Feb. 14, 1967 F. S. DEATH ET AL 3,304,169

METHOD OF DEOXIDIZING METALS

Filed Oct. 1, 1963 3 Sheets-Sheet 1

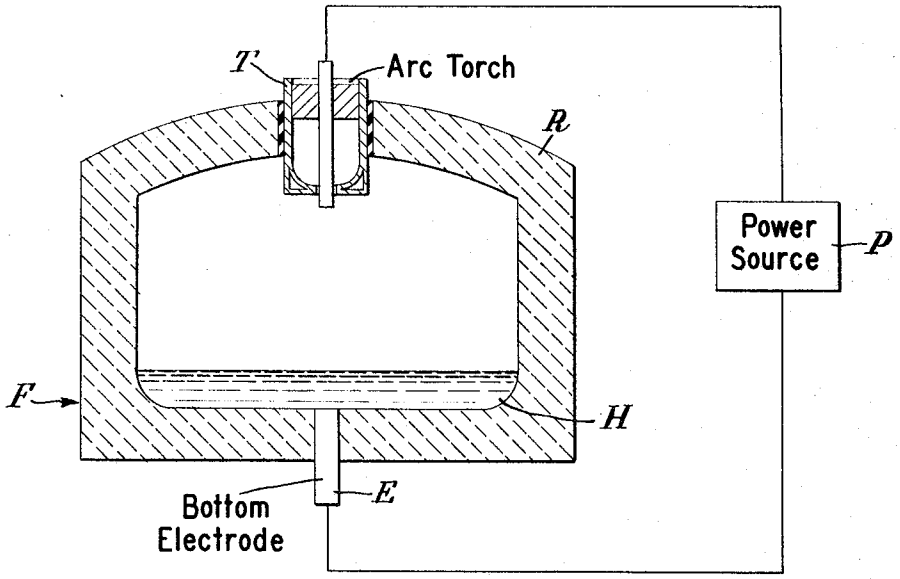


Fig. 1.

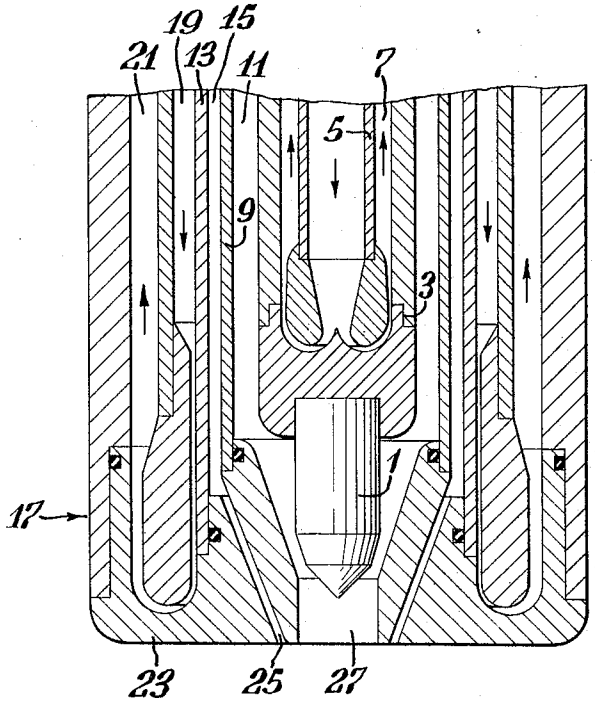


Fig. 2.

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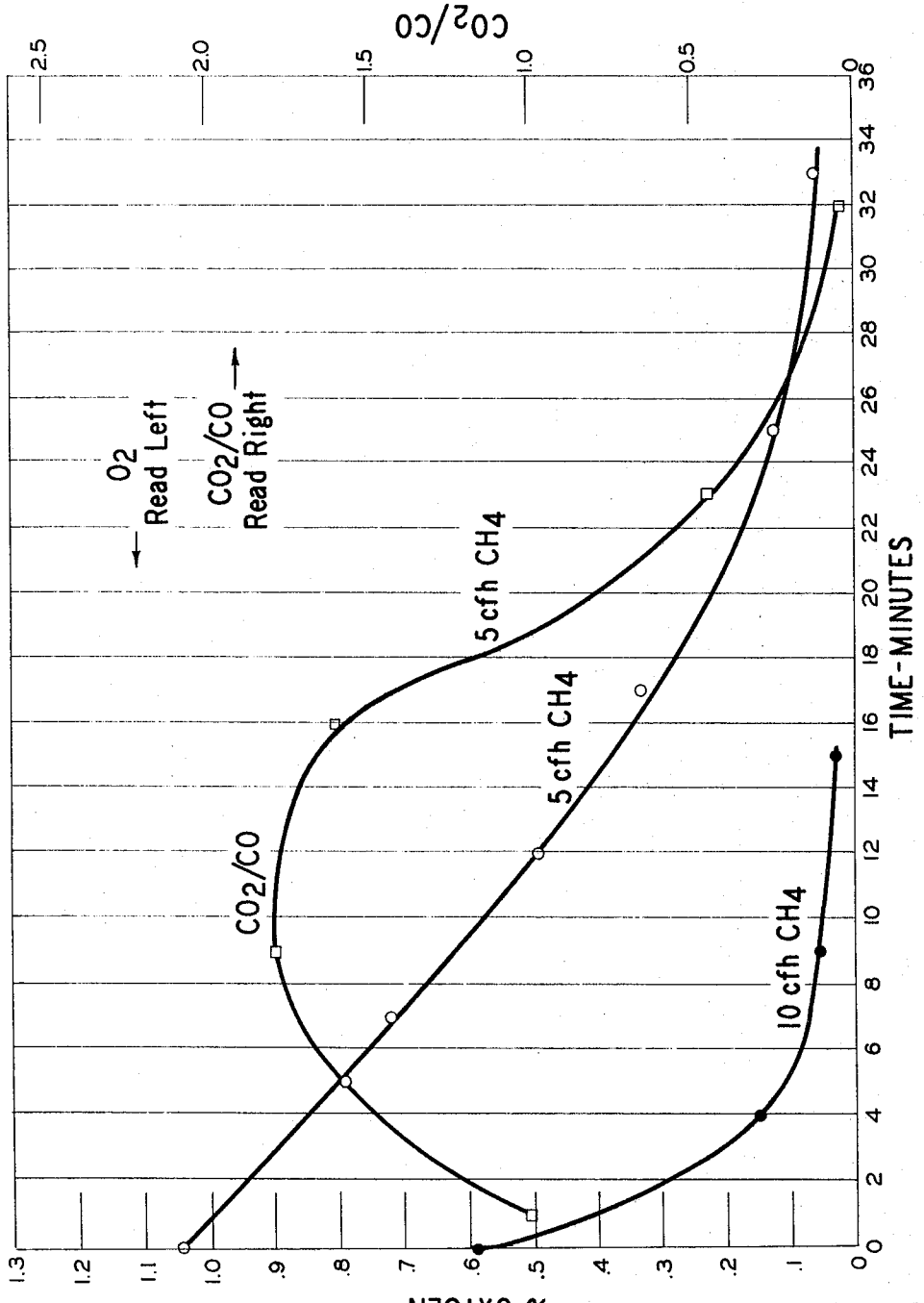


Fig. 3.

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METHOD OF DEOXIDIZING METALS

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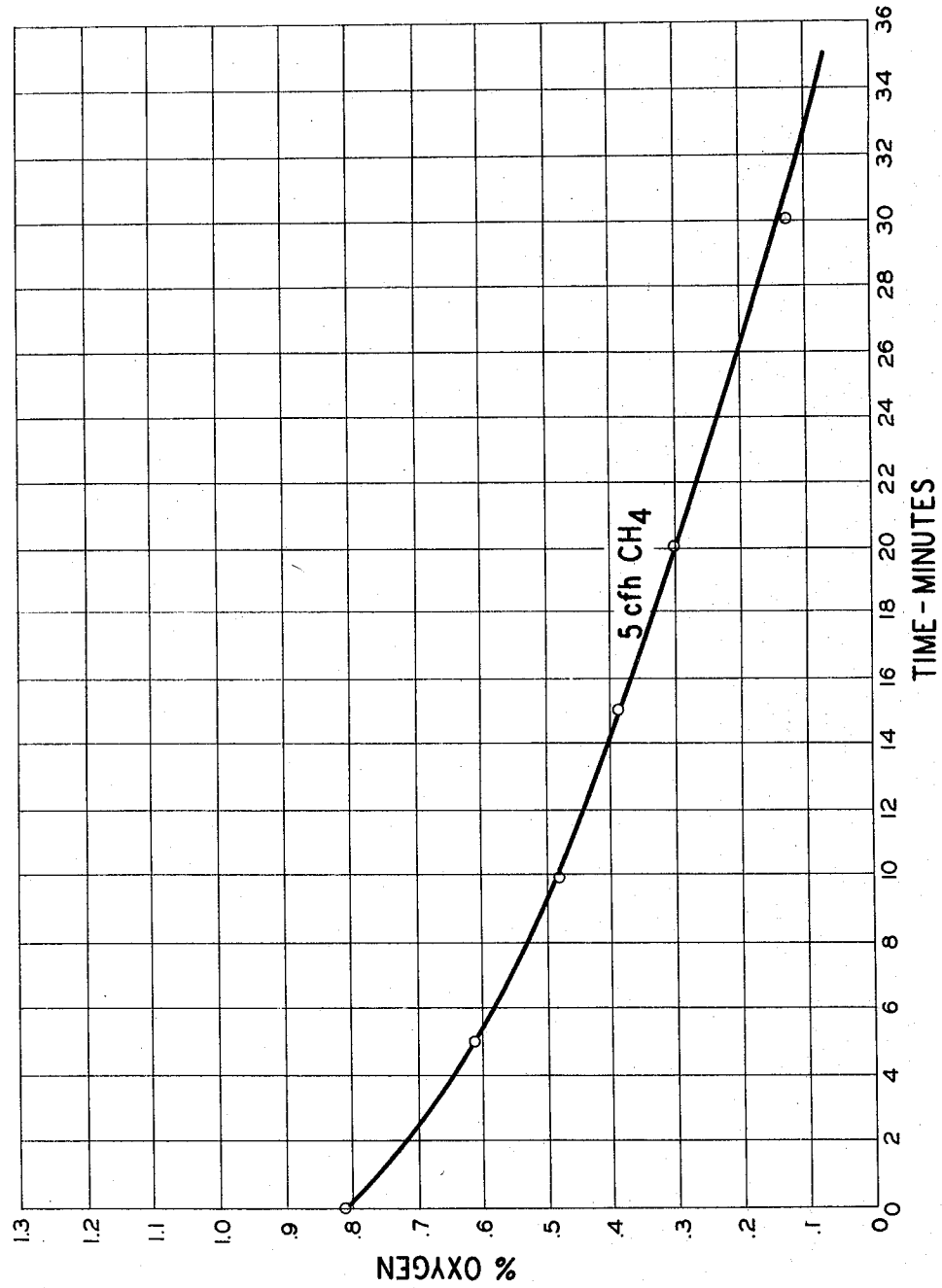


Fig. 4.

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METHOD OF DEOXIDIZING METALS

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5 Claims. (Cl. 75—10)

This invention relates to a method for deoxidizing metals and more particularly to such a process for deoxidizing metals having a low solubility for carbon. Typifying the metals contemplated by this invention are metals such as copper, silver and gold.

A particularly useful application of the process of the invention is in copper smelting. Accordingly, the discussion and following description will be directed to a process for deoxidizing copper which has utility as a step in copper smelting. However, the scope of the invention is not to be interpreted as being restricted to this specific metal.

Conventional copper smelting involves several pyrometallurgical steps in which copper concentrate melting first takes place to separate the iron-copper sulfides from gangue minerals. Next, exothermic air blowing in separate vessels called converters is employed to oxidize the sulfur and iron, with sulfur being removed in the form of sulfur dioxide gas and iron going into the slag as ferrous oxide. The remaining copper, called "blister copper," contains small amounts of sulfur and iron; along with silver, gold and trace amounts of impurities such as arsenic, antimony, bismuth, lead, selenium and tellurium. Ordinarily, refining of "blister copper" involves the following sequence of operations: (1) fire refining in a reverberatory furnace from which anodes are cast for further purification by electrolytic techniques, (2) electrolytic refining to recover precious metals and remove impurities, and (3) a second fire refining to produce copper with the physical properties required for industrial use.

In fire refining, the "blister copper" is oxidized by air blowing to remove traces of sulfur, iron, and other impurities. The dross-like slag which is formed is rabbled off (removed with an iron scraper or rake called a rabble) to be recycled to the converter. At this point, the melt, termed "set copper," will have an oxygen content of up to 0.8%, which is contained as atomic oxygen at the fire-refining temperatures. On solidification, a copper-cuprous oxide eutectic is formed which hampers further refining. Accordingly, the oxygen content has traditionally been lowered to the range of 0.2–0.3% by "poling," that is, by thrusting green tree trunks into the bath—a technique which is dirty, dangerous and archaic, although up until now, difficult to improve on. In "poling," the heat of the bath causes destructive distillation of the wood with the evolution of hydrogen, hydrocarbons, carbon monoxide and water vapor. These gases cause violent agitation of the bath and bring about effective deoxidation.

Following the initial fire refining and "poling," anodes are cast, and these are subjected to electrolytic refining in an electrolysis process in which copper goes into solution from the anode and is redeposited in a purer form at the cathode. The cathodes from the electrolytic refining are usually remelted and subjected to a second fire refining in which additional deoxidation may be required. If remelting is done in a conventional furnace, then oxidation of the melt results from contact with the atmosphere so that "poling" is again required. The product from this "poling" step is termed "electrolytic tough-pitch copper" and will have an oxygen content of 0.02 to 0.05%.

Accordingly, it is a main object of the invention to provide a process for reducing the oxygen content of an oxidized metal having a low solubility for carbon.

Another object is to provide a process for the deoxidization of copper.

Yet another object is to provide an electric arc process for deoxidizing copper wherein a hydrocarbon gas is introduced into the arc effluent providing the deoxidizing agent.

Still another object is to provide a simple convenient method for eliminating "poling" in conventional copper melting.

These and other objects will become apparent from the following description and drawings in which:

FIGURE 1 is a cross-sectional view of typical apparatus for carrying out the invention;

FIGURE 2 is a partial cross-section of a typical arc device for carrying out the invention;

FIGURE 3 is a graph showing deoxidization curves and carbon dioxide to carbon monoxide ratio obtained using the process of the invention; and

FIGURE 4 is a deoxidization curve obtained using the process of the invention on a larger quantity of copper.

Generally, the objects of the invention are accomplished by providing and maintaining a molten metallic bath containing the metal to be deoxidized, establishing an electric arc between a non-consumable electrode and said molten metallic bath, flowing a hydrocarbon containing gas through a nozzle having at least a central bore the longitudinal axis of which is aligned with the arc column; introducing the hydrocarbon containing gas into the arc column; directing the hydrocarbon gas containing arc column directly onto the surface of the molten metallic bath whereby the highly reactive products from the hydrocarbon react at the metal surface with the oxygen contained in the molten metallic bath.

In the broadest aspects, the invention contemplates introducing the hydrocarbon gas into the arc column before the arc passes through the nozzle as well as introducing the hydrocarbon gas into the arc column after it passes through the nozzle.

The invention is predicated on the discovery that when a hydrocarbon gas, typically methane is intimately mixed with the plasma of a directionally stable arc the dissociation product from the hydrocarbon, gaseous carbon and hydrogen are transported in a highly reactive state by the arc plasma to the melt surface and react with oxygen which diffuse from the bath to form reaction products.

For purposes of this disclosure, the term "directionally stable arc" is defined as an arc column the longitudinal axis of which will maintain the direction originally imparted to it.

There are several methods of producing and maintaining directionally stable arcs. Examples of directionally stable arcs of the type contemplated by our invention are described in Gage, U.S. Patent 2,806,124 and in U.S. patent application Serial No. 223,484, filed September 13, 1962, to Robert J. Baird.

The advantages of using a directionally stable arc include providing a simple method of controlling power to the bath by changing arc length; providing an arc column which can be directed to the location desired and providing a means for transporting the deoxidizing agents to the molten bath in a highly reactive state.

Typical apparatus for carrying out the invention is shown in FIGURE 1. A typical example of the invention will be described in referring to FIGURE 1 so that those skilled in the art might clearly understand how to carry out the process of the invention.

Referring now to FIGURE 1, a device for producing a directionally stable electric arc is positioned in the roof R of a furnace F. A bottom electrode is positioned in the bottom of the furnace. Power for the electric arc is provided by source P, such as a conventional direct current

power supply. The particular furnace design is any suitable electrical furnace and forms no part of the present invention.

In greater detail, a typical device for producing a directionally stable arc is shown in FIGURE 2. In this figure, an electrode 1 is carried by a hollow holder 3 having a baffle 5 positioned therein. Cooling water enters the baffle and leaves the holder through the passage 7 formed by the baffle and walls of the hollow holder. A first tubular member 9 surrounds the electrode holder and forms therewith an arc gas passage 11. A second tubular member 13 surrounds the first tubular member and forms a hydrocarbon gas passage 15 therebetween. This entire configuration is surrounded by a water jacket 17 having passages 19 and 21 for water in and water out, respectively. Depending from the plurality of tubular members and sealing the forward end of the water jacket 17 is a nozzle 23 having passages 25 arranged symmetrically and which are in registry with the hydrocarbon passages 15. Also provided in the torch is a central bore 27, the longitudinal axis of which is in axial alignment with the electrode 1.

In actual operation, the copper to be deoxidized is provided to the hearth H of the furnace F. A transferred straight polarity D.C. arc is established between electrode 1 and the bottom electrode through the metal charge. The necessary power required to bring the copper to temperature, about 1200° C., is provided by the directionally stable arc and control over the power is obtainable simply by varying the arc length or the current of the directionally stable arc. An arc gas such as for example argon, helium, nitrogen, hydrogen and carbon monoxide is passed through passages 11 and together with the arc passes out of the torch through the bore 27 of nozzle 23 as an arc plasma.

It is possible and in fact is preferred to use the hydrocarbon gas as the arc gas and eliminate the need for argon. In such case, the hydrocarbon gas would be introduced into the arc column before such column passes through the nozzle 23. The important criteria in either case is that the hydrocarbon be introduced into the arc and that the dissociation hydrocarbon products be carried in a highly reactive state to the molten metal surface by such arc.

The arc plasma carrying the reactive products of hydrocarbon dissociation are directed to and directly impinge on the molten copper bath where deoxidization takes place and the oxygen readily diffuses from the bath to the surface. The presence of a slag layer on the bath must be avoided since direct contact of the arc plasma with the molten copper is essential. Most of the deoxidation occurring in this process is attributable to carbon, although both carbon and hydrogen function as reducing agents. Carbon is only slightly soluble in molten copper so that it does not permeate the melt but reacts with the oxygen at the melt surface.

The novel method of deoxidizing molten copper disclosed herein provides a preferred alternative to the conventional technique of "poling" which is capable of producing not only "tough-pitch" copper but also "oxygen-free-high-conductivity" copper. Arc torch deoxidation of copper not only eliminates such undesirable features of "poling" as the possible hazard from the violent action within the furnace and the necessity for storing and handling wooden poles and provides instead a flexible, efficient and easily controlled process; but also provides a very significant reduction in operating costs.

The following is an example of experiments wherein oxygen content of copper was reduced to very low levels, less than 0.02% oxygen. Forty pounds of copper having an oxygen content of over 0.5% were melted with a transferred straight polarity arc operated with an argon flow of 90 to 95 c.f.h. at 40 volts. Methane was then introduced through gas passages arranged symmetrically around the bore of the nozzle at a fixed flow rate to give a total gas flow of 100 c.f.h. The voltage was 50 volts. Deoxidation progress was followed both by gas chromatographic analysis of the off-gas and by taking pin-tube samples from the bath. FIGURE 3 shows the oxygen content as a function of time for each of two deoxidation tests making up this experiment. For the run in which 5 c.f.h. methane and 95 c.f.h. argon was used, it can be seen that the oxygen was reduced to less than .1% oxygen. Chromatographic analyses were obtained and the ratio of CO_2/CO in the off-gas is also shown. Results obtained with 10 c.f.h. methane and 90 c.f.h. argon are also plotted.

Consideration of the results shown in FIGURE 3 indicates that the process of this invention provides an effective means for rapidly reducing the oxygen content of molten copper to very low levels.

A second experiment analagous to the one just described except that a fifty pound rather than a forty pound melt was used. FIGURE 4 shows the oxygen content of the bath as a function of time for the deoxidation step utilizing 5 c.f.h. of CH_4 and 95 c.f.h. argon.

Operating variables in an arc deoxidation process include total arc gas flow rate and the ratio of hydrocarbon or reactive gas to inert gas. The experimental results that have been obtained indicate that even with a moderate plasma flow, it should be possible to deoxidize to the required oxygen level in a period that is short relative to the time required for "poling." Thus, it would not be necessary to operate the torch at very high reactive gas flow rates and the total flow could be set at that level which gives optimum arc characteristics. Increasing the ratio of hydrocarbon gas to argon in the plasma at a fixed total flow rate would also decrease the time for deoxidizing a bath. More importantly, increasing the proportion of hydrocarbon results in improvement in the economics of the process, since it minimizes the requirement for argon. The optimum process would be that in which the torch is operated with a gas consisting entirely of hydrocarbons, thus eliminating the argon cost entirely.

What is claimed is:

1. Method of deoxidizing metals taken from the group consisting of copper, silver and gold which comprises providing and maintaining a molten metallic bath containing said metal to be deoxidized, establishing an electric arc between a non-consumable electrode and said molten metallic bath, supplying an arc gas into said arc, flowing a hydrocarbon contaning gas through a nozzle having at least a central bore, the longitudinal axis of which is aligned with the arc column, and introducing said hydrocarbon containing gas into said arc column, directing said hydrocarbon gas containing arc column directly onto the surface of said molten metallic bath, whereby the carbon deoxidizes the metal being treated.

2. A method of deoxidizing metals taken from the group consisting of copper, silver and gold which comprises providing and maintaining a molten metallic bath containing said metal to be deoxidized, establishing an electric arc between a non-consumable electrode and said molten metallic bath, flowing an arc gas along said non-consumable electrode, surrounding at least a portion of said arc and flowing arc gas with a water-cooled nozzle, introducing a hydrocarbon gas into the arc and arc gas stream, impinging the hydrocarbon gas containing arc effluent onto the surface of the melt to be deoxidized whereby at least the carbon acts to deoxidize said metal.

3. Method of deoxidizing metals taken from the group consisting of copper, silver and gold which comprises providing and maintaining a molten metallic bath containing said metal to be deoxidized, establishing an electric arc between a non-consumable electrode and said molten metallic bath, introducing a hydrocarbon gas into said arc, passing said hydrocarbon gas containing arc column through a nozzle having at least a central bore the longitudinal axis of which is aligned with the arc column, directing said hydrocarbon gas containing arc column directly onto the surface of said molten metallic

bath whereby the carbon deoxidizes the metal being treated.

4. Method according to claim 3 wherein the hydrocarbon gas is methane.

5. Method of deoxidizing metals taken from the group consisting of copper, silver and gold which comprises providing and maintaining a molten metallic bath containing said metal to be deoxidized, establishing an electric arc between a non-consumable electrode and said molten metallic bath, supplying an arc gas taken from the class consisting of argon, helium, nitrogen, hydrogen, and carbon monoxide into said arc column, flowing a hydrocarbon gas through a nozzle having at least a central bore,

the longitudinal axis of which is aligned with the arc column, introducing said hydrocarbon gas into said arc column, directing said hydrocarbon gas containing arc column directly onto the surface of said molten metallic bath whereby the carbon deoxidizes the metal being treated.

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