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COMPACTION OF FINELY DIVIDED METALS

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This invention relates to the compaction or conversion of powdered refractory metals into coherent masses and more particularly to novel methods and means for producing compacted masses of such metals.

As is known, refractory or high melting metals having atomic numbers between 21 and 79, including zirconium, titanium, tantalum, nickel, chromium, tungsten, cobalt, columbium, hafnium, molybdenum, vanadium, etc., are recoverable in powdered or granular state. Thus, titanium is produced in sponge form by reducing at an elevated temperature titanium tetrachloride with a reducing metal such as magnesium or sodium, the sponge product being thereafter ground or milled to the particulate powder or grain size desired. Also, columbium can be recovered in the form of free-flowing grains by reducing columbium pentachloride with hydrogen at an elevated temperature; while nickel or tungsten powders can be prepared by the reduction of their oxides in accordance with well-known techniques.

The particulate products recovered from these operations are then converted to ingot form for fabrication into mill products, e.g. bars, rods, tubes, strip, sheet or other useful articles of commerce. Ingot fabrication is commonly brought about by a melting process, but many refractory metals as well as their alloys cannot be subjected to melting while in contact with known crucible materials due to an undesired impurity contamination which ensues. To minimize or obviate this, melting by consumable electrode techniques is resorted to in which the metal undergoing melting is formed into an electrode which is then arc melted by an electric arc struck between the electrode and the ingot or a pool of the metal of the same composition within a cold crucible. The molten metal thus comes in contact only with its own solid or compatible phase frozen on the walls of the crucible and formation and production is assured of an uncontaminated ingot.

Many difficult problems attend these attempts at fabricating consumable electrodes of the particulate refractory metals mentioned. For example, if the metal powders are compressed and sintered into the desired electrode shapes, an undesired atmospheric and container material contamination takes place at the sintering temperatures used. When mere cold compaction is undertaken to avoid this contamination, disadvantageously, an undesirably low compact green strength arises which renders the compact inadequate in many instances to withstand the handling and mounting in the electrode holder to which it must be subjected. This is especially true in the case of columbium. A real need thus exists for an improved method designed to assure effective and satisfactory compacting of particulate refractory metals and their alloys without attendant objectionable impurity contamination of the metals. A salient object of this invention therefore is to overcome these and other disadvantages characterizing prior refractory metal compacting and melting procedures. A principal object is to provide novel methods and means for attaining these objects, and particularly an improved method for compacting and melting particulate forms of columbium and its alloys without the objectionable impurity contamination alluded to. Other objects and advantages will be apparent from the ensuing description.

These objects are attained in this invention which com-

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prises compacting particles of a refractory metal, a refractory metal alloy, or mixtures thereof to a coherent mass by enclosing a charge of said particles within a container comprising a relatively thin foil or sheet of a metal compatible in composition with said particles, which on completion of the compacting operation is adapted to function as a consumable electrode during subsequent arc melting of the compacted mass, enveloping said container and its metal particle content within a thin sheet of high strength, solid organic polymeric plastic material, enclosing the resulting assembly in a flexible, air- and water-tight receptacle, and subjecting the confined mass of particles while in said receptacle to hydrostatic compaction in liquid media.

In a more specific embodiment, the invention comprises compacting a powdered or granular refractory metal, such as columbium, to a coherent mass by enclosing a charge of the metal particles in a suitable container element such as a thin foil or sheet material of columbium which will function, on completion of the compacting operation, as an integral part of a consumable electrode in the subsequent arc melting of the mass produced from the compacting operation, confining said container and its metal particles within and enclosing them completely in a thin sheet of a high-molecular-weight, preferably thermoplastic organic polymeric material such as polyethyleneterephthalate, enclosing the said resulting particle mass and thermoplastic organic polymer sheet container within a relatively thick flexible, air- and water-tight rubber vessel, and subjecting the particles while confined in said container within said vessel to hydrostatic compaction.

In practically adapting the invention particles of one or more refractory metals having a melting point above 1200° C., such as titanium, silicon, hafnium, vanadium, columbium, tantalum, tungsten, nickel, cobalt, etc. or an alloy thereof are compacted to a coherent mass by introducing a suitable charge of the metal or alloy particles into a relatively thin container comprising preferably a foil of metal or alloy of substantially the same chemical composition as the metal particles being subjected to compaction whereby the body of refractory metal particles are completely enclosed in said foil. The closed container is then wrapped or otherwise enveloped in a thin plastic sheet or wrapper of a relatively high tensile strength, preferably thermoplastic organic polymer such as a polyethyleneterephthalate, or polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl fluoride, polyvinylidene chloride, polyvinylidene fluoride, polystyrene, polyurethane, or other terephthalic acid glycol polymers, polymethylmethacrylate, polyethylene, polypropylene, polybutylene, polyamides, chlorinated polyethers, polyacrylonitrile, polycarbonates, polychlorotrifluoroethylene, polymeric fluorocarbons such as polytetrafluoroethylene, and also cellulose ethers and cellulose esters such as ethyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate butyrate, cellulose nitrate, etc. If desired use can be effected of copolymers based on two or more of the above materials. The commercial thermoplastic polymers utilizable in this invention are described in the Plastics Properties Chart, Part 1, found in Modern Plastics Encyclopedia (Plastics Catalogue Corporation, Bristol, Connecticut, 1962). Preferred sheets are those composed of polyethylene, polyethyleneterephthalate, polyvinyl chloride, 6,6 nylon, and a sheet of polyethyleneterephthalate coated with polyethylene. The plastic sheet or film can range from 3-10 mils in thickness and is used to cover the metal foil enclosure at least to the extent that it separates said foil from contact with an outer flexible or rubber container to be presently referred to. When it is desired to evacuate the package, provision for the egress of air can be made. In general, the plastic films employed

herein should have a tensile strength of 10,000 p.s.i. or higher and preferably a tear strength of 10 gms. or higher, based on the well-known Elmendorf test.

The resulting package is then enclosed within a relatively strong, flexible, air-tight vessel or container which can comprise a heavy flexible sleeve or boot made of synthetic or natural rubber or similar synthetic material. The equipment and procedure at this step of the process is well known in the practice of hydrostatic compaction. The sleeve is usually closed at one end and made to fit the compact. The open end may be sealed by folding, tying, or by applying suitable adhesives against the inflow of the pressurized liquid. Frequently, it is desirable to evacuate air from the compact which may be done by incorporating a check valve in the top enclosure with provision for connection to a suitable vacuum pump.

The whole, final assembly is then immersed in a suitable liquid medium such as water, contained in a pressure vessel and subjected to sufficient hydrostatic pressure to effect desired compaction of the particular metal. Sufficient pressure is applied to compact the particles and their associated metal foil container element and provide them with a substantial degree of adherence at least within the foil and the particles contacting said foil. The pressure may be applied by mechanical means such as pumps or by explosive or spark discharge in the liquid in accordance with well-known procedures. Depending on the method of applying the pressure, the time under pressure may vary upward from a fraction of a second. The times and pressures used are selected on the basis of the material and equipment employed and are, as noted, applied in accordance with conventional procedures.

After the desired compaction has been effected the entire package or assembly is removed from the pressure vessel and the outer flexible container or boot is removed from the compact and the sheet is peeled away. Advantageously a polymeric thermoplastic organic sheet such as commercial polyethyleneterephthalate film, which is preferred for use, does not adhere to the metal and can be completely removed therefrom following the compaction. The metal foil wrapper is left on the compact, forms an integral part thereof, and is subsequently consumed with the electrode in the melting operation to which the compact is later subjected. During said compaction the metal foil becomes pressed against and into the charge of metal particles to form as noted an integral part thereof and therefore advantageously stabilizing the compacted product. The foil being integrally associated with the charge renders the whole compact rigid and strong enough for handling and use and in the subsequent arc melting of the compact the foil advantageously provides a consumable electrode. In many instances where cohesion of the particles is relatively poor, as with pure columbium and certain columbium alloys, the particles would run out of the compact if the foil is deliberately broken. Nevertheless, as long as the foil is left intact, the compact can be readily melted without spilling of solid metal particles with the foil acting as a consumable electrode. This is rendered possible because in the process of striking the arc the electrode becomes heated to sintering temperatures at least in the vicinity of the arc. In a preferred melting operation, the electrodes are initially shorted to effect the sintering condition prior to forming the arc for melting.

To a clearer understanding of the invention the following specific examples are given which are merely illustrative of and not to be construed as limiting the underlying principles of the invention.

Example I

A pure columbium sheet $11\frac{3}{4}$ " x 28" x 4 mills was wrapped about a $3\frac{1}{4}$ " diameter cylindrical wood form and lap seamed to form a tube. It was slipped off the end of the form and fitted with end caps made from

similar foil. The end caps were made from $5\frac{1}{2}$ " diameter discs by serrating and bending the edges to form caps or plugs which fitted inside the end of the tube. One end was closed with one of these caps to serve as the bottom of the container. A sheet of 8 mil commercial polyethyleneterephthalate film known as "Mylar," a trademark of E. I. du Pont de Nemours and Company, was wrapped around the cylinder and fastened with thin adhesive tape. An end support consisting of a solid aluminum disc $\frac{3}{4}$ " thick by $3\frac{1}{4}$ " diameter was placed against the lower end of the container and taped in place. This served to keep the end of the resulting compact flat to facilitate tack welding of several compacts into a longer electrode if desired. The cylindrical container was then filled with pure commercial columbium granules of approximately 0.5 mm. diameter. The top foil cap was pressed into place, the amount of granules being adjusted so that when the cap was firmly in place it was flush with the end of the cylinder. A second $\frac{3}{4}$ x $3\frac{1}{4}$ inch aluminum disc was placed on top. This assembly was then set into a fairly close fitting "Neoprene" synthetic rubber sleeve open at one end. The open end was closed by clamping. This whole package was disposed within a pressure vessel, the cover bolted on said vessel and the vessel was filled with water and connected to a high pressure force pump. The hydrostatic pressure in the pressure vessel was raised to 60,000 p.s.i. and maintained for two minutes. The pressure was let down, the vessel opened and the compact removed. The rubber sleeve was easily slipped off and was suitable for re-use. The plastic film was closely immeshed in the folds of the columbium foil but could be completely peeled off, leaving an uncontaminated columbium compact about 3" in diameter and 26" long adapted for use as the consumable electrode in a vacuum arc melting furnace. The furnace chamber contained a cooled copper crucible section in which the ingot was cast. To start the arc melting process a layer of columbium granules was placed in the bottom of the crucible. The compacted electrode was clamped in place. The electrode was lowered to make firm contact with the "striker" material in the crucible. The current was then turned on and increased to about 5000 amps. in about 5 minutes and held at 5000 amps. for one minute. The electrode was thus heated to sintering temperature. The current was then cut off and the electrode raised out of contact with the crucible. The arc current was then applied, the arc struck and the electrode melted in the usual manner. It melted off smoothly with no evidence that the solid granules were falling out.

Example II

Eight hollow cylinders of approximately 5 mil. columbium foil 4" diameter x about 14" long were prepared with end caps. A powder mixture was made up by blending 36.5 lbs. of -30+200 U.S. standard mesh low oxygen titanium, 16.0 lbs. of $-\frac{1}{8}+\frac{1}{16}$ inch zirconium granules, and 278.0 lbs. of -20+60 mesh columbium powder. A total of 5.5 lbs. of Cb foil was used. The powder mixture was moistened with 1% isopropanol, mixed in a cone blender, and transferred to the foil cylinders. The foil cylinders were then closed at the top with foil covers and wrapped in 10 mil high strength polypropylene film. These packages were then placed in heavy rubber containers which were connected to a vacuum line and vacuum applied for 1 hour to remove the residual isopropanol and entrapped air. The containers were closed and sealed, immersed in the water chamber of a hydraulic press and subjected to a pressure of 60,000 p.s.i. for 5 min. The assembly was opened and the film wrapped metal body was removed from the rubber containers and the film was stripped cleanly from the metal foil. Although the film was torn by this removal it was cleanly removed without trouble. The metal compacts could be handled normally and were

vacuum arc melted to 6 inch diameter ingots. These ingots were joined together and given a second arc melting to form an 8" ingot. The ingot composition was satisfactorily uniform and was substantially correct at the desired 10% Ti, 5% Zr, 85% Cb. Approximately 8% of the titanium was lost by evaporation in the arc. The amount of titanium used was increased by this amount to compensate for this anticipated loss.

Example III

18 lbs. of -30+200 mesh (U.S. Standard Sieve Size) titanium, 2 lbs. of -30+325 mesh V-Al alloy (60% Al) were blended in a cone blender. A four inch diameter aluminum foil cylinder was made and wrapped in a 5 mil vinyl chloride-vinylidene chloride polymer sheet having a tensile strength of 12,000 p.s.i. to give support to the foil cylinder during filling. The top end was closed with both foil and film and the package placed in a heavy flexible "neoprene" boot and subjected to hydraulic compaction as in Example II. The compacted metal was recovered cleanly from the polymer wrappings and vacuum arc melted to an ingot. The ingot composition was 6% Al, 4% V. The aluminum foil used weighed about 0.25 lb. but this amount of aluminum was lost by evaporation during the vacuum melting.

When using consumable electrodes, the foil used for the inner container is melted and usually becomes part of the ingot composition. In view of this the covering metal sheet or foil chosen should be compatible with the composition of the final ingot being produced, both in quantity and kind. The foil may have a relatively high vapor pressure and consequently is more or less volatilized during the melting process. A considerable portion of titanium foil, for example, would be lost when used during the melting of a columbium or tungsten alloy. Aluminum is lost when used with a titanium alloy. This loss may be compensated for by employing a corresponding excess of the volatile metal. It is usually preferable when economically feasible, to use foil of the metal forming the major constituent of the compact. Although aluminum foil will effect a satisfactory compaction of columbium particles, most columbium metal products are adversely effected by even small amounts of aluminum. Consequently use is preferred of a columbium foil where columbium or columbium base alloys are being compacted and melted although a foil can comprise vanadium, titanium, etc. when formation is desired of alloys containing these or other elements. During the compaction the foil is found to become indented between the metal particles, a condition which no doubt contributes to the strength of the compact. In order to withstand this action the foil should be ductile. A good measure of the desired ductility is that it be able to stand creasing, i.e. bending 180° and then opening 90° without cracking. The pure refractory metals and many of their alloys will fulfill this requirement which makes it possible to use lap seams in preparing the foil container. It also gives assurance that cracks will not open as the foil folds during compaction. Foil thickness of about 1 to 10 mils is satisfactory. The foil is not sealed in an air tight manner but merely folded with the ends capped quite closely. The cracks left should be considerably narrower than the diameter of the adjacent particles.

It is sometimes advantageous to join several of the compacts to make longer or continuously operating electrodes. To facilitate this it is helpful to place end supports at each end of the foil container inside the outer boot, which boot can consist of polymeric materials possessing elastic characteristics, such as natural or synthetic rubber, neoprene or butyl rubber, etc. These supports are strong, relatively thick discs of some suitable metal such as brass, copper, aluminum, steel or of the

metal being compacted. The commoner metals are obviously preferred. These discs are relatively thick so as not to be deformed by the compacting action. For example, they may be ¼ to 1 inch thick and having the diameter of the initial foil container or slightly less. These end supports result in flat square ends easily tack welded.

The size of metal particles compactable under the invention is subject to wide variance. A practical size ranges from about 50 microns to ½ inch in maximum diameter. The smaller particles provide smoother compacts but are more subject to contamination, segregation, and sifting out of the wrappers. Very large particles present a rough contour which may damage the protecting films or even the boot and prevent the essential exclusion of the pressurizing liquid from the interior of the compact.

The improvement of this invention resides in the combined use of a metal foil enclosure covered by a strong plastic film. The foil in itself has an advantage over heavier enclosures used in "canning" billets for working in that it is impressed into the surface interstices of the metal particles which aids in binding the assembly. The thin metal offers a minimum of resistance to the transfer of pressure and compaction of the metal particles themselves. In some cases, notably with columbium, the strength of the compact is largely due to the foil wrapper. For example, in preparing a three inch columbium compact, the columbium particles will flow out freely if the foil is opened, yet the electrode can be handled, clamped and tack welded without loss of particles. As previously mentioned the electrode may be raised, by electrical resistance heating, to sintering temperature prior to actual melting so that the solids do not fall from the compact.

If the foil is omitted, and the metal powder enclosed in plastic only, the result is unsatisfactory. In many instances the plastic ruptures during compaction. It penetrates the interstices of the compact to the extent that it cannot be removed and hence causes contamination with carbides etc. on melting.

The high strength plastic film used over the foil serves as a parting agent between the heavy outside, water proof sleeve and the metal. Without the "Mylar" or similar lining the sleeve adheres to or becomes trapped in the wrinkles of the metal and cannot be thoroughly removed. Obviously contamination will result from this.

The manner of enclosing the metal particles in the foil and plastic film may be varied. The essential feature is to have the particle mass substantially completely enclosed in a metal foil wrapper which is adjacent to and in contact with the peripheral particles. The plastic film is disposed externally of the foil covering, hence providing a substantially complete separation between said foil covering and the outer or flexible container of the assembly. The heavy flexible outer container or boot encloses this double wrapped package against the inflow of the high pressure liquid. If desired, the whole triplex enclosure assembly made up of the foil, plastic film and the flexible boot may be first assembled to form a container provided with an opening or an inlet in its top for admitting the desired particulate metal charge. The foil and plastic film can be closed by folding or capping the foil and film in the order given and then closing the boot enclosure. Alternatively, and if desired, the foil, or the foil and plastic wrapper can be shaped into a container, filled with particulate metal particles and the whole then be placed in the boot element. In another variation the exterior heavy flexible container may be applied by dipping the inner assembly in a melt of suitable plastic material or a preparation such as one of the viscous compositions used to protect or "mothball" machinery.

Briefly the process of this invention has advantages of non-contamination and better compaction over previous methods of preparing metal compacts, especially those

destined for melting as consumable electrodes. Many heretofore non-compactable metals may be compacted by this method and conveniently arc melted.

I claim:

1. A process for compacting a mass of metal particles which comprises completely confining said particles within a thin, 1-10 mils thick metal receptacle enclosure, enveloping the latter within a thin, high strength polymeric plastic material, enclosing the resulting package within a strong, flexible, liquid-tight container, and subjecting the entire assembly to hydrostatic pressure compaction.

2. A process for compacting a mass of metal particles which comprises completely confining said particles within a thin, 1-10 mils thick metal receptacle enclosure, compatible in composition to said metal particles, enveloping the latter within a thin, high strength polymeric plastic material, enclosing the resulting package within a strong, flexible, liquid-tight container, and subjecting the entire assembly to hydrostatic pressure compaction.

3. A process for compacting a mass of metal particles which comprises completely confining said particles within a thin, 1-10 mils thick metal receptacle enclosure compatible in composition to the metal particles being subjected to treatment, enveloping said receptacle and its particles content within a thin, high strength polymeric plastic film having a thickness ranging from 3-10 mils and a tensile strength of at least 10,000 p.s.i. enclosing the resulting package within a strong, flexible, liquid-tight container, and subjecting the entire assembly to hydrostatic pressure compaction.

4. A process for compacting a mass of columbium metal particles which comprises completely confining said particles within a thin, 1-10 mils thick sheet of columbium metal as an enclosure, enveloping said enclosure within a thin, high strength polymeric plastic film, enclosing the resulting package within a strong flexible, liquid-tight container and subjecting the entire assembly obtained to hydrostatic pressure compaction.

5. A process for compacting a mass of columbium metal particles comprising completely confining said particles within a receptacle comprising a thin, 1-10 mils thick columbium sheet, enclosing said sheet and metal

particles within a thin, high strength polymeric plastic film of from 3-10 mils thickness and having a tensile strength of at least 10,000 p.s.i., confining the resulting package within a strong flexible liquid-tight rubber container and subjecting the entire assembly to hydrostatic pressure compaction.

6. A process for compacting a mass of metal particles which comprises completely confining said particles within a thin, 1-10 mils thick metal foil enclosure as a receptacle, enveloping said receptacle and its metal particles content within a polyethyleneterephthalate plastic film, enclosing the resulting package within a flexible, liquid-tight rubber container, and subjecting the entire assembly to hydrostatic pressure compaction.

7. A process for compacting metal particles and melting the compacted product which comprises completely confining said metal particles within a thin-walled 1-10 mils thick metal receptacle as an enclosure therefor, enveloping said receptacle within a thin, high strength polymeric plastic material, enclosing the resulting package within a strong, flexible liquid-tight container, subjecting the resulting assembly to hydrostatic pressure compaction, recovering the resulting compacted product with said thin metal receptacle forming an integral part thereof and subjecting the recovered product to arc melting.

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