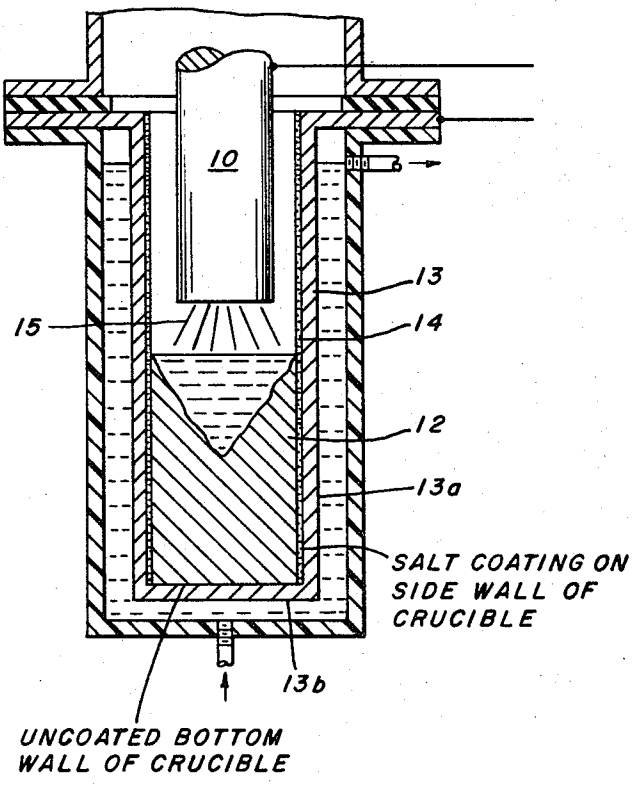
Nov. 4, 1969 L. E. STARK ET AL 3,476,171

METHOD FOR MELTING REFRACTORY METAL

Filed Feb. 14, 1967



INVENTORS.
LOUIS E. STARK &
OCTAVIAN BERTEA
By Walter P. Wood
Attorney

United States Patent Office

3,476,171

Patented Nov. 4, 1969

3,476,171

METHOD FOR MELTING REFRACTORY METAL

Louis E. Stark, Youngstown, and Octavian Bertea, Warren, Ohio, assignors to Reactive Metals, Inc., a corporation of Delaware

Filed Feb. 14, 1967, Ser. No. 615,929
Int. Cl. B22c 3/00; B22d 27/02
U.S. Cl. 164—52 6 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in the consumable arc melting of refractory metals such as titanium or zirconium which involves collecting the molten refractory metal in a cooled crucible having a coating at least 0.01-inch thick on the interior thereof of at least one halide from the group consisting of halides of alkali and alkaline earth metals.

This invention relates to a method of producing ingots of refractory metals such as titanium and zirconium. More particularly, the invention concerns an improvement in a method of producing ingots by a consumable arc melting process whereby the ingots possess superior wall surfaces and minimum internal porosity.

In processing certain refractory metals, the refining process is performed in a consumable arc furnace wherein molten metal is collected in a crucible which acts as a portion of the electrical circuit. In a typical application, such as in titanium refining, a water-cooled copper crucible is used. Contact of the molten metal against the cooled surface is responsible for the formation of a spongy and irregular ingot wall surface caused by non-uniform solidification of molten metal. There is also occasional arcing to the crucible which causes surface pitting and melting of the copper container. The pitting and deformation of the copper crucible renders the ingots difficut to remove after solidification because of the non-uniform wall surface and the contact between the ingot and crucible.

In the drawing:

The single figure is a diagrammatic vertical sectional view of a conventional consumable electrode furnace to which our invention is applied.

The present invention provides a method of casting ingots of refractory metal such as titanium and zirconium which avoids the aforementioned difficulties. According to the invention, consumable arc melted refractory metal of superior homogeneity to the original electrode **10** is collected as an ingot **12** within a crucible **13** which has a thin adherent and continuous coating **14** at least 0.01-inch thick, preferably 0.06-inch thick and not greater than about 0.25-inch thick, of at least one halide of an alkali or alkaline earth metal. The coating is preferably applied to the crucible side wall **13***a* as a slurry of the

halide and a liquid having a low vapor pressure and substantially no solubility for the halide in such a manner as to leave the bottom **13***b* uncoated to carry the electric current necessary for the consumable arc melting process. The coating is dried before melting to completely remove the liquid, in any suitable manner such as by applying a vacuum so that the liquid vehicle is removed by evaporation. After the coating is dried, the crucible **13** may be used for melting. The arc **15** used for melting is prevented from striking the crucible side wall **13***a* by the presence of the electrically non-conducting coating **14**, thus making the melting process more efficient by transferring all of the arc heat into the ingot **12**.

Metal ingots produced in accordance with the invention by consumable arc melting have a smooth improved surface. During melting, the ingot is in contact with the coating on the crucible side wall and, as a result, the heat of the solidifying metal is conducted more slowly than it would be if in direct contact with the copper crucible. The retarded cooling thus allows the solidified metal to coalesce in a smooth dense outer wall. Moreover, because of the slower heat conduction from the molten metal to the crucible, the internal solidification of the ingot can proceed more uniformly with less tendency for internal porosity by solidification shrinkage. The greater uniformity of internal solidification results in an ingot of sounder internal metallurgical structure.

After completion of the metal refining process, the ingot is cooled and subsequently extracted from the crucible with considerable ease because of the reduced friction between ingot and crucible resulting from the presence of the intermediate coating material. The crucible maintains its original surface undamaged by arcing or galling during ingot removal and consequently its useful life is materially improved.

In summary, therefore, the benefits resulting from the use of coated crucibles in accordance with the invention in consumable arc melting include (1) more efficient transfer of arc heat into the ingot because of the presence of the electrically non-conducting coating on the crucible; (2) greater ease of ingot extraction due to the reduced friction and increased space between ingot and crucible resulting from the presence of the coating; (3) increased crucible life by elimination of erosion or burn-through from the arc striking the crucible wall and from reduced surface galling during ingot removal; (4) improved smoothness and soundness for the outer wall of the ingot because of more favorable characteristics for metal solidification in contact with the salt coating; and (5) improved internal metallurgical, mechanical, and chemical characteristics of the ingot due to more uniform internal solidification and cooling characteristics resulting from heat conduction through the coating.

The following will illustrate the practice of the invention.

TABLE I

	Crucible diameter (in.)	Melting proc.[1]	Crucible Coating: Salt	Crucible Coating: Vehicle	Remarks
Sample:					
1	4	V	None		Ingot difficult to remove, coating spongy.
2	4.5	V	do		Do.
3[2]	6	P	do		Do.
4	4.5	V	50% KCl-50% NaCl	Methanol	Ingot easily removed, good surface.
5[2]	6	P	50% KCl-50% NaCl	do	Do.
6	4.5	V	CaF_2	do	Do.
7[2]	6	V	CaF_2	do	Do.
8	4.5	V	NaCl	do	Ingot difficult to remove, coating spongy.[3]
9[2]	6	P	NaCl	do	Ingot easily removed, good surface.
10	4.5	V	NaCl	Water	Do.
11[2]	6	V	NaCl	do	Do.
12	8	V	NaCl	do.[4]	Do.

[1] V denotes vacuum melted. P denotes melted under positive pressure of Argon.
[2] Second stage of double melting process.
[3] Coating less than 0.01 inch thick.
[4] Had 10 ml. wetting agent, applies as a solution.

A series of ingots were melted in crucibles having coatings as described in Table I. The coatings were applied by brushing a slurry of the indicated salt in a suitable vehicle such as methyl alcohol or water. The salt was mixed in proportions sufficient to produce a heavy paste easily applied to the crucible wall with a brush to form an adherent, continuous coating surface. In the examples illustrated, a proportion of about 100 grams of salt to about 80 ml. of liquid vehicle produced a suitable paste for application to the crucible side walls.

It is necessary that the coating be applied to the crucible wall in sufficient thickness to achieve the desired results of the invention. We have found that a thickness coating of at least about 0.01-inch is necessary to insure sufficient retardation of the cooling of the ingot and ease of the ingot removal from the crucible. In Example No. 8 of Table I, a coating less than about 0.01-inch thick was applied and as a result, the ingot was difficult to remove and had a surface not altogether satisfactory.

It has also been shown that an aqueous coating mixture may be used satisfactorily. However, the mixtures made with water have less tendency to adhere and the water does not dry as quickly as the organic vehicles and, therefore, such coatings require a longer time to dry. The coating may be applied to the crucible in any convenient manner so long as it is present as a continuous adherent coating on the crucible side wall and has a minimum thickness, as discussed above, of at least 0.01-inch.

We claim:

1. In a process for refining a refractory metal, which process includes suspending a consumable electrode of the refractory metal over a metal crucible, water cooling the crucible, and applying an electrical current through the electrode and crucible to produce an arc at the bottom of the electrode, thereby melting the electrode and building up an ingot in the crucible, a method of improving the surface characteristics of the ingot, which method comprises applying to the inside surface of the side walls of the crucible exclusive of the bottom wall

an adherent and continuous coating about 0.01 to 0.25-inch thick of a salt of the group consisting of halides of alkali metals and alkaline earth metals, said coating being applied to the crucible walls as a paste and dried before melting of the electrode begins, and conducting the arc current through the uncoated bottom wall of the crucible to the ingot during the melting operation.

2. An improvement according to claim 1 wherein said refractory metal is titanium.

3. An improvement according to claim 1 wherein said salt is sodium chloride.

4. An improvement according to claim 1 wherein said salt is calcium fluoride.

5. An improvement according to claim 1 wherein said crucible is a cooled copper mold.

6. An improvement according to claim 1 wherein said coating is about 0.06-inch thick.

References Cited

UNITED STATES PATENTS

1,940,619	12/1933	Barstow et al.	75—17
2,607,674	8/1952	Winter	75—84
3,035,318	5/1962	Campbell.	
3,271,828	9/1966	Shelton et al.	164—52
3,417,808	12/1968	Rosenberg	164—68

FOREIGN PATENTS

808,843	1/1959	Great Britain.

OTHER REFERENCES

"Slag Washing of Stainless Steels . . .," Steel, May 25, 1959, pp. 146, 149, published by Penton.

J. SPENCER OVERHOLSER, Primary Examiner

V. RISING, Assistant Examiner

U.S. Cl. X.R.

75—10, 84, 94, 95, 96; 164—68, 72, 138