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Slip Casting and Extruding Shapes of Rhenium with Metal Oxide Additives

II—Development of Grain Stabilized Rhenium Parts for Resistojets

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TABLE OF CONTENTS

SUMMARY

The adaptation of the powdered particle process used for pure metal oxides to the coprocessing of rhenium with metal oxides to produce miniature resistojet hardware has been successful. Both slip casting and extrusion processes were used. The evaluation of the benefits of addition of metal oxides to rhenium in terms of grain stabilization effects and endurance strength improvements are yet to be quantitatively evaluated. The addition of metal oxides to rhenium resulted in more dense and less porous parts. The additions of phase-stabilized zirconia most likely acts as a sintering aid.

Small, long, straight tubes, suitable in required diameter and length for use as tubular ohmic heat exchangers such as advanced resistojets have been produced. Parts which are slip cast axisymmetric bodies of varying typical shapes and wall thicknesses used in resistojet designs have been produced as well as small tubular extrusions suitable for use as ohmic heat exchangers.

The optimum amount of additives must be evaluated by future tests as well as the effects on metallurgical joining methods.

INTRODUCTION

The feasibility of utilizing commercial zirconia ceramic processing techniques for fabricating rhenium metal shapes was previously demonstrated and reported by the authors under an earlier NASA Contractor Report (ref. 1). Both slip casting and extrusion fabrication methods were able to incorporate grain stabilizing oxides such as zirconia within the rhenium matrix. The object of the tasks herein reported was to further development refinement and evolution of processing and fabricating methods leading to the establishment of grain stabilized rhenium parts of miniature shapes, such as suitable for resistojets (ref. 2).

Historically both slip casting and extrusion technology have been employed to form classical ceramic bodies based on plastic like clay formulations. In order to form nonplastic oxide ceramics, major new technology in the area of binder and media formulation had to be developed by the ceramic industry to obtain a clay like effect for such oxides as alumina and zirconia when slip cast or extruded.

While considerable attention has been devoted to nonplastic oxides, industry and researchers have reported very little on the forming of metal powders by slip casting and extrusion methods. In addition to the nonplasticity state of rhenium powder, the atomic structure and bonding mechanism is entirely different between metallic atoms than it is for oxides. Therefore, the major emphasis of this development phase was to tailor make and optimize binder systems and base composition for the particular end rhenium product desired. For example, thin wall castings of rhenium powder required a binder plasticizer system that would produce high green strength in order to remove the part from the mold and handle it without breakage. In the case of extruding rhenium powder, not only did the mixture have to be clay like, it also had to extend sufficient strength or stiffness to the extrusion to prevent collapse of the wall and/or distortion before drying and curing.

As shown in reference 1, zirconia in the cubic stabilized phase was capable of being incorporated into rhenium matrices. If not stabilized by such addition as calcium oxide, magnesium oxide or yttrium oxide, pure zirconia goes through a destructive phase change over the required temperature range. 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 volumetric 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 near normal to 80°. Since both the monoclinic and tetragonal phase 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 structure. When high temperature stability is required, yttrium oxide is the preferred stabilizing agent.

Powders of the stabilized zirconia for grain growth inhibition in rhenium were blended by standard ceramic processing methods which produce intimate mixing and interaction of the stabilizer with the zirconia particles. Heat treatment of the powder mix assures the reactivity and the desired end cubic structure. Correct particle size of the stabilized zirconia can be obtained by several grinding and attrition techniques. Two distinctly different type shapes of individual particles can be produced depending upon the reduction method used and are described as follows:

Method A produces individual particles that are spherical in shape and have a relatively smooth surface.

Method B produces irregularly shaped and fragmented type particles.

Slip cast and extruded parts of both powder types, A and B, were separately produced. Parts were never made of mixtures of A and B. Method B particles are felt to impart greater strength.

DISCUSSION AND RESULTS

The powder preparation methods described here are simple adaptations of ceramic ones and are believed to be readily understandable and adaptable by ceramists from the methods employed in the ceramics industry.

Extrusion

As previously described in reference 1, an extrusion process was employed in which a powder clay like mix was loaded into a piston extrusion chamber and forced under pressure through a conical die using a suitable center member to form tubes. The fine mesh rhenium powder with and without zirconia additives can be plasticized with organic additives and binders to become pseudo-plastic and resemble the texture of a water based clay system. The original extruded rhenium tubing, consisting of 5% zirconia additive, had a moderate degree of waviness and ellipticity throughout the tube due to an imbalance between extrusion pressure and plasticity of the mix. During the course of this program, the following basic mixtures were investigated for extrudability:

1. 100% rhenium.
2. Rhenium with 0.5% zirconia.
3. Rhenium with 1.0% zirconia.

The type A tubes with 5.0% zirconia used in the following section on sintering were extruded under the program of reference 1.

Table I lists the two basic die set sizes in the "green" unsintered state and the nominal theoretical sintered rhenium tube size expected from each.

TABLE I
EXTRUSION DIE SETS

Die set	Diameter Outer mm	 Inner mm	Theoretical sintered size mm
Type A	5.54	3.23	3.86 dia. with 0.79 wall
Type B	1.85	0.74	1.30 dia. with 0.38 wall

Figure 1 depicts some typical straight tubes of both die sizes extruded during the program. Green state lengths up to 1.22 m long have been extruded by the process. In order to obtain straightness and concentricity, the plasticity was changed by increasing the binder content from the original amount by about 10%. The resultant mix extruded at pressures about 15-20% lower than normal.

Figure 1.- Extruded straight green rhenium tubing with zirconia additives. Type A and Type B.

The type A die set was originally selected since it approximated quite closely the dimensions of an early (ref. 3) inner tubular ohm heater resistojet part (3.51 mm diameter with a 0.71 mm wall). The other die set type B was employed in order to determine the minimum diameter and wall thickness extrudability for rhenium tubing.

Sintering Extruded Rhenium Tubing.- The firing of the various extruded rhenium tubing was accomplished at an outside rhenium sintering source. The unsintered samples had a relatively high degree of green strength which allowed for being handled and forwarded to the sintering operation site. Extruded tubing was cut to about 20.3 cm length and sintering attained in general using the following steps:

1. Presintered horizontally to 1600°C to burn out and remove organic binders for a total cycle time of one to two hours under wet hydrogen atmosphere.

2. Transferred to high temperature hydrogen atmosphere furnace. Bundled vertically and sintered to 2300°C and held for one to three hours.

3. Some tubes were further densified by self heating techniques at temperatures of approximately 2500°C and held for three hours.

Table II summarizes the results obtained for sintering tubes at 2300°C which were extruded from the type A die set.

TABLE II
RESULTS OF SINTERING RHENIUM TUBES (TYPE A)
WITH STABILIZED ZIRCONIA ADDITIVE AT 2300°C

Sample weight percentage, ZrO_2 %	Time hr	o.d. green mm	o.d. fired mm	i.d. fired mm	Length fired mm	Firing linear shrinkage %	Density g/cm³	Water absorption %	Apparent porosity %
0	2	5.38	3.78	2.16	152	29.5	19.0	1.7	24.0
0.5	2	5.44	3.78	2.10	146	30.0	18.6	1.2	17.5
1.0	2	5.33	3.71	2.16	146	30.4	18.3	1.0	15.0
5.0	1	5.33	3.76	2.23	89	29.5	16.6	0.8	11.0

Tubes after firing were reasonably straight but did exhibit some twist and curl effect. Figure 2 shows a cut piece of the type A tubes. There appears to be some correlation between the zirconia content and densification as evidenced by the lowest water absorption being obtained with tube 101 containing 5% zirconia. This effect was also noted for smaller diameter tubes which are described later. In all likelihood, the zirconia acts as a sintering aid promoting densification with lowest porosity

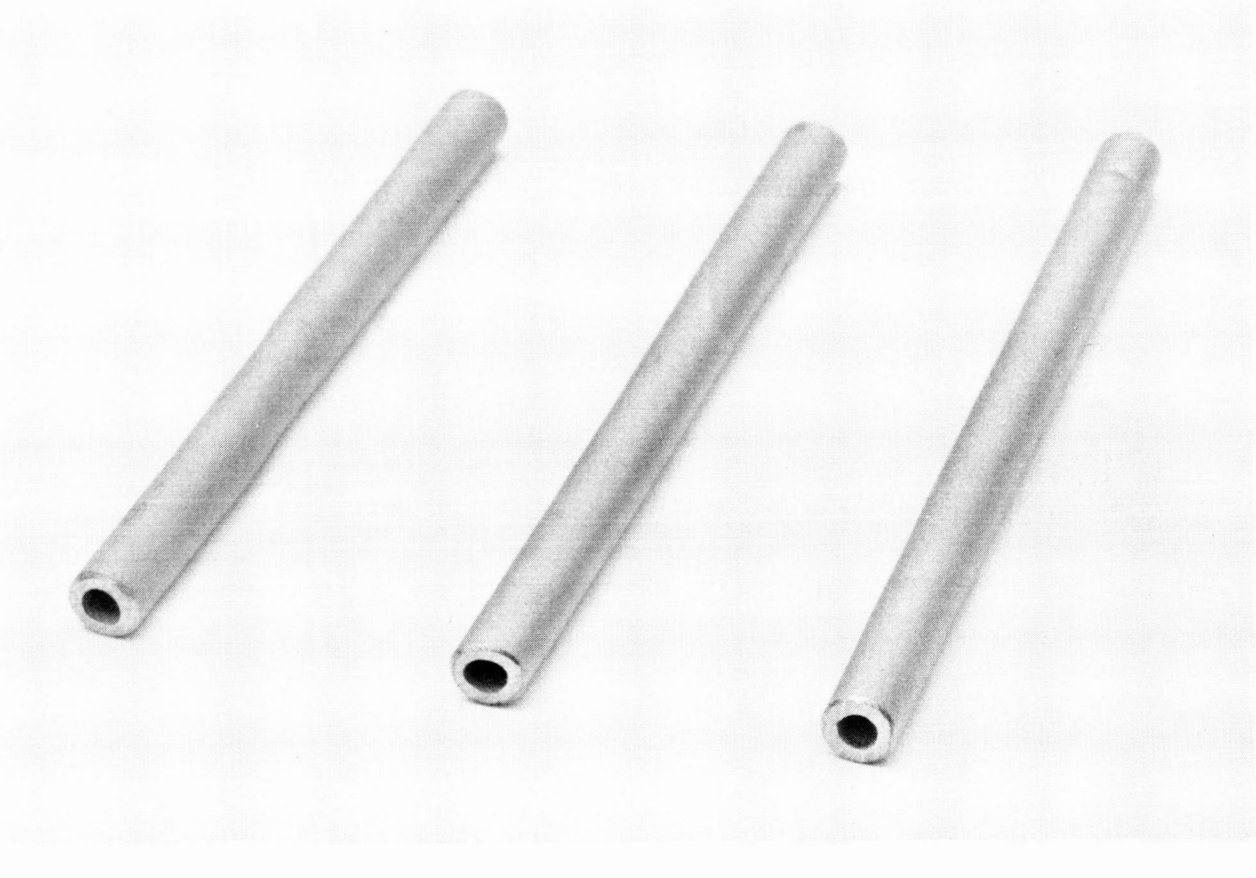


Figure 2. Samples of the type A die set sintered tubes, left to right, rhenium with 0%, 0.5% and 1.0% added stabilized zirconia.

obtained with the highest zirconia content. While apparent high densities were obtained representing ≈90% of theoretical, the fact that apparent porosity calculations were also high, indicated that true density would be considerably lower. Densities were determined by water displacement techniques based on Archimedes' principle.

Table III depicts and compares the approximate theoretical density for each composition to the adjusted density of the test specimens. The adjusted density was calculated based on the apparent porosity of parts after sintering at 2300°C.

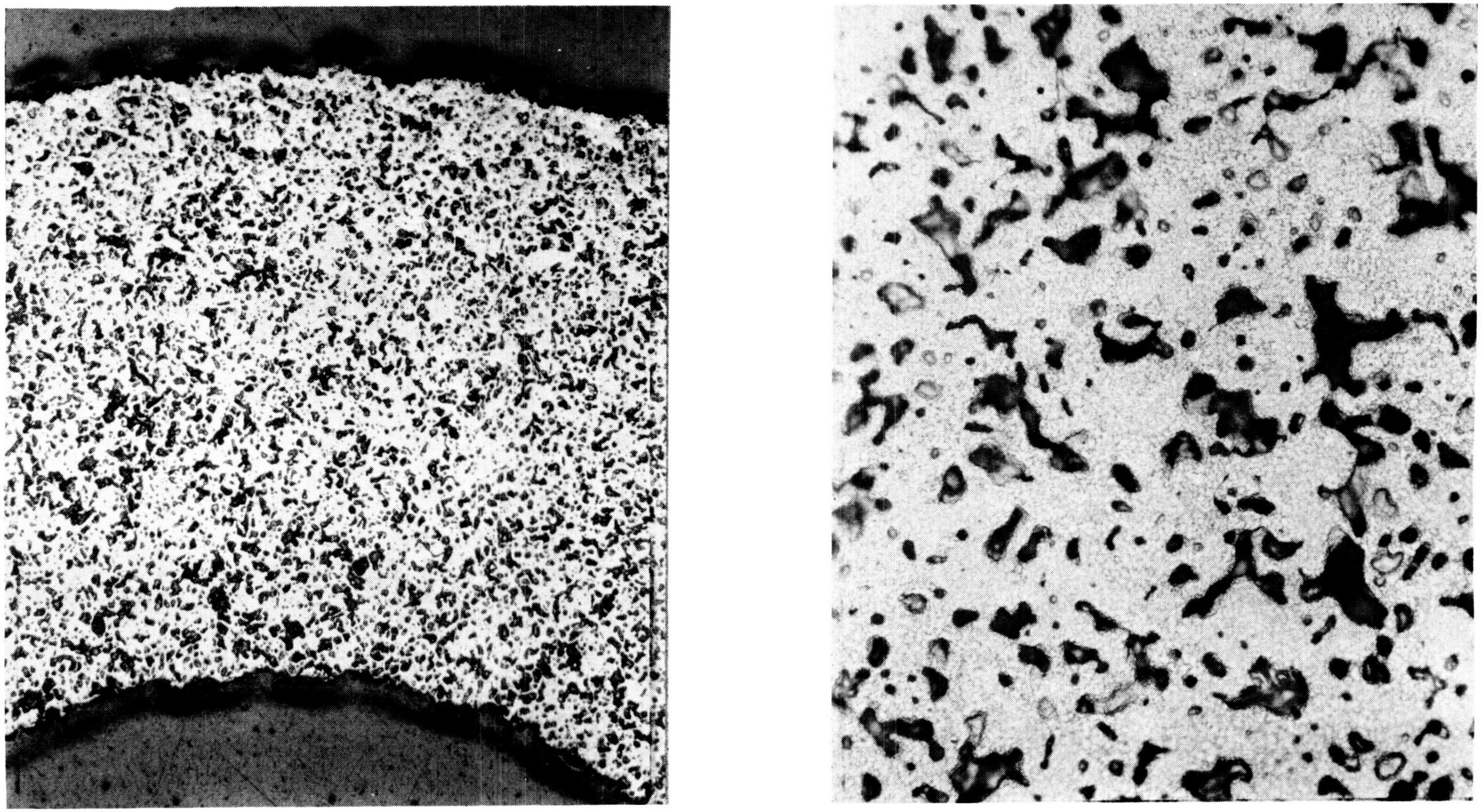
TABLE III
THEORETICAL/ADJUSTED DENSITY COMPARISON FOR RHENIUM TUBES (TYPE A) WITH STABILIZED ZIRCONIA ADDITIVE AFTER SINTERING AT 2300°C

Sample weight percentage, ZrO_2 %	Density theoretical g/cm^3	Density adjusted g/cm^3	Percentage of theoretical %
0	20.5	14.5	71
0.5	19.6	15.4	79
1.0	19.3	15.6	81
5.0	17.6	14.8	84

The various rhenium tube samples of the type A die set that were sintered at 2300°C were cross sectioned and metallurgical mounts prepared for examination of their microstructure. Results confirmed the previous findings from their physical properties that these samples all had a relatively high degree of porosity. Two photomicrocraphs are shown for each indicated sample in figures 3-6. One is at 100 x magnification and shows the entire wall thickness for each tube. The other is at 1000 x for a representative section of each tube.

The 100% rhenium, a baseline reference sample (tube 103), shown in figure 3 had voids measuring approximately 5 to 10 microns. Individual grains of rhenium were difficult to discern since the voids trapped the etchant used and tended to blur or wash out the grain boundaries. However, measurements directly under the microscope did indicate grain sizes of approximately 1-2 microns with some as large as 5 microns.

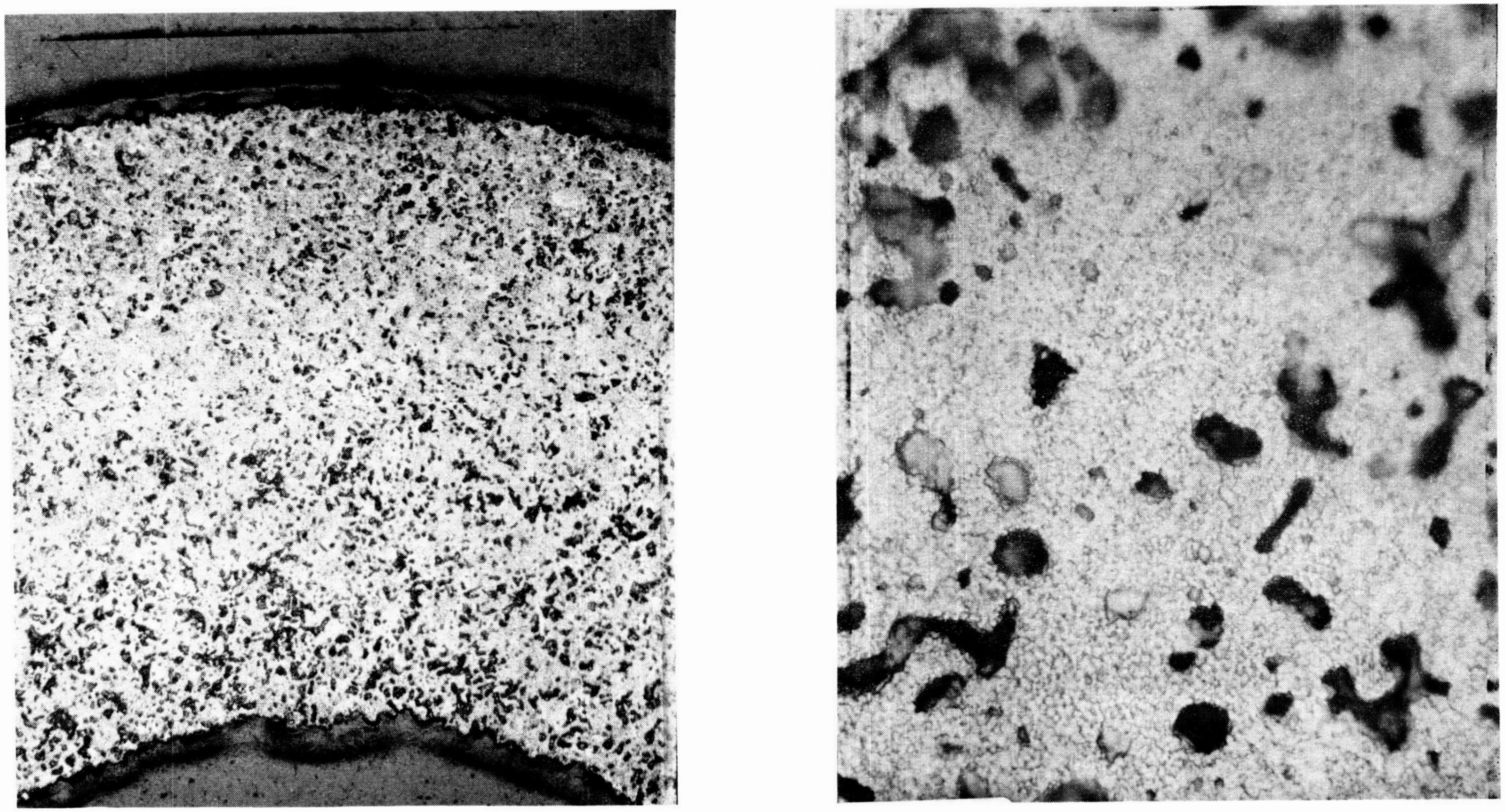
For the sample with the addition of 0.5% zirconia (tube 104), figure 4, the voids were again of the same size magnitude. The rhenium grains were also 1-2 microns with some indicating dimensions up to 5 microns. Some of the zirconia addition could be observed and showed up as relatively round particles approximately 2-2 1/2 microns in size.



a) 100X

b) 1000X

Figure 3.- Photomicrographs of tube 103, with 100% rhenium. Density = 19.0 g cm^{-3}, apparent porosity - 24.0%



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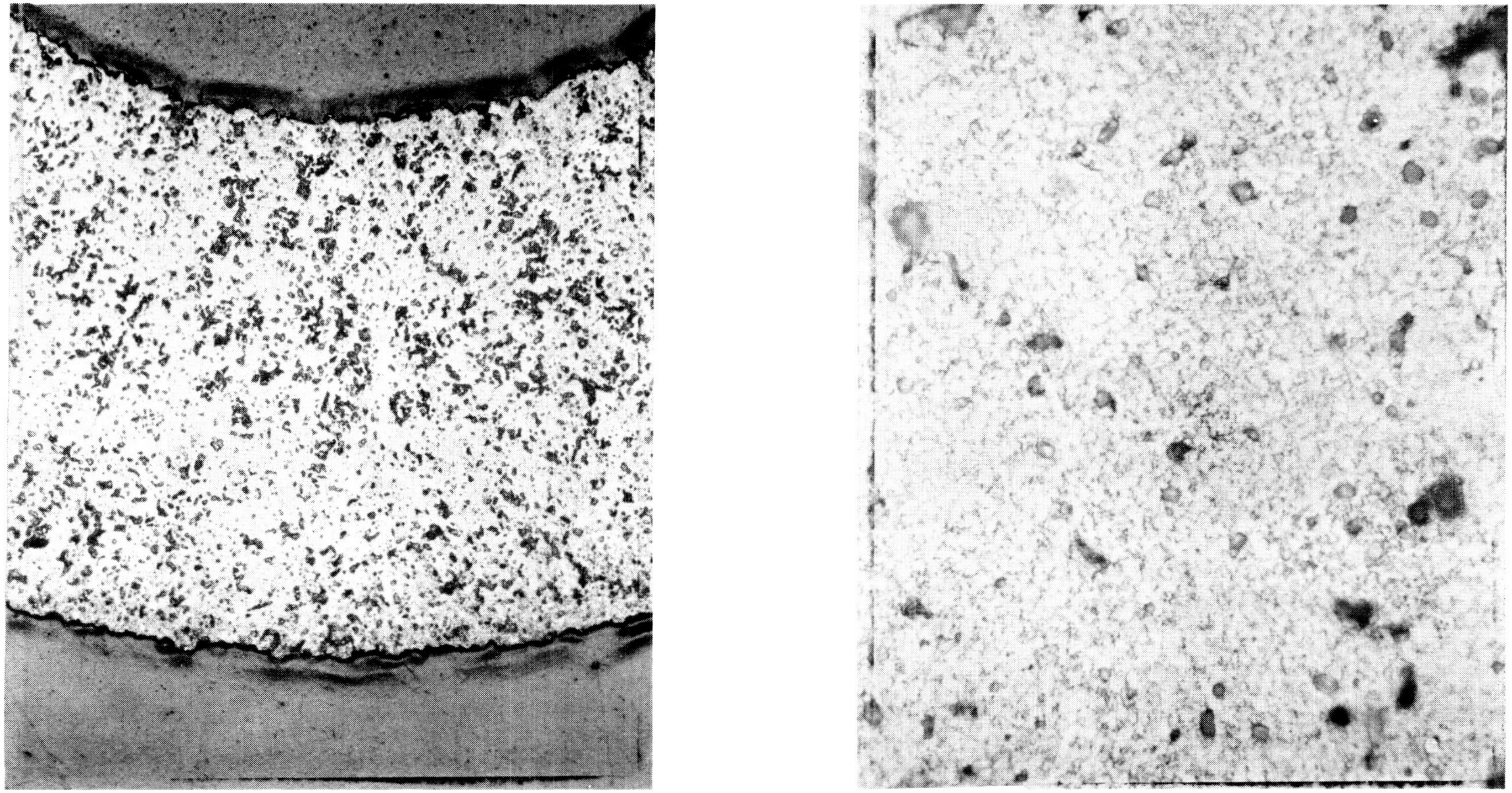
b) 1000X

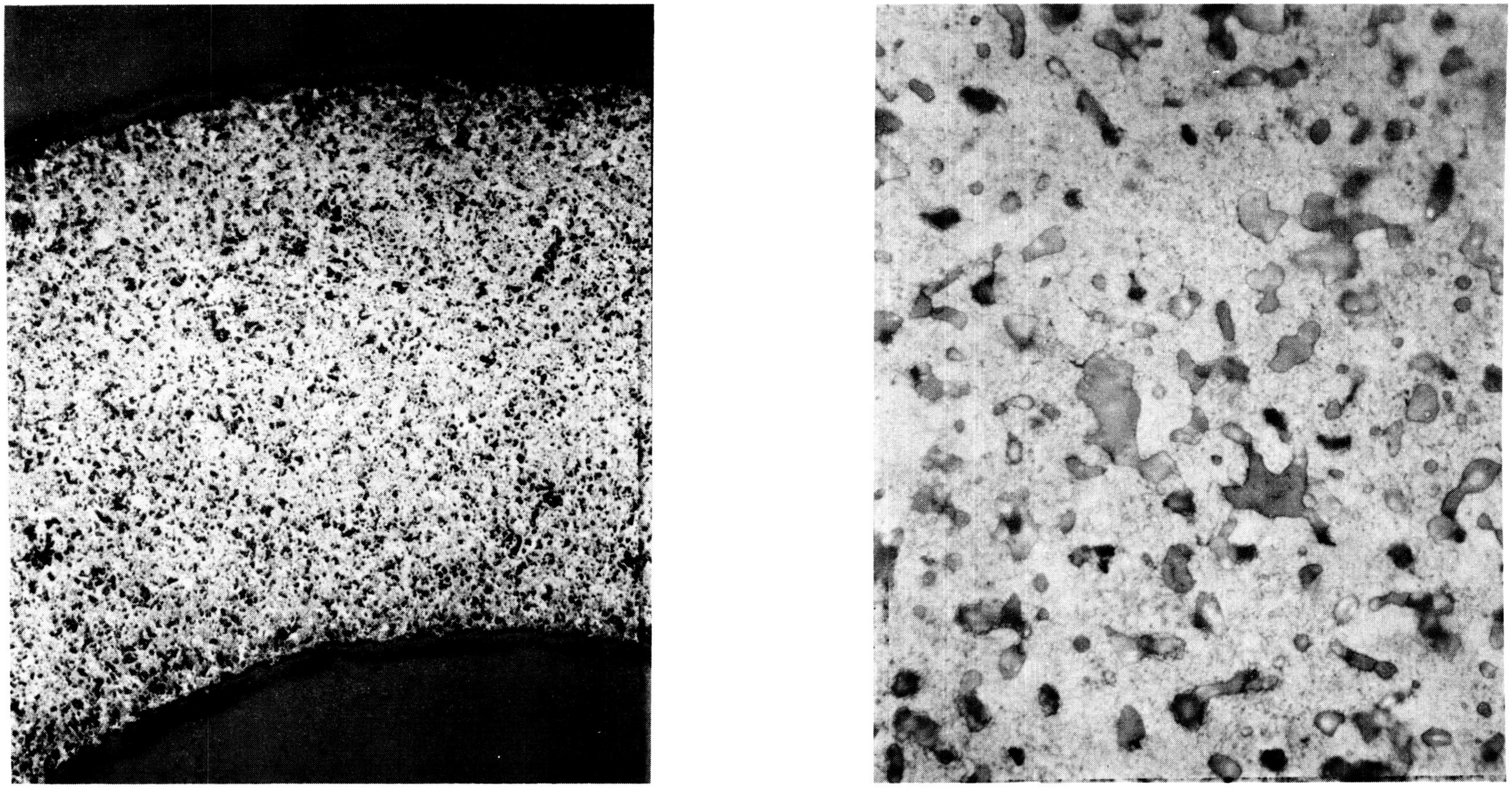
Figure 4.- Photomicrograph of tube 104, with 0.5 w/o zirconia - type A. Density = 18.6 g cm^{-3}, apparent porosity = 17.5%



a) 100X

b) 1000X

Figure 5.- Photomicrographs of tube 102, with 1.0 w/o zirconia - type A. Density = 18.3 g cm^{-3}, apparent porosity = 15.0%.



a) 100X

b) 1000X

Figure 6.- Photomicrographs of tube 101, with 5.0 w/o zirconia - type B. Density = 16.6 g cm^{-3}, apparent porosity = 11.0%.

With addition of 1.0% zirconia (tube 102), figure 5, the sample exhibited a somewhat tighter microstructure. This is also evident by its calculated apparent porosity. Voids were slightly smaller, measuring up to 5-7 1/2 microns. Round zirconia particles were also visible on the order of 2-2 1/2 microns.

With 5.0% zirconia added (tube 101), figure 6, the zirconia grains visible in this sample had irregular shapes and were as large as 5 to 7 1/2 microns. Void content, while being reduced, still had sizes approaching 10 microns. Once again, rhenium grain sizes appeared to be of the same general magnitude as in the other samples.

The tube samples were resintered to 2500°C to determine if increased densification could be obtained. Due to limitations of the technique employed, the sample (Tube 101) containing 5.0% zirconia could not be resintered since it was too short (less than 100 mm) to position it in the holding device. The results obtained at 2500°C are shown in table IV.

TABLE IV
RESULTS OF SINTERING RHENIUM TUBES (TYPE A)
WITH STABILIZED ZIRCONIA ADDITIVE AT 2500°C

Sample weight percentage, ZrO_2 %	Time hr	o.d. fired mm	Length fired mm	Firing linear shrinkage %	Density g/cm^3	Water absorption %	Apparent porosity %
0	3	3.76	92	29.8	18.3	1.0-1.3	18.0
0.5	3	3.66	102	32.5	19.0	0.8	11.0
1.0	1.5	3.63	89	32.0	18.7	0.7	10.0

All tubes that were resintered to 2500°C were quite straight. Even those that originally exhibited some twist and coil from 2300°C were almost completely straight. All samples after sintering at 2500°C indicated further densification as shown by the slightly higher shrinkage values and lower absorption and porosity levels. Again, those compositions with zirconia had better densification than the pure 100% rhenium sample.

A further example of the increased densification can be gleaned from Table V in which the adjusted density values from the apparent porosity are compared to theoretical density.

The smaller diameter tubes extruded using die set B were also sintered in similar manner to those previously described. However, due to consideration of resources, they were only sintered to 2300°C. It is anticipated that these small diameter samples can be subsequently employed to study the effect of prolonged self heating at 2500°C on grain growth. The results of sintering at 2300°C showed that small diameter rhenium tubing

TABLE V
THEORETICAL/ADJUSTED DENSITY COMPARISON FOR RHENIUM TUBES (TYPE A) WITH STABILIZED ZIRCONIA ADDITIVE AFTER SINTERING AT 2500°C

Sample weight percentage, ZrO_2 %	Density theoretical g/cm^3	Density adjusted g/cm^3	Percentage of theoretical %
0	20.5	15.0	73
0.5	19.6	16.9	86
1.0	19.3	16.8	87

could maintain relative concentricity without collapse or distortion of the thin wall. Table VI summarizes the results obtained for these rhenium tubes with and without 1% zirconia.

TABLE VI
RESULTS OF SINTERING RHENIUM TUBES (TYPE B) WITH STABILIZED ZIRCONIA ADDITIVE AT 2300°C

Sample weight percentage, ZrO_2 %	Time hr	o.d. green mm	o.d. fired mm	i.d. fired mm	Approx. length fired mm	Firing linear shrinkage %	Density g/cm^3	Water absorption %	Apparent porosity %
0 (5 tubes)	3	1.80	1.26	.45	146	29.8 to 30.8	18.2	0.4 to 0.7	6.5 to 10.0
1.0 (2 tubes)	3	1.78	1.26	.45	89 to 146	29.0 to 30.0	18.0	nil to 0.3	<1.0 to 6.0

The tubes were relatively straight but did exhibit some twist and curl characteristics of method used to support them during sintering. See figure 7. The surprising fact of the results was that these tubes were densified more at 2300°C than the larger diameter tubes were at 2500°C. While having similar firing shrinkage, the 1.27 mm diameter tubes had much lower water absorption values and apparent porosity. Either erroneous sintering temperatures may have been recorded during the sintering operation or the smaller cross section of the 1.27 mm tubes accounts for the increased sintering. In any event, the increased densification is evident when comparing adjusted density values to theoretical. For these particular samples, the following were calculated:

100% rhenium - 81.5% of theoretical
w/1.0% zirconia - 92% of theoretical

Figure 7.- Samples of the type B die set sintered tubes, left to right, rhenium with 0%. 0.5% and 1.0% added stabilized zirconia.

An additional set of tubes, including a 0.5% added zirconia member, was made to provide test hardware for possible further study.

Another aspect of sintering 1.27 mm tubes was the fact that originally 5 tubes each with and without 1.0% zirconia addition were supplied to the sintering operation. None of the pure 100% rhenium tubes were damaged in shipment or subsequent sintering. However, those with 1.0% zirconia had one tube broken in transit and two others broken by handling during the initial sintering stage. In the case of these extruded tubes, the zirconia powder used was from Method A with smooth spherically shaped particles. Since the cross section of the 1.27 mm tubes was relatively small, the strength may have been weakened by the use of the spherical particle. It was thought that the irregular particles from Method B might impart greater strength through an interlocking effect to small cross sectional extrusions and decrease breakage potential.

Slip Casting

The major emphasis on slip casting resistojet type parts was to try to tailor make the slip formulation to provide for the necessary strength required for ultra thin wall castings of ≈0.13 - 0.38 mm. This involved changing types and amounts of binder used, as well as the solids content of the slip. Another approach was to try and precisely control the particle size and distribution of the rhenium powder to provide for maximum particle packing and strength. Initially trial tubes, about 12.7 mm diameter x 50.8 mm long were cast from rhenium powder using a 1.0% zirconia additive (Method B particles). Using plaster mold casting techniques as previously reported in reference 1, several trials were made to determine the minimum wall thickness that could be cast and still allow the part to be successfully removed from the mold. A qualitative check indicated the following:

Tube	Cast Wall Thickness mm	Estimated Sintered Thickness mm
A	0.25 - 0.43	0.18 - 0.30
B	0.33 - 0.53	0.23 - 0.38
C	0.76 - 0.89	0.51 - 0.64

Only Tube C could be removed entirely intact while A and B had insufficient strength to hold completely together without cracking. The wall thickness of Tube C met the requirement for some of the resistojet parts, mainly for the nozzle throat and initial expansion section. However, the wall thickness for such parts as the tubular heater pressure vessel and funnel type require the 0.13 to 0.38 inch thickness values.

Some time based separation studies of rhenium powders were performed to determine if an aqueous sink-float method would be adequate to separate the finer smaller particles from relatively larger heavier ones. If successful, the finer particles could then be used to cast denser and stronger thin wall parts. The general results showed that only a very short settling period could be employed. At even less than 5 seconds of settling, only 6-7% of finer particles were deemed recoverable from one type of rhenium powder and only ≈13% for another powder. It was obvious that more practical and higher yield separation methods would have to be devised which were beyond the scope of this contract. Therefore, emphasis was placed on changing and/or modifying the basic slip constituents to gain the desired amount of strength in slip cast thin wall parts. In addition to affecting strength, the slip formulation also had to be closely coordinated with casting rates and mold removal techniques.

A green strength binder slip formulation was developed which provided adequate strength for thin wall parts. While providing for sufficient handling strength, the following problem areas were revealed:

1. The casting rate was very rapid and allowed for excess thickness build up within the part.

2. The "drying" temperature of the mold/part assembly was extremely critical. A temperature variation as little as 10°C could cause hairline cracking.

A suitable decrease in casting rate was accomplished by controlling the moisture content of the plaster molds prior to casting. This allowed for slower absorption of the liquid phase from the rhenium slip. It was also determined that a minimum peak drying temperature was critical and had to be used with an increased drying time factor to compensate for total heat effect if cracking was to be prevented.

Improvement in casting simulated test type type parts from rhenium with 1.0% zirconia was obtained using the closer controls described above. Figure 8 shows some of the shapes cast. The contoured tube, typical of a resistojet-like pressure case part, on the left is in the green state. To its right is such a part after being fired to 1600°C. Full firing would produce further shrinkage to the approximate 30% linear reduction of the original green state. Wall thickness approximately 0.51 mm were cast on several parts. This would yield an approximate sintered wall thickness of about 0.38 mm. Some parts were able to be cast with walls approaching 0.25 mm but still require some slip adjustment before reproducibility can be obtained.

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Figure 8.- Typical cast shapes.

Since the sintering process represented such a complicated and time consuming operation, slip cast parts were not able to be fully sintered during the program length. However, in order to determine the effect of the modified "high strength" binder system, sintering investigations were conducted using a model system to simulate rhenium. This consisted of substituting zirconia powder for the rhenium while keeping the same binder system. Similar parts were then cast from the zirconia slip and sintered under normal oxidizing conditions. Sintering results showed that there were no adverse effects such as slumping or distortion during densification. The only significant effect of the binder appeared to be an increase in firing shrinkage of about 18-20% higher than the normal rate. If the same degree of shrinkage is assumed for rhenium based formulations, the final fired shrinkage rate for rhenium parts would increase from about 30% to approximately 35%.

CONCLUSIONS & RECOMMENDATIONS

1. The metal oxide extrusion process of reference 1 has now been refined to produce thin walled fully sintered rhenium parts with grain stabilizing metal oxide of small diameter tubing (1.3 mm outside diameter x 0.5 mm wall) suitable for ohmically heated resistojet tubing heat exchangers.

2. The rhenium tubing extruded could be ohmically heated by NASA to evaluate the degree of grain stabilizing effects of additions of wt/0.5%, 1.0% and 5.0% of ZrO_2 as compared to the baseline pure rhenium formed by the same technique. The tubes will be required to establish ultimately the best percentage of additives for grain stabilization and the degree of the benefits.

3. Thin walled rhenium parts have been slip cast of representative wall thicknesses and shapes typical of resistojets and their process variables are now well established.

4. The weldability of cast and extruded grain-stabilized parts is yet to be established. Basic test samples are now available for such investigations by NASA.

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16. Abstract

The adaptation of the powdered particle process used for pure metal oxides to the coprocessing of rhenium oxides suitable to produce pure miniature resistojet hardware has been successful. Both slip casting and extrusion processes were used. The metal oxide ZrO_2 was stabilized into the cubic phase with Y_2O_3, for use as a potentially grain stabilizing additive to rhenium. Straight meter long tubing in two sizes are reported. Tubing suitable for resistojet ohmic heater use of fully fired dimensions of nominally 3.8 mm o.d. x 2.2 mm i.d. and 1.26 mm o.d. x .45 mm i.d. with 0, 0.5, 1.0 and 5.0% zirconia additives were produced for further study. Photomicrographs of these are discussed. The addition of the metal oxide zirconia to rhenium resulted in more dense and less porous parts. The additions of phase stabilized zirconia most likely acts as a sintering aid. Tubes of varying diameter were slip cast which were representative of miniature pressure cases.

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