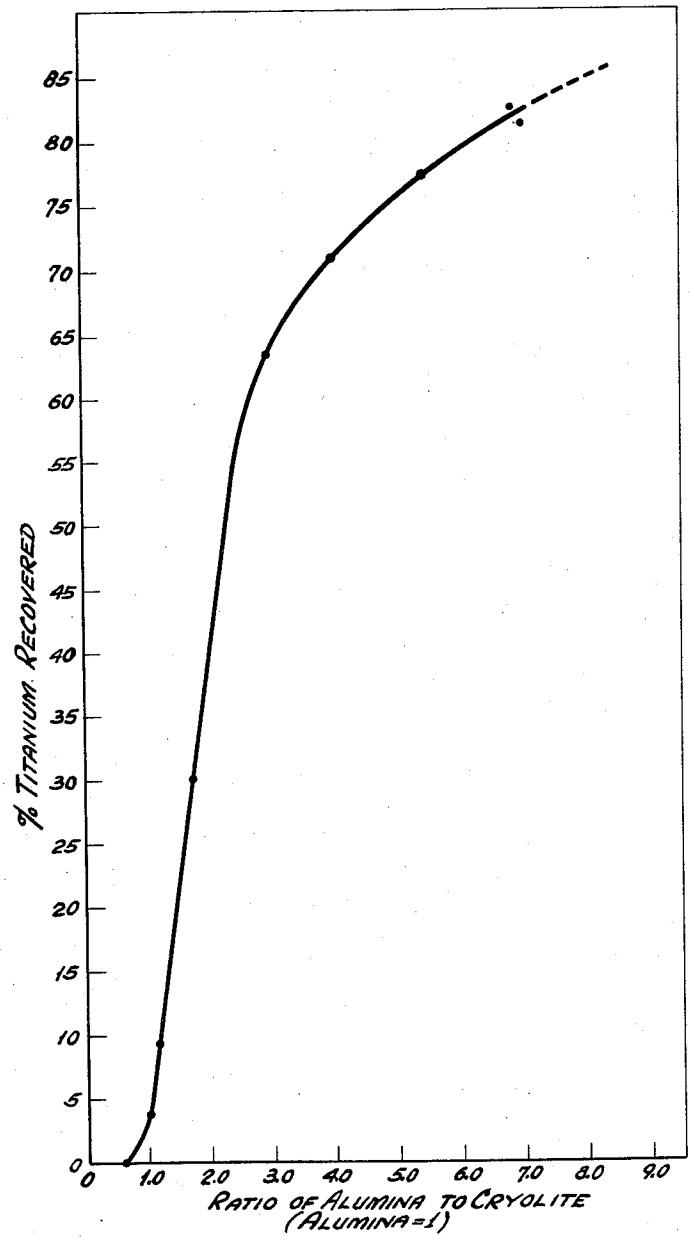
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PROCESS FOR THE PREPARATION OF ALLOYS

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PROCESS FOR THE PREPARATION OF ALLOYS

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This application is a continuation-in-part application of our co-pending application Serial No. 573,614, filed on March 26, 1956, now abandoned.

This invention relates to metal alloys and more particularly to a process for the preparation of alloys of refractory metals. For the purpose of this specification and the appended claims the term "refractory metals" is deemed to mean metals such as, for example, titanium, zirconium, molybdenum, chromium, manganese, vanadium etc., the oxides of which are not readily reduced by carbon by conventional methods.

Alloys containing relatively small percentages of refractory metals have recently gained increased technical importance. It has, for example, been found that as little as 0.5% of titanium confer upon certain aluminum alloys an increase in strength of as much as 30%, that relatively small amounts of Ti improve the corrosion resistance of magnesium alloys, refine the grain of steel, retard age hardening in aluminum alloys etc.

The preparation of these alloys, however, is fraught with considerable difficulties. These difficulties are due to the fact that the melting point of refractory metals such as titanium, zirconium, molybdenum and the like, is relatively high, and generally considerably above the melting point of most metals or alloys, the properties of which are to be influenced by additions of such refractory metals. In fact, the melting point of most refractory metals is above 1700° C.

In the customary methods for the production of alloys containing refractory metals, the other metal constituents have to be melted and heated to a temperature which is close to the melting point of the refractory metal or metals. When titanium, for example, is to be alloyed with major amounts of such metals as aluminum, magnesium, iron, manganese, or copper, which have melting points considerably below that of titanium, it is very undesirable to heat the major constituent or constituents almost to the melting point of titanium. Such overheating substantially beyond the melting point of the major constituent results in appreciable losses of metal due to evaporation and oxidation. Moreover, a considerable amount of heat energy is lost.

The metallic forms of titanium, zirconium etc. are relatively expensive, and the preparation of an alloy prepared from even a small percentage of refractory metal is thus very costly. The use of very high temperatures in the preparation of the alloys, furthermore, calls for melting pots or crucibles extremely resistant to heat which pots or crucibles are expensive and difficult to manufacture.

It is, therefore, an object of the present invention to provide a process for the preparation of alloys comprising refractory metals together with major amounts of non-refractory metals which may be carried out at temperatures considerably below the melting point of the refractory metals to be incorporated in the alloy.

Another object of the invention is the provision of such a process in which the losses of metallic constituents are held to a minimum.

A further object of the invention is the provision of a process for the preparation of alloys comprising refractory metals, wherein said refractory metals are supplied to the process in the form of relatively inexpensive and readily available starting materials.

Still another object of the invention is the provision of such process which may be carried out in a simple manner and without requiring expensive apparatus while resulting in alloys of excellent quality at high yields.

Furthermore, it is an object of the invention to provide a process for the preparation of alloys comprising refractory metals which lends itself to continuous operation and to the reclamation and reuse of auxiliary materials and by-products.

It is still a further object of this invention to improve generally on processes for the preparation of refractory metal alloys as now customarily practiced.

Other objects and many of the attendant advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description and to the specific examples of embodiments of the process of the invention.

In its more specific aspects, the present invention contemplates the preparation of alloys comprising refractory metals by reacting one or several oxides of refractory metals with an equivalent amount of reducing metal in the presence of an amount of non-reacting metal and of a molten salt solvent as hereinafter defined.

A reducing metal for the purposes of the process of the invention is a metal having a lower position in the electromotive series at the relevant reaction temperature and under the relevant reaction conditions than the refractory metal of the oxide or oxides to be reduced. Generally, such reducing metals may also be defined in terms of the free energy of formation of their oxides per atom oxygen at the reaction temperature, the energy of formation of the oxide of the reducing metal being generally higher than that of the refractory metal oxide or oxides which it is desired to reduce. It has been found, however, that metals the oxides of which have a free energy of formation equal to or even slightly greater than that of the reducing metal may be successfully prepared in good yields by the process of the invention.

According to the process of the invention, additional metal oxides other than those of refractory metals may be reduced simultaneously by the reducing metal. Iron oxide (Fe_2O_3) may be mentioned as an example of such additional non-refractory metal oxide.

The non-reacting metal in the presence of which the reaction between the refractory metal oxide or oxides and the reducing metal is carried out may either constitute an excess or the reducing metal or it may consist of another metal or metals capable of alloying with the refractory metal or metals. This non-reacting metal, which thus will be a constituent of the alloy to be obtained, acts as a diluent and moderates the rate of the reaction between the reducing metal and the oxide or oxides.

The molten salt solvent to be employed in the inventive process is a salt or a mixture of salts having a melting point below the temperature at which the reaction between the oxide or oxides of the refractory metals (hereinafter referred to as "primary oxide") and the reducing metal is performed, which salt or mixture of salts is capable of dissolving the oxide of the reducing metal formed by the reaction and hereinafter referred to as "secondary oxide." Since the preferred reducing metals for the inventive process are aluminum and/or magnesium, the molten salt solvent should consequently be capable of dissolving aluminum oxide and magnesium

oxide. It has been ascertained that the readily available fluorides and chlorides of the metals of the first through the third groups of the Periodic System, such as for example Ca-, Na-, Al- and K-chlorides and fluorides having a boiling point above 700° C. are particularly suitable for the intended purpose.

The process of the invention thus comprises essentially reacting at least one primary oxide of a refractory metal with an equivalent amount of reducing metal in the presence of an amount of non-reacting metal at a temperature above the melting point of the reducing metal and the non-reacting metal, but below the melting point of the refractory metal or metals, and dissolving the secondary oxide formed by the reaction in the molten salt solvent.

It has been established by us that the removal of the secondary oxide of the reducing metal or slag has an important bearing on the process of preparing alloys of refractory metals from their primary oxides by reaction with reducing metals in the presence of non-reacting metals.

It has formerly been proposed to reduce oxides of refractory and other metals by aluminum in a continuous operation by adding small batches of primary oxide at frequent intervals to a molten bath of the reducing metal while keeping the metal bath at the proper reaction temperature by means of an electric arc or by another heating device.

We have now ascertained that this procedure is practical only in very short runs and becomes virtually inoperative as soon as the surface of the molten metal is completely covered by a slag of secondary aluminum oxide formed by the reaction of the aluminum with the primary metal oxide. Aluminum oxide or alumina has a melting point above 2000° C. As soon as a cover of tough impermeable slag or solid alumina forms on the melt, no further reaction takes place.

A continuous operation at much lower temperature than heretofore proposed is possible by the process of our invention wherein the molten salt solvent is used for continuously removing the secondary oxide. When the metallic melt to which the oxide or oxides of the refractory metal is added comprises aluminum or a heavier metal as the major constituent, the molten salt solvent will usually float on top of the metallic phase much in the manner of a conventional salt cover. While the invention will be illustrated largely by examples referring to such floating molten salt solvents, it will be well understood by those versed in the art that it is entirely within the scope of the invention to employ molten salt solvents of a specific gravity such that they will largely or entirely drop to a position below the molten metal in the melting and reaction vessel.

We have also found that the percentage of refractory metal recovered in the alloy obtained by the process of the invention from refractory metal oxide or oxides varies within certain limits as a function of the excess of molten salt solvent over the secondary oxide formed by the process. The relationship is not a linear one. With a very small excess of molten salt solvent over the secondary oxide formed, the improvement in yield of refractory metal is noticeable, but not economically significant. Beyond a certain excess of molten salt solvent, on the other hand, the recovery of refractory metal in alloy form improves at such an insignificant rate, that the additional expense for additional salt solvent and its handling is no longer warranted. Generally, we prefer, therefore, to use an amount of molten salt solvent the weight of which is about 2.2 to eight times the weight of the secondary oxide formed in the process of the invention by the oxidation of the reducing metal to a non-metallic slag.

As previously mentioned, the preferred reducing metals for the process of this invention are aluminum and magnesium because of the high heat of formation of their oxides at the preferred reaction temperatures, because of their low cost and ready availability, and, further, because of the relative simplicity of operation which they permit.

The preferred molten salt solvents for the process of the invention thus comprise molten salts or mixtures of salts which readily dissolve aluminum oxide or magnesium oxide at the preferred reaction temperature. Molten cryolite is of special advantage where aluminum is employed as the reducing agent. Although the initial cost of cryolite is relatively high, it may be recovered and reused almost indefinitely. A molten cryolite solvent may be readily separated from the molten alloy formed in the process of the invention and may be subjected to electrolysis by the well known method employed in the recovery of aluminum from bauxite which yields cryolite substantially depleted of alumina and ready to be returned to the process of the invention, and metallic aluminum which may also be returned to the reduction process of the invention.

As previously mentioned, fluorides other than cryolite, chlorides and mixtures of fluorides and chlorides of metals of the first through the third groups of the periodic system are suitable for performing the process of the invention in a temperature range of 800 to 1600° C. They must be selected so as to show high dissolving power for the secondary oxide formed while only sparingly dissolving the primary oxide of the refractory metal which is to be produced. Molten cryolite dissolves up to 18% of its weight of alumina while still maintaining the free fluidity required for ready separation of the molten salt solvent with the secondary oxide dissolved therein from the alloy formed. Cryolite, on the other hand, does not readily dissolve refractory metal oxides such as titanium dioxide.

It will be appreciated that use of a substantial excess of molten salt solvent in the process of the invention has a function entirely different from that of a small amount of oxide-dissolving fluxes customarily used in melting operations. Such fluxes are adequate only to dissolve films of oxide formed on the metal surface by oxidation with atmospheric oxygen or the like and to permit coalescence of individual metal particles into a homogeneous metal body. The fluxes commonly employed are useful in melting a metal or alloy already produced in another operation, they would, however, be of no assistance in a primary smelting process such as the process of the invention in which a metal is to be prepared from its oxide, and the slag formed by oxidation of the reducing agent must be removed. The basic difference between the function of commonly known fluxes and the non-metallic solvent melt of our invention is thus emphasized and should be borne in mind so as to facilitate the understanding of the inventive process. It should also be noted that the relatively large amount of molten salt solvent present in the reaction mixtures acts as an acceptor of thermal energy, thus further serving as a reaction moderator.

The inventive process is performed at a temperature intermediate the melting point of the metallic constituents present before the reaction and the melting point of the refractory metal or metals the oxide or oxides of which are being reduced. It is one of the principal advantages of the invention that the reduction of the oxides of the refractory metals may be performed at a temperature substantially below the melting point of the refractory metals proper and, therefore, at a temperature much lower than that required in processes in which a refractory metal in the metallic state is alloyed with other constituents. The maximum temperature reached in the inventive process is much lower than that of the aluminothermic processes of the prior art. The use of the molten salt solvent of the invention has been found to give superior yields of refractory metal at lower temperatures than are obtainable under otherwise similar conditions, but without molten salt solvents and at the higher temperatures required for this reason.

The process of the invention is preferably carried out in an electric furnace having an inert atmosphere, but furnaces heated in any other manner may be used as well as will be obvious to those skilled in the art.

It will be realized that the inventive process is very economical since the refractory metal constituents, which usually determine the cost, are supplied in the form of their oxides which are much less expensive and are generally more readily available than refractory metals in their metallic state.

The inventive process is particularly advantageous for the production of so-called "master alloys," that is of alloys containing a relatively high percentage, for example 5–40%, of a refractory metal. The melting point of such a master alloy is somewhat higher than that of the non-refractory base alloy or metal, but well below that of the refractory metal proper. In order to produce an alloy of relatively low refractory metal content from such a master alloy, the alloy or metal base need to be melted and heated only to the melting point of the master alloy, whereupon a predetermined amount of master alloy is added. The refractory metal content of the master alloy is thus diluted by the molten base alloy or metal whereby a refractory metal alloy of lower refractory metal content than that of the master alloy is obtained. Since—as previously set forth—the melting point of the master alloy is below that of the refractory metal proper, it will be realized that the drawbacks of conventional processes are substantially eliminated by the process of the invention.

The reducing metals of this invention may be employed in powder, ingot or shredded form.

The invention will now be described by several examples but it should be understood that the examples are given by way of illustration rather than by way of limitation and that many changes may be made herein without departing in any way from the scope and spirit of the invention.

Example 1

75 grams of aluminum are melted by an electric arc in a magnesia crucible under an atmosphere of argon gas.

48 grams of iron oxide (Fe_2O_3), 59.5 grams of manganese oxide (Mn_3O_4) and 62.3 grams of titanium dioxide (TiO_2) are pulverized and mixed intimately. The mixture is added to the molten metal with stirring and 300 grams of a molten mixture of 98% cryolite and 2% zinc chloride is added. The reaction between the molten aluminum and the metal oxides is initiated by the electric arc. The heat of reaction gradually raises the temperature of the mixture to 1600° C. When the reaction subsides, this temperature is maintained by the electric arc.

Aluminum oxide is formed by the reaction of the aluminum with the metal oxides and dissolves in the molten mixture of non-metallic compounds. This molten mixture forms a layer which floats on top of the alloy formed and is easily separated therefrom. The alloy formed weighs 99 grams and contains:

	Percent
Titanium	19
Aluminum	21
Manganese	33
Iron	24
Insoluble	Balance

This alloy may advantageously be used as a master alloy in the production of low-titanium steel.

Example 2

A master alloy consisting almost entirely of titanium and aluminum is prepared in the following manner:

215 grams of aluminum are melted and heated to about 1000° C. in a crucible under an argon atmosphere. The melt is covered with 125 grams of a molten mixture of sodium chloride and calcium fluoride having a melting point of about 800° C., 22.5 grams of TiO_2 powder are then added.

Two distinct layers are formed after the reaction of the aluminum with the titanium dioxide, that is a molten aluminum-titanium layer, and a molten salt solvent layer containing the aluminum oxide formed by the reaction of the aluminum with the titanium oxide. The crucible is permitted to cool to about 1000° C. and the solvent layer which is still quite fluid is poured off.

156 grams of a master alloy of the following composition are obtained:

	Percent
Titanium	4.6
Aluminum	93.8
Insoluble	Balance

Example 3

157 grams of ingot aluminum and an intimately mixed powdered blend of 100 grams of titanium oxide, 50 grams of aluminum powder, and 750 grams of cryolite are packed into a magnesia lined graphite crucible. The crucible is placed in an induction furnace and heated until the reaction starts. The reaction subsides after approximately 60 seconds and the charge is reheated to its melting point of approximately 1260° C. It is then allowed to cool under an argon atmosphere.

The non-metallic layer formed is readily separated from the alloy which latter weighs 202 grams and has the following composition:

	Percent
Titanium	25.05
Aluminum	67.73
Insoluble	Balance

Example 4

388 grams of ingot aluminum are melted in a magnesia crucible by induction heating and the temperature of the melt is raised to approximately 1000° C.

A powdered mixture of 175 grams of titanium dioxide and 600 grams of cryolite is added gradually in several small batches, while an argon atmosphere is maintained over the melt. The reaction of the molten aluminum and of the titanium dioxide is initiated instantly by the heat of the molten metal. After the last addition has been made, heating is continued until the temperature of the melt reaches 1310° C. and is sufficiently high for pouring. The melt is poured into a steel mold and cooled.

Metal and non-metallic solvent phase separate in the mold and 395 grams of alloy of the following composition are obtained:

	Percent
Titanium	18.8
Aluminum	80.2
Insoluble	Balance

Example 5

In order to determine the influence of the excess of molten salt solvent on the yield of refractory metal, a series of aluminum-titanium master alloys was prepared by the method of Example 4 with the following results:

Batch No.	Composition of Starting Batch			Alumina Formed Theoretically, Grams	Ratio Alumina to Cryolite	Titanium Recovered in Alloy	
	Aluminum, Grams	TiO_2, Grams	Cryolite, Grams			Grams	Percent
1	646	200	200	170	1:1.18		9.5
2	374	100	150	85	1:1.77		30.2
3	352	100	255	85	1:3.0		67.3
4	388	175	600	149	1:4.02		70.7
5	444	140	594	119	1:5.0		75.8
6	356	100	583	85	1:6.85		82.4

The results of the six experiments have been plotted on the accompanying graph which illustrates the rela-

tionship of the ratio of alumina to cryolite to the percentage of titanium recovered in the final alloy. From the curve obtained it will be readily seen that the yield of titanium is rather poor (less than 40%) when the ratio of alumina to cryolite is below 1:2. When this ratio is increased to above 1:2.2, the yield of titanium increases considerably. It will be seen that a very favorable yield is obtained in the range covering an excess of cryolite of 2.2 to 8 times whereafter the additional recovery of titanium increases at such an insignificant rate that the expense for further excess of cryolite is not warranted. Consequently, the ratio of cryolite to alumina should advantageously be 2.2–8.0:1.

Example 6

200 grams of cryolite are intimately mixed with 100 grams of sodium chloride, 50 grams of titanium dioxide, and 10 grams of calcium chloride. A block of 135 grams of magnesium metal is placed in a magnesia crucible and the prepared mixture is packed around the block. The magnesia crucible is placed inside a graphite crucible and mounted in the coil of an induction furnace. The charge is heated under an argon atmosphere until melted and is then allowed to cool. Metal separates in several small buttons at the top of the fused non-metallic phase. The buttons are remelted with a mixture of 85 grams of sodium chloride and 15 grams of calcium fluoride to form a single button of 65 grams containing

	Percent
Titanium	5.6
Magnesium	93.2
Insoluble	Balance

Example 7

789 grams of ingot aluminum are melted in a magnesia crucible by induction heating. An intimate mixture of 144 grams of molybdenum trioxide and 560 grams of cryolite is then gradually added to the molten aluminum under an argon atmosphere at such a rate as to keep the temperature of the melt above 1000° C.

The reaction of the molten aluminum with the molybdenum trioxide is initiated instantly by the heat of the melt. After the last addition of molybdenum oxide, the melt is heated until its temperature reaches 1180° C. and is sufficiently high for pouring. The melt is then poured into a preheated steel mold and permitted to solidify. Metal and non-metallic phase separate in the mold. The alloy obtained weighed 704 grams and had the following composition:

	Percent
Molybdenum	8.94
Aluminum	89.6
Insoluble	Balance

Example 8

454 grams of ingot aluminum are heated to the melting point in a magnesia crucible by induction heating.

A powdered mixture of 109.2 grams of vanadium pentoxide and 510 grams of cryolite is added under an argon atmosphere in several small batches to maintain the temperature of the melt substantially at 1000° C. The reaction between the aluminum and the vanadium pentoxide is initiated spontaneously by the heat of the molten metal. After the last addition has been made and the reaction subsides, the reaction mixture is heated to approximately 1200° C. when it is fluid enough to be poured into a pre-heated steel mold where it is allowed to cool. Metal and non-metallic phase separate in the mold.

395 grams of an alloy having the following composition are obtained:

	Percent
Vanadium	10.1
Aluminum	88.1
Insoluble	Balance

Example 9

584 grams of ingot aluminum are melted in a zirconia crucible by induction heating.

A mixture of 96.1 grams of zirconium oxide and 271 grams of cryolite is added to the molten aluminum at a temperature of about 980° C. under an argon atmosphere. The reaction between the molten aluminum and the zirconium oxide is initiated spontaneously under the prevailing conditions. After the reaction subsides, the melt is heated to 1185° C. to make it sufficiently fluid. It is then poured into a pre-heated steel mold in which the non-metallic solvent phase solidifies separately from the metal alloy.

The alloy obtained weighs 562 grams and has the following composition:

	Percent
Zirconium	6.43
Aluminum	92.3
Insoluble	Balance

Example 10

376 grams of ingot aluminum are melted in a magnesia crucible by induction heating.

69.1 grams of boron oxide (B_2O_3) and 495 grams of cryolite were mixed intimately and are added in several small portions to the molten aluminum under an argon atmosphere at a temperature of approximately 970° C. The reaction between the aluminum and the boron oxide is initiated spontaneously at this temperature by the heat of the molten metal. After the reaction subsides, the reaction mixture is heated until the temperature reaches 1120° C. and the melt is fluid enough for pouring into a preheated steel mold. The alloy, separated from the non-metallic phase after solidification, has the following composition:

	Percent
Boron	4.3
Aluminum	93.8
Insoluble	Balance

331 grams of alloy are obtained.

Example 11

392.5 grams of copper are melted in a zirconia crucible by induction heating. 138 grams of aluminum are then added to the molten copper.

An intimate powdered mixture of 209 grams of manganese dioxide and 590 grams of cryolite is prepared and is added under an argon cover in several small portions to the molten base alloy. The reaction between the aluminum and the manganese dioxide is initiated spontaneously by the heat of the molten metal. After the reaction subsides, the contents of the crucible are heated until the temperature of the supernatant non-metallic melt is 1100° C. and the melt is ready for pouring. It is then poured into a pre-heated steel mold. The alloy separated from the non-metallic phase weighs 421 grams and has the following composition:

	Percent
Manganese	7.9
Aluminum	3.1
Copper	88.95

Example 12

617 grams of copper are melted in a zirconia crucible by induction heating and 51 grams of aluminum metal are dissolved in the molten copper.

A powdered mixture of 122 grams of titanium dioxide and 500 grams of cryolite is added under an argon atmosphere. The reaction between the aluminum and the titanium oxide starts spontaneously at the melting point of the copper-aluminum alloy. After the reaction subsides, heating is resumed to make the alloy fluid enough for pouring. The melt is then poured into a pre-heated steel mold and allowed to cool.

630 grams of an alloy of the following composition are obtained:

	Percent
Titanium	7.6
Copper	85.05
Aluminum	3.6
Insoluble	Balance

As can be seen from Examples 1 to 12, 60 to 85% of the refractory metals introduced in oxide form into the process of the invention are recovered in the alloys. Results were particularly favorable in the alloys of titanium and aluminum which show a titanium recovery of 72 to 90% of the titanium added in the oxide form. The common metals added were recovered in the alloys at yields varying between 90 and 95%.

Even better recovery of the refractory metals and greater heat economy can be achieved by continuous operation of the process of the invention as illustrated in the following example:

Example 13

715 grams of ingot aluminum are melted in a crucible by induction heating. The crucible is provided with two taps, one being located near the bottom, the other one about one third of the height below the top of the crucible.

165 grams of titanium dioxide are carefully mixed with 86 grams of aluminum powder and 904 grams of cryolite. The mixture is added under an argon atmosphere to the molten aluminum in small batches. External heat is applied as needed if the reaction becomes too sluggish.

The reaction between the aluminum and the titanium dioxide is initiated spontaneously. After approximately one half of the cryolite-titanium dioxide mixture is added, the reaction is permitted to subside, the contents of the crucible are heated to 1070° C. and the greater part of the supernatant non-metallic melt is drawn off through the upper tap.

The power supply of the furnace is again switched on and the second half of the titanium dioxide and cryolite is added in small batches as above. After completion of the last addition the contents of the crucible are heated to 1300° C. and the metal at the bottom of the crucible is drawn off through the lower tap into a steel mold together with a portion of the non-metallic phase.

714 grams of an alloy of the following composition are obtained:

	Percent
Titanium	12.98
Aluminum	84.3
Insoluble	Balance

The collected non-metallic phase has the following composition:

	Percent
Aluminum oxide	13.9
Titanium dioxide	1.1
Cryolite	85.0

It is thus essentially a solution of alumina in cryolite.

The non-metallic melt is fed to an electrolytic cell having a carbon anode and walls covered with a carbon lining which serves as cathode. The solution is kept at a temperature of 950° C. by the passage of electric current and electrolyzed in a well-known manner. A voltage of 5 volts applied to the electrodes of the cells produces a current density of 1,000 amps. per sq. ft. at the anode. Aluminum metal in the molten state collects at the bottom of the cell and is drawn off from there to be returned to the melting crucible of the reduction process. The cryolite depleted of alumina is drawn from the top of the cell and is ready to be reused in the process of the invention.

While a continuous batch process was described in the above example, the process can readily be made fully continuous by adding to the reaction vessel a mixture of aluminum and titanium oxide in a ratio substantially corresponding to the composition of the alloy which is to be prepared, and containing the necessary small amounts of cryolite required to compensate for losses which mainly occur by evaporation. The cryolite melt is circulated between the reaction vessel, in which the reaction between the aluminum and the titanium dioxide is performed and the electrolytic cell in which the alumina is removed. We have found that the titanium dioxide does not accumulate in the non-metallic phase but reaches a maximum equilibrium value substantially at 1.1% corresponding to the solubility of TiO_2 in cryolite at approximately 1000° C.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not limited thereto, but is to be construed broadly and restricted solely by the scope of the appended claims.

What is claimed is:

1. A one-step process for the preparation of an alloy, which comprises reacting an oxide of at least one refractory metal with an equivalent amount of reducing metal above the melting point of said reducing metal, whereby said refractory metal oxide is reduced to the metallic state and a slag-forming oxide of said reducing metal is formed, said reaction being carried out in the presence of an amount of molten, non-reacting metal capable of alloying with said refractory metal and in the presence of a molten salt solvent capable of dissolving the slag-comprising reducing metal oxide formed during the reaction, said reducing metal having a lower position in the electromotive series at the reaction temperature than said refractory metal, and said molten salt solvent being present in an excess sufficient to dissolve said slag formed by said reducing metal oxide.

2. In a process as claimed in claim 1 wherein said refractory metal has a melting point of above 1700° C.

3. In a process as claimed in claim 1, wherein said refractory metal oxide is an oxide of a refractory metal selected from the group consisting of titanium, zirconium, molybdenum, vanadium, boron, chromium and manganese.

4. In a process as claimed in claim 1, wherein said reducing metal is selected from the group consisting of aluminum and magnesium.

5. In a process as claimed in claim 1, wherein said non-reacting metal and said reducing metal are identical metals.

6. In a process as claimed in claim 1, wherein said non-reacting metal is copper.

7. In a process as claimed in claim 1, wherein said molten salt solvent is selected from the group consisting of metal chlorides, metal fluorides and mixtures of metal chlorides and metal fluorides having a boiling point above about 700° C. and wherein the metal constituent thereof belongs to the first through third groups of the periodic system.

8. In a process as claimed in claim 1, wherein said molten salt solvent comprises cryolite.

9. In a process as claimed in claim 1, wherein said molten salt solvent comprises sodium chloride and calcium fluoride.

10. In a process as claimed in claim 1, wherein said molten salt solvent comprises cryolite and zinc chloride.

11. In a process as claimed in claim 1, wherein the ratio between reducing metal oxide slag formed by the reaction and molten salt solvent is between about 1:2.2 and 1:8.0.

12. In a process as claimed in claim 1, wherein the reaction is performed at a temperature substantially between 900° and 1600° C.

13. In a process as claimed in claim 1, wherein at least one non-refractory metal oxide is simultaneously reacted

with an additional equivalent amount of reducing metal to be reduced to the metallic state.

14. In a process as claimed in claim 1, wherein said molten salt solvent and said reducing metal oxide slag dissolved in said solvent are separated from the metal constituents, whereafter the solvent melt thus obtained is electrolysed to recover reducing metal and salt solvent for recycling.

15. A one-step process for the preparation of an alloy, which comprises reacting in a reaction zone an oxide of at least one metal selected from the group consisting of titanium, zirconium, molybdenum, vanadium, chromium, manganese and boron with an equivalent amount of a reducing metal selected from the group consisting of aluminum and magnesium above the melting point of said reducing metal, whereby said metal oxide is reduced to the metallic state and a slag-forming oxide of said reducing metal is formed, said reaction being carried out in the presence of an amount of a molten, non-reacting metal capable of alloying with said refractory metal and in the presence of a molten salt solvent capable of dissolving the reducing metal oxide slag formed during the reaction, the ratio between said molten salt solvent and said reducing metal oxide slag being between about 2.2:1 and 8:1 and said molten salt solvent being selected from the group consisting of metal chlorides, metal fluorides and mixtures of metal chlorides and metal fluorides having a boiling point above about 700° C. wherein the metal constituent of said salt solvent belongs to the first through third groups of the periodic system, whereby a molten alloy layer and a second layer comprising said molten salt solvent with said reducing metal oxide slag dissolved therein are obtained, and separating said alloy layer and said second layer from each other.

16. In a process as claimed in claim 15, wherein said molten salt solvent comprises cryolite.

17. In a process as claimed in claim 15, wherein said second layer is electrolysed for recovering said reducing metal and said salt solvent for recycling.

18. In a process as claimed in claim 15, wherein portions of said alloy layer and said second layer are substantially continuously withdrawn and fresh amounts of said refractory metal oxide, equivalent amounts of said reducing metal, said non-reacting metal and said molten salt solvent are supplied in predetermined amounts to said reaction zone, whereby fresh amounts of alloy layer and second layer are continuously formed.

19. A one-step process for the continuous preparation of an alloy, which comprises reacting in a reaction zone an oxide of at least one refractory metal with an equivalent amount of aluminum above the melting point of aluminum, whereby refractory metal and aluminum oxide are formed, said process being carried out in the presence of an amount of molten, non-reacting metal capable of alloying with said refractory metal and in the presence of cryolite, the ratio of cryolite to aluminum oxide formed being between about 2.2:1 and 8.0:1, whereby an upper layer comprising cryolite and aluminum oxide dissolved therein and a lower alloy layer are obtained, continuously drawing off from said reaction zone said alloy layer and said upper layer, and continuously supplying fresh amounts of refractory metal oxide, aluminum, non-reacting metal and cryolite to said reaction zone.

20. In a process as claimed in claim 19, wherein said upper layer is electrolyzed for separating the aluminum and the cryolite from each other, and recycling said aluminum and said cryolite to said reaction zone.

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