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PROCESS FOR PRODUCING METAL COMBINATIONS OR ALLOYS

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This invention is a novel process for producing metal combinations or alloys, as well as particular alloys producible by such process; and more particularly it comprises a thermal or metallurgical process for the industrial production of various desirable alloys or other mixtures of selected sets or pairs of metals. The invention is practically useful for the combining or alloying of different sets of metals, for various purposes and uses, starting with the ingredient metals of merely commercial grade of purity, or materials containing such metals, and adapted to yield products consisting of particular alloys or mixtures of high purity. A single one of many instances may be the combining in high purity of the metal pair beryllium and manganese, (for example into an alloy of the proportions Be. 20%, Mn 80%) believed to be novel and affording properties highly desirable for a variety of practical purposes. As an instance of a set comprising more than two metals may be taken the combination of mixture of cobalt with nickel and zirconium, or beryllium and manganese with silver. Many other pairs and sets of metals may be combined in accordance with the principles of this invention. Certain non-metals may be included on account of their importance in forming alloys, notably carbon.

The general object of the present invention is to afford an improved process for alloying or otherwise combining or mixing selected metals, adapted to afford a more thorough and perfect combining thereof, along with greater freedom from contamination. A further object is to make practical the production of various particular alloys possessing useful properties to a degree unobtainable in the absence of high purity of the product. Other and further objects and advantages of the invention will be explained in the hereinafter following description of several practical embodiments or examples thereof, or will be understood to those conversant with the subject.

The invention hereof may be said to rest upon the conception and discovery that certain sets or pairs of metals, desirable to be combined or alloyed, may be selected as having boiling points that are the same or are substantially adjacent in the scale of boiling points and may on this account be simultaneously, or in the same step, distilled for the several purposes of separating the

respective metals from their impurities, combining them in vapor form and condensing them into the molten or solid combination of the composition and purity desired. The invention consists in such process for producing the desired combinations or alloys, and consists further in certain of such combinations or alloys per se; and contemplates further the predetermining of the proportions of the ingredient metals in the product by treating measured initial quantities of the starting materials. In its preferred form the process involves the premixing or heating of the starting materials in the same furnace or chamber, to a temperature beyond the boiling point of the ingredient metal having the highest boiling points; but in some cases it may be desirable to employ parallel operation with heating of the respective materials in separate chambers; in either case the several vapors being brought into mutual admixture, conducted away to a suitable receiving point or vessel and there condensed. By the use of furnace chambers in series any impurities of relatively low boiling point may be blown off or distilled away in an earlier chamber or chambers, the residue being advanced to a later chamber or chambers for evaporation and mixing of the vapors of the desired metals; and by this means the entire process may be performed continuously and economically.

In a different aspect the process hereof may be said to consist in the combining or alloying of selected metals having the same or adjacent boiling points, comprising the distilling of the metals by vaporization and condensation, and characterized in that the metals are brought into combination prior to the condensation step, that is, either while in the vapor phase or preferably earlier, so that a product is obtained comprising thoroughly combined selected metals, and of such high purity as to afford non-brittleness and other desirable properties.

For the purposes hereof a scale or table of metals and certain other elements, arranged according to boiling points, will be useful; including a selection of elements deemed to be of utility for alloying purposes, and others which are likely to be present as objectionable impurities; such a scale being presented as illustrative and not as limitative of the present invention. In the following table the first column states the symbol

of the metal or element, the second and third columns the boiling and melting points, in centigrade, and the fourth column the ratios of boiling to melting points.

Boiling points from 1,120 to 2,310				Boiling points from 2,400 to 4,400			
Mg	1,120	651	1.7	Sc	2,400	1,200	2.0
Ba	1,140	850	1.3	Rh	2,500	1,250	1.2
Ra	1,140	960	1.2	B	2,550	2,300	1.1
Sr	1,150	752	1.5	Au	2,600	1,063	2.4
Sp	1,350	630	2.2	Si	2,600	1,420	1.8
Te	1,390	452	3.1	Ni	2,900	1,452	2.0
Ca	1,400	840	2.2	Co	2,900	1,480	2.0
Bi	1,430	271	5.4	Zr	2,900	1,900	1.5
Li	1,470	186	8.7	Fe	3,000	1,535	1.9
Pb	1,613	327	4.9	Ti	3,000	1,715	1.7
Tl	1,650	303	5.4	V	3,000	1,800	1.7
Al	1,800	559	2.7	Hf	3,200	1,845	1.6
La	1,800	826	2.2	U	3,500	1,857	1.4
Mn	1,900	1,260	1.5	Cb	3,700	1,950	1.9
Be	1,900	1,350	1.4	Mo	3,700	2,620	1.4
Ag	1,950	960	2.0	Ta	4,100	2,850	1.4
Pd	2,200	1,555	1.5	Ru	4,150	2,450	1.7
Cr	2,200	1,615	1.4	C	4,200	3,527	1.2
Sn	2,270	232	9.8	Pt	4,300	1,773	2.4
Cu	2,310	1,083	2.1	Ir	4,400	2,440	1.8

In its preferred form the present invention involves the premixing of the starting materials or metals, such as commercial beryllium and manganese, as in crushed, granular or other reduced condition, and introducing the mixture into a furnace or furnaces of a character capable of raising the temperature of the materials through the melting points and to and beyond the boiling points of the respective metals to be included in the product. For this purpose an available and efficient furnace is one operating on the principles disclosed in United States Patent of Gardner No. 2,195,453 granted April 2, 1940, with which of course is to be provided a suitable in-feed means and a refractory outgoing conduit leading the vapors to suitable receiving or condensing points. There must also be protection against oxidation as by maintaining an atmosphere of hydrogen or other reducing or non-oxidizing atmosphere. With such apparatus the process hereof may be performed as a continuous process, using successive furnaces or chambers if necessary, as already indicated.

In the above table of elements will be seen several cases of identity of boiling points, and in its fullest embodiment the invention contemplates utilizing such identity. Typical is the case of Be and Mn both boiling at 1900°; or for a three-metal alloy Co and Ni and Zr all boiling at 2900°. Such identity is not always essential, as in the case of Be and Mn with Ag, the boiling points being 1900° or 1950°, sufficiently close to permit the process to be practiced when considering the substantial adjacency of the three metals on the scale, there being no intermediate metal that might otherwise remain as an impurity in the product.

Having thus indicated the general character and utility of the process hereof and its broad features of novelty, the principles of the invention will next be more specifically disclosed by means of particular examples of industrial or commercial utility.

Example A—Beryllium and manganese

The following example discloses the application of the principles in order to produce a beryllium-manganese alloy of, for example 50 percent content of each of the ingredients. In order to obtain a satisfactory result it is preferred to start with commercially pure beryllium, e. g. 98.5 to 99 percent, which in crushed form is mixed with crushed manganese of the same quantity and approximately the same purity. At the start of course each of the metals is very brittle and can therefore be easily crushed.

Heretofore an attempt to obtain a relatively much purer beryllium than 99 percent has been described in the Patent No. 1,435,742 of 1920; but the metal obtained is still quite brittle and contains substantial impurities. These impurities have been found to be present by whatever known method the metal has been refined. Naturally, the impurities in the metal vary; but as a rule they are either some beryllium compounds, such as beryllium nitride, Be₃N₂, or the carbide, Be₂C, or the sulphide, BeS; although other impurities may be present, such as compounds of aluminum or silicon, or traces of iron, sufficient to preclude the advantages of high purity and the properties due thereto. Although very few researchers have actually worked with beryllium of a very high degree of purity, there has nevertheless been definitely established an important role which beryllium can play in modern industry, namely, it can increase materially the tensile strength of many alloys, as well as hardness and resistance to corrosion. Heretofore chiefly beryllium has been alloyed with copper; but of late beryllium is more and more used in steel production, and in light metal alloys, or as alloyed with nickel.

A great bar to an early development of uses of beryllium industry has been the unduly high price of the metal, rather than scarcity, since beryllium ores are widely found, and beryllium forms perhaps .01 percent of the earth's crust, although the ores are scattered and are seldom found in large deposits.

With regard to tensile strength of the pure metal, beryllium comes next highest to tungsten, as seen from standard tables, e. g. W 590,000 lbs. per square inch; Be 480,000; steel wire 250,000; Ni 155,000, Ta 130,000; Cu 60,000, etc.

The very high tensile strength of beryllium drew the attention of the industrialists, who experimented to introduce beryllium into multiple alloys, but with no appreciable success. It remained to produce cheaper metal and especially to increase by all possible means its purity; for some of the contradictory data tended to confirm the fact that purer metal was required for the best possible results. Fichter in 1913 showed that the modulus of elasticity of beryllium is higher than 30,000 kilos per square mm. This figure gives the ratio of the internal stress to the strain giving rise to it, and it must be expected to be high, considering the high tensile strength above stated.

The atomic volume of beryllium is about 5.

All the above data lead to the indication that the introduction of beryllium into other metals must improve their tensile resistance and the limit of their elasticity without increasing their density. The magnetic susceptibility of beryllium is taken to be $.72 \times 10^{-6}$ at 18°. It may also be stated, that beryllium is valuable as a scavenger and helps to remove into the slag certain impurities when added in small quantities in the manufacture of steel.

Referring next to manganese, modern industry supplies the commercial metal up to about 99.5 percent purity, containing a series of impurities, such as smaller amounts of iron compounds, also often magnesia, silica, sulphur, phosphorus, carbon etc. Even this degree of purity was available only after distillation in vacuo of the metal in a high frequency furnace. But the metal of such purity is still brittle, and has a hardness of approximately 6. The earth's crust contains about .125 percent manganese which is thus the fifteenth on the list of elements, headed by oxygen

which represents about 49 percent of the hydrosphere and lithosphere. There exists therefore about 12 times more manganese than beryllium. In the standard tables the tensile strength of manganese is given as about 15,900, as found by W. C. Robertson-Austen, who also gave the elongation as 29.7 percent, experimenting with 3-inch test pieces. Besides T. W. Richards found the value of $.82 \times 10^{-6}$ for the compressibility of the metal in sq. cm. per kilo (between 100-500 kilos). The magnetic susceptibility of manganese is about 10.1×10^{-6} at 18° , and about 20.0×10^{-6} at 1000° .

On research for verification of these figures, it has now been established in connection with the present invention that a series of data concerning manganese have been erroneous, this fact being due to the metal heretofore tested being in an insufficiently pure state. It has now been found that if manganese is distilled with certain precautions in an efficient high-temperature furnace, such as that mentioned, the metal no longer appears to be brittle when attaining a purity not under 99.99 percent, and its tensile strength is far higher than the standard figure as hereinabove stated.

It may be added, that manganese is highly considered by the metallurgist; it has found various applications in the art, particularly in the steel industry, being used in multiple alloys, and also being useful as a scavenger.

The hardness of Mn is high, being 6 in a table in which Be is 7 and steel wire is 8, but cast iron only 4.5 and most metals well under these figures.

Having thus indicated the chief pertinent data concerning beryllium and manganese, there will now be set forth the process or steps by which a pure combination of these metals may be produced, for example by starting with a mixture of the commercially pure metals, and considering the fact that both metals, different as they are in many respects, have the same boiling point, for joint or simultaneous distillation.

In demonstrating the invention, tests were carried out in a continuous operation in the aforesaid patented furnace, the reaction chamber being lined with beryllia (M. P. 2570° C.), or zirconia (M. P. 2700° C.), or preferably with magnesia (M. P. 2800° C.) applied molten; other linings, such as of carbides, and highly refractory, can also be used. The atmosphere maintained in both the reaction and condensing chambers was either hydrogen or an inert gas, as argon; special measures being taken to avoid leakage at joints or entrance of air from without. The temperature should be upkept at about 200 degrees above the boiling point of the two metals, that is to say at about 2100° . Such impurities as distill below the boiling point of the two metals are preliminarily removed in the course of the process, for example by using successive furnace chambers, one to dispose of the vapors of such impurities, and the next for the Be and Mn. However, in the same furnace the impurities may be distilled out through special tubes in the upper part of the reaction chamber, which always is full of the hydrogen or inert gas. The powdered metals are fed in continuously through a special charging valve and are progressively slowly carried by a feed mechanism or endless screw towards the discharge part of the reaction chamber; the charging being preferably above and the advancing travel downward toward the discharge.

As both metals distill away at the same temperature, their vapors, in mutual admixture and

high purity, may be conducted to a cooling and condensing place or chamber, resulting, in molten or solid form, in a pure combination of the set or pair of metals. The proportions in which the metals are thus to be alloyed are predetermined in measuring the components of the initial crushed mixture of the two metals.

By this method it is possible to obtain any desired proportions of the constituent metals or elements; but it has been found that a particularly valuable alloy is obtainable containing beryllium 20 and manganese 80 parts. This alloy is useful itself; or it may be introduced to advantage into steel in any proportions desired. Owing to the high tensile strength of such alloys, they can serve for many applications. Thus Be 20 Mn 80 can be usefully employed in the manufacture of ball bearings, and affords a remarkable resistance to wear and tear. In certain cases, where the question of tensile strength is of less importance, it may be found advisable to introduce, besides the two metals, also another metal, such as aluminum (B. P. 1800° C.), or silver (B. P. 1950° C.), or both of these; which can be done with this invention on account of the adjacency thereof on the boiling point scale. Irrespective of boiling points other metals can be introduced that are obtainable on the market in high purity; for example they can be introduced in a molten state into the condensing chamber, and into this molten material the vapors of beryllium and manganese can thereupon be introduced or bubbled in measured quantities, as required for the particular alloy desired. A high grade of purity of the alloy to be produced is always attained, if the distillation be carried out with great care.

From the condensing chamber, in all cases, the liquid alloy may be directly poured into moulds and ingots of high grade of purity are thereby produced.

As already stated, particularly drastic steps must be taken to avoid oxidation by preventing leakage or penetration of air or moisture from outside, since manganese tends to oxidize, while beryllium has a great affinity for oxygen and for nitrogen as well, whereby its oxide and nitride tend to form according to the following equations:



The properties of the pure alloys of Mn and Be, believed to be new, are such as to permit many uses in modern industry. But these alloys and uses are not practically available if the two metals are attempted to be alloyed without passing them through the vapor phase, as described, and if they are not thus freed from all appreciable impurities which were present in the commercial grade metals.

The obtainable alloys are many. Combining the Be and Mn by distillation gives purity, hence non-brittleness and other high properties as stated. The proportions may be varied with the uses, and may be 50-50, though Mn will usually be the major constituent, as in the very useful alloy Be 20 Mn 80 mentioned whose proportions are critical. For ball bearing surfaces the Be content may be as low as 8 or 5 or even 3 percent. Another metal or other metals adjacent on the scale may be added to the Be and Mn before condensation; and still others at the condensation place as described. The Mn-Be combination, of whatever proportions, may be used mere-

ly as a minor constituent in an alloy composed mainly of another metal or metals, as by adding the combination to the composition of a steel.

In all cases the above-mentioned thorough protection against oxidation should be carried not only through the furnaces and to the condensation chamber, but even therebeyond, since in flowing the molten alloy from the condensation place to the molds in which the ingots are formed there might be quite harmful oxidation, tending not merely to loss of the metal, but to impairment of the ingots by introducing voids or inserts therein, wherefore the casting should be effected within a closed chamber supplied with non-oxidizing atmosphere.

In the table given above are recited not only the boiling but the melting points of the elements, and their ratio, for the reason that these data have certain significance. The ratio should not be excessive, as it is with mercury and certain other low boiling point elements omitted from the scale. There should be approximate similarity of ratios for the pair or set of metals selected, so that they will first melt and later evaporate at substantially adjacent points.

Example B—Cobalt and nickel

Among many other combinations producible by the present process are alloys of cobalt and nickel. It has already been pointed out that these, when obtained of extreme purity, have the same boiling point, namely 2900° C. For various metallurgical processes nickel is required in some cases where cobalt has been considered undesirable. In these cases the simultaneous distillation of the two metals of commercial grade purity according to the present invention is excluded. However in various other cases this may not be so, and then the joint distillation of Co and Ni becomes of great interest. As the tensile strength of nickel per se is much higher than that of cobalt, this point must be particularly studied in order to obtain an alloy of required properties. The process may closely follow that described for Be and Mn.

With Co and Ni may be combined other elements. For example as zirconium has a boiling point only slightly over 2900° C., it is readily introduced into the combination. Zr is a particularly recommended scavenger in the steel industry, but is also often recommended in various alloys, more especially in nickel-containing alloys.

As with Example A the increase of the purity of the commercial grade metals is of utmost importance; with ordinary purity they may be crushed to powder and mixed, and the present invention acts to purify and combine them for high properties. Tests have confirmed that the alloys obtained with any example can be produced of varying percentages of the ingredient elements.

Other examples

Many other examples may be mentioned or developed. Thus with the furnace already mentioned it was found possible to distill jointly even such metals as iron, titanium and vanadium. The distillation of such a cheap metal as iron is of course a costly operation. But the mere fact that in case of necessity modern industry has the means, in this invention, to distill metals having such high boiling points as 3000° C. and even higher, and thus to combine and alloy them

with great purity, permits improved latitude in technical development and production, as of special alloys and particular properties. This is particularly the case if high grade purity vanadium or thorium are required in a combination or alloy.

Vanadium is considered to be the hardest of all metals; it is usually separated from the other ingredients of its ore by chemical means. Herebefore it has been very difficult to obtain the metal of high degree of purity. But as vanadium is today much used to increase the toughness of steel, and its resistance to shock, a vanadium of highest purity has become a necessity to modern industry. The same can be said of titanium of high purity, since titanium in steel also increases toughness; besides titanium is considered to be a valuable deoxidizer and also is useful for the removal of nitrogen from steel, as titanium is known to be the only metal which burns in nitrogen. These two metals have the same boiling point, 3000°, and may be combined in pure form by this invention, or both combined with iron, or thorium, or both; all boiling at 3000°.

Another case of identical boiling points is gold and silicon, 2600°, which also represents a case of combining a metal and non-metallic element.

It is obvious that other metals and even non-metals can be subjected to the present method of joint distillation, on the principles described. However, before embarking on any particular case of this method of obtaining metals, or alloys of highest purity, it is naturally requisite to examine the conditions and the requirements to be put to the metals or alloys to be manufactured, and only to apply the present invention when such high degree of purity is really necessitated by the industrial demands and when distinct technical advantages can be achieved.

There have thus been described a number of representative processes for producing metal combinations or alloys in accordance with the principles of the present invention, and as well a number of alloys producible by such process; and since many matters of operation, proportions, temperature, and duration may be reasonably varied within such principles, and within the practical utility of the invention, it is not intended to limit the claims of invention to the specific data described.

What is claimed is:

1. The metallurgical process for industrially producing a combination or alloy of a certain set or pair of metals, with boiling points above about 1120° C., and selected as having boiling points that are substantially identical in the scale of boiling points, with no other metal intermediate them, comprising heating up in an inert atmosphere substantial portions of such selected metals above a temperature sufficient for vaporization of the metals, conducting away more volatile impurities as waste vapors below the boiling points of the selected metals, conducting away the vapors of such metals in mutual admixture, and condensing the vapor mixture at a suitable receiving point.

2. The process as in claim 1 and wherein the starting materials in measured proportions are brought together in a heating chamber before vaporization; and the resulting vapor mixture is condensed into a molten mass containing predetermined proportions of the selected metals.

3. The process as in claim 1 and wherein the

materials are brought into mixture before melting, in the solid state.

4. The process of combining or alloying selected metals having substantially the same boiling points, comprising distilling the metals by vaporization and condensation; characterized in that the metals are brought into combination before condensation; and that impurities of lower boiling point than the selected metals are removed during progressive rise of temperature; whereby later the selected metals evaporate in purified condition and a product is obtained of thoroughly combined selected metals, and of high purity to afford non-brittleness.

5. The metallurgical process for combining a set or pair of metals having proximate boiling points on the scale of boiling points such that no other metal has an intermediate boiling point between the same, comprising distilling the metals in the same heating operation, with purification of both during heating up followed by joining of their vapors, and then condensation.

6. The process of claim 5 and wherein the starting metals are commercially pure but brittle and in crushed condition and premixed before heating and have the same boiling points thereby, after melting, to evaporate simultaneously in pure condition for distillation and simultaneous condensation.

7. The process of combining or alloying of a set of selected metals having substantially the same boiling points, comprising distilling the metals by vaporization and condensation; characterized in that the metals are brought into combination before their vaporization and their vapors are conducted away in admixture; whereby a product is obtained of thoroughly combined

selected metals, both of high purity and affording non-brittleness thereof.

8. The process of combining or alloying of a set of selected metals having substantially the same boiling points, comprising distilling the metals by vaporization and condensation; characterized in that the metals are brought into combination before condensation and all impurities of lower boiling points are vaporized and eliminated during heating up of the selected metals; whereby a product is obtained of thoroughly combined selected metals, and of high purity to afford non-brittleness.

9. The process of combining or alloying in a minor part beryllium and a major part of manganese having the same boiling point, comprising distilling the metals by vaporization and condensation; characterized in that the metals are brought into combination and thorough mixture before vaporization and are condensed simultaneously at the common boiling point; whereby a product is obtained of thoroughly combined beryllium and manganese of high purity and free of brittleness.

10. The process of producing and combining in a high state of purity measured proportions of beryllium and manganese of the same boiling point, comprising first combining and then fractionally vaporizing suitable starting materials containing the desired proportions of said metals thereby to eliminate and separate impurities of lower boiling points, followed by vaporizing and combining in thorough mixture the beryllium and manganese, and conducting away a mixture of their vapors and condensing the same simultaneously at their common boiling point.

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