereafter subjecting said molten bath to the action of an oxidizing flame and adding to said molten bath a predetermined quantity of metal oxids selected from the group consisting of the oxids of Cu, Ni, Mn, and Zn, the quantities of the less noble element added being such that at least a trace thereof remains in the refined metal or alloy, and that the quantities of the oxids added are proportioned to the maximum quantities of gaseous impurities possible in the molten mass, and absorbing the excess oxids and reaction products by said slag.

2. Process according to claim 1, in which the less noble element is selected from the group consisting of Zn, Mn, Fe, P, Na, Cd, and Mg.

3. Process according to claim 1, in which the less noble element is selected from the group consisting of Zn, Mn, Fe, P, Na, Cd, and Mg, and the slag is composed of a mixture of an alkaline barium compound, and an alkaline alkali metal compound.

4. Process according to claim 1, in which the less noble element is selected from the group consisting of Zn, Mn, Fe, P, Na, Cd, and Mg, and the slag consists of a mixture barium carbonate, and at least the same weight of sodium carbonate.

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