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Slip Casting and Extruding Shapes of Rhenium With Metal Oxide Additives

I—Feasibility Demonstration

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16. Abstract

The feasibility of fabricating small rhenium parts with metal oxide additives by means of slip casting and extrusion techniques is described. The metal oxides, ZrO_2 and HfO_2 were stabilized into the cubic phase with Y_2O_3. Additions of metal oxide to the rhenium of up to 15 weight percent were used. Tubes of 17 mm diameter with 0.5 mm walls were slip cast by adapting current ceramic oxide techniques. A complete cast double conical nozzle demonstrated the ability to meet shapes and tolerances. Extrusion of meter long tubing lengths of 3.9 mm o.d. x 2.3 mm i.d. final dimension is documented. Sintering schedules are presented to produce better than 95% of theoretical density parts. Finished machining was found possible where required by electric discharge machining and diamond grinding.

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SUMMARY

The processing of most metal oxides (zirconia, alumina, etc.,) is normally done by the preparation of finely sized powders, forming the powders into shapes, and sintering at much less than melting temperatures. Slip casting and extrusion of these powders in a fluid state into finished forms is one of these techniques. Some refractory metals such as molybdenum and tungsten have adapted slip casting successfully. No such reference to the successful formation of rhenium by these methods is known. Further, the coprocessing of rhenium with metal oxides by powdered particle methods is new and could produce grain stabilized parts unavailable by any other known method.

The objective of this initial study is verification that the same methods used with metal oxides is directly transferable to rhenium.

The process variables and methods for slip casting rhenium with metal oxide additives and the extrusion of these as cermets was found possible. Stabilized zirconia additives as high as 15 weight percent were successfully incorporated into rhenium matrices. Photomicrographs show a continuous phase of rhenium surrounding individual stabilized zirconia particles. The zirconia is shown uniformly disbursed through the rhenium matrix with the rhenium showing good wetting even at sintering temperatures as low as 2300°C.

Part shapes were formed as slip cast conical rocket nozzles and cylindrical tubes typical of resistojet pressure cases. Tubing was extruded approximately a meter in length. The final tube outside diameter after sintering would be 3.91 mm. The sintering of the extruded tubes was not demonstrated in this phase. Thin walls were successfully slip cast with walls of .5 mm with projections for .1 mm being obtainable. The basic casting, extruding and sintering of variables are summarized.

INTRODUCTION

The main purpose of the program is to demonstrate the feasibility of utilizing commercial processing techniques for forming zirconia for fabricating rhenium hardware. While rhenium is usually fabricated by chemical vapor deposition (CVD) and to some extent by powder metallurgy techniques, neither of these methods readily lends itself to grain stabilization of small shaped parts typical of resistojet hardware. Rhenium grain stabilization is desired to prevent grain growth during resistojet operation for extended times at high temperature. On the other hand, both the slip casting and extrusion fabrication methods are able to accurately incorporate well-known stabilizers such as zirconia and thoria. Stabilizer concentration level and uniformity can be readily controlled. Zirconia and thoria are used to grain stabilize metals such as nickel, tungsten and platinum through dispersion strengthening (ref. 1).

No reference was found to any previous slip casting of rhenium. However, other refractory metals (molybdenum and specifically tungsten) have been fabricated by the slip casting process for a considerable time. In fact, early works with tungsten used suspending vehicles (media) that were chemically reactive in nature. Obviously, not only were these vehicles detrimental to the tungsten itself unless precisely controlled, but also were very reactive toward the plaster molds used for obtaining the desired shape. More recently (ref. 2), investigators developed an improved slip casting system for tungsten which permitted the use of a simple aqueous vehicle. The processes emulated a ceramic oxide slip by forming an oxidized coating on the metallic particles. This work pointed out the complicated nature of the slip media involved for adequately suspending particles of high density refractory metals. This point is very significant when comparing densities of materials which can be slip cast commonly, such as:

Alumina (Al_2O_3) $\simeq$ 3.9 g/cc
Zirconia (ZrO_2) $\simeq$ 5.6 g/cc

as compared to:

Tungsten (W) $\simeq$ 19.5 g/cc
Rhenium (Re) $\simeq$ 20.5 g/cc

A survey of the general ceramic slip casting process indicates that methods previously used for casting ceramic oxides were more than adequate to cast most shapes of refractory metals. The processing allows casting parts of high content of solids. In any slip casting operation, the higher the solids-to-liquid ratio the more dense the part is in the unfired state and, thus, less susceptible to cracking from high shrinkage. The process closely controls vital factors required for obtaining stable slips such as pH, viscosity, particle size distribution and chemical stability.

It was also recognized and anticipated that the casting of rhenium would be quite similar to tungsten on the basis of similar basic properties.

TABLE I
COMPARISON OF PROPERTIES

Metal	Atomic Number	Atomic Weight	Density $g\text{-}cm^{-3}$	Melting Point °C
Tungsten	74	186.2	19.5	3410
Rhenium	75	183.3	20.5	3180

It was also expected that rhenium would be easier to suspend into a slip since rhenium gradually oxidizes in moist air at 20°C to form $HReO_4$. Therefore, it was not necessary to require a separate processing step to obtain an oxide coating on the rhenium particles.

Some additional background information regarding grain stabilization of rhenium was gained from cermet applications between oxide ceramics and refractory metals. Valuable information regarding chemical reactivity and wetting between the metals and the metal oxides have been published (ref. 3). The stability of both yttria stabilized hafnia and zirconia, as well as thoria, was determined in combination with the refractory metals rhenium, tungsten and molybdenum. Calculations of the change of free energy of reaction for metal oxide systems showed large positive values indicating the refractory metals were very stable in contact with thoria, stabilized zirconia and hafnia at 2000°K and at 2500°K. Results of compatibility tests performed in vacuum at 2350°C for an exposure time of two hours are summarized in table II.

TABLE II
CHEMICAL COMPATIBILITY AT 2300°C IN A VACUUM (Ref. 3)

Metal (wt %)	Ceramic (wt %)	Remarks
Mo-40Re	ThO_2	No reaction
Re	ThO_2	No reaction
Mo-40Re	91 HfO_2 + 9Y_2O_3	Slight discoloration
Re	91 HfO_2 + 9Y_2O_3	Slight discoloration
W	91 HfO_2 + 9Y_2O_3	Slight discoloration
Mo-40Re	91 ZrO_2 + 9Y_2O_3	Slight discoloration
Re	91 ZrO_2 + 9Y_2O_3	Slight discoloration
W	91 ZrO_2 + 9Y_2O_3	Slight discoloration

Metal and ceramic compatibility was necessary since any severe reaction between metal and oxide would deplete the metal phase which in turn would cause embrittlement and loss of strength.

Another part of the published work pointed out the importance of having a liquid metal phase or a liquid ceramic eutectic wet the ceramic particles and flow between them during liquid phase sintering. While pure rhenium was not investigated, a molybdenum - 40 weight percent rhenium alloy was studied for wetting with thoria and hafnia ceramics at temperatures of 2500°C - 2750°C. The results indicated that sufficient wetting occurred to have facilitated bonding and tie-up of metal and oxide phase during sintering.

In this investigation of grain stabilizing rhenium, only cubic stabilized zirconia and hafnia were used. Pure zirconia oxide, for example, is known not to meet phase stability conditions over the required temperature range unless stabilized. Pure zirconia goes through a destructive phase change. When heated past approximately 1150°C, zirconia transforms from the monoclinic to the tetragonal crystalline structure. With the transformation from the monoclinic to the tetragonal phase, zirconia undergoes a considerable volume contraction and vice versa amounting to about a 9% volume change. The three crystalline axes in the zirconia are almost equal and the angles between them vary from a near right angle to 80°. Since both the monoclinic and tetragonal phases differ only slightly from a cubic form, additives having a cubic structure form a solid solution inducing a permanent cubic structure with only a small stress on the lattice. Zirconia once stabilized assumes a fluorite type of lattice. Common stabilizers for zirconia are calcium oxide, magnesium oxide and yttrium oxide. When high temperature stability is required, yttrium oxide is normally used.

INVESTIGATION OF NEW FABRICATION METHODS FOR GRAIN STABILIZING RHENIUM

A series of experiments were conducted to determine suitable means of suspending rhenium powder and forming a stable slip. This included the amount and types of liquid vehicle, binder and electrolyte (suspending media). The vehicle furnished the necessary fluidity and good drainage during casting while the binder supplied the strength required for handling and to some extent acted as a thickening agent helping to hold the particles in suspension. The electrolyte supplied the ionic environment around each particle creating a like-electrical charge on each particle. The electrolyte caused a particle repelling force and resulted in a uniform suspension. Slips were monitored and controlled for solid-to-liquid ratio, viscosity, pH, and specific gravity.

As expected, the major problem was determining the correct trade-off between slip components in order to suspend the high density rhenium powder. Resulting aqueous based slip formulations are shown in the appendix. Slip formulations are shown for pure rhenium and for composites containing stabilized zirconia. The use of the zirconia also served to aid in suspending the relatively heavy rhenium powder. Slips with the stabilized zirconia have been found to be usable for relatively long periods of time (at least 4-6 months) with very little settling occurring during this interval. The properties of a grain-stabilized rhenium slip are listed in the appendix.

Casting

The mold material used in most slip casting operations was plaster of paris. The plaster acts as an absorbent of the liquid phase of the slip by nature of its chemistry and crystalline structure. During the manufacture of plaster, the gypsum-$CaSO_4$-$2H_2O$ is calcined to remove approximately 75% of its chemically combined water, thus forming $CaSO_4 \cdot 1/2H_2O$. It is a combination of this built-in desire to accept water and the needle-like crystal structure forming a series of capillary passages in the plaster mold which result in removal of liquid from the casting slip. Thus, the liquid vehicle carrying the suspended particles is absorbed by the wall of the plaster mold leaving a uniform deposit on the walls which have been shaped to the desired geometry with due regard to shrinkage for sizing. The thickness of the part is determined by the time the slip is in contact with the mold and the complex interaction of the key process variables. In most instances, the relative shrinkage rate of the cast (green) part (after moderate air drying) and the mold allow the part to be freed and removed. It is at this point that green strength imparted by the binder phase of the slip is extremely important. At best, the green part is fragile and must be carefully removed from the plaster mold. Subsequent heat treatment (which is discussed in a later section) can set up the binder within the part for added strength prior to sintering.

A unique aspect of the rhenium slip casting process is the fact that cast parts do not exhibit any or at best only minimal shrinkage when cast in plaster molds. This phenomenon is in part most likely explained by the fact that optimum (or maximum) packing is obtained among the individual rhenium powder particles in conjunction with the high solids content of the slip. A method employed for removal of a cast rhenium part is to use an ash free paper-like insert in the plaster mold prior to casting. This procedure is also advantageous for casting thin walled parts since the absorbent paper becomes an integral part of the cast piece and provides handling strength to a thin walled part.

Tubes were cast which were typical of resistojet pressure cases of 17 mm in o.d. with walls of 1 mm. See figure 1.

During the course of the program, it was found that the rhenium slip with stabilized zirconia could be modified to slow down the casting rate and thus allow thinner walled parts to be cast. Using this modification, rhenium tubes with walls on the order of 0.5 mm (20 mils) thickness were cast and sintered. Subsequent study indicated the ability to cast ultra-thin walled parts in the 0.1 to 0.3 mm (4-12 mil) range might be realized provided precise control of particle size and distribution of the powder can be established.

A rhenium shaped part, with 1.5 mm wall, representative of a conical nozzle was processed with approximately 15 weight percent stabilized zirconia. See figure 2.

Extrusion

Extrusion methods used to extrude ceramic oxides (alumina and zirconia) were investigated as a possible means of forming tubular rhenium shapes to meet the requirements of resistojet parts. An extrusion process was employed in which a power clay-like mix is loaded into a piston extrusion chamber and forced under pressure through a conical die using a suitable center member to form tubes or rods. The rhenium powder and finely ground zirconia can be plasticized with suitable organic additives and binders to become pseudo-plastic and resemble the texture of a clay-like composition. The blending and mixing process for extruding incorporated 5 weight percent of zirconium oxide for grain stabilization into fine particle size rhenium powder. The appendix details the composition and extrusion data for this series of experiments. The green size selected from available die sizes for extrusion was approximately 5.54 mm o.d.x 3.25 mm i.d. which upon sintering would shrink and produce fired tubing of 3.91 mm o.d. x 2.29 mm i.d. A 29.3% shrinkage was observed for the tubing shown in figure 3.

It was observed that extruded rhenium tubing had considerable green strength from the binder system. Thus, tubing could be stored and handled prior to sintering, representing a significant accomplishment. While only moderate pressure was required to extrude a continuous meter length of tubing, there was some degree of waviness and ellipticity observed. This indicated that improvement could be obtained by establishing a better balance between the extrusion pressure and plasticity of the rhenium mix.

Sintering

A literature review uncovered very little information on sintering techniques required to promote densification of rhenium compacts. In general, the basic guidelines are that rhenium is

Figure 1.- Cast tubing of rhenium with zirconia as an additive of 17 mm o.d. x 1 mm wall.

Figure 2.- Representative sample. Conical nozzle shapes of rhenium with metal oxide additives.

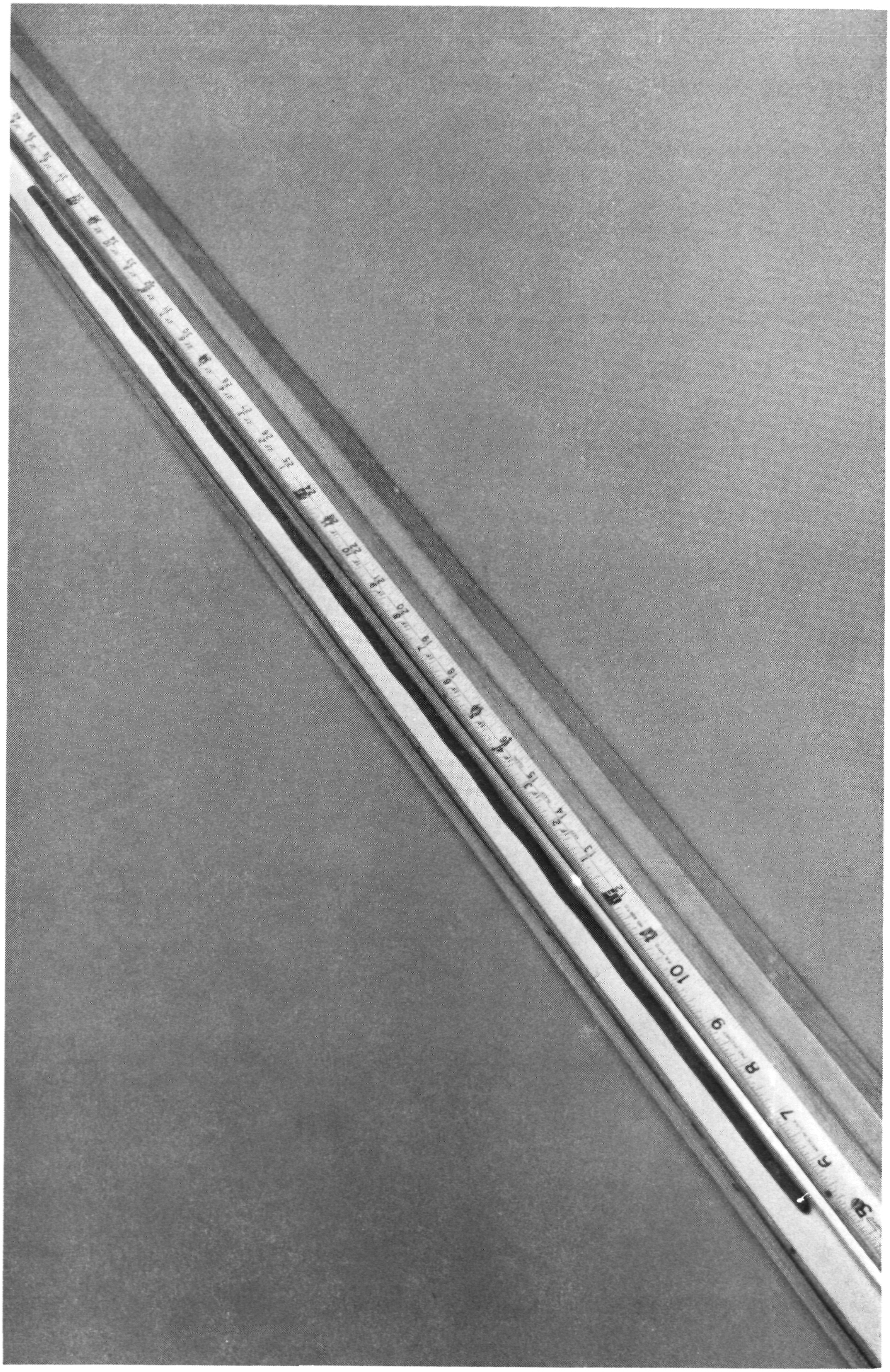

Figure 3.- First extruded "green" tubing of rhenium with zirconia additives.

sintered in vacuum to some intermediate temperature followed by firing in a hydrogen atmosphere to temperatures as high as 2600°C.

The rhenium sintering process is made difficult by the fact that other materials are incorporated in our rhenium samples. It is a requirement that the organic binder for casting the rhenium part be removed prior to final densification under hydrogen. In normal ceramic practice, the binder is removed and volatilized under ambient air atmosphere during heating. Obviously, this is not the case with the rhenium since even low temperatures readily oxidize and burn up the rhenium particles. By using vacuum for low temperature sintering, the binder was effectively removed with subsequent complete removal under a wet hydrogen atmosphere. The presence of the zirconia additive also is to be considered since zirconia is reduced to zirconium or lower oxide forms under vacuum if sintered to a high temperature.

A successful trade-off of the sintering variables was accomplished by using sintering schedules as shown in the appendix. The high degree of densification was evident by the apparent porosity as exhibited by water absorption values of about 0.3% or less. In addition, actual density values were within 95% of the theoretical samples having zirconia additives. Typical density values for samples containing 10-15 weight percent of zirconia range from 14.0 to 14.9 g/cc.

Stabilized zirconia additives as high as 15 weight percent have been successfully incorporated into rhenium matrices. Photomicrographs of polished specimens revealed that a continuous phase of rhenium surrounded individual stabilized zirconia particles. The zirconia was uniformly dispersed throughout the rhenium matrix with good wetting by the rhenium even at sintering temperatures as low as 2300°C.

Results of hot isostatic pressing (HIP), investigated on a cursory basis as a possible alternative technique for densification of rhenium parts, were not conclusive. Equipment available is limited to about 1600°C and 2000 psi of pressure which does not allow for adequate sintering and densification. Parts sintered under these conditions were quite porous and structurally very weak. In addition to these limitations, intricate encapsulating and canning techniques are required of parts prior to attempting the HIP process.

During the sintering trials a helium atmosphere was determined to be unsatisfactory for promoting void free, dense rhenium parts. Instead, a protective/reducing atmosphere as provided by hydrogen or in combination with argon was found adequate.

The state-of-the-art furnaces available for the required temperature regimes of 2500°C with hydrogen atmosphere are limited in size to about 100 mm in diameter and up to 230 mm high. Their present operating modes prohibit sintering extruded lengths of 1 meter of rhenium tubing produced. In order to sinter tubing, a special processing facility is required to affect densification. The semi-continuous heating of meter lengths would require some intricate sealing and atmosphere enclosure techniques combined with possible self-resistance or RF induction heating. Such methods were beyond the scope of the present contract.

Machining Investigation

Several techniques for machining rhenium parts were considered both before final sintering and after full densification. Machining could provide an alternative method for obtaining thin walled sections. One method used a preliminary low temperature bisque-like firing to provide adequate part strength for subsequent grinding or machining followed by final sintering. Cast rhenium parts can be bisque-fired at about 1500°C under vacuum and hydrogen and then ground to shape. The part in the bisque state has sufficient strength to allow handling and grinding operations. After grinding, the parts are sintered to full densification under hydrogen at about 2500°C.

Intricate parts were also successfully machined to very precise tolerances by electric discharge machining methods. The parts prior to machining were completely sintered and represent fully densified, grain-stabilized rhenium. The ability to machine parts to final dimensions allows for simpler mold design for casting parts. Thus, approximate shapes or even "billets" can be slip cast case and subsequently sintered before machining in areas where close tolerances are necessary or complex geometries are involved.

CONCLUSIONS

1) The variables and methods for adapting the metal oxide ceramic slip casting process to rhenium with metal oxide additives have been thoroughly demonstrated.

2) Special techniques for casting thin wall tubes of rhenium with metal oxide additives have been experimentally confirmed. Such tubes are suitably shaped for resistojet parts.

3) The metal oxide extrusion process has been adapted to the formation of rhenium tubing. Final firing techniques of multimeter length tubing is yet to be experimentally defined, but

the process is believed to be completely feasible. Methods employed in the processing of metal oxide ceramic tubes could be readily adapted.

4) A set of sintering process variables have been found to make finished hardware.

5) Finished machining was found possible by using electric discharge machining or diamond grinding.

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APPENDIX

a) RHENIUM SLIP FORMULATION AND PROPERTIES

	Pure Re Slip Weight percent	Re-ZrO_2 Slip Weight percent
# 154 (Rhenium powder)	79.3	53.0
# 156 (Rhenium powder)		15.4
Stabilized ZrO_2 powder		12.1
Water (vehicle)	14.3	6.2
# 235 (electrolyte)	0.3	1.2
# 217 (electrolyte)	2.5	
BB Solution (binder)	3.6	12.1
975/944 water based defoamer	trace	trace
# 221 oil based defoamer for thin walls	trace	trace
Specific gravity	~ 3.9	~ 4.0
Viscosity cps	~ 350 @ 60 rpm ~ 500 @ 30 rpm	~ 1175 @ 60 rpm ~ 1450 @ 30 rpm
pH	8.5 - 9.0	5.6 - 6.0

b) CASTING USING PAPER LINED MOLDS TO PREVENT STICKING AND SEIZURE OF RHENIUM SLIP TO PLASTER MOLDS

1. Cut high quality thin (>10 mils) filter paper to fit mold configuration.
2. Line plaster mold with paper and moisten paper with slight water spray. Air dry 1 - 3 hours.
3. Fill mold with slip and allow to cast for required time before drying.
4. Allow 12 - 16 hours for ambient air drying.
5. Cure mold and part at about 40°C for >16 hours.
6. Remove paper covered part from mold.
7. Cure at 120°C - 130°C for 2 - 3 hours.
8. Remove paper carefully if possible or burn off during sintering operation.

c) RHENIUM EXTRUSION COMPOSITION AND PROCESSING

# 154 (Rhenium powder)	71.3 wt/%
# 156 (Rhenium powder)	23.7 wt/%
Stabilized ZrO_2 powder	5.0 wt/%

1. Above composition is dry blended together to assure a homogeneous mix.

2. Following binders and plasticizers are added:

   # 258 - 1.5% by weight
   # 281 - 1.5% by weight
   # 600 - 1.5% by weight
   # 40 binder solution - 13.5% by weight

3. Binders and plasticizers are worked into the rhenium/ZrO_2 powders by kneading techniques until a clay-like mix is obtained.

4. The prepared clay is loaded into a hydraulic type extruding chamber (~ 1/1/4" diameter) and extruded at pressures of about 1000 psi.

d) TYPICAL SINTERING SCHEDULE FOR CAST RHENIUM PARTS

Temperature range	Time period	Atmosphere
Room temperature - 500°C	0.5 hours	vacuum
500°C - 1000°C	1.5 hours	hydrogen
1000°C - ~2500°C	4 hours	hydrogen
at 2500°C	4 hours	hydrogen
2500°C - room temperature	cool in furnace	hydrogen

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