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METHOD OF MAKING ALUMINUM ALLOYS

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This invention relates to the production of aluminum alloys containing from 45 to 90% of aluminum and from 10 to 55% of at least one high melting metal having a melting point above 1000° C., such as, for example, vanadium, molybdenum, chromium, tantalum, columbium, titanium, zirconium, tungsten, manganese, copper and iron.

Since aluminum alloys according to this invention are master alloys intended to be added to other metals or alloys, they should be of great purity, in respect to metallic contaminants, non-metallic interstitials and inclusions. For instance, the 40% canadium-60% aluminum alloy is in considerable demand for the production of a titanium base alloy which contains 4% vanadium and 6% aluminum.

It is an object of this invention to provide a method of making by simple techniques an alloy containing from 45 to 90% of aluminum.

It is another object of this invention to provide a method of making an alloy containing from 45 to 90% of aluminum, which is of great purity having low levels of other metallic and non-metallic contaminants as well as a great freedom from inclusions.

Other useful objects will become evident from the following detailed specifications.

For purposes of illustration, the invention will be described particularly in connection with the production of an alloy containing about 40% vanadium and 60% aluminum, an alloy containing about 30% molybdenum and about 70% aluminum, and an alloy containing about 40% chromium and 60% aluminum.

Vanadium-aluminum alloys have in the past been prepared by reduction of oxides in electric furnaces and also by aluminothermy. In the former case it has not been possible to reduce the carbon levels in the resultant alloy to the desired low levels, and in the latter, considerable difficulties have been encountered because this 40% vanadium-60% aluminum alloy is relatively poor in vanadium and high in aluminum. Consequently, in aluminothermic reduction, as commonly practiced, it is not possible to achieve a sufficiently high temperature to obtain the 40% vanadium-60% aluminum alloy.

According to this invention, a pool of molten aluminum is provided in a reaction vessel. A very suitable reaction vessel is a specially shaped ladle provided with a side tap hole, as more particularly described hereinafter.

To this molten aluminum is added a charging mixture consisting essentially of an exothermic reaction mix and a flux. The exothermic reaction mix consists essentially of vanadium pentoxide and aluminum in such proportion as to produce an exothermic reaction, capable of generating a vanadium rich, aluminum-containing alloy which is absorbed by the molten aluminum. The flux consists essentially of a proper mixture of lime and fluorspar, sufficient to generate a fluid slag capable of protecting the underlying metal. As the reaction proceeds, this

layer of slag will absorb more and more of the alumina generated as a result of the reaction between the aluminum metal and the vanadium pentoxide.

An important feature underlying this invention consists in the idea of generating a slag layer which is fluid as long as additions are made of the exothermic charging mixture and which either allows this mixture to pass through it or acts to ignite the charging mixture and permits the resultant vanadium rich alloy to go through it and into the metal beneath. At the completion of the production run, however, the slag is high in aluminum, forms a cover which protects the metal beneath it, solidifies upon slight cooling from the reaction temperature and is capable of sustaining itself, i.e., roofing-over when the finished alloy is tapped from the reaction pot. Furthermore, the vessel in which the reaction is performed preferably is shaped so as to give to its side wall an adequate angle against which the solidified refractory roof can support itself.

In practice, these features are achieved by a combination of factors, the principal of which are the proportioning of flux and exothermic reaction mix and the proportioning of the lime to the fluorspar at different stages of the operation.

At the start of the operation, i.e., during the "start-up" period, the reaction is initiated by contacting the molten aluminum with a few shovelfuls of "start-up" charging mixture. This addition is followed by charging a small amount of barium peroxide and aluminum grain to initiate a vigorous reaction. Thereafter more of the "start-up" mixture is charged until a molten slag cover has become established as the result of the reaction of aluminum and vanadium pentoxide and the absorption of the resultant alumina in the lime and fluorspar charged with the "start-up" mixture.

After this molten slag cover has become established, it is sufficiently hot to set-off the reaction when further additions of exothermic charging mixture are made. Thus the weight ratio of total flux ($CaO+CaF_2$) to exothermic reaction mix (V_2O_5+Al) and the weight ratio of CaO to CaF_2 in the flux are different during the start-up period than they are during the running period.

Because the slag cover should remain hot enough to initiate the reaction in the exothermic charging mixture and not become too hot to boil over, a charging rate should be maintained which is capable of complying with these needs.

Pebble lime and fluorspar are differently proportioned for the first short "start-up" period and for the later "running mix" period, also because the early slag should be highly fluid in order to permit the later charge to pass through this slag layer.

The operation proceeds by placing a pool of molten aluminum at the bottom of the reaction vessel, then charging the "start-up" charging mixture containing a relatively heavy proportion of flux for a period ranging between about three and ten minutes, depending on the quantity of alloy to be produced. Thereafter, the "running mix" continues to be charged for between thirty and ninety minutes, depending again, on the quantity of alloy to be produced.

The weight ratio $CaO:CaF_2$ in the "start-up" charging mixture is high, about 1.8:1 (i.e., 64% CaO), but can be between 1.4:1 and 2.8:1, because the Al_2O_3 generated in the course of the reaction will be tied to CaO and its

availability is important. At the 1.8:1 ratio, the melting point of the $CaO:CaF_2$ composition is about 1800° C., compared to 2560° C. for 100% CaO. CaF_2 is necessary to keep fluidity high and melting point low.

The weight ratio of total flux constituents ($CaO+CaF_2$) to total exothermic reaction mix (V_2O_5+Al) in the "start-up" charging mixture is high, and is usually about 0.23:1, but can range from 0.17:1 to 0.40:1. In the "running mix" this ratio is preferably about 0.075:1, but can vary between 0.05:1 and 0.15:1.

Later, when the "running mix" is charged, it becomes important to have a slag capable of absorbing alumina, while maintaining a relatively high degree of fluidity, thus the weight ratio $CaO:CaF_2$ is low, about 0.6:1 (33% CaO), i.e., ranging between 0.20:1 (18% CaO) and 1.0:1 (50% CaO). The slag becomes increasingly richer in alumina until the end point of the reaction has occurred at which time this largely alumina slag will solidify on even slight cooling and turn into a refractory roof covering the molten alloy. The composition of the slag at that point is aimed to be between about 80 to 85% Al_2O_3 by weight.

As mentioned before, the sides of the reaction vessel preferably form an angle which permits the solidified slag to find sufficient support to form an arch or roof, i.e., the sides form an angle of between about 100 and 110°, preferably about 104°, with the bottom of the reaction vessel, assuming that this bottom is completely level.

As discussed hereinabove, the composition of the slag cover at the end of the production run combined with the design of the reaction vessel, produces a cover over the metal which very quickly solidifies when heat is no longer supplied by exothermic reactions taking place in the metallic bath in the vessel. The metal being tapped from the bottom of the vessel leaves the slag resting as a solid roof behind in the ladle, minimizing entrapment of slag or reaction products in the metal. Thus a clean metallic product is obtained which contains a minimum of non-metallic inclusions.

Conversely, the metallic bath is heated owing to the exothermicity of the reaction between aluminum and vanadium pentoxide, so that it is capable of absorbing progressively increasing amounts of vanadium until the desired composition is reached. At the same time, the reaction product of V_2O_5 and Al goes into the supernatant slag and during passage of the reaction mix through the slag, impurities contained in the charge can be absorbed therein.

A feature of considerable importance of this process is the fact that cleanings from previous production runs can be recycled and absorbed into the melt while they are purified as they pass through the slag. Such remelt additions are most suitably made when the operations reach the 40% V level at which time there exists sufficient excess heat to absorb the remelt cleanings in amounts up to about 20% of the final alloy weight.

After completion of the reaction, the heat is tapped through a tap hole level with the bottom of the reaction vessel and passes into a cast iron chill mold which is lined with a special high purity refractory mix and which contains a small charge of cryolite at the bottom. Mold and cryolite must be preheated to prevent the tapped alloy from freezing and to permit a clean metal-slag separation to occur. The cryolite acts to purify the alloy in two ways: (1) by chemically dissolving entrapped alumina, and (2) by mechanically sweeping slag inclusions upward to the surface which is later cropped during the cleaning operation. Such cryolite additions are made to the extent of between 0.25 and 1.50% of the gross cast weight, but an addition of about 1.25% is preferred.

Immediately after tapping, the reaction vessel is placed on its side and the refractory roof is removed. It is thus possible to produce 20–25 heats with only minor repairs to the refractory lining. The lining is 90–95% MgO and very low in iron and silica. The same material is used for the mold.

Charging of the "start-up mix" and the "running mix" should be as constant as possible. This can be accomplished easily by mechanical charging. In the case of hand charging, this is more difficult but with some care a constant rhythm of charging at a steady controlled rate is also possible.

The advantages of the above-described invention will be more evident to those skilled in the art as shown in the embodiment presented below.

Example 1.—40% V–60% Al

A 109 cu. ft. reaction vessel equipped with a tap hole in its bottom and with trunnions for crane handling was used. This vessel had an inside diameter of 76" at the top and 43" at the bottom with a 66" inside height. It had been provided with a 6" lining around the side wall and 15" bottom consisting of a high purity magnesia refractory containing between 90 and 95% MgO and very low in iron and SiO_2.

Into this vessel was charged 4,000 lbs. of aluminum which was then heated by means of gas burners until it was molten. The "start-up mix" consisted of 800 lbs. of V_2O_5 containing material (analyzing about 90% V_2O_5, balance largely Na_2O, but also other, minor amounts of oxides of Fe, Si and Al), 428 lbs. of grained aluminum, 180 lbs. pebble lime, and 100 lbs. of fluorspar. This charge was well mixed and then charged in shovelfuls over a period of five minutes into the molten aluminum, undergoing a reaction upon contacting the hot metal. To make sure that the reaction proceeded satisfactorily, a paper bag full of a total of 4.5 lbs. of BaO_2 and 1.5 lbs. of Al was added after the first five shovels of "start-up mix" had been charged.

After this "start-up mix" had been charged, a second mix, the "running mix" consisting of 5,960 lbs. of V_2O_5 containing material, same grade as above, 3,416 lbs. of grained aluminum, 280 lbs. of pebble lime and 448 lbs. of fluorspar was charged in 43 minutes at a rate as constant as possible by hand charging methods. The reaction continued to proceed satisfactorily and after the entire "running mix" had been charged, the vessel and its contents were allowed to stand for five minutes for alloy grains that had not yet separated from the slag layer to trickle into the underlying metal, and for the refractory roof to form and solidify.

Thereafter, the alloy in the reaction vessel was tapped into a 66 cu. ft. cast iron chill mold lined with a high-purity refractory mix consisting of 90–95% MgO to a thickness of 1", troweled to a little above the metal level. 100 lbs. of cryolite had been placed at the bottom of this mold and both mold and cryolite had been preheated. Ten to fifteen minutes were required for the metal to flow into the mold. The final gross weight of the alloy was 8,533 lbs. which analyzed as follows:

	Percent
V	40.60
C	.024
Mn	.087
Al	58.27
O	.059
S	.002
Si	.31
N	.015
H	.001
Fe	.34
Mo	.20

and represented a total yield of 87.5% with respect to vanadium. There were no appreciable losses of aluminum.

The reaction vessel was then placed on its side, the refractory roof was pierced and then following that it was further loosened and removed by a crane. After a small patching job, the reaction vessel was ready for the next heat.

The following Examples 2 and 3, respectively, illustrate the production of a molybdenum-aluminum alloy and of a chromium-aluminum alloy. The methods employed are essentially similar to that of Example 1.

Example 2.—30% Mo–70% Al

Start-up mix:	Pounds
CP MoO_2	520
Al grain	335
Pebble lime	141
Ground fluorspar	78
Running mix:	
CP MoO_3	3865
Al grain	2498
Pebble lime	205
Ground fluorspar	327
Molten aluminum	5000
Final alloy	8500

Analysis:	Percent
Al	69.13
Mo	30.04
Fe	0.30
Si	0.30
C	0.03

Example 3.—40% Cr–60% Al

Start-up mix:	Pounds
Green chrome oxide	351
Potassium dichromate	678
Al grain	540
Pebble lime	55
Ground fluorspar	126
Running mix:	
Green chrome oxide	2572
Potassium dichromate	4976
Al grain	3959
Molten aluminum	3429
Final alloy	8000

Analysis:	Percent
Cr	40.05
Al	59.13
Fe	0.30
Si	0.30

The above described invention is not restricted to the embodiment here presented, but may be practiced within the scope of the following claims.

We claim:

1. A method of making vanadium-aluminum alloys containing from 45% to 90% of aluminum and from 10% to 55% of vanadium, which comprises providing in a reaction vessel a pool of aluminum, establishing, during a start-up period, a slag cover on the pool of aluminum by charging onto the pool of aluminum a start-up charging mixture consisting essentially of an exothermic reaction mix and flux, the exothermic reaction mix consisting essentially of V_2O_5 and Al, the flux consisting essentially of lime and fluorspar, the weight ratio of said flux to said exothermic reaction mix in said charging mixture being between 0.17:1 and 0.40:1, and the weight ratio of lime to fluorspar in said flux being between 1.4:1 and 2.8:1, and after a slag cover has been established, charging onto the slag, during a running period, a charging mixture consisting essentially of an exothermic reaction mix and flux, the exothermic reaction mix consisting essentially of V_2O_5 and Al, the flux consisting essentially of lime and fluorspar, the weight ratio of said flux to said exothermic reaction mix in said charging mixture being between 0.05:1 and 0.15:1, and the weight ratio of lime to fluorspar in said flux being between 0.20:1 and 1.0:1, whereby the V_2O_5 and Al react to form alumina which is absorbed by the slag and vanadium metal which alloys with the aluminum in the pool.

2. A method according to claim 1, wherein the charging of the charging mixture during the running period is continued until the slag contains such a high proportion of alumina that it will solidify on slight cooling, stopping the charging, thereby allowing the slag to cool and form a solidified roof covering the molten alloy, maintaining the solidified roof supported by the reaction vessel, and tapping the molten alloy from the vessel while the solidified roof remains in the vessel.

3. A method according to claim 2, wherein the charging of the charging mixture during the running period is continued until the slag contains about 80–85% alumina by weight.

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