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PROCESS FOR THE PRODUCTION OF
ALLOYS OF BERYLLIUM AND COPPERAndrew J. Gahagan, New York, N. Y., assignor
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a corporation of DelawareNo Drawing. Application November 14, 1938,
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3 Claims. (Cl. 75-10)

This invention relates to a process for the isolation of alloys of beryllium and copper. Moreover, this invention affords a process for the continuous manufacture of commercial beryllium-copper alloys directly from the oxide, such continuous manufacture having hitherto been impossible in actual practice.

The fact that aluminum could be reduced from its oxide by carbon in the presence of copper and other metals, thereby yielding alloys of these metals, has been known ever since the work of Cowles in 1884. The process was technically quite feasible on a large scale, but it failed to survive commercially because the cheap electrolytic method for manufacturing pure aluminum from bauxite made the co-reduction procedure unnecessary. In view of the resemblance of beryllium to aluminum, it seemed, from the very first, reasonable to assume that this procedure of co-reduction would succeed just as well with beryllium. The first technical work along this line was that of Lebeau, who, in 1897, formed small amounts of alloys of beryllium by co-reduction of the oxides, or by reduction of beryllium oxide in the presence of the metals, using the electric arc as a source of heat. In connection with the work of Lebeau, see *Comptes rendus*, vol. 125, 1897—pages 1172-1174.

At about the same time Liebmann (see German Patent No. 94,507) discussed the same general type of process. Later developments and disclosures were made in this field by Rohn (U. S. Patents Nos. 2,025,614 and 2,025,616) and Burgess (U. S. Patent No. 1,905,340). As late as 1932, scientific work was carried on by Kroll (Wiss. Veroffent. Siemens Konzern, 11, 88-92).

While the foregoing accomplished the production of some alloys, especially in small scale or experimental operations, a number of difficulties were inherent in the processes proposed, especially when considering commercial operation on any practicable scale. For instance, alloys produced were found to be non-homogeneous, so that on liquating, what appeared to be a veritable felting or skeleton of crystals remained behind; these being of a red color, representing a double oxide of the two metals employed in the process. Furthermore, the prior work was hampered by impurity of the alloys produced. Still further, at least some of the prior processes involved the use of special equipment. Thus, even though Rohn obviated the presence of the mixed oxide compound in beryllium-copper, this was only accomplished by the use of a special at-

mosphere, thereby displacing the normal carbon equilibrium.

The present invention has as one of its primary objects to overcome difficulties of the type mentioned and to provide a procedure which would be at once simple and effective, yet require nothing but relatively standard equipment. This I have accomplished as set forth below, my new procedure yielding an alloy free from the above-mentioned red double oxide, and flowing readily out of the furnace. Thereby I have made possible a continuous process, in itself a sharp differentiation from previously known procedures, wherein it was necessary to stop a batch run, dig out the arc-treated material, and separate the metal from the residue.

Not only does the beryllium-copper alloy formed under normal operating conditions contain what appears to be a skeleton of double oxides, as indicated by Lebeau, but I have also observed that much of it remains physically entrapped in the larger mass of beryllium oxide-carbon mixture. This latter condition interferes, certainly because of physical factors, and probably also by virtue of mass action, with the further continuance of the reduction. I have found, as one part of my invention, that if after the usual preliminary heating of a mixture of carbon, beryllium oxide, and finely divided copper (or an oxide of copper with sufficient excess of carbon to reduce it to metal) I subsequently add more metal and permit it to melt and flow down through the reaction mass, the metal washes down the beryllium-copper alloy already formed and thereby permits the reaction to be renewed. Simultaneously, the alloy is freed, by this molten metal washing action, from the skeleton of double oxide, which latter is then left, in open, highly reactive condition, unprotected by the alloy, for further reduction.

This washing down procedure, of course, dilutes the alloy somewhat, but not merely to the extent that might be assumed from earlier workers' results. For example, alloys of about 5% beryllium can be obtained in small quantity by remelting away from the oxide skeleton in accordance with the procedure first indicated by Lebeau; my procedure permits manufacture, on a much larger scale, of an alloy running regularly 3½% in beryllium, and occasionally considerably higher. Yields are high; practically all the beryllium values are recovered, either as metal or as re-usable oxide.

It will be understood that the addition of massive copper to wash down the alloy formed

can be made with copper metal of any reasonable macroscopic particle size. There is no advantage to using finely divided metal at this point of operation, but it will be understood, in the claims, that "massive metal" refers to any copper suitable for washing down the alloy already formed.

I have found that good results are obtainable from the use of "massive metal" in the form of chunks or pieces of copper, such chunks or pieces being introduced into the furnace preferably alternately with charges of a mixture of carbon, finely divided copper and beryllium oxide.

Thus, after the preliminary heating of a batch of carbon, finely divided copper and beryllium oxide in the furnace, some massive copper is added so as to initiate the washing down action and operation of the furnace is carried out continuously, with periodic additions, desirably alternated, of a mixture of carbon, finely divided copper and beryllium oxide, on the one hand and massive copper, on the other hand. I have found that in a furnace appropriate for carrying out the present process, introduction of a mixture of carbon, copper and beryllium oxide may suitably be effected at intervals of the order of about one hour. Massive copper may suitably be added at similar alternate intervals, although when using chunk copper, the addition thereof is effected at more frequent intervals; for instance several times between each addition of the mixture of carbon, copper and beryllium oxide.

The intervals of introduction of both the mixture and the massive copper will, of course, vary in accordance with a number of conditions, including furnace size, size of particles of massive copper used, etc., although as a general guide it may be stated that the massive copper should be added in a manner which will practically continuously maintain a reserve of copper present adequate to perform the washing down process above referred to.

It is obvious that not only beryllium oxide as such, but any of the compounds which will break down under heat and/or reduction to yield the oxide, can be equally well used. For example, the hydroxide, the basic carbonate, the sulfate, the nitrate, and organic derivatives, are all equally well usable for the purpose of my invention. In general, the oxide has been found most economical to use, and the phrasing of this patent is therefore in terms of the oxide itself. In the claims, it will be understood that "beryllium oxide" refers to ore and to the compound itself whether added as such to the mixture or whether formed by decomposition or dissociation in situ.

While I have found it most convenient and economical to use finely divided copper in elementary form for the preliminary reduction, it is an obvious alternative, which I have found equally satisfactory, to use a mixture of finely divided oxide of copper, with sufficient excess carbon or other reducing material to yield copper on heating. Where the term "copper" is used in the claims, it should therefore be understood that such copper may be added either in elementary form or in the form of an oxide or similarly reducible compound to yield the metal in the reacting zone.

In carrying out my process the following conditions, at least in part, must be taken into account to obtain maximum success.

In arc reduction, there is a central core of very small volume, in which the full temperature of the arc (about 4000° C.) holds sway. Beyond

this, the following various zones may be considered to exist.

(1) The first of these zones may be viewed as represented by the sphere wherein occurs the greatest temperature drop, from about 4000° C. to about 2300° C. In this sphere, no liquid metal can exist, since both beryllium and copper are vaporized above 2300° C.

(2) This volume will, in turn, be followed by a shell representing the 2300° C. to 1900° C. drop. In this shell, carbon is soluble in copper (a factor of great importance in the reduction of the beryllium oxide), while any beryllium which may form will have a very high vapor pressure, even in the presence of alloying copper.

(3) In the next shell, from 1900° C. to 1500° C., molten copper will no longer dissolve carbon, but the other conditions are essentially the same. Copper is in the fused state, while beryllium vapor pressure is still quite high.

(4) In the zone which follows, from 1500° C. to 1285° C., there is both copper and beryllium still in a state of free fusion, with comparatively low vapor pressure on the part of the beryllium. This represents the condition of optimum alloying if reduction problems were not inherent in the situation, and nothing else were involved but the union of free elementary beryllium and copper.

(5) In the next shell, from 1285° C. to 1083° C., the former being the melting point of beryllium and the latter the melting point of copper, one of the components, beryllium, is no longer in the molten state.

(6) Below 1083° C., and reaching to about 850° C., we have a zone of primarily theoretical although not devoid of practical interest, wherein beryllium-copper alloy remains liquid, freezing at some point within that temperature range, corresponding to its composition. Below 850° C., the melting point of the copper-beryllium eutectic, all possible components are of course solid, and neither reaction nor alloying can take place.

Experiment has shown that conditions for reduction of the beryllium oxide, for alloying of the nascent metal, and for maintenance of the alloy undecomposed, are all different, and that, therefore, furnace construction must be such as to give each of these essential factors opportunity to play its normal part. It appears, from the unpublished work of others, that while they did maintain conditions satisfactory for the reduction of the beryllium oxide, and perhaps also for alloying action, these conditions were such as to decompose the alloy almost as rapidly as it was being formed. As a consequence, recoveries were always so low as to make the arc reduction method impractical.

Whether carbon can reduce beryllium oxide alone in the 4000° C.-2300° C. core is purely of theoretical interest; even if reduced to metallic state, the beryllium so formed, lacking copper as a collecting agent (the zone is above the normal boiling point of copper), would immediately be volatilized away or, more likely, converted to carbide. What little did escape carbonization, or reoxidation by reversal of the reaction:



would condense in the cooler portions of the furnace in the form of thin metallic films on the reaction mass, or be volatilized completely out of the furnace.

Where reduction reaction does occur is pri-

marily in the 2300° C.-1900° C. shell. It is here that carbon dissolves in copper, and it is this copper-carbon alloy that appears to react best with the beryllium oxide, dissolving the beryllium immediately as formed.

But this zone, in which beryllium can best be divorced from its oxygen, is not conducive to maintenance of the alloy just formed. The high vapor pressure of elementary beryllium in that temperature range will gradually cause that element to volatilize away from the alloy; once alone as an element, either as vapor or as condensate and unprotected by a preponderance of copper around it, the beryllium is rapidly carbonized or oxidized.

It is consequently essential that there be, best completely surrounding the 2300° C.-1900° C. zone, or certainly above and below it in the furnace, an appreciable zone in which the temperature ranges of 1900° C.-1500° C. and 1500° C.-1285° C. exist. It is in the latter zone that vaporized beryllium will tend to condense, in liquid form, and will alloy with liquid copper to reform the alloy. It is even desirable to have sufficient cross section of reaction material to have a surrounding zone of from 1285° C. to about 850° C.

The furnace construction factors therefore called for in my invention are: There must be sufficient heat conductivity from the bottom of the crucible or container, or, more accurately, from the liquid alloy already formed, to maintain its temperature below the point where the beryllium vapor pressure becomes strong enough to afford material loss. This may be done by water cooling, for example. There should be a sufficient "head" of reaction material above the arc zone to permit the existence of at least a 1500° C.-1285° C. shell, without that shell overheating, by conduction and by contact with the heated carbon monoxide resulting from the chemical reduction, to beyond the 1500° C. where beryllium begins to vaporize away appreciably. It is also very desirable that the 1500° C.-1285° C. zone extend around the sides of the arc as well as around the top and bottom; to accomplish this, it is necessary that the arc furnace be of sufficient diameter to permit conduction and convection effects to counteract the heat of the arc, and reduce the temperature on the outside periphery to 1500° C.-1285° C. desired for alloy maintenance. And finally, it is preferable although not essential to have a diameter which provides a surrounding zone of from 1285° C. to 850° C.

In practice, I find it preferable to maintain, above the arc, sufficient charge so that there is a full temperature drop to as low as 850° C. This insures that all beryllium vapor rising out of the more heated zones will be trapped, either physically by condensation on the relatively cold surface, or by surface solution in the molten copper or molten copper-beryllium alloy.

It is not necessary that the heat source be an electric arc; any other appropriate method of central heating will accomplish the same result. For example, a carbon rod heated by electrical induction can serve as heat focus, acting as a central point equivalent to an arc. The conditions surrounding arc operations will not be significantly changed as regard temperature zones even if the mode of heating is thus changed. To indicate the type of heating wherein the maximum temperature is at a focal point, around or

adjacent which there are zones of lesser temperature, I have chosen to term "focal heating," and in the claims this term is to be understood as covering arc heating, inductive heating, etc.

Where the arc is used, I prefer to use a three phase furnace (three electrodes with alternating current). The electrodes should be of ample cross section to carry the current without overheating because of resistance.

Reference has already been made to the necessity for using finely divided copper in the preliminary reduction. That the factor of metal coarseness or fineness plays an important role in this matter, from the standpoint of optimum results, can be judged from the following quantitative tests, all being run under conditions as identical as possible other than for the changes in the particle size of the copper used.

A beryllium oxide containing 3.04% Al_2O_3 , 0.22% SiO_2 , 0.2% Fe_2O_3 was used throughout. With a relatively coarse copper powder, varying in mesh from 38 to 60 to the inch, an alloy of only 1.47% beryllium was obtained, with aluminum at 0.20%. With copper at 60 to 100 mesh in particle size an alloy of 2.68% beryllium was obtained, aluminum being 0.26%. When identical reduction was accomplished, but using a copper powder of still finer size, specifically 100 to 200 mesh, beryllium was 2.72%, and aluminum remained the same as before. When copper powder ran to finer than 200 mesh, approaching a copper dust, the beryllium content of the resulting alloy dropped somewhat, to 2.38%, while aluminum rose to 0.34%. In all cases reported, silicon was 0.08%-0.10% and iron from 0.07%-0.09%, indicating that particle size does not significantly affect their ratio in the final alloy.

It will be seen that there is a definite preferability for copper powder of smaller than 60 mesh size. Beyond this, extreme fineness does not significantly increase the yield. Because the percentage of impurities remains constant in the final alloy, it follows that the ratio of impurities to beryllium is relatively higher in alloys corresponding to the use of coarse powder.

In all, the optimum alloy is to be obtained by use of a copper powder of less than 60 mesh average particle size. Where, therefore, the term "finely divided copper," or its equivalent, is used in this specification or in the claims, it is to be understood as referring to such metal preferably less than 60 mesh average in particle size.

The invention is not to be limited to copper-beryllium alloys, but is intended to include other alloys producible by the process.

This application is a continuation-in-part of my application Serial No. 184,930.

I claim:

1. The process of forming copper-beryllium alloys in the electric arc furnace by reducing beryllium oxide by means of carbon in the presence of copper which includes charging the furnace with a mass of reaction material comprising beryllium oxide, carbon and copper, the mass providing sufficient reaction material laterally around the arc to produce a drop in temperature to at least about 1285° C., and sufficient reaction material above the arc to trap beryllium vapor, maintaining the temperature below the arc below the point where the beryllium vapor pressure causes material loss, and adding massive copper to the reaction mass in an upper region thereof after preliminary reduction to wash down alloy formed.
2. In the process of forming beryllium-copper

alloys by thermal carbon reduction of beryllium oxide in the electric arc furnace, the step of adding massive copper to the reaction mass subsequent to preliminary reduction in the presence of copper of less than 60 mesh average particle size.

3. The process of continuous formation of beryllium-copper alloys characterized by the

heating of beryllium oxide, carbon, and copper of less than 60 mesh average particle size, in admixture, with separate addition of more copper to the heated mass and withdrawal of the resultant beryllium-copper alloy in fluid form.

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