

UNITED STATES PATENT OFFICE

2,008,731

TREATMENT OF EASILY OXIDIZABLE
ALLOYS

Philip T. Stroup, New Kensington, Pa., assignor
to Aluminum Company of America, Pittsburgh,
Pa., a corporation of Pennsylvania

No Drawing. Application July 24, 1934, Serial
No. 736,720

7 Claims. (Cl. 75—17)

This invention relates to the treatment of molten easily oxidizable metals and it is more particularly concerned with preventing excessive burning of aluminum base alloys to which certain elements are added that are especially susceptible to reaction with the air at elevated temperatures.

It is a matter of common metallurgical knowledge that certain elements such as the alkali and alkaline earth group of metals are attacked by air under ordinary conditions with the resultant formation of various non-metallic products. The severity of this attack increases with a rise in temperature until an actual visible burning or ignition may occur. The product of the reaction is a non-metallic appearing substance which, in the case of a molten metal bath, will float upon the surface. Molten alloys containing alkali and alkaline earth metals are also subject to burning, especially during the operation of adding the oxidizable element to the molten base metal. Under conditions frequently prevailing in foundries the base metal is melted and the alloying constituents added without any attempt to exclude air from contact with the molten charge. In consequence of this practice a thick dross scum accumulates on the surface which represents a loss of metal, especially the most oxidizable elements present in the alloy.

The production of an excessive amount of dross on molten alloys might not be particularly objectionable if no ill effects were carried over to the final product. Such is not the case, however, for particles of dross may become mixed with the metal when it is agitated to secure a uniform mixture of the alloying ingredients and later poured into the mold. The inclusion of insoluble, non-metallic particles in the solid metal may interfere with machining operations because of the existence of hard spots. Furthermore, the presence of particles imbedded in the matrix produces discontinuities in the metallic structure which are a source of weakness. In some instances the non-metallic impurities may serve as focal points for corrosive attack and thus tend to promote disintegration of the metal article. The production of dross also represents a loss of metal which is distinctly disadvantageous where small amounts of easily oxidizable elements are added to a base alloy and where it is essential to retain such elements in the alloy. Under ordinary melting conditions a large proportion may be lost through burning and the desired effect of the added element is not obtained or is greatly diminished. In addition to the

aforementioned deleterious effects of dross, the oxide skin formed on the stream of metal entering a mold may also hinder the flow of liquid metal and thus prevent the production of satisfactory castings.

The amount of dross or oxide scum produced by the addition of easily oxidizable elements to a molten base metal under normal conditions depends in large part upon the character of the furnace atmosphere in which the melting is done, the metal temperature, and upon the nature and amount of the elements added. A high furnace temperature with an abundant flow of air across the surface of the molten charge yields an excessive amount of burned product. Again there is a difference in susceptibility to oxidation among the various elements, some burning more readily than others. An appreciable amount of dross is usually formed under the conditions commonly prevailing in foundries and melting rooms. The reaction that occurs between the air and the added oxidizable element or subsequent alloy, where melting is done under normal atmospheric conditions, is herein referred to as burning or oxidation and is not limited to the sole production of oxides within the strict meaning of the latter term. Other constituents of the atmosphere than oxygen may react with the added element or alloy and form compounds other than oxides. The terms burning and oxidation are therefore employed in a broad sense to designate the general reaction and not the particular action of oxygen alone on the metal.

Various means of decreasing or preventing the burning of easily oxidizable metals have been tried with varying degrees of success. Such expedients as conducting the operations under a vacuum have been employed, but this practice requires special equipment which is expensive to maintain and operate. The use of a fused salt covering on the molten charge has been advocated as an effective means of preventing contact of the air with the oxidizable elements or alloys, but this method possesses certain inherent handicaps such as difficulty in maintaining the desired composition, drying before using, losses in melting, and removal of the fused mass from the molten charge prior to pouring into the mold.

One of the objects of my invention is to provide a simple but effective means of decreasing the burning of easily oxidizable elements when added to molten metals as well as the subsequently formed alloys. A further object is to employ a means of effecting the foregoing purpose without resorting to the use of special equipment or

technique in handling. Still another object is to decrease the burning without leaving any objectionable residue on the surface of the melt or intermingled with the metal itself. Another object is to use a means of diminishing burning which is devoid of water vapor and which constantly maintains its dry character. A further object is to provide a material for the desired purpose that is not noxious to the workmen.

My invention is based upon the discovery that when compressed solid carbon dioxide, commonly known as dry ice, is placed in thermal association with a molten charge under normal atmospheric conditions a copious, dry, protective atmosphere of carbon dioxide is produced which greatly diminishes, if it does not entirely prevent, a burning of the added element or oxidizable alloy. Carbon dioxide is comparatively inert in respect to reacting with readily oxidizable elements and hence it may be used as a means of protecting the element at the time of being added to the molten bath and the subsequently formed alloy against the action of the oxygen, nitrogen and water vapor in the air. It has heretofore been regarded as being extremely dangerous to bring a piece of solidified gas at a temperature considerably below the freezing point of water in contact with a body at an elevated temperature. Contrary to what might be expected in view of precautions hitherto exercised in handling a solidified gas we have found that dry ice may be safely placed on the surface of the molten charge without causing an explosion or eruption of the metal. The dry ice gradually sublimates and forms a protective layer of dry carbon dioxide gas next to the surface of the liquid bath thereby substantially preventing access of air to the molten metal. The gas is evolved rapidly enough to maintain a fresh supply of carbon dioxide next to the metal that is undiluted with air.

Dry ice and the carbon dioxide atmosphere derived therefrom possess certain properties which afford distinct advantages over former attempts to utilize this gas as a means of protecting an oxidizable metal against oxidation. For example, exhaust combustion gases containing carbon dioxide have been tried as a protective atmosphere but the high temperature of the gas and the presence of other constituents, notably nitrogen and water vapor, have not served to give the desired degree of protection. I have found that water vapor is a particularly insidious constituent of the atmosphere that promotes attack of the metal. Even carbon dioxide which is ordinarily commercially available in compressed or liquid form in steel cylinders is contaminated with water vapor in sufficient amount to render it undesirable for use in preventing the oxidation or burning according to my tests. The only practicable method heretofore employed to extract water vapor from a furnace atmosphere has been to pass it through a dehydrating apparatus but this practice has been objectionable from a commercial standpoint because of the expense involved.

In contrast to the foregoing difficulties associated with the use of a protective atmosphere of carbon dioxide I have found that dry ice provides a readily available and convenient source of the dry cool gas. The gas is more easily handled in solid form since no special equipment is required to control the flow of gas or its introduction into the furnace chamber or about the crucible holding the liquid metal. It is only necessary, for example, to place a small piece of the solid mate-

rial on the surface of the metal bath, and a protective atmosphere of high efficiency is quickly created. The gas evolved is initially very cool since it sublimates from the solid at a temperature of about -78°C . By reason of the fact that the gas is cold it is heavier per unit volume than the same gas at an elevated temperature and it therefore tends to stay near the surface of the metal for a longer time. The low temperature of the gas in itself also tends to hinder any reaction since the reaction rate usually increases with a rise in temperature. The dry ice, furthermore, contains no water vapor in amount sufficient to promote oxidation as far as I have been able to detect. The use of dry ice offers still other advantages in that no residue is left after sublimation of the gas and no cleaning of the metal handling equipment is required after each heat because of the accumulation of any reaction product. The concentration of the gas near the melting pots under ordinary conditions is not great enough to be disagreeable or injurious to the workmen.

In the application of my discovery to the treatment of molten metals, it is not absolutely necessary that the solid carbon dioxide be actually placed on the surface of the bath in order to afford protection against burning. It is only essential that the dry ice be placed in such thermal association with the molten charge that heat from it, or the furnace heating means, causes a relatively rapid and abundant evolution of gas, and that such gas effectively covers the exposed surface of the metal. I have found that placing the solid material directly on the surface of the molten metal is a very satisfactory method of providing a protective atmosphere at the metal surface. When the dry ice has been used on a crucible or container filled with metal and the metal is subsequently poured into a mold, the protective atmosphere tends to follow the molten stream and prevent burning. A more effective method of protecting metal in the mold is to place pieces of dry ice near the mold openings prior to pouring the metal thus permitting the mold cavity to become completely filled with the gas before the metal is introduced. The low temperature and greater specific gravity of the gas cause the carbon dioxide to settle down in the mold and displace the lighter and warmer air.

It is not essential that a carbon dioxide atmosphere be provided during the entire period of melting and adding of alloy ingredients where the base metal of the alloy does not burn readily. In making an aluminum-magnesium alloy, for example, we have found that the dry ice need not be employed until just prior to the addition of magnesium. Magnesium and similar readily oxidizable metals are usually added shortly before casting the alloy, hence the carbon dioxide need be used for only a brief period of time between the addition of such alloying constituents and pouring of the metal into the mold.

The dry, relatively cool carbon dioxide atmosphere is also useful in protecting the alloy after the easily oxidizable element has been added. Burning can be prevented as long as desired by maintaining some solid carbon dioxide on the surface of the melt. It is also desirable to employ a protective atmosphere of carbon dioxide when remelting the alloy, and dry ice may be conveniently used for this purpose.

The amount of dry ice used must be sufficient to provide a continuous and copious supply of gas which will keep the air away from the metal. The constant evolution of a fresh supply of car-

bon dioxide will also prevent adulteration with air at the metal surface. The actual quantity of dry ice required for a particular charge of metal depends upon the area of the surface exposed to the air, the length of time needed to dissolve the added alloying elements, and the temperature of the bath. In the case of treating aluminum base alloys I have found that about 5 $\frac{1}{4}$ pound of dry ice per square foot of exposed surface is enough to protect the alloy against 10 burning for a period of several minutes. In using the solid carbon dioxide I have found it preferable to employ comparatively small pieces, and add them from time to time rather than to place a large piece in contact with the metal which 15 would yield the same amount of gas. Dry ice of commercial purity is satisfactory for our treatment of easily oxidizable metals and alloys. The term dry ice as herein employed is merely a convenient designation of solid carbon dioxide and is not intended to indicate any particular source or method of manufacturing solid carbon dioxide. 20

The easily oxidizable elements herein referred to include potassium, sodium, magnesium, lithium, 25 calcium, barium, strontium, beryllium, phosphorus, arsenic, selenium, tellurium and others of a similar nature which burn in contact with the air when added to a molten metal bath. The term oxidation or burning is here understood to mean the reaction of the foregoing elements with 30 any one or all of the constituents normally found in the air or in a furnace atmosphere. Aluminum base alloys within the purview of this invention are those that contain 50 per cent or more of aluminum. Aluminum or any other metal constituting the predominant portion of an alloy is regarded as being the base metal of the alloy. In referring to the melting of an alloy in the appended claims, this term is to be understood as 35 comprehending both the initial preparation of the alloy, that is, the addition of alloying constituents

to the molten base metal, and to holding the prepared alloy in a molten state or remelting the alloy after it has once solidified. The product of the melting operation may be conveniently referred to as the melt and is herein employed in that sense. 5

I claim:

1. A method of treating easily oxidizable metals to produce a molten alloy thereof comprising placing solid carbon dioxide on the surface of the 10 melt.

2. A method of treating aluminum to produce a molten alloy containing easily oxidizable elements comprising placing solid carbon dioxide on the surface of the melt. 15

3. In the process of melting an alloy containing easily oxidizable elements the step of placing solid carbon dioxide on the surface of the molten charge. 20

4. In the process of melting an alloy containing easily oxidizable elements the steps comprising placing solid carbon dioxide on the surface of the molten charge and generating a dry relatively cool atmosphere of carbon dioxide. 25

5. A method of protecting an alloy containing easily oxidizable elements against burning during the melting operation comprising placing solid carbon dioxide on the surface of the molten metal. 30

6. A method of protecting an alloy containing easily oxidizable elements against burning comprising maintaining solid carbon dioxide on the surface of the molten charge and generating a dry relatively cool atmosphere of carbon dioxide. 35

7. A method of substantially preventing access of air to an alloy containing easily oxidizable elements while being melted comprising placing solid carbon dioxide on the surface of the molten charge to provide a dry relatively cool atmosphere of carbon dioxide.

PHILIP T. STROUP.