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**DEVELOPMENT OF
A
DISPERSION STRENGTHENED CHROMIUM ALLOY**

By

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Westinghouse Astronuclear Laboratory

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA-Lewis Research Center

Contract NAS 3-10487

John Merutka, Project Manager

Thomas Herbell, Research Advisor

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FOREWORD

The work described herein was done at the Astronuclear Laboratory, Westinghouse Electric Corporation, under NASA Contract NAS 3-10487 with Messrs. John Merutka and Thomas Herbell, Materials and Structures Division, NASA-Lewis Research Center, as Project Manager and Research Advisor, respectively.

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ABSTRACT

A ZrO_2 -chromium alloy was produced. Submicron ZrO_2 -coated chromium powder was prepared by thermally decomposing $\text{Zr}(\text{OR}')_4$ (zirconium tetratertiary butoxide) onto gas phase nucleated chromium particles. Powder particle size could be controlled to within a few hundred angstroms. The as produced powder was contaminated with both excessive amounts of carbon and oxygen. However, carbon content was reduced to <100 ppm by hydrogen sintering. The powder product was consolidated by cold pressing plus extrusion. The as-extruded product was dense and contained a uniform ZrO_2 dispersion. However, the dispersion was unstable at high temperatures. This is attributed to the combination of the inherent relative instability of the ZrO_2 with respect to the chromium matrix, plus the excessive oxygen contamination.

The inability of vendors to synthesize $\text{Th}(\text{OR}')_4$ prevented development of a ThO_2 -chromium alloy.

SUMMARY

An investigation of the feasibility of producing oxide dispersion strengthened chromium by gas phase nucleation of an oxide coated powder was carried out. It was intended initially that a ThO_2 dispersoid be used. However the inability of three suppliers to synthesize its parent compound made the substitution of ZrO_2 as the dispersoid necessary. A process was developed for producing ZrO_2 -coated submicron chromium particles. In this process zirconium tetratertiary butoxide, $\text{Zr}(\text{OR}^t)_4$, was thermally decomposed on chromium particles condensed from the vapor emanating from an inductively melted pool. Some features of the process include: (1) control of chromium particle size within a range of several hundred angstroms, (2) confinement of the vapor stream by the Bernoulli effect to allow its contact by the alkoxide, and (3) control of ZrO_2 content.

Oxygen and carbon contamination was a serious problem. Carbon content was reduced below the goal level (100 ppm) by hydrogen sintering the powder in the presence of titanium powder. Consolidation of a chromium plus 3.5 volume percent ZrO_2 powder was achieved by cold pressing the powder to 61% of its theoretical density into a molybdenum container which was electron beam seal welded and extruded at 1250°C (1523°K) with a 10/1 reduction ratio. A final density of greater than 95% theoretical was obtained.

A dispersion of ZrO_2 particles in a chromium matrix was obtained. These particles were in the form of platelets having the average dimensions of 0.1μ (1×10^{-7} m) thickness and 0.7μ (7×10^{-7} m) diameter, much larger than the desired size (up to 0.1μ (1.5×10^{-6} m) with 50% less than 0.05μ).

The ZrO_2 dispersion was not stable during heating in vacuum at either 1316°C (1590°K) or 1427°C (1700°K) for periods up to 100 hours. Oxide contamination was at least partially responsible for this instability. Cr_2O_3 was evident in the microstructures. Electronmicrographs showed a large decrease in the number of dispersoid particles and a spheroidization of those that remained following heat treatments.

INTRODUCTION

General Discussion

The objective of this program was to establish the feasibility of producing thorium oxide (ThO_2) dispersion strengthened chromium by gas phase nucleation of an oxide coated powder. However the inability of suppliers to furnish $\text{Th}(\text{OR})_4^*$, the parent compound for ThO_2 , forced substitution of ZrO_2 as the dispersoid. The dispersion strengthened alloy was to have the following characteristics:

- Volume fraction of dispersoid — less than 8 volume percent
- Dispersoid particle size — up to 0.1 micron, with 50% less than 0.05 micron
- Interparticle spacing — up to 1.5 micron
- Unalloyed chromium matrix density $\geq$ 98% theoretical
- Total impurities $<$ 1000 ppm with no single impurity $>$ 100 ppm.
- Microstructure stability for at least 100 hours at temperatures up to 1427°C (1700°K).

Chromium, by virtue of its high melting point, high elastic modulus and relatively good oxidation resistance, has long been of interest as a high temperature structural material. However, alloying chromium with substitutional solutes to improve high temperature strength has almost invariably lead to serious aggravation of the low temperature brittleness problem associated with pure chromium. In contrast, with dispersion hardened alloys, excellent high temperature strength can be achieved without sacrifice of low temperature ductility. This is illustrated by the results achieved by Westinghouse^(1, 2) with a W- ThO_2 alloy, which has high temperature strength greatly superior to unalloyed tungsten and a ductile-brittle transition temperature comparable to pure tungsten.

Notable success has been achieved in a number of systems strengthened by inert oxide particles, the most significant being SAP and TD-nickel. The initial results reported with SAP stimulated a great deal of research on dispersion hardened alloys with major

*Thorium tetratertiary butoxide

emphasis on methods of preparation. Most of the processes explored however are not suitable for alloys with a reactive metal matrix. This is mainly the result of instability of the dispersed phase due to contamination of the matrix by interstitial elements. In addition many processes provide insufficient control of dispersoid spacing and particle size.

In the conventional powder metallurgy technique ultra-fine metal and metal oxide particles are comminuted, mixed and consolidated. Contamination of the metal powder by interstitial elements is usually excessive. Particle segregation during mixing makes uniform distribution of dispersoid difficult to achieve.

In the SAP technique, sub-micron metal flakes are ball milled to permit their surfaces to become oxidized. The particles are consolidated and the product worked to break up the oxide to yield a dispersion of oxide particles in a continuous metal matrix. This technique is limited to metals which form an adherent oxide and which have a low oxygen solubility. To date, success with this method has been achieved only with the low melting metals — aluminum, lead, tin and zinc.

In a dilute solid solution system in which the oxide of the solute has a much greater free energy of formation than the oxide of the solvent the solute can be selectively oxidized by internal oxidation to yield a dispersion strengthened alloy⁽³⁾. This method is limited to systems in which the diffusion rate of oxygen in the solvent metal is high. Large oxide particles are usually formed at the grain boundaries since the rate of grain boundary diffusion is greater than volume diffusion. Only silver and copper base alloys have been dispersion strengthened by this method.

By co-precipitation a complex salt is precipitated from an aqueous solution of solvent and solute salt. The precipitate is dried and selectively reduced to yield a dispersed oxide in a matrix of the solvent metal. The outstanding examples of alloys made by this

technique are TD nickel and thoriated tungsten. The method is not suited to chromium because of the stability of Cr_2O_3 .

The homogeneous nucleation technique investigated in this program offered a number of potential advantages. This process can be briefly described with reference to Figure 1, in which ZrO_2 is used as an example of the dispersoid. Chromium atoms ($\diagup$) escape from the surface of molten chromium ($\sim\sim\sim$), nucleate and grow by collision with other chromium atoms to form submicron particles (X). These particles are entrained by a high velocity stream of He ($\square$) and carried to a point where they are contacted with $\text{Zr}(\text{OR}')_4$ (zirconium tertiary butoxide) vapor ($\cup$). The $\text{Zr}(\text{OR}')_4$ thermally decomposes to produce ZrO_2 coated chromium particles ($\otimes$). The coated particles are then collected and consolidated in an inert environment to avoid contamination.

The initial approach selected was to produce chromium particles by hydrogen reduction of a chromium halide. However, initial experiments indicated that the problem of preheating hydrogen to the necessary temperature would be very difficult to solve. In addition, the high halide content of the product produced by this method was of serious concern. Consequently, the evaporation technique was selected for the production of chromium powder.

Theoretical Considerations

The factors considered in developing the experimental program were:

- 1) Selection of approximate conditions required to homogeneously nucleate submicron chromium particles.

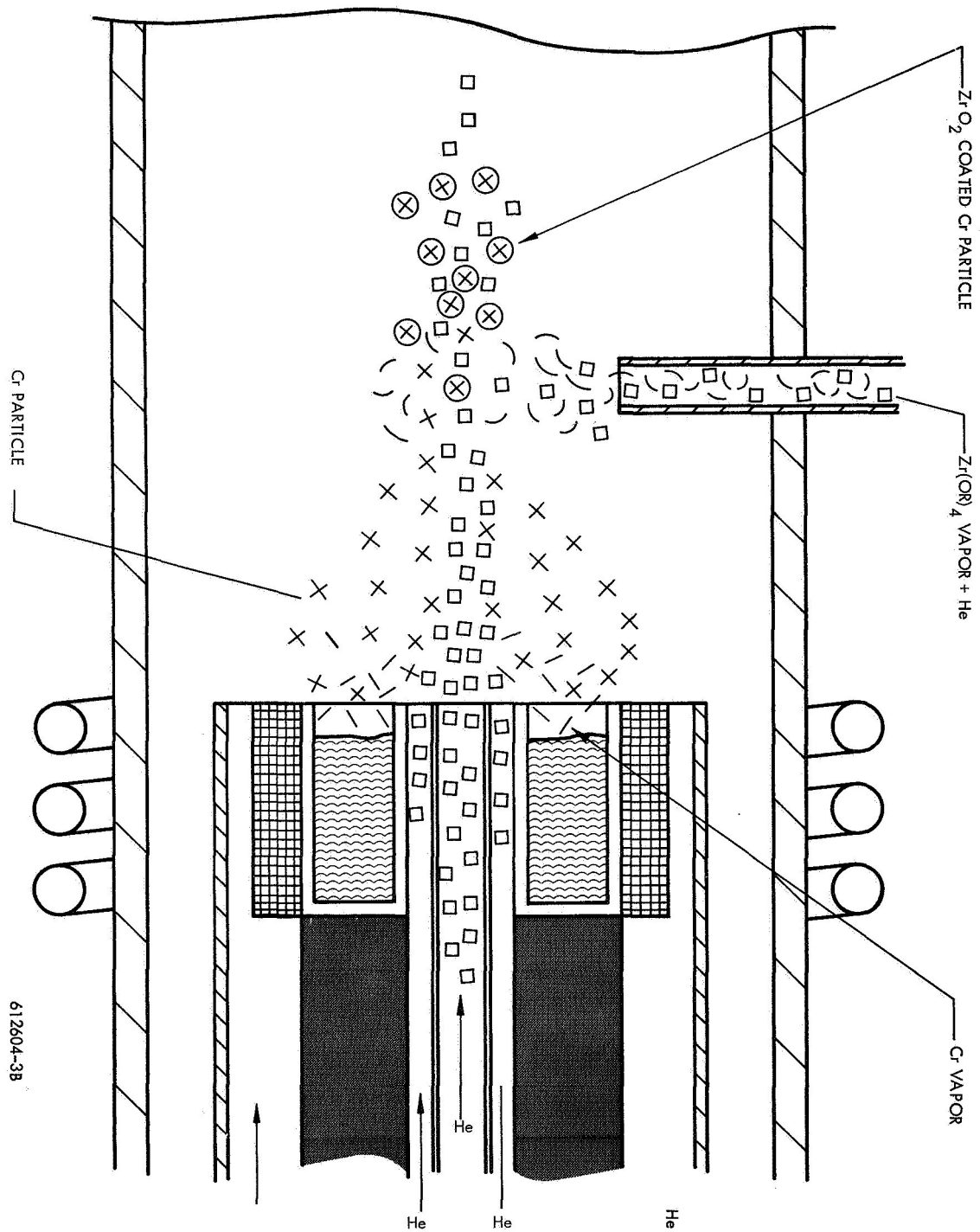


FIGURE 1 - Schematic Representation of Homogeneous Gas Phase Nucleation Process to Produce Submicron ZrO_2 -Coated Chromium Particles

- 2) a. Selection of methods to produce the chromium powder.
b. Methods of controlling chromium particle size.
c. Means of collecting ultra-fine particles.
- 3) Stability of ThO_2 and ZrO_2 particles in a chromium matrix.
- 4) Deposition of ThO_2 or ZrO_2 onto the chromium particles.

These factors are discussed in the above sequence.

1) Results of the following analysis show that the formation of submicron chromium particles should readily be achieved. Supersaturation* of the nucleated species above a specified minimum value must be achieved if particles are to be formed by homogeneous nucleation. At low supersaturation ratios, α , whisker-like growths are formed from condensation of the metal vapor. Greater supersaturations are required for the crystal growth rate needed to yield submicron powders⁽⁴⁾. The minimum supersaturation for particle growth is termed the critical supersaturation, α_{cr} , and can be calculated from the relation

$$\ln \alpha = \frac{\alpha \sigma^2 M}{\phi k T^2 R \ln B/N} \quad (5) \quad (1)$$

$$\text{*Supersaturation} = \frac{\text{actual vapor pressure of material}}{\text{equilibrium vapor pressure of material}}$$

where:

α	= interlayer spacing	R	= molar gas constant
φ	= density	T	= absolute temperature
σ	= surface free energy	N	= surface nucleation rate
M	= molecular weight	B	= 10^{20}
k	= Boltzmann's Constant		

Morelock⁽⁶⁾ found α_{cr} values for chromium, nickel, iron, copper, and gold to be slightly greater than 2, while Sears⁽⁷⁾ measured an α_{cr} value of 20 or less for cadmium, zirconium, and silver.

By assuming a condensation temperature of 1000°C (1273°K) and a reasonable nucleation rate of 10^{10} nuclei/cm²/sec (10^{14} nuclei/m²/sec) and using the values of chromium for M, φ , and an α_{cr} value of 3 is obtained for the above relation.

By vaporizing chromium at 2000°C (2273°K) a supersaturation ratio of $\sim 10^8$ will be achieved. The above critical supersaturations or any of the others noted in the literature^(8,9) can be far exceeded. Therefore, no problem in producing sub-micron chromium particles was anticipated.

2-a) Two methods of producing chromium powder were considered. In the first method, CrI₂ vapor is reduced by hydrogen to yield homogeneously nucleated chromium particles. This method is essentially that developed by Lamprey and Ripley^(10,11). Residual iodine content of the powder would be expected to be high (several 1000 ppm). Sub-micron powders produced by other workers by halide vapor reduction have yielded a product containing considerable amounts of the halide. For example, tungsten powder produced by reduction of WCl₆ contained 3,000 ppm chlorine⁽¹²⁾. Group VB and VIB element powders made by Brutvan, et al⁽¹³⁾, contained between 3,000 and 6,000 ppm chlorine. The impurity level can be reduced by adjusting the process parameters and by post-treatments but the chlorine content remains relatively high⁽¹⁴⁾. In the other method evaporation and homogeneous nucleation are used to form condensed particles in free space. Evaporation rate is given by the following relation which is derived from the kinetic theory of gases⁽¹⁵⁾.

$$W = (p_o - p') \sqrt{\frac{M}{2 \pi R T}} \quad (2)$$

W = rate of evaporation

p_o = vapor pressure (equilibrium)

p' = pressure of vapor in contact with surface of evaporating metal

M = molecular weight

R = gas constant

T = absolute temperature

Chromium's relatively high vapor pressure makes powder formation possible by this method even though the presence of a gas above the evaporating metal [represented by the p' term in equation (2)] reduces the rate of evaporation considerably below the maximum theoretical rate predicted by the Langmuir-Knudsen equation.

2-b) Particle size of the product can be expected to be in the sub-micron range. Particle growth takes place by collision of atoms with the nuclei in the gas phase. This growth is very slow since the nuclei tend to be perfect⁽¹⁶⁾. A high rate of nucleation also contributes to the formation of very small particles. The following analysis demonstrates that extremely high nucleation rate could be expected.

The free energy of formation of a nucleus (assumed to be spherical) is the sum of a bulk and a surface term⁽¹⁷⁾.

$$\Delta F = \frac{4 \pi r^3 \Delta F_v}{3} + 4 \pi r^2 \sigma \quad (3)$$

where:

- ΔF_v = bulk free energy change/unit volume = $\frac{-kT}{\Omega_L} \ln p/p_o$
- Ω_L = molecular volume of stable phase = $\frac{M}{\rho N_A v}$
- p = partial pressure of unstable phase (supersaturated vapor)
- p_o = partial pressure of stable phase (solid)
- p/p_o = supersaturation ratio
- r = nucleus radius

M	=	molecular weight
φ	=	density
Nav	=	Avogadro's number
σ	=	surface energy
T	=	absolute temperature of condensation
k	=	Boltzmann's constant

The critical radius, r^* , required for the formation of a stable nucleus is found by maximizing the above equation to give:

$$r^* = \frac{2\sigma M}{\varphi k N_{av} T \ln p/p_o} \quad (4)$$

Using the values for chromium of $\sigma = 1500 \text{ erg/cm}^2$ (1.500 J/m^2), $M = 52 \text{ gm/mole}$ ($5.2 \times 10^{-2} \text{ kg/mole}$), $\varphi = 7.19 \text{ gm/cm}^3$ ($7.19 \times 10^3 \text{ kg/m}^3$), $T = 1273^\circ\text{K}$ and $p/p_o = 10^8$, the critical radius is found to be $1.11 \times 10^{-8} \text{ cm}$ or $1.11 \text{ \AA}$ ($1.11 \times 10^{-10} \text{ m}$).

The atomic radius of chromium is $1.27 \text{ \AA}$ ($1.27 \times 10^{-10} \text{ m}$). Therefore only one chromium atom is required to form a stable nucleus under our conditions of very great supersaturation. Needless to say, the rate of nucleation will be extremely high.

Some degree of control over particle size is to be expected within the submicron range since growth rate is an inverse function of the mean free path of chromium. Thus decreased system pressure and decreased evaporation and condensation temperature should reduce particle size by lengthening the mean free path. Particle agglomeration can be minimized by operation at low pressure⁽¹⁸⁾.

2-c) The mean free path must also be restricted by adjusting these same parameters to control the size of the condensation zone (the space adjacent to the evaporation source inside of which particle growth takes place and outside of which only particle agglomeration occurs)⁽¹⁹⁾. If the boundaries of the condensation zone exceed the dimensions of the chamber condensation of chromium will occur on the walls of the chamber to produce a foil product.

Atoms emitting from a vapor source will follow paths determined by optical line of sight. This would make coating of the condensed particles with the dispersoid oxide virtually impossible. Advantage can be taken of the Bernoulli effect, however, to confine the vapor in a stream. Bernoulli's theory states that the sum of pressure, kinetic energy and potential energy at two points in a stream are equal⁽²⁰⁾.

$$p_1 + 1/2 \varphi v_1^2 + \varphi g Z_1 = p_2 + 1/2 \varphi v_2^2 + \varphi g Z_2 \quad (5)$$

where:

- p = pressure
- φ = density
- v = linear velocity
- g = gravitational constant
- Z = height in vertical stream

and subscripts 1 and 2 refer to locations in the stream.

Since the potential energies are virtually equal for small differences in height the equation can be reduced to:

$$p_1 - p_2 = 1/2 \varphi (v_2^2 - v_1^2) \quad (6)$$

The pressure differential created by the difference in velocity can be used to pull a slowly moving chromium stream into a rapidly moving stream of inert gas. With the stream of chromium particles confined to a vertical stream away from the walls of the vaporization chamber they can be coated with the oxide.

3) The dispersed particles of oxide must be stable in the chromium matrix at the maximum temperature of anticipated use of 1371°C (1644°K). The relative stability of particles at this temperature can be determined by calculating the standard free energies of the reactions for the oxide going into solution in the matrix. For ZrO_2 and ThO_2 these reactions are



where the underlined elements are in solution and the standard state of the solute is taken as 1.0 weight percent.

The standard free energies of these reactions can be determined by summing the standard free energies of the constituent reactions as follows:



The same procedure is used to obtain the ΔF° for $\text{ThO}_2 = \underline{\text{Th}} + 2\underline{\text{O}}$. The method of calculation is similar to that of Cochard⁽²¹⁾ and is given in Appendix A.

Standard free energy values for equations (7) and (8) are +88,200 cal (368,200 J) and +126,400 cal (528,500 J). Both oxides should be stable in a chromium matrix with ThO_2 being much the more stable of the two.

4) Either oxide particles or coating deposits can be formed by the thermal decomposition of a metal alkoxide. For example, ZrO_2 can be deposited from $\text{Zr}(\text{OR}')_4$, zirconium tetratertiary butoxide. Submicron particles will result from homogeneous nucleation⁽²⁷⁾ while deposits will result from heterogeneous nucleation on a solid substrate such as submicron chromium particles to produce a duplex powder. Decomposition temperature must be controlled in a range above that where decomposition will be incomplete and below that where carbon bonds will be broken to provide a contaminant for the oxide.

EXPERIMENTAL PROGRAM

A flow diagram showing the experimental program and relation of the subtasks is given in Figure 2. These subtasks are described as follows.

I. Determine Optimum Method of Making Chromium Powder

Two methods were considered, evaporation-condensation and H_2 reduction of CrI_2 . In both, powder is formed by homogeneous nucleation in the gas phase. Three methods of melting to permit evaporation were chosen for investigation—induction, arc and levitation melting.

II. Determine Means of Controlling Chromium Powder Formation

This rate must be controlled as a function of system pressure and temperature to match it to the ZrO_2 formation rate to form an alloy of desired composition. ZrO_2 formation rate is dictated by the flow rate of $Zr(OR')_4$ into the reaction chamber.*

III. Study $Zr(OR')_4$ Decomposition

The decomposition must be studied to determine the minimum temperature required to form ZrO_2 . A special apparatus for this study was necessary. ZrO_2 particle size requires measurement.

IV. Design and Assemble Equipment for Producing ZrO_2 Coated Chromium Powder

A leak tight reaction chamber was needed in which the stream of chromium particles can be confined away from the chamber walls and combined with a $Zr(OR')_4$ stream. The temperature at the juncture of these streams must be controllable.

V. Produce ZrO_2 Coated Chromium Powder

Powder has to be produced and evaluated for ZrO_2 coverage, particle size, composition and impurity content.

* This flow rate is given by

$$\text{flow rate } Zr(OR')_4 = \frac{\text{vapor pressure } Zr(OR')_4}{\text{system pressure}} \times \text{flow rate He carrier gas} \quad (12)$$

The $Zr(OR')_4$ vapor pressure⁽²⁸⁾ is fixed by controlling the temperature of the saturator. Therefore, for a given system pressure the amount of ZrO_2 formed is controlled simply by controlling the flow rate of He carrier gas.

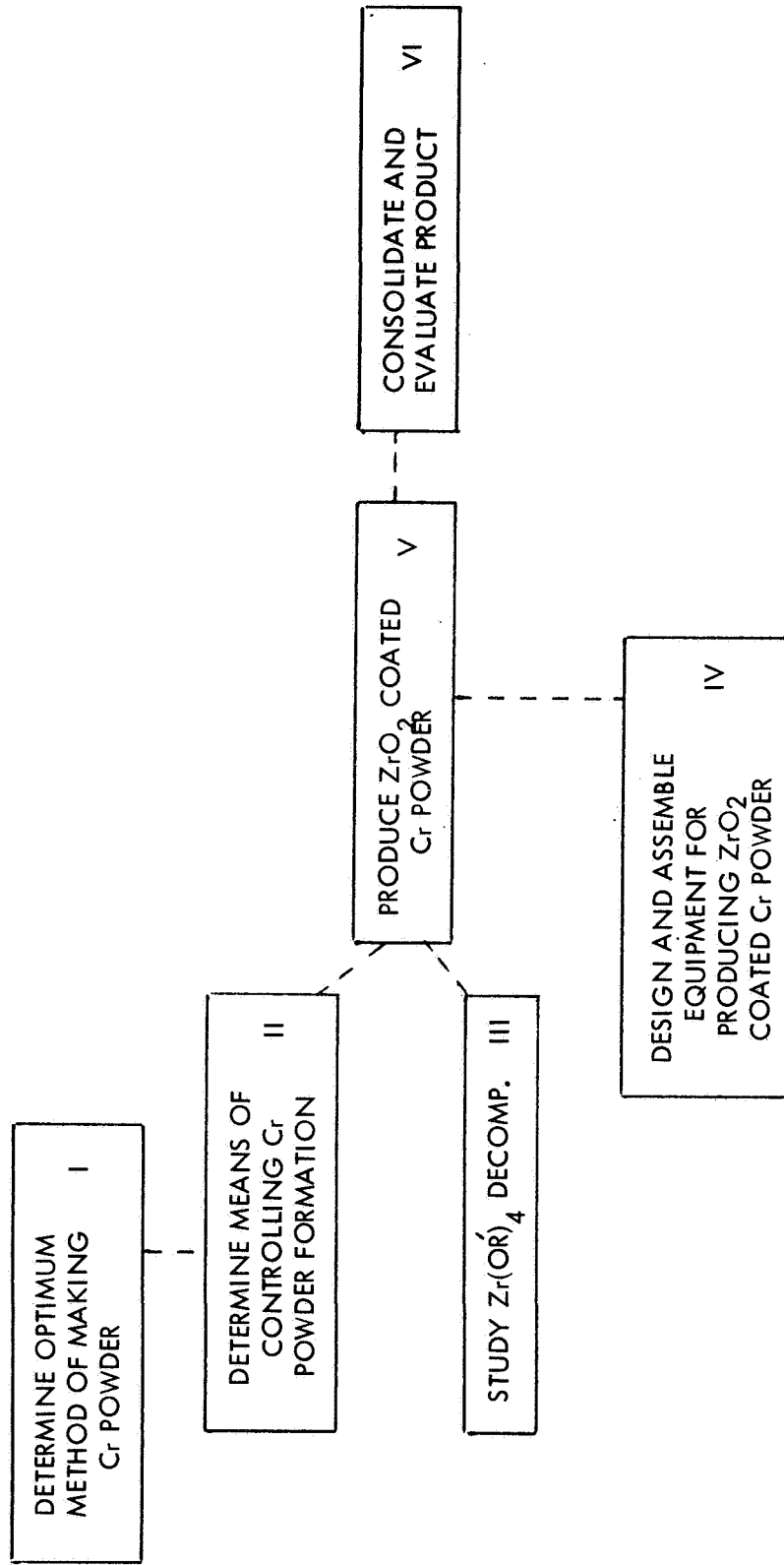


FIGURE 2 - Flow Diagram of Experimental Program Sub-Tasks

VI. Consolidate and Evaluate Product

Cold pressed and Dynapak extruded product was evaluated for:

- 1) density
- 2) impurity content
- 3) microstructure
- 4) dispersoid particle size and spacing
- 5) dispersion stability

EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

The results are presented according to the experimental program subtasks outlined in the preceeding section of this report.

Subtask I. Optimum Method of Making Chromium Powder

Chromium powder formation by the hydrogen reduction of CrI_2 vapor proved difficult. The desired reduction temperature of 1200°C (1473°K) could only be achieved by preheating the H_2 to above 1700°C (1973°K). Attainment of this temperature resulted in repeated failures of the tungsten wound Al_2O_3 heater cores. While this problem could have been overcome by major equipment modification, the large number of references found reporting high halide content in the product produced by this method indicated that the most promising approach was the evaporation-condensation method.

The evaporation-condensation method using induction heating proved to be the most workable means of forming submicron chromium powder. This work was done in equipment very similar to that shown schematically in Figures 3 and 4. The only difference was that a single walled crucible and He flow through inlet (3) were used instead of the chromium stream confining portion of the apparatus consisting of the double-walled crucible, Al_2O_3 injection tube and He streams (1) and (2).

Of the crucible materials evaluated - BN, Al_2O_3 , ZrO_2 and TaC - the latter was the only acceptable one. Al_2O_3 reacted with chromium at 2000°C (2273°K). The vapor pressure of BN and ZrO_2 proved to be prohibitively high. ZrO_2 crucibles also exhibited very poor resistance to thermal shock.

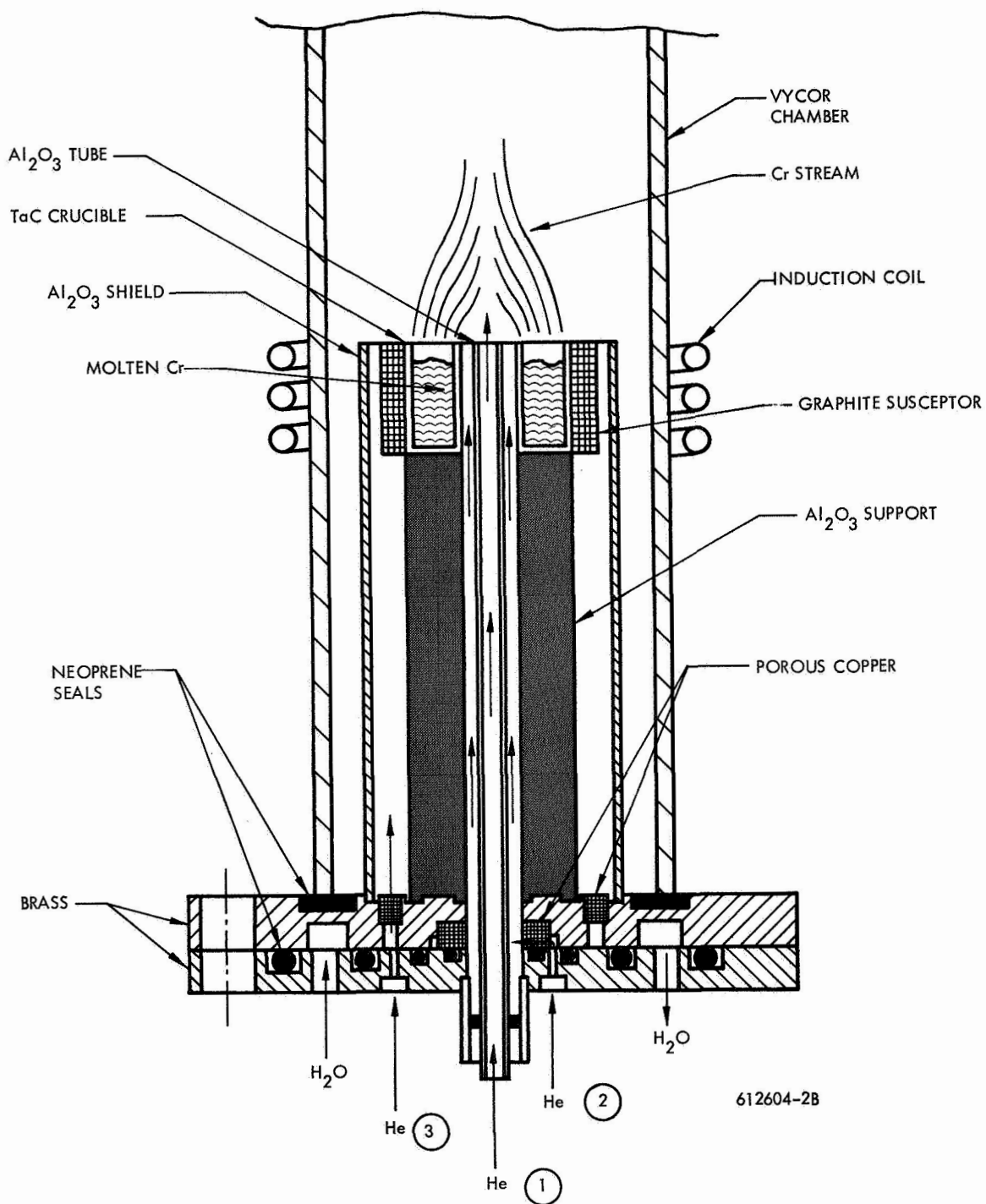


FIGURE 3 - Schematic Drawing of Deposition Chamber

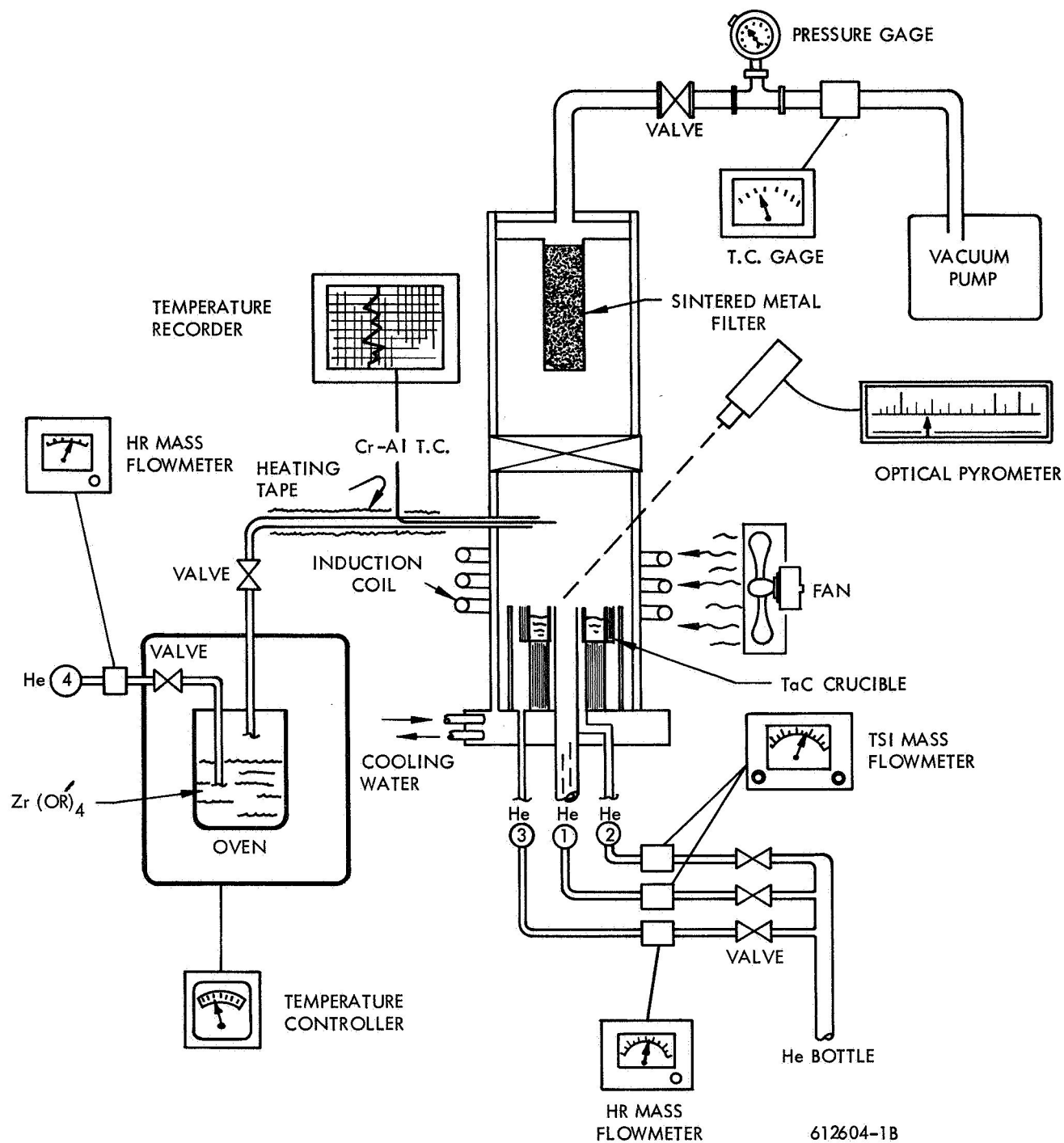


FIGURE 4 - Schematic Drawing of Equipment Used for Making ZrO_2 -Coated Chromium Particles

Evaporation by arc melting produced a high rate of powder formation. The method was not pursued further, however, because of the anticipated difficulty in confining the evaporant to a laminar stream. Levitation melting was also investigated but not pursued because of difficulty in making extended runs. In addition, as can be seen in Figure 5 the particles were large, 1000 to 10,000 Å, (1×10^{-7} to 1×10^{-6} m), compared to those produced by induction melting where the temperature could be controlled at a lower value.

Subtask II. Control of Chromium Powder Formation

Preliminary evaporation-condensation experiments were run to determine the effect of evaporation temperature on chromium particle size and rate of evaporation. The system pressure was held constant at 1/2 atmosphere throughout. The condensation temperature could not be determined but is known to be greater than 600°C (873°K). Powder was collected by valving off the collection portion of the particle formation chamber and transferring it to a glove box which was then evacuated to 10^{-6} torr (1.33×10^{-4} N/m²) and backfilled with helium. A sample of the powder was removed from the box, dispersed and replicated*. The electronmicrographs obtained are included as part of the experimental results shown in Figure 6. Several conclusions are evident from this figure:

- 1) Evaporation rate is extremely low below the melting point of chromium.
- 2) Evaporation rate increases rapidly with temperature. This is to be expected since the vapor pressure of chromium increases rapidly over the temperature range studied.
- 3) Particle size is directly proportional to evaporation temperature and can be controlled within a small size range at any given temperature. For example, the particles prepared at 1910°C (2183°K, the melting point of chromium) range in size from 150 to 1200 Å (1.5×10^{-8} to 1.2×10^{-7} m).

*Particles are ultrasonically dispersed in amyl acetate, spread on a glass slide and allowed to dry. The particles are covered with replicating plastic into which grids are inserted. The dried plastic is stripped from the glass and made a substrate onto which carbon is deposited by an evaporation technique. The plastic is dissolved in ethyl acetate leaving a carbon replica in which the particles are embedded.

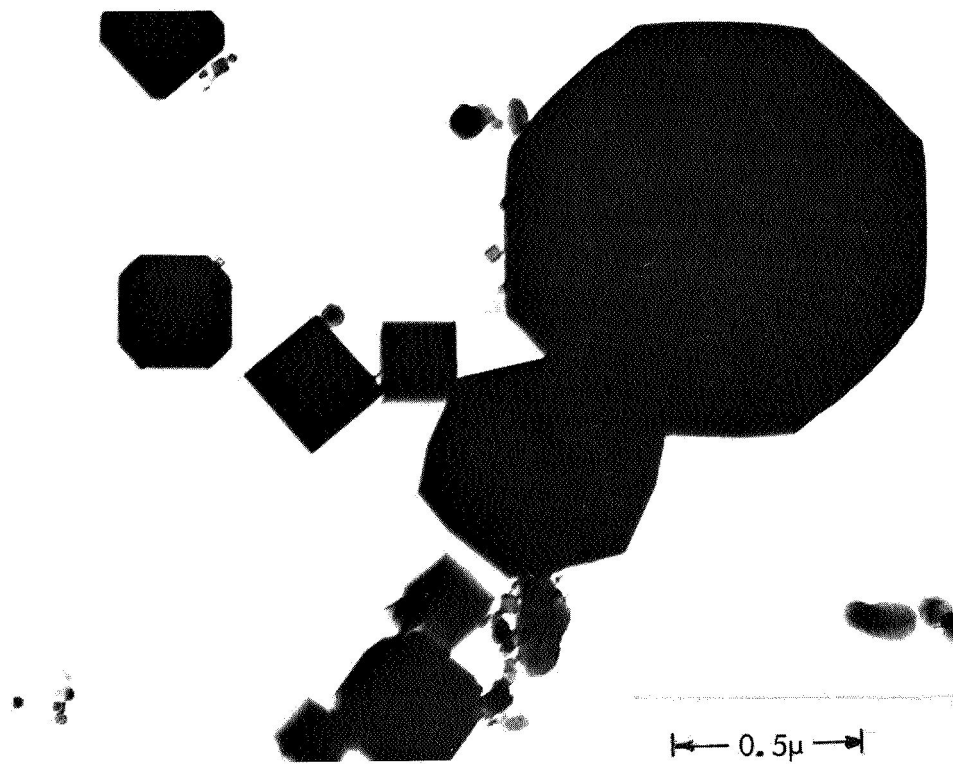


FIGURE 5 - Chromium Particles Prepared by Nucleation from Vapor Above Levitated Melt

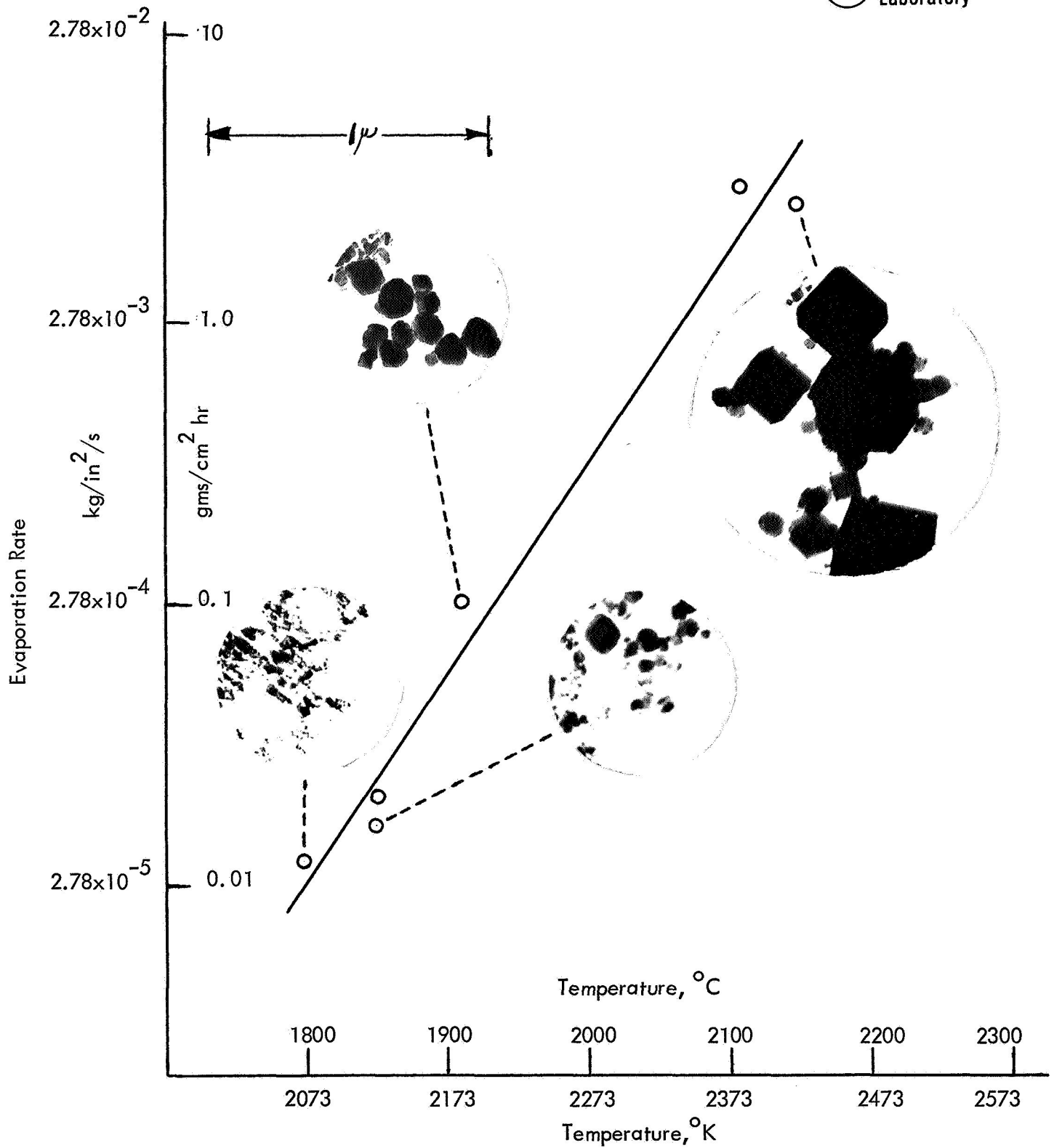


FIGURE 6 - Evaporation Rate of Chromium as a Function of Temperature (System Pressure of 1/2 Atm.) Typical Particles Formed at Each Temperature Are Shown in 50,000X Electromicrographs.

Other size controlling parameters are condensation temperature (not determined experimentally but known to be an inverse function of the linear velocity of the helium confinement stream, v) and system pressure. *

Growth rate and hence particle size increases with increasing evaporation temperature since the partial pressure of chromium atoms adjacent to the molten metal is raised and the mean free path of chromium atoms in this region is shortened to produce a greater frequency of collision among chromium atoms.

In an equation presented previously (Equation (4)), the critical radius required to form a stable nucleus was found to vary inversely with T , the temperature of condensation. This critical radius, r^* , can be related to particle growth rate, G , by the expression

$$r^* = k' \frac{1}{N} = k'' G \quad (13)$$

where k' and k'' are proportionality factors and N is the nucleation rate. T varies inversely with the linear velocity of the helium confinement stream, v . Thus particle growth rate is directly proportional to T and therefore inversely proportional to v in accordance with our experimental results.

In the powder formation chamber evaporated chromium atoms lose their thermal energy by collision with helium atoms. This energy loss is a function of the frequency of collision. (Should other gases be present it would also be a function of their atomic weights.) Collision frequency, and hence both the cooling and particle growth rates, is proportional to the system pressure. In turn, particle size is also proportional to system pressure.

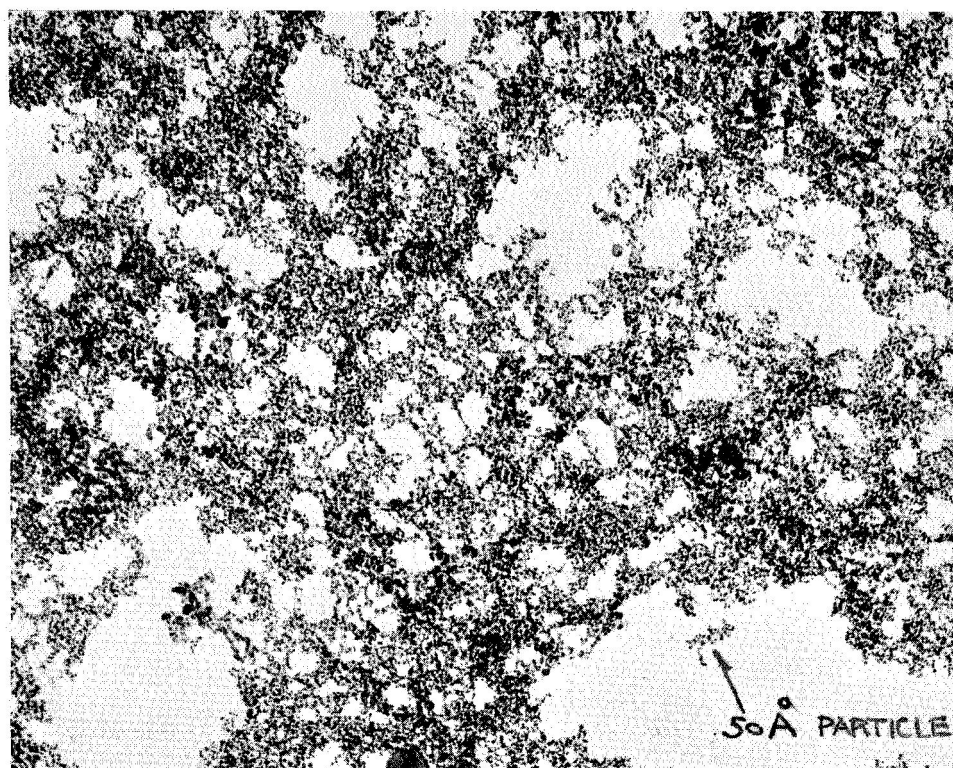
*In the study of more than one metal, consideration would also have been given to crystal structure. There is evidence that, for constant conditions, larger particles would be obtained for metals for hexagonal structure than for cubic structures⁽³⁰⁾.

Subtask III. $Zr(OR')_4$ Decomposition

It was initially intended that ThO_2 would be the dispersoid utilized. Prior to initiation of the program firm quotes were obtained from two suppliers for $Th(OR')_4$ (thorium tetratertiary butoxide), the starting compound for ThO_2 synthesis. Three suppliers accepted orders for the compound, but were unable to successfully produce the product. Consequently $Zr(OR')_4$ was used as a substitute, with recognition that this would penalize the chances of obtaining a stable alloy since ZrO_2 is significantly less stable in chromium than ThO_2 (see Appendix A).

$Zr(OR')_4$ decomposition was studied to determine the temperature range within which ZrO_2 would be produced. This work was done in the particle formation chamber (see Figures 3 and 4) but without the presence of chromium. Helium streams (1) and (2) were heated by passage over the hot walls of Al_2O_3 injection tube and inner wall of the double-walled TaC crucible. $Zr(OR')_4$ vapor was swept into the chamber from the saturator where it was contacted with the hot helium. A chromel-alumel thermocouple located at this stream juncture was used to measure the temperature of thermal decomposition. This temperature was varied for each experiment by substituting Vycor chambers having $Zr(OR')_4$ inlets at different heights from the chamber bottom. The particles produced were extremely small; on the order of 50 to 100 Å (5×10^{-9} to 1×10^{-8} m) as shown in the electron micrograph of Figure 7. Electron diffraction analysis was necessary to confirm the identity of ZrO_2 since the very fine particles produced extreme line broadening in x-ray diffraction studies. The results of the decomposition studies are as follows:

Decomposition Temperature		Product Obtained
$^{\circ}C$	$^{\circ}K$	
220	493	produce intermediate to $Zr(OR')_4$ and ZrO_2
330	603	product intermediate to $Zr(OR')_4$ and ZrO_2
430	703	cubic ZrO_2
480	753	cubic ZrO_2



50,000X

FIGURE 7 - ZrO_2 Particles Formed by Gas Phase Decomposition - Nucleation of Zr(OR)_4

No higher temperatures were investigated since no further decomposition is possible. An electron diffraction pattern of the ZrO_2 produced by decomposition at 430°C (703°K) (Figure 8) showed the product to have the cubic structure. Normally, unless a cubic structure is stabilized by oxide additions such as CaO or Y_2O_3 , ZrO_2 is monoclinic at all temperatures below about 1000°C (1273°K). Above this temperature the tetragonal structure is stable. Mazdidasni⁽²⁷⁾ has reported that submicron cubic ZrO_2 particles formed by thermal decomposition of an alkoxide transform to the monoclinic structure above 300°C (573°K).

Subtask IV. Equipment for Producing ZrO_2 Coated Chromium Powder

Details of the deposition chamber are shown in Figure 3. Chromium is melted in the double-walled TaC crucible by heat transferred from the surrounding inductively heated graphite susceptor. An Al_2O_3 tube is used to shield the Vycor chamber walls from thermal radiation from the susceptor. The water cooled brass chamber bottom is designed to allow three separately controllable helium streams to enter the chamber through porous copper flow distributors to confine the stream of chromium to the vertical axis of the chamber. Stream No. 3 was only used in preliminary studies of chromium evaporation where a single-walled crucible was used. Streams 1 and 2 were not used in these preliminary trials.

Figure 4 is a schematic drawing of the complete experimental setup showing the chamber and its auxiliary control equipment. Following a run, the collection cylinder with its sintered metal filter cartridge was valved out and loaded into a dry box where the powder was removed.

Two methods of introducing the $\text{Zr}(\text{OR}')_4$ vapor were investigated. In the first, helium and $\text{Zr}(\text{OR}')_4$ were injected through the Al_2O_3 tube passing through the center of the crucible (this would take the place of the helium (1) stream shown in Figure 3). Decomposition temperatures in excess of 1000°C (1273°K) were encountered. Since it was felt that decomposition temperatures of this magnitude would produce ZrO_2 high in carbon content this method was abandoned.

In the adopted method $\text{Zr}(\text{OR}')_4$ was injected perpendicular to the chromium stream. The height of the injection point above the crucible was fixed to give a temperature at the point of injection of 400 to 600°C (673 to 873°K).

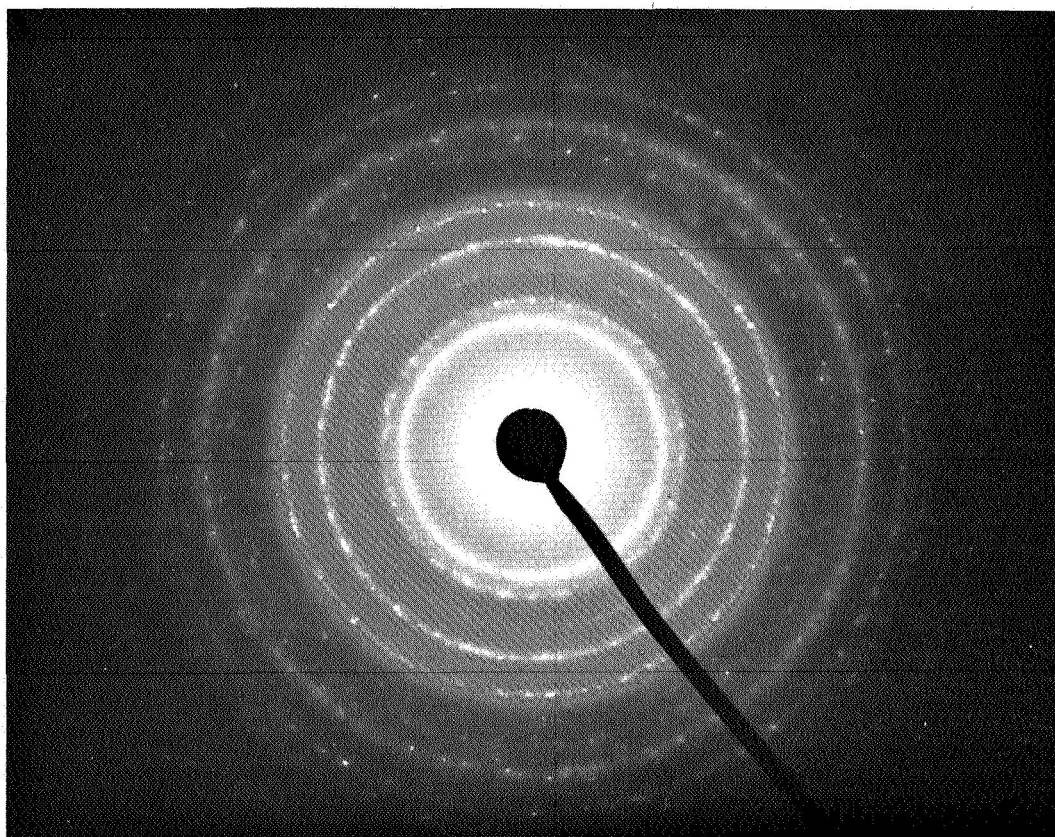


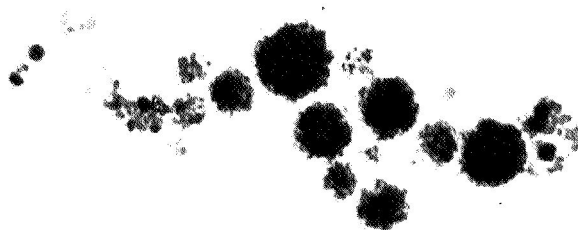
FIGURE 8 – Electron Diffraction Pattern of Submicron Cubic ZrO_2 Particles

Subtask V. Production of ZrO_2 Coated Chromium Powder

Trials were made to produce a duplex powder, one in which chromium particles were coated with ZrO_2 . The feasibility of producing such a powder was established. With fairly rapid cooling of the chromium particles the product shown in Figure 9 was obtained. It is reasoned that the ZrO_2 was not formed by $\text{Zr}(\text{OR}')_4$ decomposition on the chilled chromium particles but rather homogeneously nucleated and then deposited as ultra-fine particles. This type of deposit will be referred to as a particle deposit in subsequent discussion. Slower cooling produced the duplex powder of Figure 10. Here ZrO_2 appears to have deposited on the chromium particles to form spiny growths. This type of deposit will hereafter be referred to as a growth deposit.

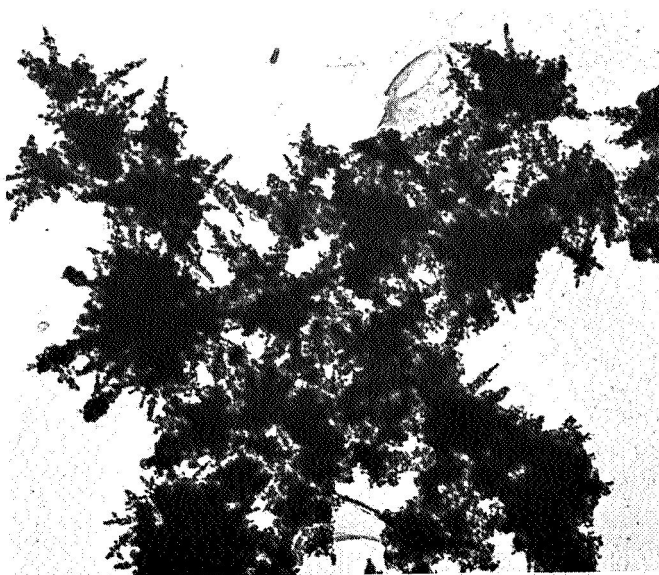
The effect of system pressure on the rate of formation of product was studied. Results are shown in Figure 11 for a constant evaporation temperature of 2000°C (2273°K). This temperature was selected to yield chromium particles of the most desirable size range. Larger chromium particles might adversely affect the spacing of dispersoid particles in the final product. Smaller chromium particles would tend to increase the possibility of contamination by adsorption of trace amounts of gaseous impurities and would increase the difficulty of consolidation. To confine the streaming particles sufficiently so that an appreciable amount of product could be collected in the filter trap, the linear velocity of the helium confinement stream was varied inversely with the system pressure. The cooling effect of this helium stream on the deposition mode of ZrO_2 onto the chromium particles is evident from the electron micrographs of Figure 11. A linear velocity of approximately 1500 cm/sec (15 m/s) appears to mark the transition from particle mode deposition to growth mode deposition.

The ZrO_2 content of each powder preparation was determined by stoichiometry from the analyzed Zr content. Sufficient samples were analyzed for Zr, both chemically and by x-ray fluorescence to obtain a relation between the results of the two methods (see Figure 12). In the x-ray fluorescence method, $\text{ZrK}\alpha$ radiation diffracted by a LiF crystal and corrected for background radiation was counted for two minutes. With this relation subsequent Zr analyses could be made rapidly by fluorescing a small amount of powder.



50,000X

FIGURE 9 - Chromium Particles to Which ZrO_2
Particles have Adhered



50,000X

FIGURE 10 - Chromium Particles onto which ZrO_2
has been Deposited

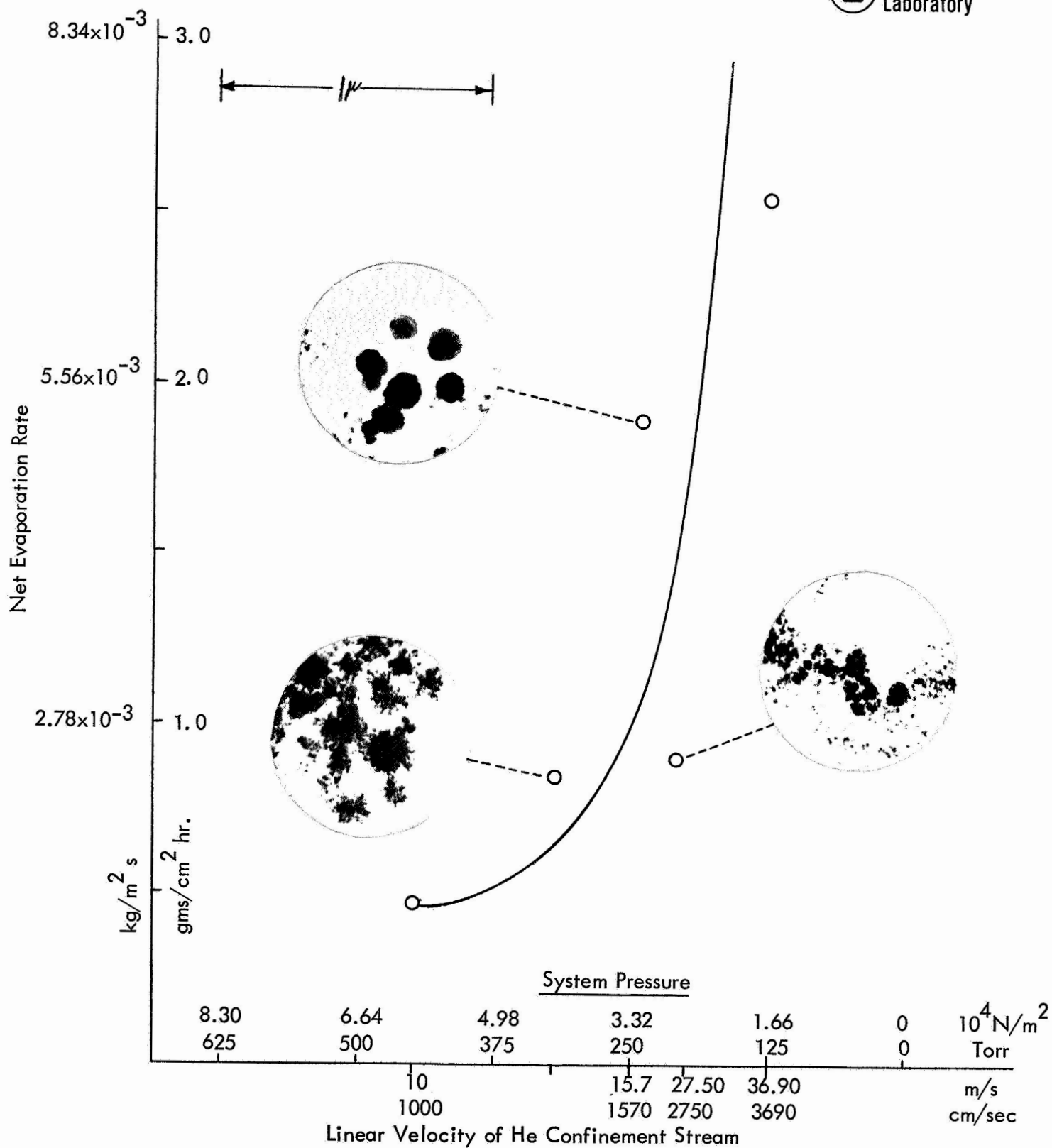


FIGURE 11 - Evaporation Rate of Chromium as a Function of System Pressure (Melt Temperature of ~2000°C) Typical Particles Formed at Each Pressure are Shown at 50,000X.

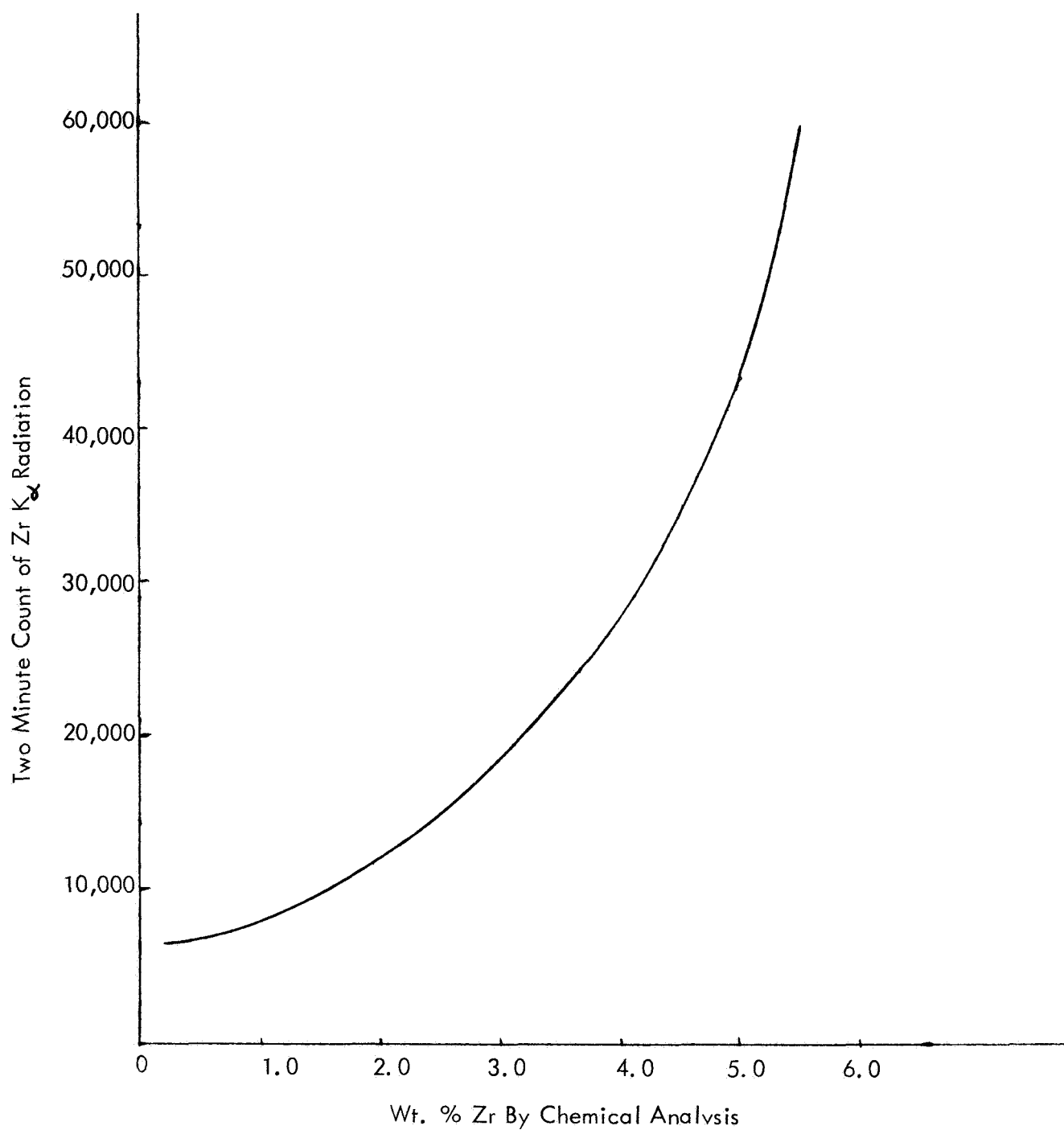


FIGURE 12 - Relation Used to Determine w/o Zr in Cr-ZrO₂
Powder by X-Ray Fluorescence

After examination of the results of a large number of coating trials, duplex powder produced by growth mode deposition was prepared for consolidation and subsequent evaluation. Runs to produce approximately 5 gm (5×10^{-3} kg) quantities were carried out at an evaporation temperature of 2000°C (2273°K) and a system pressure of approximately 250 torr ($3.32 \times 10^4 \text{ N/m}^2$). The nominal ZrO_2 level was selected to be 3.5 to 4.0 volume percent.

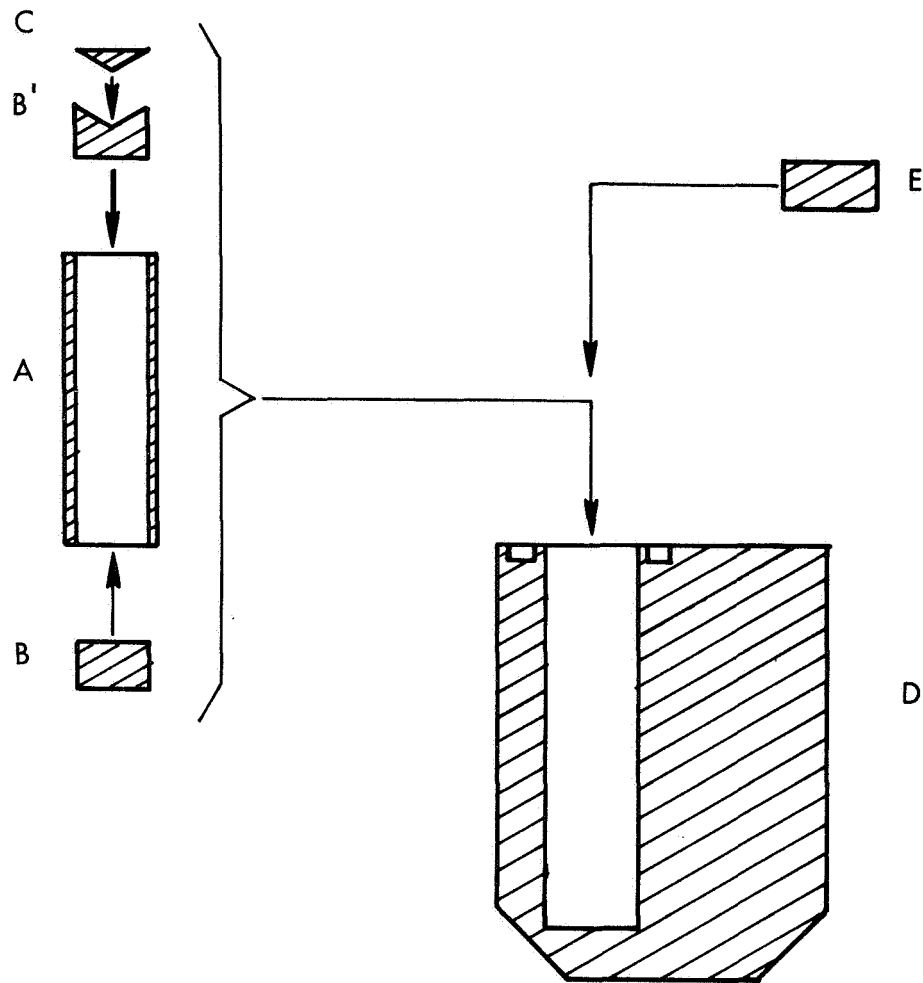
Sub-Task VI. Consolidation and Evaluation of Product

Consolidation

Duplex powder containing 3.5 volume percent ZrO_2 was produced for consolidation and subsequent evaluation. The theoretical density of this material is 7.12 g/cc ($7.12 \times 10^3 \text{ Kg/m}^3$). The powder was collected in the filter trap and transferred to an inert atmosphere dry box for loading into the extrusion billet. During transfer and loading, the duplex powder was exposed only to high purity helium (<1 ppm total active impurities) or vacuum. The dry box was evacuated to 10^{-6} torr ($1.33 \times 10^{-4} \text{ N/m}^2$) prior to backfilling with helium. The powder was cold pressed into a 3/8 inch ($9.5 \times 10^{-3} \text{ m}$) I.D. x 1/16 inch ($1.6 \times 10^{-3} \text{ m}$) wall 304 stainless steel tube, which was evacuated and then sealed by electron beam welding. The as-pressed density was about 50 percent of theoretical. The tube was then inserted into a cavity in a 1-7/8 inch ($4.76 \times 10^{-2} \text{ m}$) diameter mild steel extrusion can.

The composite billet was then Dynapak extruded at 1250°C (1523°K), using a 10 to 1 extrusion ratio. Three extrusions were made using this technique, but they were unsuccessful since very little densification beyond the cold pressed density was achieved. The mild steel merely flowed around the stronger Cr-ZrO_2 compact. Extrusion was next attempted by cold pressing powder into a molybdenum extrusion can, electron beam seal welding on a cap, and loading the capsule into an eccentrically positioned cavity of a molybdenum extrusion can, as shown in Figure 13. This billet was also extruded at 1250°C (1523°K) and a 10 to 1 extrusion ratio. A product density of 93% of theoretical was obtained. However the Cr-ZrO_2 extrusion fragmented into a number of irregularly shaped pieces.

One of the problems in handling the Cr-ZrO_2 powder was its extremely low bulk density (≤ 1.4 percent theoretical density). To aid handling and cold pressing into the extrusion capsule, subsequent lots of powder were sintered in purified hydrogen at 1127°C (1400°K) in the presence of titanium powder. This treatment raised its bulk density to approximately 31 percent of theoretical in addition to drastically lowering the carbon content of the as-prepared powder, as will be described later. The powder was sintered in a molybdenum boat. The sintering chamber was designed to allow it to be loaded and



TIG Weld B into Bottom of A
 Press Cr-ZrO₂ Powder into A
 Press B' into A to Contact Powder
 EB Weld B' into Top of A
 Position C into B'
 Load Assembly (A+B+B'+C) into D
 Press E into D
 TIG Weld E into D

FIGURE 13 - Schematic Representation of Assembly for Extruding ZrO₂
Chromium Coated Powder

unloaded in a helium containing glove box to prevent exposure to atmospheric contaminants. After sintering, the powder was transferred to the dry box where it was cold pressed to approximately 60 percent density into a molybdenum capsule. A schematic drawing of the capsule and the other components of the extrusion assembly is presented in Figure 14. A molybdenum spacer and plug were pressed into the cavity of the can. Electron beam welding provided a seal between the plug and the can. A molybdenum punch having the same face contour as the plug was then fitted into a stainless steel follower block. The volume of this punch was slightly greater than the void volume of the powder. With this arrangement a space was provided between the steel follower block and the extrusion can to prevent contact from being established between them during Dynapak extrusion until the punch was first forced into the cavity of the can to hot press the powder. Extrusion was carried out at 1250°C (1523°K) with a reduction ratio of 10 to 1.

This successful extrusion was radiographed to establish the location of the chromium alloy, sectioned and treated with hot concentrated HNO_3 acid to dissolve the molybdenum. Samples of the chromium alloy were taken for evaluation.

Density was determined to be 95 percent theoretical density by water immersion technique. However, the presence of contained micro cracks would make the apparent density of the material be less than its actual value. The actual density is therefore greater than 95 percent of theoretical.

Chemical Analysis

Impurity levels in the duplex powder, both in the as-prepared and as-sintered conditions, were established (Table 1) and compared with the maximum target level. Carbon contamination in the as-prepared powder was extremely high. Sintering the powder at 1123°C (1400°K) in hydrogen and in the presence of titanium powder reduced the carbon content below 100 ppm, the maximum target level. Free energy calculations justifying the selection of this method of decarburization are given in Appendix B. Calculation of the rate of evaporation of carbon from TaC at conditions of operation (see Appendix C) discounts this process as a source of contamination. The vapor pressure of graphite (used as a susceptor to induction

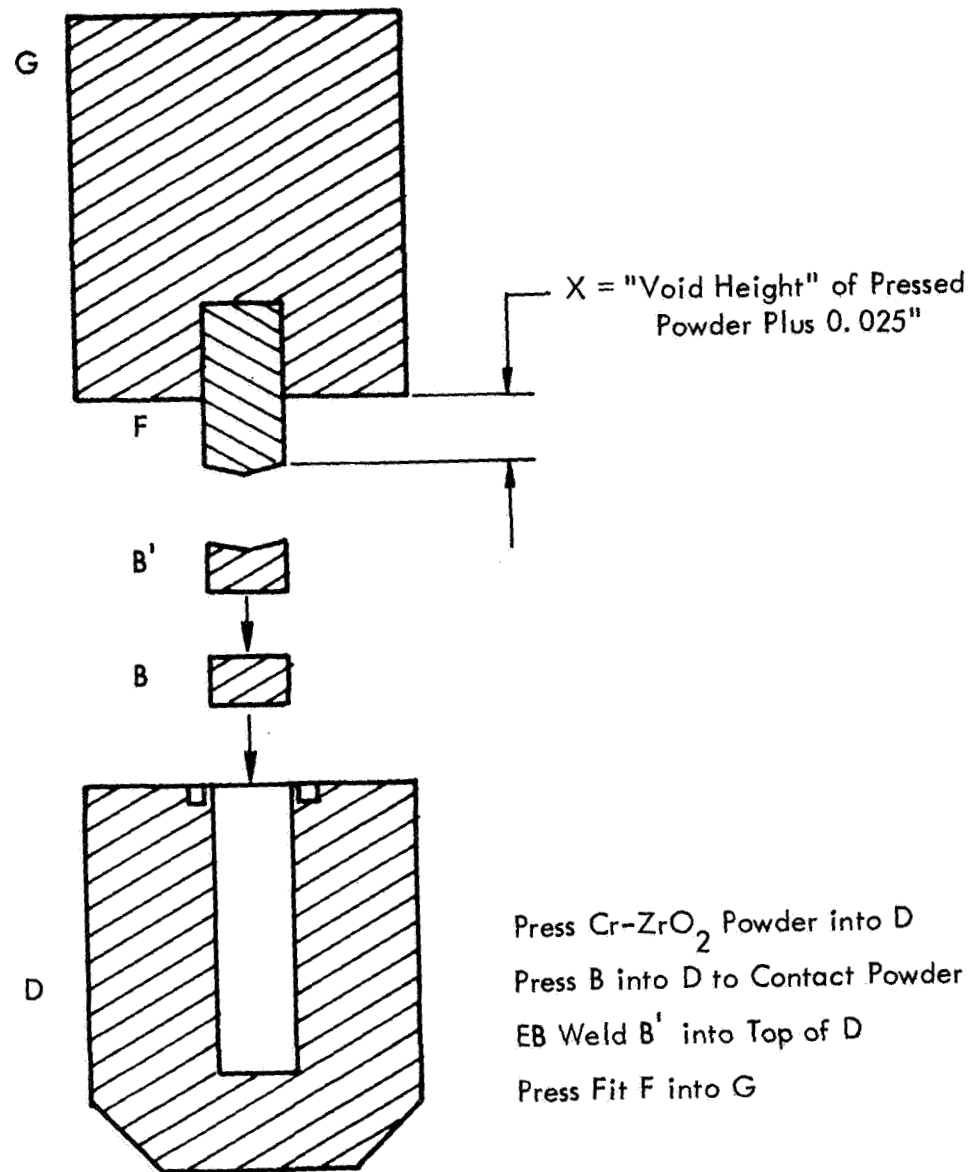


FIGURE 14 - Schematic Representation of Assembly for Hot Pressing-
Extruding ZrO₂ Coated Chromium Powder

TABLE 1 - Chemical Analyses of Cr-ZrO₂ Powder and Cr Starting Material, ppm

Element	Max. Target Level	Cr Starting Material*	Submicron Cr+ZrO ₂ (As Prepared)	Submicron Cr+ZrO ₂ (H ₂ Sintered)
S	100	90	<30	ND
O	100	50	+	+
C	100	70	23,000	<100
N	50	80	<<600	ND
Fe	100	90	170	ND
Mg	↓	NR	300	↓
Si		90	300	
Ni		NR	70	
Cu		NR	<30	
Ca		NR	<30	
Ti		NR	<30	
Zr		NR	20,000	

NR - Not Reported

ND - Not Determined

* - Electrodeposited Cr supplied by Union Carbide Corp. as lot No. 37589

+ - Insufficient oxygen found to account for that in ZrO₂

These analyses were obtained from samples taken from powder preparation lots 46, 47, 49, 54, and 55.

heat the TaC crucible) is far too low for this source to be considered. A batch of uncoated chromium powder [prepared by the normal method but with no injection of $\text{Zr}(\text{OR}')_4$] was analyzed for carbon and found to contain 21,700 ppm. This amount is within the range of carbon content of ZrO_2 coated powder. By this process of elimination it is concluded that carbon contamination results from its direct transfer from the TaC crucible into the molten chromium. Contamination does not, therefore, originate from the decomposition of $\text{Zr}(\text{OR}')_4$. Elimination of the TaC crucibles (which served well in all other respects) would mean designing, shielding, and utilizing entirely new power formation equipment. This effort could not be made within the funding limits of the program. Fortunately, as described above, hydrogen sintering in the presence of titanium powder reduced the carbon content of ZrO_2 coated powder to <100 ppm.

The reported analysis for nitrogen of 600 ppm is in error and is therefore reported as <<600 ppm. The error is the result of the highly active powder (it has an extremely high surface area) being inadvertently exposed to air while loading it into the vacuum fusion apparatus. Sulfur content was well below the target level.

Chemical samples for oxygen analysis of the powder were obtained in the dry box. For each analysis a tin ampoule was filled with powder and cold-weld sealed. The tin encapsulated powder was removed from the box and sealed in another capsule formed from a Pyrex test tube. The samples were then analyzed by vacuum fusion in a platinum bath. The oxygen analyses were inconclusive. In powder containing ZrO_2 , less oxygen was found than can be accounted for by combination with zirconium, as shown below.

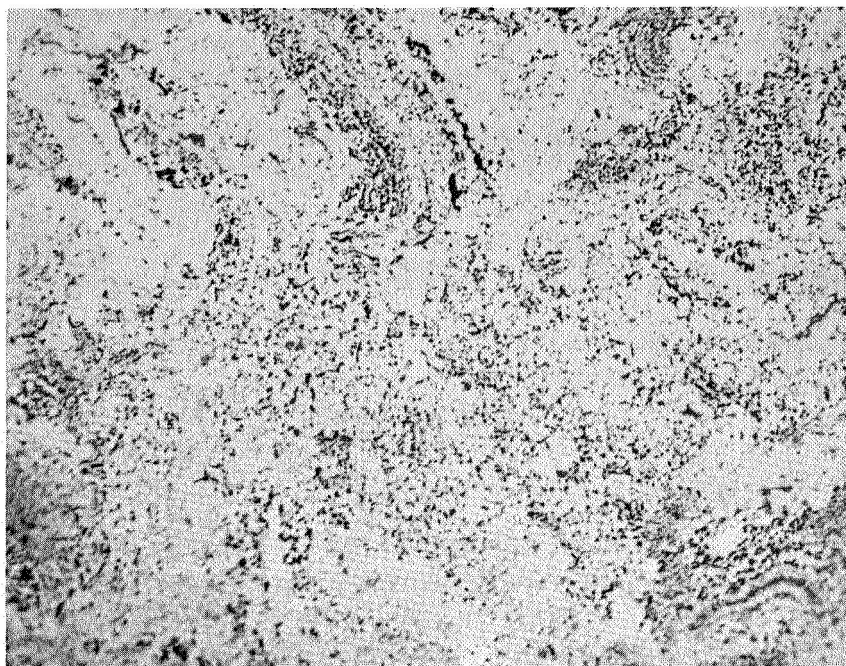
Powder Preparation Trial No.	Analyzed Zr (w/o)	Analyzed Oxygen (w/o)	Calculated O_2 in Combination with Zr (w/o)
49 (as-prepared)	4.9	0.71	1.72
49 (as-prepared)	4.9	1.68	1.72
55 (H_2 sintered)	2.0	0.33	0.7

Since it is difficult to conceive of zirconium being present in the unoxidized state, the oxygen results on the Cr-ZrO₂ powder were considered to be erroneous. Subsequently, one run of chromium powder was prepared without the addition of ZrO₂ (powder preparation lot No. 56) and analyzed and found to contain >1.85 w/o oxygen. This result indicated severe oxygen contamination of the powder. A section of the as-extruded Cr-3.5 v/o ZrO₂ compact was analyzed and found to contain 1.2 w/o oxygen. Of this amount, 0.7 w/o oxygen is combined with zirconium as ZrO₂. This leaves a remainder of 0.5 w/o present either as Cr₂O₃ or a mixed oxide of chromium and zirconium. At the present time it is not possible to determine if the oxygen contamination of the powder occurs during powder production, or during transfer from the deposition chamber. The powder, because of its very fine particle size, is extremely reactive, and powder exposed to air was extremely pyrophoric.

As shown in Table 1 the other impurities were all either less than target level or close to it. The probable sources of the contaminants are: iron and nickel (particle trap), silicon (vacuum seals) and magnesium (Zr(OR')₄).

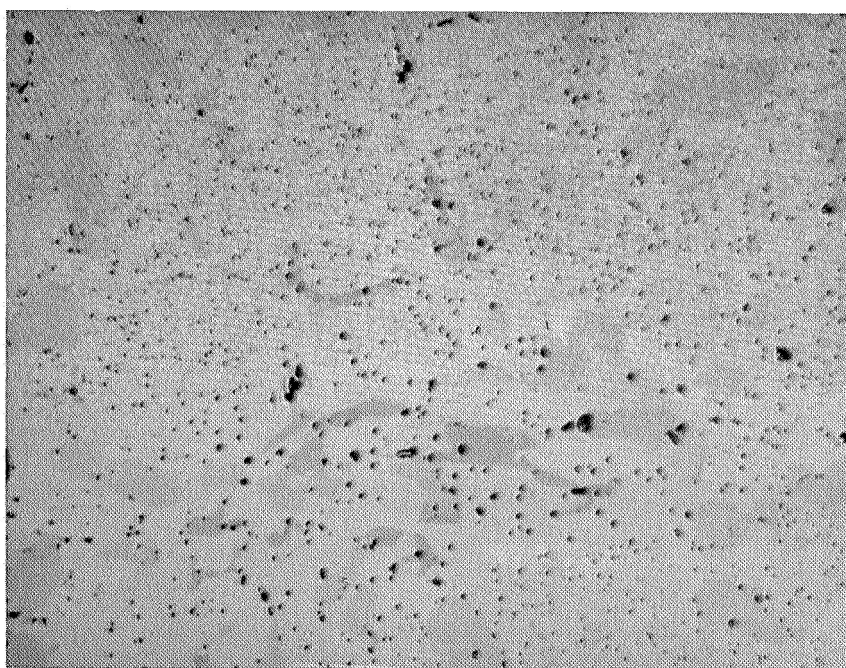
Thermal Stability

Microstructure of the as-extruded alloy is shown in Figures 15 and 16. The 1000X optical micrograph was taken with oblique lighting to provide a distinction between voids (dark spots) and ZrO₂ particles (much smaller dark spots each with an adjoining larger white area, the "shadow" of the particle). The particle dispersion is fairly uniform. Electron-micrographs of the as-extruded alloy at 10,000X and 40,000X are presented as Figures 17 and 18. The ZrO₂ particles appear as platelets. Lineal analysis^(32,33) of three 10,000X micrographs (total sampling length of 123 inches) (3.13 m) gave average platelet dimensions of 0.1μ (1 × 10⁻⁷ m) thick by 0.7μ (7 × 10⁻⁷ m) diameter. On the average, the particles are larger than the desired maximum particle size of 0.1μ (1 × 10⁻⁷ m). The volume fraction of dispersoid obtained by this analysis is 1.5 v/o compared to 3.5 v/o obtained by two minute count of ZrK_α radiation on the uncompacted powder. This discrepancy could be the result of several factors, including insufficient sample size and inability to resolve some particles at 10,000X. Interparticle spacing was calculated to be 13μ (1.3 × 10⁻⁵ m). This is much greater than the desired spacing of 1.5μ (1.5 × 10⁻⁶ m).



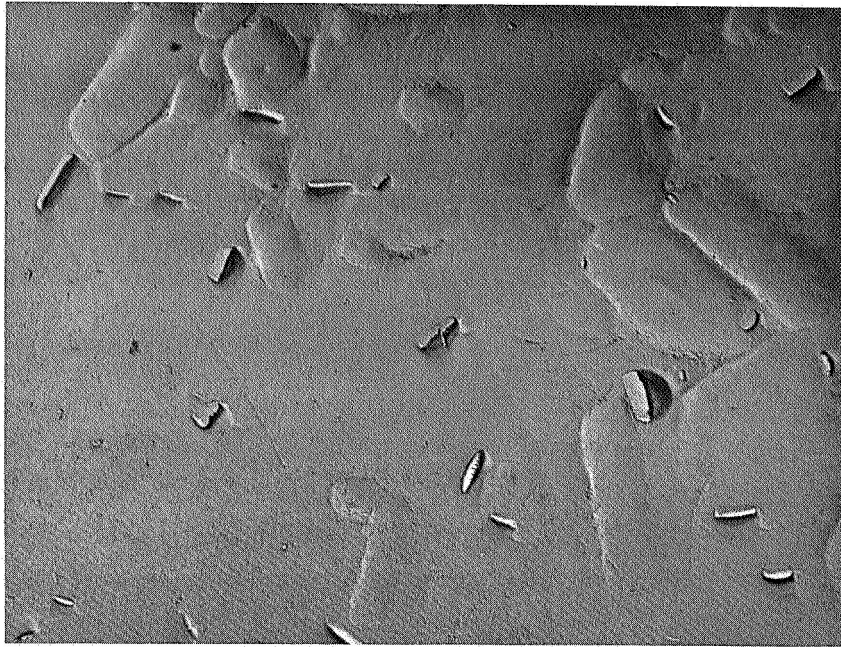
250X

FIGURE 15 - Microstructure of As-Extruded Alloy



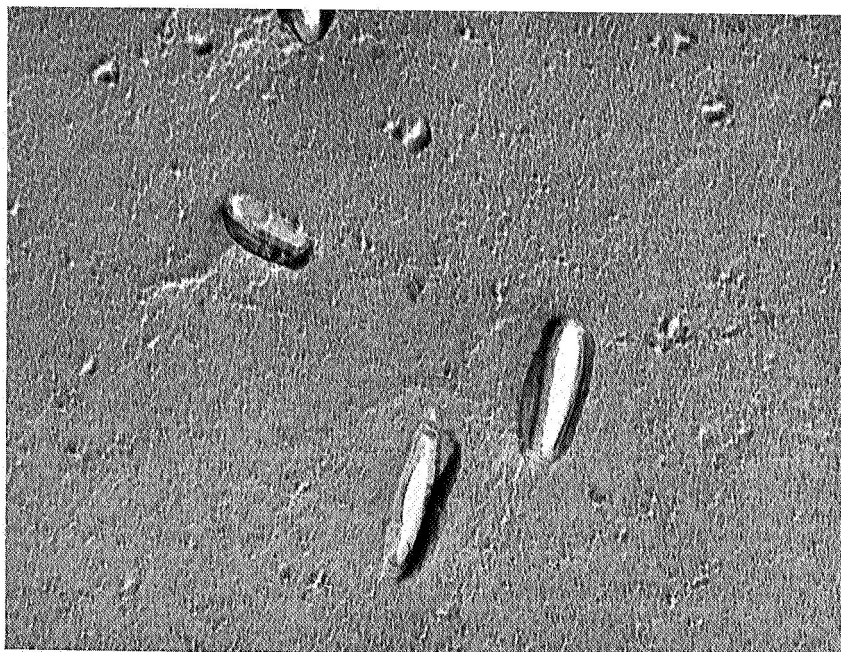
1000X

FIGURE 16 - Microstructure of As-Extruded Alloy Using Oblique Light



10,000X

FIGURE 17 - Electronmicrograph of As-Extruded Alloy



40,000X

FIGURE 18 - Electronmicrograph of As-Extruded Alloy

Thermal stability of the dispersoid was determined by heat treating samples of the extruded alloy at these conditions: (a) 1316°C (1590°K) for 10 hours, (b) 1316°C (1590°K) for 100 hours, (c) 1427°C (1700°K) for 10 hours and (d) 1427°C (1700°K) for 100 hours. The samples were contained in evacuated electron beam welded cans during vacuum heat treatment at 5×10^{-5} torr (6.65×10^{-3} N/m²) to prevent evaporation of chromium.

Microstructures of the heat treated alloy are shown at 1000X in Figures 19 through 22. From these figures, it is evident that oxygen contamination has occurred at some step in the consolidation process. In these figures Cr₂O₃ appears as straight-sided, medium-gray colored inclusions (see example in Figure 20). Its presence was established both by x-ray diffraction analyses and microscopic analyses with polarized light. Under polarized light Cr₂O₃ displayed a characteristic green color and exhibited alternate increased brilliance and extinction of image as the metallograph stage was rotated. This latter property is the result of Cr₂O₃ having an anisotropic structure (hexagonal to be specific).

The small round particles, the larger of which appear white in the photomicrographs, (see Figures 20, for example) are ZrO₂. This identification was made at 1000X under polarized light by comparing their appearance in the alloy with the appearance of ZrO₂ particles mixed with chromium powder and metallographically mounted and polished. In both cases, the particles are white and anisotropic (ZrO₂ being monoclinic at room temperature).

The dark gray, glassy areas probably represent mixed oxides. They were usually found adjacent to Cr₂O₃ and, therefore, likely contain this oxide (see Figure 20). Note also that this glassy area is dark grey where it contacts the Cr₂O₃ and becomes progressively lighter at increased distances from the Cr₂O₃. This is indicative of lessening Cr₂O₃ content in the mixed oxide at increasing distance from the Cr₂O₃ phase.

More detailed information on oxide identity, morphology and distribution is required. In an attempt to obtain these data, samples of the as-extruded and thermally exposed material were placed in a bromine-methanol-tartaric acid solution. This technique of bulk extraction has been used successfully to extract oxide, nitride, and carbide phases in V, Cb, Ta, and Mo alloys. However, after several weeks exposure in the solution no residue was obtained.

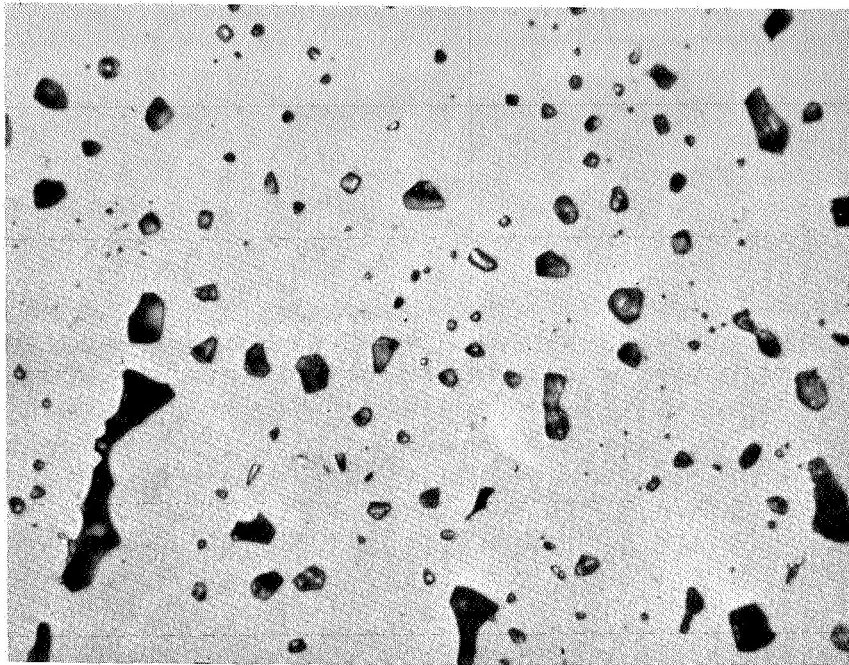


FIGURE 19 - Microstructure of Alloy Heat Treated 2400°F - 10 Hours

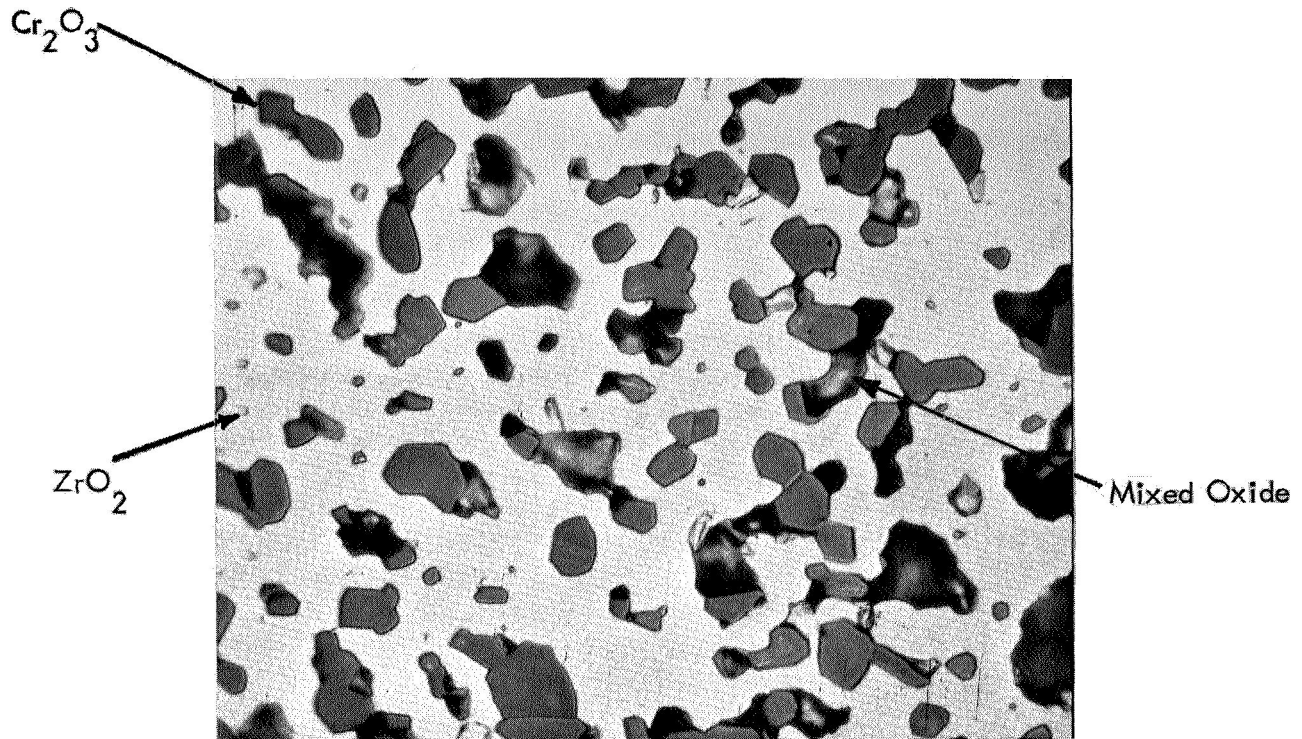


FIGURE 20 - Microstructure of Alloy Heat Treated 2400°F - 100 Hours

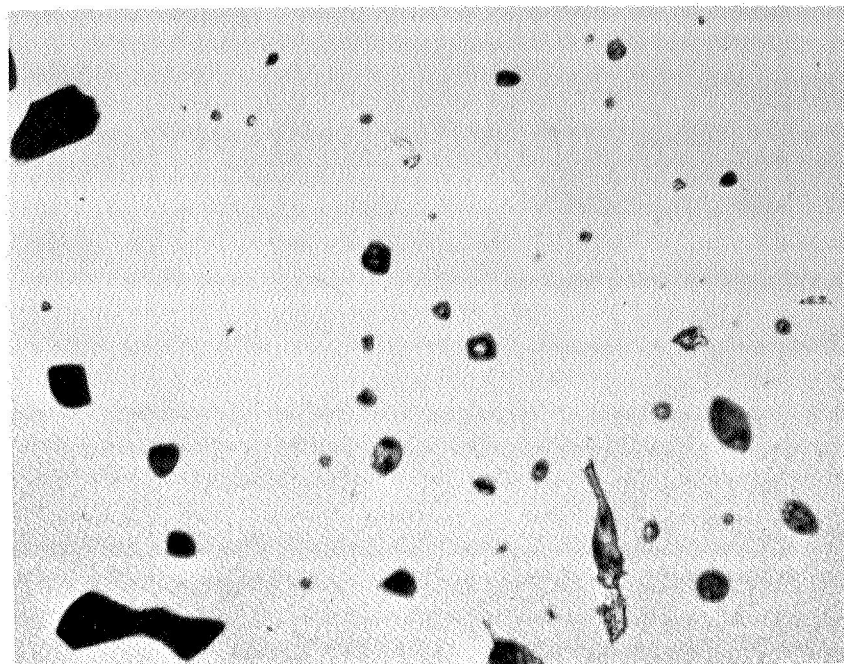


FIGURE 21 - Microstructure of Alloy Heat Treated 2600°F - 10 Hours 100X

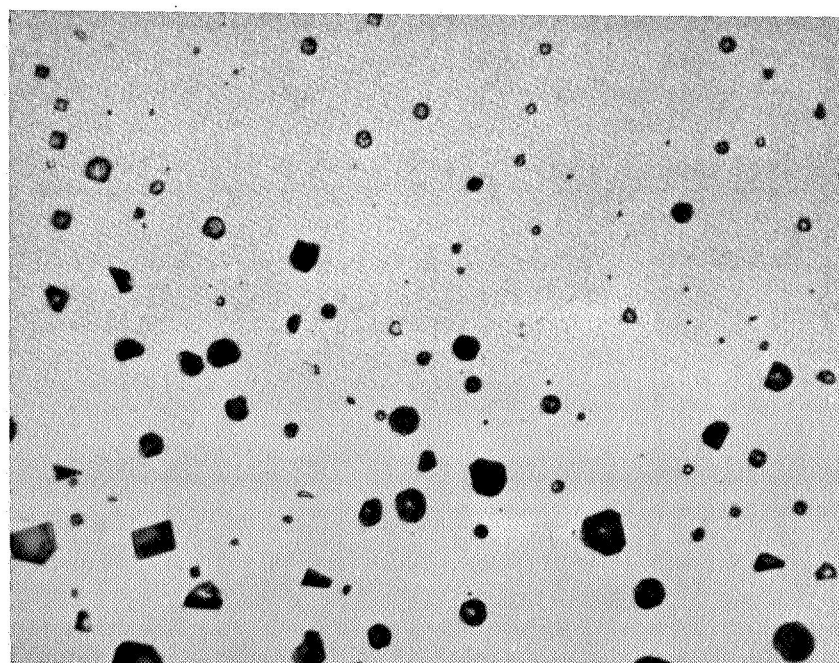


FIGURE 22 - Microstructure of Alloy Heat Treated 2600°F - 10 Hours 1000X

The number of ZrO_2 particles was considerably less than in the as-extruded alloy. Those that remained after heat treatment are large in comparison to those in the as-extruded state. The concentration gradient which exists (and decreases) from smaller to larger particles results in the growth of larger particles at the expense of smaller ones. Other evidence for the instability of the ZrO_2 particles is their change in two-dimensional shape from elongated-angular (as-extruded condition, Figures 17 and 18) to rounded (heat treated condition, Figures 23 through 30). Many strain markings exist in the replicas as the result of replica adhesion in the pores of the metallographically prepared specimens, which may be a result of particle removal during metallographic preparation.

Considering the extent of ZrO_2 particle coarsening and solution, it is surprising that the hardness of the heat-treated specimens only decreased slightly (with the exception of the anomolous behavior of the 1316°C (1590°K)-100 hour heat treated specimen) from the as-extruded hardness level. The hardness results are as follows:

	Condition of Alloy	DPH(10 Kg Load)
1.	As-Extruded	375
2.	Heat Treated 1316°C , 10 hours	355
3.	Heat Treated 1316°C , 100 hours	653
4.	Heat Treated 1316°C 10 hours	257
5.	Heat Treated 1316°C , 100 hours	296

No logical explanation for the high hardness of the material heated 100 hours at 1316°C (1590°K) can be given. It can be noted from the microstructure, however, that the contaminant phases are present to a greater degree than they are in the other heat treated specimens. These oxides have greater hardness than chromium.

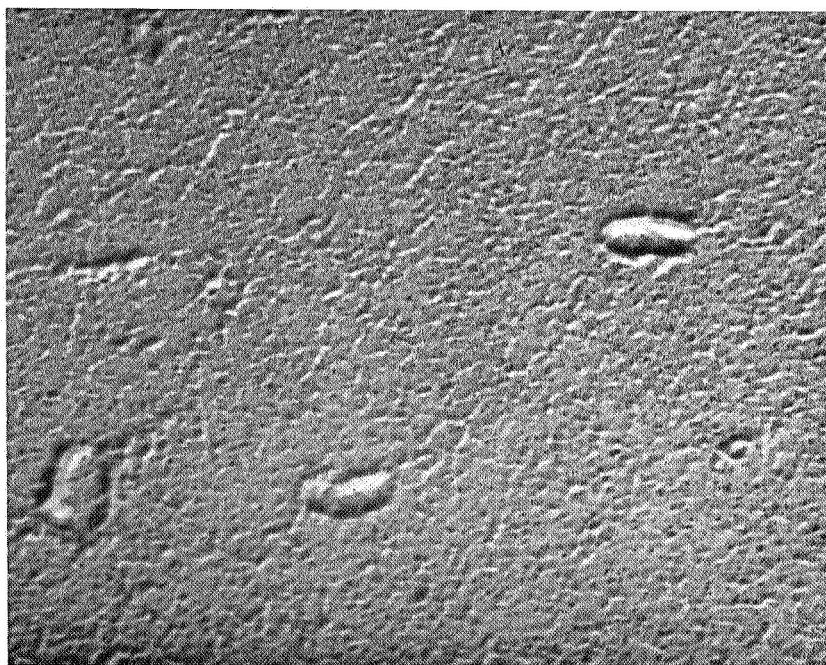
Another factor, besides oxygen contamination, contributing to the instability of ZrO_2 in chromium is its transformation from a cubic to a monoclinic structure upon heating above 300°C (573°K). This transformation could destroy particle-matrix coherency, thus creating an interface. Interfacial energy (that energy associated with the interface between phases) is a driving force for particle growth at high temperature. This energy is increased with this ZrO_2 transformation. A further transformation to the tetragonal structure upon

heating above about 1000°C (1373°K) could be even more disruptive since it is accompanied by a 9% volume decrease. These factors would have presented no problem had the alkoxide for producing ThO_2 been successfully produced since ThO_2 is cubic at all temperatures.



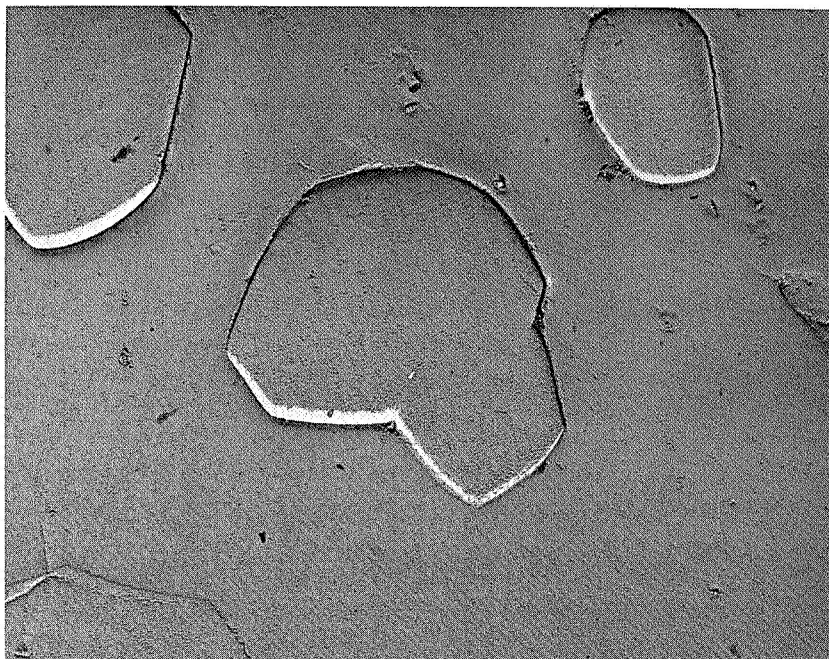
10,000X

FIGURE 23 - Electronmicrograph of Alloy Heat Treated 2400°F - 10 Hours



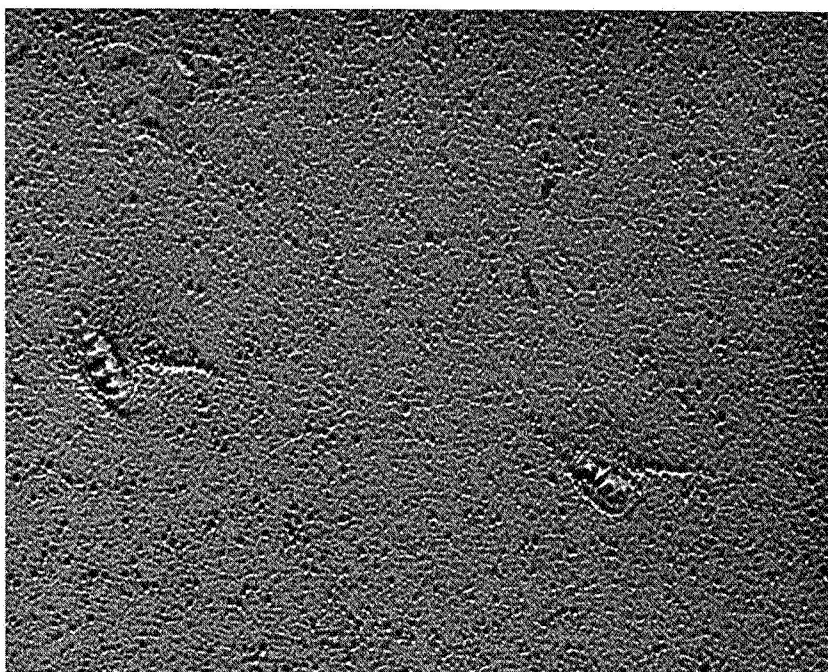
40,000X

FIGURE 24 - Electronmicrograph of Alloy Heat Treated 2400°F - 10 Hours



10,000X

FIGURE 25 - Electronmicrograph of Alloy Heat Treated 2400°F - 100 Hours



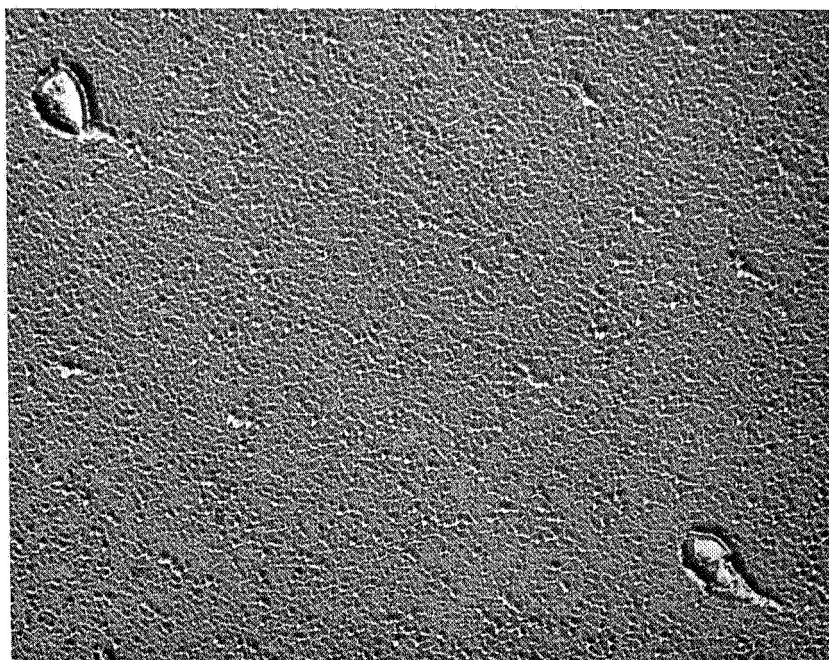
40,000X

FIGURE 26 - Electronmicrograph of Alloy Heat Treated 2400°F - 100 Hours



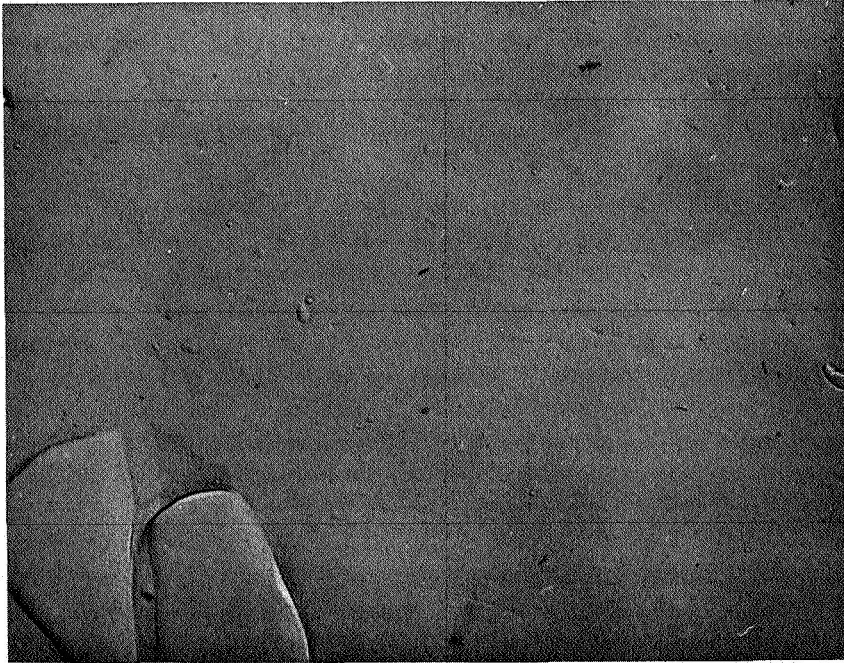
10,000X

FIGURE 27 - Electronmicrograph of Alloy Heat Treated 2600°F - 10 Hours



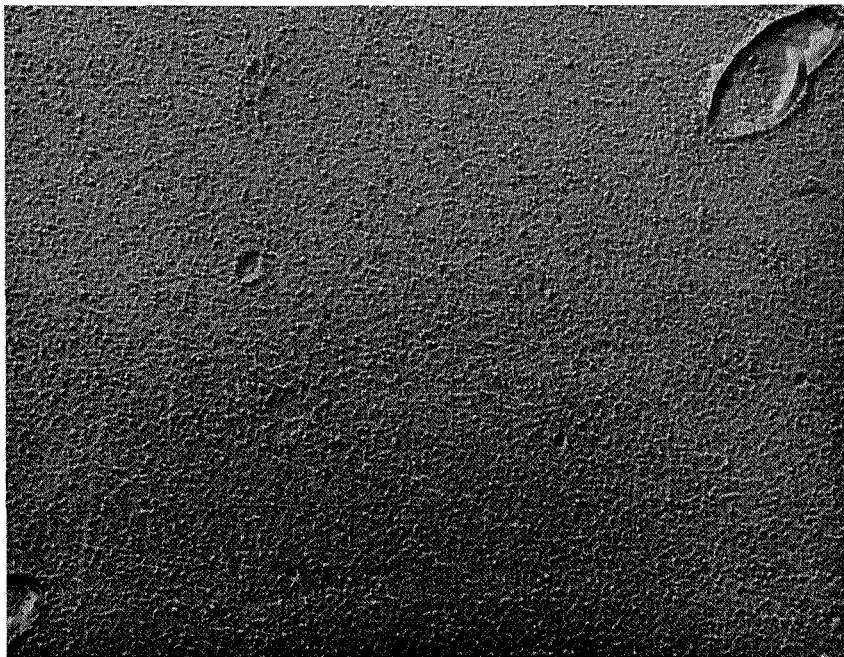
40,000X

FIGURE 28 - Electronmicrograph of Alloy Heat Treated 2600°F - 10 Hours



10,000X

FIGURE 29 - Electronmicrograph of Alloy Heat Treated 2600°F - 100 Hours



40,000X

FIGURE 30 - Electronmicrograph of Alloy Heat Treated 2600°F - 100 Hours

CONCLUSIONS

Several conclusions can be drawn concerning this development of a process for producing an oxide dispersion-strengthened chromium alloy.

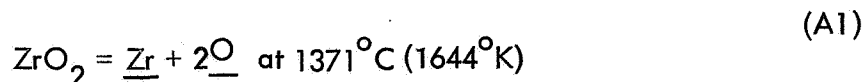
1. The particle formation step of the process is capable of producing submicron chromium particles individually coated with ZrO_2 . This technique appears to be adaptable to any dispersoid-matrix combination in which there exists a volatile, readily decomposed parent compound of the dispersoid and a matrix metal of high vapor pressure. The latter restriction could be eliminated by substituting other means of vaporizing the metal such as with an electron beam or plasma arc.
2. Oxygen and carbon contamination of the powder is a serious problem although carbon content can be reduced below 100 ppm by a hydrogen reduction.
3. A fairly uniform dispersion was achieved by cold pressing to 61% theoretical density followed by 10/1 extrusion at 1250°C (1523°K) to produce a compact of greater than 95% theoretical density.
4. Dispersoid particle size of 0.1μ thickness by 0.7μ diameter was greater than the desired size of $< 0.1\mu$ with 50% less than 0.05μ . The interparticle spacing of 13μ was much greater than the target spacing of 1.5μ .
5. The ZrO_2 particles were not stable in the chromium matrix when heated in vacuum for up to 100 hours at temperatures up to 1427°C (1700°K). This is due, in part at least, to contamination by oxidation.
6. The program was hampered by lack of $\text{Th}(\text{OR})_4$, the parent compound for preparing ThO_2 . Calculations of free energy of solution of ThO_2 and ZrO_2 in chromium revealed the former oxide to be considerably more stable. The use of ThO_2 (which undergoes no transformations from its cubic structure) as the dispersed phase instead of ZrO_2 would have eliminated the possibility of disruptive oxide volume changes which accompany the

transformations of ZrO_2 . Lower particle-matrix interfacial energy would also result with the substitution of ThO_2 for ZrO_2 .

While this program did not provide an alloy with the desired microstructure and thermal stability, because of excessive oxygen contamination of the powder, extremely fine ZrO_2 -coated powder of controllable particle size and ZrO_2 content was produced.

APPENDIX A

The standard free energy ΔF° of the reaction



is the sum of the standard free energies of these reactions at the same temperature



where (A3) and (A4) are respectively the reactions for the solution of zirconium and oxygen in chromium.

ΔF° for (A2) is reported to be +187,000 cal/mole⁽²²⁾ (+782,000 J/mole)

ΔF° for (A3) is the sum of the ΔF° for



ΔF° for (A5) is estimated to be -4,000 cal/mole (-16,750 J/mole) based on the free energies of formation of several other intermetallics involving chromium, e.g., TaCr_2 ⁽²³⁾.

ΔF° for (A6) at 1371°C (1644°K) is taken from the relation

$$\Delta F^\circ(\text{A6}) = RT \ln a_{\text{Zr}} = RT \ln C_{\text{Zr}} = 3,600 \text{ cal/mole } (-15,000 \text{ J/mole}) \quad (\text{A7})$$

where the weight percent composition is substituted for the activity since the solubility of Zr at 1371°C (1644°K) is only 3 wt. pct.⁽²⁴⁾ and the standard state was taken as 1 wt. pct.

ΔF° (A3) is therefore $-4,000 + (3,600) = -7,600 \text{ cal/mole } (-31,850 \text{ J/mole})$.

ΔF° for (A4) is the sum of ΔF° for



ΔF° for (A8) is $-114,000 \text{ cal/mole}^{(22)}$ ($-476,000 \text{ J/mole}$) while ΔF° (A9) is calculated

from

$$\Delta F^\circ (\text{A9}) = 2 RT \ln a_{\text{O}} = 2 RT \ln C_{\text{O}} = +22,800 \text{ cal/mole } (+95,500 \text{ J/mole}) \quad (\text{A10})$$

The error in ΔF° (A9) introduced by using this relation is small since the oxygen concentration in chromium is only 0.03 wt. pct.⁽²⁴⁾.

ΔF° (A4) is $-114,000 + 22,800 = -91,200 \text{ cal/mole } (-380,500 \text{ J/mole})$

Therefore, the standard free energy of



is $+88,200 \text{ cal/mole } (+368,400 \text{ J/mole})$. The free energy ΔF° for $\text{ThO}_2 = \underline{\text{Th}} + 2\underline{\text{O}}$ is found in analogous manner using a calculated* value of the solubility of thorium in chromium at 1371°C (1644°K) of 2 wt. pct. and allowing for the absence of intermediate phases in the Cr-Th system.

This value is $\Delta F^\circ = +126,400 \text{ cal/mole } (+529,000 \text{ J/mole})$

* It is assumed that the limit of solid solubility of a transition metal in chromium is inversely proportional to the sum of energies associated with a solubility factor and the lattice strain due to difference in atomic size⁽²⁵⁾.

The energy related to the solubility factor is given by

$$F(S-S') \quad (A11)$$

where F is a constant equal to 23,060 cal (96,500 J) and S and S' are the solubility factors for chromium and the transition metal respectively.

The energy related to the lattice strain is given by

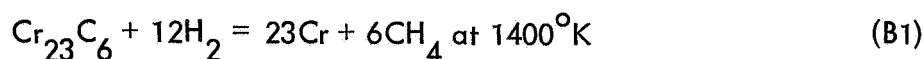
$$\frac{2}{3} GV \left[\left(\frac{D}{D'} \right)^3 - 1 \right]^2 \quad (A12)$$

where G is the shear modulus, V is the molar volume and D and D' are the Goldschmidt radii for coordination number 12 for transition metal and chromium respectively. The value of GV is taken as 60,000 cal (251,000 J).

The solid solubility of thorium in chromium is found to be 0.5 at. pct. or 2 wt. pct. This agrees qualitatively with the finding that thorium is less soluble than zirconium in chromium⁽²⁶⁾.

APPENDIX B

At the level of carbon contained in the as-prepared ZrO_2 -coated chromium powder (2.0 – 2.3 w/o) the stable carbide phase is Cr_{23}C_6 . This carbide can be reduced according to the equation

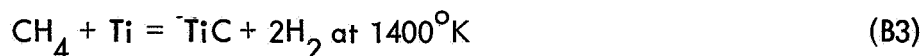


For this reaction $\Delta F^\circ = +120,500 \text{ cal}$

$$RT \ln K = 2.3 RT \log \frac{p(\text{CH}_4)^6}{p(\text{H}_2)^{12}} \quad (\text{B2})$$

Since $p(\text{H}_2)$ can be made to essentially equal unity a CH_4 pressure of less than 0.001 atmosphere makes the reaction thermodynamically favorable.

To assure a CH_4 partial pressure of less than 0.001 atmosphere, titanium powder was placed in the reaction chamber to provide CH_4 gettering by the reaction



For this reaction (with $p(\text{H}_2) = 1 \text{ atm.}$ and $p(\text{CH}_4) = 0.001 \text{ atm.}$)

$$\Delta F = \Delta F^\circ + RT \ln K = -21,000 \text{ cal/mole} \quad (\text{B4})$$

APPENDIX C

The final step in the manufacture of the TaC crucibles is high temperature sintering. During this operation the crucibles are subjected to a temperature of 3000°C (3273°K) for one-half to one hour. Resultant preferential evaporation of carbon would give a carbon poor structure, say for example 46 a/o carbon.

The evaporation rate of carbon from TaC of this composition at 2477°C (2750°K) under vacuum is reported to be 2.0×10^{-8} moles/cm²/sec⁽²⁹⁾ (2.0×10^{-4} moles/m²/s) or 8.65×10^{-4} gms/cm²/hr (2.4×10^{-6} Kg/m²/s). At 125 torr (1.66×10^{-4} N/m²) (a common operating pressure for powder preparation) this rate would be very much less. The rate of chromium evaporation during powder preparation is approximately 3.0 gms/cm²/hr (8.3×10^{-3} Kg/m²/s). The ratio of evaporation rates of carbon and chromium is several orders of magnitude less than the ratio of carbon and chromium contents in the powder. It is therefore concluded that evaporation of carbon from the TaC crucible is not responsible for the high carbon content of the chromium-ZrO₂ powder prior to hydrogen sintering.

APPENDIX D

EXPLANATION OF SYMBOLS USED IN THIS REPORT

<u>Symbol</u>	<u>Definition</u>	<u>U. S. Customary Units</u>	<u>SI Units</u>
α	supersaturation ratio = p/p_o	---	---
α_{Cr}	critical supersaturation ratio	---	---
a	interplanar spacing	cm	m
ρ	density	gm/cm ³	Kg/m ³
σ	surface free energy	ergs/cm ²	J/m ²
M	molecular weight	gm/mole	Kg/mole
k	Boltzmann Constant	erg/°K/mole	J/°K/mole
T	absolute temperature	°K	°K
N	surface nucleation rate	nuclei/cm ² /sec	nuclei/m ² /s
B	10 ²⁰ (constant)	nuclei/cm ² /sec	nuclei/m ² /s
p_o	equilibrium vapor pressure	dyne/cm ²	N/m ²
p	actual pressure of vapor in contact with solid	dyne/cm ²	N/m ²
W	evaporation rate	gm/cm ² /sec	Kg/m ² /s
R	Gas Constant (8.3144)	erg/°K/mole	J/°K/mole
Ω_L	molecular volume = $\frac{M}{\rho N_{av}}$	cm ³ /mole	m ³ /mole
N_{av}	Avogadro's Number (6.0254×10^{23})	---	---
ΔF	change in free energy of formation	cal/mole	J/mole
r	radius of nucleus	cm	m
r^*	critical radius of nucleus	cm	m
P	pressure	gm/cm ²	N/m ²
v	linear velocity	cm/sec	m/s
g	gravitational constant	cm/sec ²	m/s ²
Z	height in vertical stream	cm	m
ΔF^o	change in standard free energy of formation	cal/mole	J/mole

APPENDIX D (CONTINUED)

<u>Symbol</u>	<u>Definition</u>	<u>U. S. Customary Units</u>	<u>SI Units</u>
a	activity	---	---
C	concentration (w/o)	---	---
F	constant for solubility factor effect	cal/mole	J/mole
S	solubility factor value for Cr	---	---
S'	solubility factor value for Th	---	---
G	shear modulus	gm/cm ²	N/m ²
D	Goldschmidt radius for coordination number 12 for Th	KX units	KX units
D'	Goldschmidt radius for coordination number 12 for Cr	KX units	KX units
p(CH ₄)	methane partial pressure	atm	N ² /m
p(H ₂)	hydrogen partial pressure	atm	N ² /m
K	equilibrium constant	---	---

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