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Directional Solidification of the Alumina-Zirconia Ceramic
Eutectic System

by

Boldt, Christopher

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Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

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I. INTRODUCTION

Recently, a revival of research has taken place in the area of directionally solidified eutectics. Significant work in this area was carried out in the mid 1960's but soon tapered off. Research was revived again in the late 1970's as a result of interest surrounding in situ composites. This work continued through the early 1980's. Now, as technology continues its rapid acceleration, directionally solidified materials are again in the spotlight, especially eutectic materials. Directional solidification is of extreme interest because it can be used to control the production of well aligned and finer scale microstructures within a material [1]. Eutectic systems are also of interest because of their composite nature, microstructural stability, and their anisotropic properties [1]. Directional solidification of eutectics has been applied to high temperature engine components and other structural materials, where control of the eutectic microstructure is of the utmost importance [2]. The focus has been on the superalloys and their use for blades for gas turbine engines.

The superalloys have encountered difficulties as the operating temperatures of these turbine engines are pushed to the limits. Metal eutectics, depending upon the system, can melt around 1300 degrees centigrade [2]. Also, as the operating temperature increases, these material's creep resistance decreases markedly. Usually, metal eutectics are only stable to perhaps half of their melting temperatures. Unfortunately these temperatures are too low for practical application in these engines. Therefore, new materials are needed which could

withstand the high operating temperatures required. Ceramic materials seemed to be a logical choice.

Refractory oxide ceramic eutectics have become the ceramics of choice for high temperature structural material research. They have very high melting temperatures, usually around the 2000 degree centigrade mark. They also resist oxidation and perform well in corrosive environments like sea water [2]. These ceramics also tend to be very creep resistant and retain their microstructural stability to approximately 90% of their melting temperature. These properties as well as their relatively high strengths and light weights make them very attractive as replacements to the metals currently used.

Unfortunately ceramics do have certain drawbacks. The main problem with most ceramics is the tendency toward brittle behavior. This is generally attributed to porosity and the lack of a uniform structure within the material. The pores and other flaws can act as crack initiation sites thus forming microcracks. Once these cracks form, they often cause catastrophic failure of the ceramic material. In traditionally prepared ceramics, solutions to this problem were sought through the addition of ductile metals to the matrix, or through the use of ceramic components which undergo transformational toughening. Hopefully, directional solidification research on ceramics will provide a different solution to the microcracking problem by focusing on microstructural control.

Directional solidification of ceramics can result in the formation of fine structures of long range uniformity. This directional, uniform

microstructure could act to enhance various anisotropic properties. It is also hypothesized that the fine microstructure might limit the size of the initial flaws and that the uniformity of the structure could act to blunt or halt crack propagation through the medium [1]. As a crack travels through the ceramic, it will continuously encounter other phases in the solidified eutectic ceramic. As it meets a new phase the crack may be deflected along the phase boundary. This increases crack length, which increases the fracture toughness of the ceramic.

Unfortunately, directional solidification with ceramic eutectics is very difficult to accomplish. First of all, extremely high temperatures are required to achieve a melt. Proper care must be taken to safely insulate the melt from the furnace used. Secondly, it is difficult to find a container for the melt that remains nonreactive at the temperatures required. As most ceramic systems of interest melt at or above the 1800 °C mark, viable crucible materials must be stable to temperatures well above 2500 °C. Thirdly directional growth is difficult to achieve in ceramic systems due to their poor heat flow properties. The insulating solid ceramic does not allow for directional heat flow downward through the solidifying sample. Lastly, the optimum condition of a planar growth front within the solidifying ceramic is difficult to establish. This usually requires a steep temperature gradient or a very slow rate of growth. In addition to these problems, solidified materials typically experience porosity problems. Present economic constraints also act as a barrier. Finding

a reliable, cost effective method for producing bulk quantities of ceramic for structural use has been elusive.

Current research will concentrate on alleviating some of these problems in ceramic processing. Using the alumina-zirconia eutectic ceramic system and a Bridgman type furnace, crucible materials will be examined for their viability in containing the ceramic melt while remaining nonreactive. Various solidification rates will be attempted to correlate the microstructure with growth rate. The optimum microstructure and the necessary processing conditions to attain this microstructure will be established. The heat flow difficulties will be analysed and solutions will be tested. The ceramic system will be compared to existing theoretical models of eutectics to see if any correlations can be made. And finally, the physical properties of the ceramic will be studied in order to see how solidification effects them.

II. GENERAL THEORY

A. Eutectic Growth

The main goal for each of the aforementioned solidification processes is the control of the ceramic microstructure in the growth direction. Eutectic means 'lowest melting', which describes its behavior quite well. Materials comprised of a eutectic structure, have melting points which exist below the melting temperature of either of the two components. In addition to this, eutectics typically exhibit a zero or a small freezing range which means the material will experience good flow properties [6]. Eutectic structures are also much finer than other microstructures such as dendrites, and finer structures can be equated with enhanced mechanical properties.

Eutectic structures form from a coupled growth of two phases from a liquid state. For a particular system at equilibrium, eutectics form at one specific composition and temperature. But in real, nonequilibrium systems, the eutectic microstructure can form under many different conditions. In these real systems, a range of experimental conditions exists where the eutectic can form, and the growth of the eutectic becomes dependent upon undercooling [6]. The range in which the eutectic forms is called the "coupled zone". This zone can either take a regular symmetrical shape below the eutectic point, or it may be skewed to one side of the phase diagram. Figure 1 shows typical phase diagrams with (a) skewed, and (b) symmetrical coupled zones result [6].

Eutectic microstructures appear either as rods or as lamellae.

(a)

(b)

Figure 1. Eutectic phase diagrams where the shaded regions depict (a) a skewed coupled zone, and (b) a symmetrical coupled zone

Both can have desired effects on the properties of ceramics. Rods can act as tougheners if they are more ductile than the surrounding matrix. Lamellar growth can yield nice, sandwich-like composite properties. Even though both structures can be desirable, it is important to understand under what conditions each structure will result.

Rods usually form if the volume fraction of the minor phase of the eutectic is below 32% [7]. When the minor phase volume fraction is above this amount, a lamellar structure is predicted. This convention arises from a minimization of the surface area to volume of the phase in question [1]. By minimizing surface area, the surface energy factor is reduced which aids in nucleation and growth. The 32% volume fraction level is an approximation, however. Additional factors such as growth orientation also influence the amount surface energy contribution. Lamellae can grow in very low energy, preferred orientations, thus reducing surface energy, while rods are forced to grow in a multitude of higher energy orientations due to their circular nature. This can act to increase the overall surface energy of the minor phase. Since coherent lamellar interfaces tend to propagate a crack readily, rod eutectics are preferred.

In addition, impurities have an effect on determining the formation of a rod or lamellar eutectic. It has been suggested that in the presence of impurities in the melt, that a rod structure is more likely to form [7]. Impurities also tend to cause instabilities in the solidifying interface which can lead to colony growth. Colonies exhibit extreme curvature at their boundaries, and this curvature lends itself

well to the formation of a rods eutectic. Colony growth will be discussed further in a later section.

It has also been suggested that solidification rate might affect which type of eutectic microstructure would form. At faster growth rates the Jackson and Hunt (J &H) model for eutectic spacing loses its validity, but growth rate seems to have little effect on the type of eutectic structure [7]. Hunt and Chilton experimented on several metallic lamellar eutectic systems using growth rates between 0.01 and 1.2 cm/min. No breakdown of the lamellar structure into rods was seen at the higher rates. however, further research in this area needs to be accomplished before growth rate can be ruled out as a factor in the selection of eutectic structure.

Even though resulting from different conditions, one aspect is shared by both the rod eutectic and the lamellar eutectic formations. The rate of solidification for a eutectic alloy directly affects the interlamellar or interfiber spacing of the solidified material. Jackson and Hunt developed a model to predict this behavior [8]. They first divided the interfacial undercooling term into two parts: solutal and capillary undercooling. This can be expressed through the equation:

$$\Delta T_{int} = \Delta T_{sol} + \Delta T_{cap}$$

The solutal undercooling was obtained through solving the steady state diffusion equation:

$$\nabla^2 C + (V/D)(\partial C/\partial Z) = 0$$

where C is the composition, V is the growth velocity, D is the diffusion coefficient in the liquid, and Z is a measure of distance and extends parallel to the growth direction.

In order to solve this equation, several basic assumptions had to be made. First, it was assumed that the overall undercooling experienced at the interface was relatively small. Next, it was assumed that the ratio of diffusion to velocity was much larger than the resulting eutectic spacing. A constant planar interface was also assumed.

The capillary undercooling term was obtained through the Gibbs-Thompson equation:

$$\Delta T_{\text{cap}} = (\gamma/\Delta S)\kappa$$

where γ is the interfacial free energy term, ΔS is the entropy of fusion, and κ is the average curvature of the interface for either phase. Here a planar interface is no longer assumed.

In order to form a useful relationship between the amount of undercooling, the growth velocity and the resulting eutectic spacing, several more assumptions were made. It was assumed that the amount of undercooling from the eutectic temperature for each phase was identical. Also, since only small undercooling values were used, it was assumed that the compositions of the two phases at the interface were

independent of the undercooling and were equal to their equilibrium value at the eutectic temperature. In addition, any sort of kinetic effects at the solidifying interface were discounted. Jackson and Hunt were then able to produce this relationship:

$$\Delta T = K_1 \lambda V + K_2/\lambda$$

K_1 is a system dependent constant and contains liquidus slope, composition, volume fraction, diffusion and Bessel function terms. K_2 is also system dependent and contains liquidus slope, surface energy, contact angles and volume fraction terms.

It was discovered that during eutectic growth, a range of possible spacings can manifest, but that minimum and maximum spacing values can be determined by shape and stability of the interface. The minimum eutectic spacing has been well defined over the years and a simplified relationship between the growth velocity and the minimum spacing can be written as follows:

$$V\lambda_{\min}^2 = K_2/K_1$$

This model for the maximum spacing values shows that the maximum stable spacing is several times the minimum stable spacing. However, eutectic spacing in faceted/nonfaceted systems such as Fe-C and Al-Si show an average spacing that is 3 to 5 times the minimum stable spacing.

The minimum spacing model is used to describe most eutectic solidification behavior. For general applications, the model is further simplified into:

$$V\lambda^2 = K$$

where λ becomes the average eutectic spacing and K becomes a generalized system constant.

Because several key assumptions have been made in order to create this model, it is by no means an exact prediction of behavior. Most of the main assumptions are valid, yet the validity of discounting the kinetic effects present during the solidification process remains in doubt for ceramic systems. For simple metal eutectic compounds, kinetics do indeed play a minor role during solidification, especially when considering undercoolings on the order of 1 °C and for growth velocities of less than 1 cm/sec. Therefore, most metallic eutectic systems researched have followed the Jackson and Hunt model for predicting eutectic spacing at various growth velocities quite well. Current research concerning ceramic systems is trying to discover if the same model can be applied.

B. Planar Front Growth and Constitutional Supercooling

In order to achieve well aligned microstructures within the solid, control must be maintained over the solidification interface. The greatest degree of microstructural control results from the

establishment of a stable planar growth front. A planar eutectic front may result in fine, evenly spaced microstructures which continue over long ranges. Unfortunately, sometimes planar growth fronts can incur instabilities which cause the solidification interface to break up.

The perturbations seen in a previously planar eutectic growth situation commonly result from a phenomenon called constitutional supercooling [1,9,10]. In a condition of constitutional supercooling, solute or impurity particles are ejected ahead of the advancing solid. These particles pile up along the interface and this acts to depress the freezing point of the liquid. This freezing point depression occurs in systems whose ratio of solidus to liquidus compositions is less than unity.

When the temperature gradient of the system is sufficiently low, the freezing point for the system incurred from the solutal or impurity buildup drops below the system's equilibrium freezing temperature. At this point the liquid ahead of the advancing interface is said to be supercooled. Any asperity or perturbation of the solid can then extend beyond the rest of the interface, as they readily reject latent heat of fusion into the supercooled melt. Thus the planar interface breaks down into colonies or dendrites.

Constitutional supercooling should not be present in a pure eutectic system. Eutectic systems when solidifying exhibit no solute buildup ahead of the interface as they experience controlled coupled growth of the two phases. Only a system far away from its eutectic composition would experience a buildup of a solute boundary layer.

However, colony formation has also been associated with impurity elements present within a given system, which enhances a constitutional supercooling effect. At higher imposed growth rates, the amount of impurity needed to cause an instability in the growth front can be extremely small. Thus the amount of impurities present becomes a very important consideration in any system.

To avoid the constitutional supercooling effect, two variables can be modulated. Constitutional supercooling depends upon both rate and temperature gradient. If the temperature gradient is increased in the liquid by enhancing the heat removal in the system, the constitutional supercooling effect can be avoided. As the gradient increases, the zone affected by constitutional supercooling is diminished. With a steep enough gradient, the effect can be nullified altogether. The other method of maintaining a planar interface is by decreasing the growth rate. If the rate of the advancing solid interface is slowed by decreasing the growth rate, the solute ejected is given more time to diffuse into the liquid and the supercooling effect caused by solute or impurity buildup can be avoided.

As has just been discussed, to remove colonies from a system, either a sharp temperature gradient or a slow rate must be used when solidifying. A simple mathematical relationship developed by Gruzleski and Winegard [33] describes the conditions for planar growth in a eutectic system, and is as follows:

$$G/R \geq -(mC_0/D)[(1-k_0)/k_0]$$

where G is the temperature gradient, R is the growth rate and m , C_0 , k_0 and D respectively represent the slope of the liquidus, concentration, distribution coefficient, and diffusion coefficient in the liquid for the impurity element. For the greatest amount of eutectic microstructural control, a condition of planar front growth needs to exist. The minimum G/R ratio where planar growth occurs is called the critical G/R ratio, and this value is system dependent.

C. Colony Growth

Important as it is to control the eutectic growth of the directionally solidified material, it is just as important to control the solid's overall microstructure. This means elimination of the colony structure which can develop within certain solids. Colonies, or cells as they are sometimes called, are groupings of collective eutectic microstructural growth regions within a solidifying material [8]. They are an example of the disruption which can result from constitutional supercooling. A colony may contain a fine eutectic microstructure itself, but this structure may not be in conjunction with the neighboring microstructures. In fact, the colonies tend to have curved interfaces which butt up against one another causing boundary problems. Figure 2 shows a typical fan colony structure [7]. Not only do colonies result in fan shapes, but they also can exhibit a needle like appearance. Needle like colonies have very sharp, well defined boundaries and contain highly oriented eutectic structures.

Multidirectional microstructures are often the result in colony structures because the curved interface offers many growth directions. This multidirectional growth front lends itself very well to rod eutectic growth [7]. It is because of this multidirectionality that colonies need to be eliminated from a directionally solidified material. It is also important to remove the colony structure because it tends to limit the strength of a material [2]. Possibly because of impurity segregation to these boundaries, or because of the microstructural inconsistency present at the colony boundaries, colony boundaries weaken materials. Thus two good reasons exist for the removal of the colony structure from directionally solidified materials.

When directionally solidifying ceramics, colony growth of some sort is almost always reported. This is mainly due to the impurity contamination of the melt. Even if the starting powders for the ceramic are relatively pure, since the Bridgman method is the most popular for directional solidification, the crucible becomes a major factor in providing contaminants. At the temperatures required for ceramics to melt, some sort of contamination of the melt from the crucible is generally present. This can then lead to colony formation. So, to avoid this, the gradient or the rate must be modulated. In most typical ceramic systems, the critical G/R ratio is on the order of 6×10^7 K/sec m^2 [2]. Unfortunately, as stated earlier, only low level gradients are possible with the Bridgman method. That leaves the decrease of the growth rate as the only viable option. But by decreasing the rate, the time the crucible is in the hot

Figure 2. Representation of a fan colony growth pattern

zone of the furnace is increased, thus increasing the chances for further contamination. Also, longer growth processes are less economical. Crucibleless growth methods, such as floating zones, seem to offer a solution to this problem.

D. Faceted/Nonfaceted Growth

Another wrinkle in the area of eutectic microstructures lies in their ability to grow either with or without facets. Non-faceted microstructures are associated with regular rod/lamellar structures. Faceting can cause definite irregularities within the structure. Facets are caused by slow growing crystallographic planes which act as boundaries to the growing phase [8 - 10]. These planes are typically smooth on the atomic level, and thus it becomes energetically unfavorable to add any more atoms. This energy barrier must be overcome before any additional growth can occur.

Whether a system is faceted or nonfaceted depends both upon the entropy of fusion and the growth rate. A study of the effect of entropy of fusion has led to the formation of an approximate relationship describing faceting behavior in solidifying systems:

$$\Delta S/R < 2 \quad \text{for faceted systems}$$

$$\Delta S/R > 2 \quad \text{for nonfaceted systems}$$

where ΔS is the change in entropy of fusion for the solid, and R as it turns out, is the gas constant. According to this approximation, when

the left hand side is greater than two, faceting behavior may occur, and when less than two, nonfaceted behavior can be dominant. If very slow rates are used, all materials will experience faceted growth as there will be enough time to allow for the atomic ordering required [7]. However, at moderate rates the surface roughening of the system that decides behavior.

Within a eutectic system, it is possible for the two phases to demonstrate different behavior. Faceted/nonfaceted systems are not uncommon. The faceted phase can complicate the problem, though, as its orientation is very crystallographically dependent. This dependency often has to struggle with the other phase for orientation dominance which has the tendency to force odd growth behaviors. Although, there are certain faceted/nonfaceted systems which exhibit normal growth behavior.

III. LITERATURE REVIEW

An extensive search of all literature pertaining to the alumina-zirconia ceramic system as well as the yttria stabilized system was performed. The results from this survey were compiled and appear in Table 1. This table displays the composition, method of solidification, temperature gradient, solidification rates, microstructures, as well as any other pertinent data. The basic experimental methods pertaining to this system can be placed into four major categories: Bridgman, Float Zoning, Edge defined Film-fed Growth (or E.F.G.), and atomization. The first three will be the subject of primary focus, as they are designed to produce monolithic ceramic structures.

A. Experimental Techniques

Progress in the field of ceramic directional solidification has basically taken place through the use of three main directional solidification methods: Bridgman, float zoning, and Edge-defined Film-fed Growth. The Bridgman method is probably the most widely used out of the three. It makes use of a crucible which travels through a zone heated by induction. As the crucible is lowered through this zone, freezing of the charge takes place. Thus directional growth ensues.

The Bridgman method's main advantages lie in its ability to fabricate moderate sized pieces and in the fact that it is relatively easy to perform. Its major drawback is that it uses a crucible which can lead to contamination of the ceramic and possibly to cracking due to thermal expansion differences between the ceramic and the crucible.

Table 1. Compilation of data from the literature review concerning alumina-zirconia

SOURCE	COMPOSITION	METHOD	RATE cm/hr	TEMP.GRAD. degrees/cm	STRUCTURES	OTHER DATA
12	Al ₂ O ₃ -37 mol% ZrO ₂	Bridgman	1.29-15.56	220	colonies w/ ZrO ₂ rods	vapor deposited tungsten crucibles
13	Al ₂ O ₃ -37 mol% ZrO ₂	gradient furnace	0.75 and 1	1200	no colonies w/ lamellar eutectic	molybdenum crucibles
16	Al ₂ O ₃ -42 wt.% ZrO ₂	flame press. atomization	_____	>10000	amorphous eutectic	_____
15	Al ₂ O ₃ -ZrO ₂	E.F.G.	1.39, 12.7, and 50.8	_____	colonies w/ rod eutectic	_____
14	Al ₂ O ₃ -ZrO ₂ - Y ₂ O ₃ eutectic	float zone r.f. heating	0.8, 2, 20	1000	~20, colonies ~0.8, none	seed crystal helps strength:524 MPa at 1575 C
17	Al ₂ O ₃ -ZrO ₂ eutectic	Bridgman	_____	200	colonies w/ ZrO ₂ rods	Al ₂ O ₃ to ZrO ₂ (001)//{100} (110)//<100>
18	Al ₂ O ₃ - 42.7 wt% ZrO ₂ - 4.4 wt% Y ₂ O ₃	Stepanov	2 - 10	_____	colonies	bending strength: 417 MPa, room T 276 MPa, 1300C
18	"	Verneuil	0.5 - 2	_____	colonies	_____
20,21	Al ₂ O ₃ - 34.5 mol% ZrO ₂ - 3.5 mol% Y ₂ O ₃	"	1 - 2	-----	"	[2110]//[100] faceting along these planes

Table 1. continued

SOURCE	COMPOSITION	METHOD	RATE cm/hr	TEMP. GRAD. degrees/cm	STRUCTURES	OTHER DATA
22,23	Al ₂ O ₃ - ZrO ₂ - 0,1.2,2.1,5.3 mol% Y ₂ O ₃	float zone w/Xe arc	1 - 9	600	colony growth only w/ higher Y ₂ O ₃ additions	hardness best w/ 1.2 mol% Y ₂ O ₃ fract. tough. best without Y ₂ O ₃
24	Al ₂ O ₃ - 34 wt% ZrO ₂ - 10 wt% Y ₂ O ₃	Bridgman	<1.09	-----	Colony growth w/ rods ZrO ₂	3 pt bend strength 181-274 MPa at 1500 C
25		electrohydro dynamic rapid solidification	-----	> 10 ⁴	Amorphous and eutectic structures	

Also problematic is the fact that only relatively low temperature gradients of around 200 degrees centigrade per centimeter can be achieved with this method [3].

Another method used to directionally solidify ceramics is the float zone method. This method uses a prefabricated charge rod of the ceramic of which a small zone is then heated until molten. This zone is then translated up the rod which causes the directional solidification. Several methods are used to heat the ceramic in float zoning including: electron beam, laser beam, plasma beams, arc plasmas and imaged arcs [4].

This method has several advantages over the Bridgman method. Because no crucible is used, there is little chance for contamination. Also, very high temperature gradients can be achieved with this method. Gradients around 2000 °C/cm are quite common [3]. However, typically only small diameter rods of ceramic can be made. So this technique, although of great scientific importance, has little practical industrial use.

The third method used is entitled Edge-defined Film-fed Growth, or E.F.G. for short. This method makes use of a crucible and a die setup. Capillary action draws the ceramic from the crucible up through small holes in the die. The die's surface, once wetted, then has the ceramic drawn from it a thin layer thus causing directional solidification [5]. This method is good at growing aligned fibers and can produce a great deal of material. Industry uses this method to produce ribbons of directionally solidified ceramic by the ton. Once again, though, this

method requires a crucible and a die which lead to contamination of the ceramic melt. Also, sometimes the ceramic doesn't wet the surface of the die effectively, thus creating problems.

For this research, the alumina-zirconia eutectic system was chosen. A eutectic system was chosen for its natural composite structure. This ceramic has a high melting temperature, and both of the components are already industrially useful. Solidification on this system will be carried out through the use of a Bridgman crystal growth unit.

B. Bridgman and Related Experiments

The Bridgman method of solidification was used to examine the eutectic composition of the alumina-zirconia eutectic system [11, 12, 16], as well as to examine the stabilized system containing 10 wt% yttria [23]. For this type of solidification, growth rates were reported in a range of 0.75 and 15.56 centimeters per hour with registered temperature gradients of between 200 and 220 °C/cm in the solid [11, 16]. A gradient furnace was also used in this research [12], and provided a gradient of 1200 °C/cm. The gradient furnace uses basically a Bridgman type of growth. The main difference lies in the method of heat exchange. The gradient furnace keeps the crucible fixed on top of a helium gas heat exchanger, and then uses a gradual decrease in furnace power to control the growth rate. The types of crucibles used are similar for both and are typically made of molybdenum [12] or of vapor deposited tungsten [11].

Most of the experiments using the Bridgman technique reported similar eutectic microstructures resulting upon solidification. Typically colony growth was prevalent, and a eutectic structure consisting of rods of zirconia growing within an alumina matrix was reported [11, 16, 23].

With the gradient furnace, however, a substantially lamellar eutectic was witnessed, while almost no colony growth was produced [12]. This result can be attributed to the presence of a steeper temperature gradient within the solid, thus helping to avoid a constitutionally supercooled regime. Unfortunately, the growth rate was difficult to keep constant, and banding occurred within the ceramic.

More quantitative results were also produced from the Bridgman experiments. Measurements of eutectic spacing with respect to growth velocity were reported to have conformed to the $\lambda^2 R$ relationship [16] derived by Jackson and Hunt. Also reported from this experiment, the eutectic system seems to prefer a [011] or an [100] growth direction and the general orientation relationship between the two phases was $\{100\}\text{ZrO}_2 \parallel (0001)\text{Al}_2\text{O}_3$. For the system stabilized with 10 wt% yttria [23], a three point bending test reported that at a temperature of 1500 C, the measured bending strength was anywhere between 181.3 and 274.4 MPa. These reported strength values were higher than those reported for other eutectic systems solidified with the Bridgman technique, and substantially higher than the strengths shown by non-stabilized alumina-zirconia.

C. Floating Zone Experiments

The floating zone method was used extensively with the alumina-zirconia-yttria system and generally required the use of a Xenon arc lamp heating source [19 - 22]. This method was used most commonly because an RF heating source experiences difficulty in coupling to a ceramic due to its insulating nature. It is believed, however, that once the alumina-zirconia system reaches 1000 °C, it becomes conductive. One reported experiment employed RF heating during solidification [13]. For float zoning the ceramic, growth rates between 0.8 and 20 centimeters per hour were used, but the main body of work centered around rates between 1 and 2 cm/hr. The temperature gradients achieved with this method were reported to be between 600 °C/cm [19, 20] and 1000 °C/cm [13].

Upon solidification, the stabilized ceramic demonstrated colony growth and a fine rod eutectic microstructure. Only when the amount of yttria added did not exceed the 1.2 mol% level was colony growth suppressed [21]. When this amount was used, a substantially lamellar microstructure resulted, with its growth occurring perpendicular to the float zone. With higher amounts of yttria, the system not only exhibited more colonies but also less directionality as well. Directional solidification was able to be enhanced through the use of a seed sapphire crystal [13]. This seed crystal was aligned so that its [0224] direction was parallel to the supposed growth axis. This did provide an increase in directionality as well as a uniform lamellar structure within the ceramic.

When tested the ceramic with the yttria additions demonstrated some plastic deformation at higher temperatures [13]. A strength value was reported in this case to be approximately 524 MPa when tested at a temperature of 1575 degrees centigrade. When tested with varying amounts of yttria, it was discovered that hardness of the ceramic increased significantly with addition of yttria up to the 1.2 mol% level [22]. After that, any more yttria in the system did not significantly effect the hardness. This effect is attributed to the stabilizing of the zirconia. The tetragonal zirconia phase is not only tougher than the monoclinic phase, it also decreases microcracking because no phase change occurs. However, reported values for the fracture toughness were higher in samples without any yttria, and as the amount of yttria increased, the toughness decreased [22].

For the alumina-zirconia-yttria system, the epitaxial relationships and growth directions were also studied. It was noted that the alumina preferred to grow along either the [0001] or the [0110] direction. Between the alumina and stabilized zirconia phases, it was discovered that three main epitaxial relationships exist [19]. They are as follows: $(0001)\text{Al}_2\text{O}_3 \parallel (010)\text{ZrO}_2$, $[2110]\text{Al}_2\text{O}_3 \parallel [100]\text{ZrO}_2$, and $[0110]\text{Al}_2\text{O}_3 \parallel [001]\text{ZrO}_2$. When faceting occurred within the system, it was also most likely along these planes and directions.

D. Experiments using E.F.G. and Related Processes

The technique of directionally solidifying the ceramic system through Edge-defined Film-fed growth was used for both the yttria

stabilized as well as the simple alumina-zirconia eutectic [14, 17, 18]. The traditional ceramic ribbon producing method of E.F.G. was used to solidify the eutectic mixture ceramic, while the Stepanov technique was used to solidify alumina-zirconia stabilized with the addition of 4.4 wt% yttria. The Stepanov method of E.F.G. uses a double walled cylindrical die in order to create tubular ceramic samples. Growth rates ranging from 1.39 to 50.8 cm/hr were used but again, most of the work used a more centralized range of between 2 and 10 cm/hr. Molybdenum seemed to be the material most often used for the dies and crucibles [17,18]. Because of the difficulty involved in the measurement, no temperature gradients were reported for these experiments.

Colonies containing a eutectic structure were once again discovered in each solidified sample regardless of growth rate. This could be due to impurity contamination from the dies used in the process. Impurities are often responsible for a breakup of the solidification interface (and subsequent colony growth) in metal systems. With the more traditional E.F.G. setup [14] a lamellar eutectic was noted to exist at lower growth rates, while a rod eutectic took over for higher rates. Higher growth rates increase the concentration gradient at the interface, thus creating a constitutionally supercooled condition. The higher rates also tended to increase the segregation reported at the cell boundaries.

From the samples solidified with the Stepanov method [18], the colony diameter was measured for the ceramic as a function of rate.

The plot of this data showed a decrease in colony size with increasing rate, but only until the velocity of 8 cm/hr had been reached. After this point the trend leveled off, as if a minimum diameter was reached. This behavior might be due in part to a limit imposed on the system as to how fast the heat may be removed, thus limiting actual growth velocity. This theory will be discussed later in more detail.

The strength of the material achieved through E.F.G. was measured [17, 18]. The bending strength of this ceramic was reported to be around 417 MPa at room temperature. This total decreased with increasing temperature until a value of 276 MPa was reported at a temperature of 1300 °C. From another series of experiments also using the same technique and composition, a strength of 261 MPa was achieved at 1650 °C.

E. Rapid Solidification Experiments

In order to study the microstructures achieved under rapid solidification, several techniques were used. Among the methods used were Shock Wave Quenching (SWQ), Flame Pressure Atomization (FPA), High Pressure Water Atomization (HPWA), and Electrohydrodynamic Rapid Solidification [15, 24]. Eutectic compositions of powders were solidified with all of these techniques. A hypoeutectic sample consisting of 17 wt% zirconia was also solidified using the Electrohydrodynamic process. All methods used reported ceramic cooling rates on the order of 10^4 °C/second or greater. SWQ has a reported cooling rate of 10^8 °C/second.

The microstructures found in the rapidly solidified particles ranged anywhere from a glassy/amorphous structure to a typical eutectic. With electrohydrodynamic solidification, both amorphous and two phase results were seen [24]. For the hypoeutectic samples, alumina dendrites were prevalent in larger particles, with small regions of eutectic phase between the dendrite arms. Smaller particles at the hypoeutectic composition often resulted in a single phase structure. With the same process but using eutectic composition starting charges, two phase eutectic powders resulted with very fine eutectic spacings on the order of 0.2 microns.

The other methods produced similar results. SWQ produced splats with completely amorphous natures [15]. FPA produced amorphous structures when particle size was below 80 μm , and fully eutectic structures when sizes were above 200 μm . Between 80 and 200 μm , the microstructures existed as a microcrystalline eutectic [15].

F. A Summary of Previous Work

The previous work concerning the alumina-zirconia ceramic eutectic system has mainly concentrated on qualitative analysis. The efforts to date have surrounded different methods of solidification and the microstructures produced. Little work has been done on the isolation of conditions and processes that will yield the finest structured, directionally solidified product. It has been seen that most solidification methods yield colony type structures in the ceramic. Eliminating these colonies is best accomplished through the use of

float zoning equipment. Significant strengths can be achieved with this ceramic, yet overall, these reported strengths still leave much to be desired. Research in the future should concentrate on setting down parameters for controlling ceramic growth. Eutectic spacing versus growth rate should be more closely examined to determine if it truly follows the Jackson and Hunt prediction. The heat flow of the ceramic system should also be more closely examined, as it is a definite controlling factor in solidification.

IV. EXPERIMENTAL PROCEDURE

A. Materials and Preparation

The first series of experiments used powders with reported purity levels of 99.8% for the alumina and 99.0% for the zirconia. Analysis of the powders showed typical impurities for the alumina to be Na, Fe, and Si with each registering under the 300 ppm level. The zirconia showed impurities of approximately 1% corresponding to HF, while other major impurities were listed as Ti and Si, each below 550 ppm. The latter experiments used a higher grade of powders with reported purities of 99.999% for the alumina and 99.9975% for the zirconia. The reported analysis of this alumina powder showed the major impurities for to be Mg, Fe, and Si, but each was recorded to be under the 3 ppm level. The higher purity zirconia listed Ba, Na, Nb, and Sr as major impurities, with all being under 300 ppm in concentration.

All experiments were carried out at the reported eutectic composition for this system. This composition, as taken from the phase diagram is approximately 58.5 weight percent alumina and 41.5 weight percent zirconia. The phase diagram for the alumina-zirconia ceramic system is shown in Figure 3 [11].

At first, 500 grams of both alumina and zirconia powders were placed in separate glass containers and baked in a furnace at approximately 200 degrees centigrade. This was done to remove any water absorbed by the powders. Then large volumes of each powder were carefully weighed, combined in the eutectic composition, and mixed mechanically. This final product was stored in clean glass jars.

Figure 3. The alumina-zirconia eutectic ceramic phase diagram

B. The Crucibles and Casting Experiments

The first experiments performed on the alumina-zirconia eutectic system were accomplished through the use of a rhenium crucible. Rhenium was chosen after preliminary research on the melting of refractory oxides unearthed a paper in which rhenium was successfully used to contain melts of yttria [20]. Further research suggested that rhenium should work as a container for the alumina-zirconia system also. A rectangular rhenium crucible was welded together and a simple quench experiment of the ceramic was performed by taking the system up to a melt, and then turning off the furnace power.

For this experiment, a chill casting induction unit was used, the schematic of which appears in Figure 4. The furnace consisted of a large helical induction coil surrounding a quartz tube chamber approximately 8 inches in diameter. The coil can be positioned to effectively surround the sample, which sits on a water cooled base. The rhenium crucible containing the ceramic, was surrounded with tungsten sheet and then fitted inside a tantalum canister. The canister was to act as secondary containment in case of a breach in the rhenium primary crucible. The tungsten was used to keep the rhenium out of contact with the tantalum, as tantalum and rhenium can form compounds at the temperatures necessary to achieve a ceramic melt. Next, the tantalum canister was placed inside a thick walled graphite crucible, which was then subsequently surrounded in graphite felt. As the tantalum/rhenium setup was not bulky enough to allow for sufficient heating by induction, the thick graphite crucible was needed

Figure 4. Schematic of the Chill Casting Induction Furnace

to act as a radiative heat source for the melting procedure. The felt was necessary for insulation purposes.

The entire assembly was sealed inside the quartz tube and a vacuum was pulled. The temperature was brought up slowly and was monitored through optical pyrometry. Upon achieving the target temperature of 2100 °C, the temperature was maintained for 15 minutes to ensure a complete melt. At this time, instead of performing a bottom pour chill cast, the power was simply switched off, and the sample allowed to cool. Upon examination of the cooled product, it was noted that the rhenium contained the melt with no apparent contamination of the sample. Unfortunately, due to the expense of rhenium metal as well as the difficulty involved in fabricating appropriate crucibles, alternate crucible materials were investigated.

Instead of a solid metal rhenium crucible, a graphite crucible plasma sprayed with rhenium was fabricated. A small crucible was prepared by first plasma spraying the graphite with a 10 mil layer of tungsten, and then spraying a 10 mil layer of rhenium on top. The tungsten was used as a buffer layer between the carbon and rhenium in order to prevent reactions and possible contamination of the ceramic. The crucible was filled with pressed pieces of eutectic composition alumina-zirconia and then loaded into the same induction furnace as used previously. A similar experimental setup was used along with the same melt conditions. The crucible was successful at containing the melt, but closer examination of the ceramic showed some rhenium

contamination. In addition, the expense of crucible fabrication was still a considerable drawback to the process.

Tantalum was then chosen as a replacement material for these crucibles. It was chosen for three main reasons. First, the melting temperature of tantalum (3030 °C) is well above the melting points of both alumina (2100 °C) and zirconia (2400 °C). Second, tantalum appeared to be relatively nonreactive with the ceramic system. And third, it was readily available as a crucible material and at very little processing expense. To test the tantalum, initial experiments were performed using the same setup as described for the rhenium crucibles. These experiments demonstrated the viability of tantalum as a crucible material, so the decision was made to continue to the next series of experiments.

C. The Crucibles and Preparation for Directional Solidification

Tantalum tubes of 1.90 centimeters in diameter (3/4 inch) were cut into lengths of between 3.5 and 4 centimeters. These tubes then had bottoms welded onto them, thus forming the crucible. A thin tantalum top was made for each, with a hole punched through the center. This allowed for optical pyrometric readings of the ceramic while still enclosing the system to reduce heat loss. Later, longer crucibles of 9 centimeters were used. The reason behind this will be explained later in detail.

The tantalum crucibles, were finished and cleaned, and then packed with the ceramic eutectic powder. The packing of the ceramic

was accomplished through three different methods. First, the ceramic was cold isostatic pressed (CIPed) into rods, and these rods were placed in the crucibles for melting. CIPing proved to be time consuming and difficult, as the ceramic would often come out of the press in disks or in small pieces. Next, packing using methanol was tried. The ceramic powder was mixed with methanol to form a slurry. This was then poured into the crucibles and then baked at 200 degrees centigrade until dry. This method seemed to fill the crucibles well, but after melting and solidification, several new problems were noted. The methanol seemed to add impurities to the ceramic which caused nonuniformity within the microstructure. Also noted was the lack of proper solidification in the bottom of the crucibles. Because of this, the methanol process was abandoned. Third, simple mechanical packing of the powders was tried. The ceramic powder was basically pressed and pounded into the crucibles. This method seemed to work reasonably well and was cheap and relatively easy to perform. After directional solidification, however, it was noted that all packing methods only produced an initial charge around 50% dense.

D. The Bridgman Apparatus and Directional Solidification

The Bridgman unit used in all of the directional solidification experiments was an Arthur D. Little crystal growth furnace. A schematic diagram of the furnace can be viewed in Figure 5. A two inch diameter helical coil was used for the induction heating of the samples. The ceramic-packed tantalum crucibles were wrapped in carbon felt in

Figure 5. Schematic diagram of the A.D. Little crystal growth unit

order to insulate the furnace and surrounding material from the incredible heat radiated by the melting ceramic. The felt also served to hold the heat in, to insure proper melting conditions. The punched tantalum lids were then placed on the crucibles and carbon felt disks (with identical holes) were placed on top. Then the whole setup was placed inside an alumina crucible for containment. The alumina crucible was then placed in the coil of the unit. The furnace was sealed and a vacuum was pulled. After the vacuum stabilized, the furnace was backfilled with argon gas to a pressure of 5 psi. The argon was used in order to reduce the chances of arcing within the furnace during the experimental runs.

Each sample was then heated to approximately 2100 degrees centigrade with the temperature being monitored through optical pyrometry. After the ceramic had become fully molten, the crucibles were drawn from the hot zone of the furnace at rates varying between 0.72 and 72.0 centimeters per hour. Once the ceramic was clear of the hot zone and solid, the power was turned off and the samples allowed to cool the rest of the way to room temperature.

E. Metallography

After being removed from the unit, the crucibles and ceramic were examined briefly to note specifics about the run. As tantalum was cheaper and in more abundant supply than rhenium, less care was taken to keep the crucibles in tact. The upper portions of the tantalum crucibles were then clipped off, to get down to the solidified ceramic.

These portions were then sectioned using a high speed diamond saw. The cut ceramic was then mounted in epoxy and allowed to set. After mounting, each sample was baked at a temperature around 100 degrees centigrade for at least 24 hours to remove any oil obtained from the cutting process. Each sample then underwent polishing using diamond mesh wheels, until 1 micron grit could be used. From there the samples could be examined optically or through the use of a scanning electron microscope. In order to use the SEM though, it was necessary to coat the ceramic with a fine layer of gold to eliminate charging caused by the electron beam.

V. RESULTS

A. Initial Casting Experiments

Initial studies were carried out by melting the ceramic in a rectangular rhenium crucible. The melt was quenched by turning the furnace power off. There was little or no degradation of the rhenium under the extreme temperatures used, and it did not appear to react with the melting ceramic. Upon removal from the furnace, it was instantly apparent that a successful melt had been achieved. The ceramic was milky white in appearance and had a vitreous luster. It was also fused quite well into the bottom of the rectangular crucible. Also noted was the fact that some of the ceramic had wetted the corners of the crucible. This seemed to indicate that the molten ceramic perhaps was not quite as viscous as previously thought.

In order to preserve the rhenium crucible as much as possible, nondestructive means were tried in order to remove the ceramic. In the end, the solidified ceramic was beaten out of the crucible with a hammer. This did deform the rhenium, but upon rewelding, the crucible was as good as new. Unfortunately, the crucible was destroyed later upon cleaning with a nitric acid solution. The intense heat from the welding and solidification processes had caused tremendous grain growth to occur, and it was these enlarged grain boundaries that the acid attacked.

The ceramic pieces removed from the crucible were mounted, polished and examined under the SEM. In the SEM, the light phase was

identified as the zirconia while the dark phase was the alumina. Micrographs of this cast sample can be viewed in Figures 6 a and b. The microstructure appeared very irregular, as heat dissipation and growth was multidirectional during the cooling process. However, a rod type of eutectic structure prevailed, with the zirconia forming the rods inside an alumina matrix.

Analysis of the sample through Energy Dispersive Spectrometry (EDS) showed that the sample contained no visible rhenium contamination. A copy of the x-ray analysis can be viewed in Figure 7. This result favored continued use of rhenium as a crucible material, yet as was stated before, the sheer materials expense precluded any further experiments using solid rhenium metal crucibles.

The plasma sprayed rhenium crucible experiment appeared to be a positive solution to the expense problem. The ceramic melt was contained well, yet problems manifested after closer examination of the final product. A large amount of porosity was apparent in the solidified ceramic, and there was a color shift in the ceramic from milky to grey. When the sample was cut in half, it was noted that the layers of tungsten and rhenium had pulled away from the graphite crucible. When examined under the SEM, a microstructure similar to that of the previous run was noted. Micrographs of these microstructures appear in Figures 8 a and b. Figure 8b shows a very light colored irregular phase to be present within the solid. EDS examination showed this other phase to be rhenium metal. Therefore, these plasma sprayed crucibles allowed for contamination of the

(a)

(b)

Figure 6. Micrographs of alumina-zirconia ceramic, cast in rhenium.
(a) General microstructures, (b) grain boundary formations

Figure 7. EDS analytical results from the sample cast in rhenium, showing no rhenium contamination

(a)

(b)

Figure 8. Micrographs of alumina-zirconia ceramic cast in plasma sprayed rhenium crucible. (a) General microstructures, (b) rhenium contaminant

ceramic. Assumably, the rhenium coating was porous and not well bonded, thus allowing the ceramic to interact more easily with the crucible wall.

The tantalum crucible casting experiments were very similar in nature to the rhenium crucible experiments. Once again casting the ceramic was successful, but this time, upon removal of the crucible, some differences were noted. The tantalum crucible did not seem to hold up as well in the high temperature environment. Pronounced grain growth as well as a general discoloration of the metal was noted. The solidified ceramic experienced a color change again. Instead of milky white, the ceramic was a grayish color. This might indicate that the alumina-zirconia was driven nonstoichiometric somehow.

Examination of the sample underneath the SEM showed similar behavior to that observed in the rhenium crucible. An irregular microstructure containing the same grain boundary phenomenon was noted. Micrographs depicting the results of the tantalum experiments can be seen in Figure 9. The only difference noted between the two casting experiments was the slight presence of tantalum in the latter sample. EDS analysis showed the presence of tantalum within the ceramic near the crucible boundaries. There was not a great deal of metallic pickup experienced which was a very positive result. The tantalum impurities within the sample appeared as very light blobs within the ceramic matrix. A copy of the EDS analysis can be seen in Figure 10. Even though some tantalum contaminated the sample, the decision was made to carry out directional solidification experiments

(a)

(b)

Figure 9. Micrographs of the alumina-zirconia eutectic ceramic cast in tantalum. (a) Grain boundary microstructures, (b) tantalum impurities

Figure 10. EDS analysis of the ceramic sample cast in tantalum showing the slight presence of tantalum impurities

using tantalum as a crucible material, since the tantalum pickup was only observed near the crucible walls.

B. Directional Solidification Experiments

A series of directional solidification experiments was planned in order to get a wide range of data and results. Experiments were run at varying withdrawal rates, to test the effect of rate on microstructure of the ceramic. The rates used spanned two orders of magnitude and consisted of the velocities 0.72, 3.6, 7.2 and 72 centimeters per hour. For each of these experiments, commercially available powder of lower purity was used. When these samples were examined with the SEM several trends were noted.

Colony growth and a severe lack of directionality pervaded each sample. The colonies consisted mainly of a very fine rod eutectic structure with a coarsened structure apparent at the colony boundaries. Unfortunately, these colonies appeared to grow in every direction throughout the sample. If a growth direction existed within the samples, it was a radial one, instead of the desired longitudinal direction. Figure 11 contrasts the four different rates and the resulting microstructures. Within these micrographs in general, it can be seen that the eutectic spacing decreases with an increase in growth rate. This spacing, as well as the spacing of the colonies, was measured for each run and plotted versus withdrawal rate in Figures 12 and 13. For comparison, data from previous experiments are also shown in these plots.

Figure 11. Micrographs of longitudinally sectioned alumina-zirconia at the eutectic composition of 41.5 wt% zirconia, withdrawn at (a) 2, (b) 10

(c)

(d)

Figure 11 cont. Micrographs of longitudinally sectioned alumina-zirconia at the eutectic composition of 41.5 wt% zirconia, withdrawn at (c) 20 and (d) 200 microns per second

Figure 12. Plot of the rod eutectic spacing versus the withdrawal rate for alumina-zirconia with an additional line of slope $-1/2$ shown

Figure 13. Plot of colony spacing versus withdrawal rate for alumina-zirconia

The effect of the tantalum crucible on the microstructure of the ceramic was also examined. The amount of tantalum visible in the ceramic near the crucible wall can be directly correlated to the solidification time. The samples run at faster rates showed less tantalum than the experiments run at slower rates. It is hypothesized that this behavior is due to an increase in the amount of time spent in the hot zone of the furnace. The longer the crucible remains within the coil, the greater the chance for reaction between the ceramic and the crucible, and the more time for diffusion of tantalum into the samples. A comparison of microstructures and tantalum contaminants of two different velocity runs appears in Figure 14. The lightest phase present is tantalum.

An interesting result from this tantalum impurity was seen in the sample solidified at 7.2 centimeters per hour. It was noted within this sample, in certain areas, a phenomenon existed where the tantalum formed tiny spheres along the alumina-zirconia eutectic boundaries. The tantalum was absorbed neither by the zirconia, nor the alumina. One explanation for these spheres existence is perhaps that originally, while solidifying, a thin sheath of tantalum existed around the zirconia rods. This sheath, after a time experienced a Rayleigh instability.

In addition to the eutectic structures, the sample solidified at 7.2 centimeters per hour also showed a significant amount of alumina dendrites. Occasional dendrites of either alumina or zirconia were registered in the other samples, but this particular sample was dominated by their presence. Micrographs of these dendrites are shown

Figure 14. Micrographs depicting tantalum contamination at withdrawal rates of (a) 0.72 and (b) 72.0 centimeters per hour

in Figure 15. These dendrites have a strongly faceted nature and they greatly disrupt the eutectic microstructure. Colonies are not readily apparent in this sample. This result is attributed to improper mixing of the initial powders thus resulting in a higher concentration of alumina which drove the sample off-eutectic.

C. The Yttria Stabilized Experiment

After reviewing some of the literature, yttria was noted to stabilize the zirconia by keeping it in the tetragonal phase down to room temperature. Otherwise, at approximately 1000 °C zirconia undergoes a phase change from tetragonal to monoclinic. This adds incredible stress which often is relieved through cracking. As microcracking was viewed in the nonstabilized experiments, an addition of yttria was deemed worthy to attempt.

Yttria was added to the alumina-zirconia system at the 3.5 weight percent level. Initially this appeared to be an appropriate choice as this amount should have fully stabilized the zirconia. The preparation of the samples and the process of solidification were the same as those used for the nonstabilized experiments. This sample, when solidified, appeared to be a darker shade of gray than the majority of other samples to date. The sample polished quite well and the presence of yttria did seem to minimize the formation of microcracks within the ceramic. The bonding between phases was also quite good. However, the yttria additions of this magnitude seemed to further disrupt the order of the microstructure. There was less

(a)

(b)

Figure 15. Micrographs a and b depict the formation of alumina dendrites within the sample withdrawn at 7.2 centimeters per hour

uniformity among the zirconia rods in this sample than seen in the previous work. Micrographs of the stabilized ceramic can be viewed in Figure 16. Later, through literature research, it was discovered that any additions of yttria above the 1 mol% level are severely detrimental to the ordering of the solidified structure.

D. Additional Impurity Experiments

When it was discovered that tantalum was a constant possibility for contamination to the ceramic samples, the question of what effect the addition or subtraction of impurities might have on the alumina-zirconia system arose. Four experiments were designed to test this. Yttrium fluoride, tantalum, and vanadium were all added to individual experiments to test their effect on the microstructure.

The first impurity addition to the system consisted of 1 weight percent YF_3 . Yttrium fluoride was chosen as an additive in the hopes that it would getter some of the impurities from the ceramic as it solidified. It was supposed that the yttrium and the fluoride would dissociate at the high temperatures. Thus the fluoride would be free to combine with any impurities within the ceramic and form volatile compounds. The yttrium left behind would then hopefully dissolve into the zirconia and act as a stabilizer.

Two yttrium fluoride containing experiments were run. A solidification rate of 3.6 centimeters per hour was used for the first. The second experiment contained 2.5 wt%, and was run at the same rate for comparison purposes. Each sample was sectioned and examined

(a)

(b)

Figure 16. Micrographs a and b depict the effect of 3.5 wt% additional yttria in the eutectic ceramic system. Withdrawal rate was 5.4 centimeters per hour

with the SEM. Upon examining the microstructure, it became apparent that the desired impurity gettering behavior never materialized. The yttrium fluoride did not seem to remove any impurities, rather it seemed to act as an impurity itself. Directional growth of the microstructure was even more lacking in these samples as compared with previous runs. In addition, more pronounced colony growth was found, coupled with a significant change of the zirconia rods occurring at the colony boundaries. As the amount of YF_3 added to the system increased, so did the amount of random microstructure formation. A comparison of micrographs depicting this behavior for the two YF_3 experiments can be viewed in Figure 17. Also noted in these experiments was an increase in the amount of tantalum contamination. It appeared that by combining a slower withdrawal rate, along with the yttrium fluoride, more severe degradation of the tantalum crucible resulted. Perhaps, the YF_3 preferentially attacked the crucibles.

Amidst the complex microstructures, one quite interesting result was seen. There was a reoccurrence of the tantalum beading between the eutectic phases, a micrograph of which is displayed in Figure 18. This behavior had not been witnessed since the first directionally solidified experiment, and it was curious why it would be seen again here. Admittedly there was more tantalum contamination in these samples, thus the duplication of this behavior was a distinct possibility. However, this beading was noted in only the 1 wt% yttrium fluoride sample. Thus, more systematic experiments are needed to establish conditions for Tantalum beading to occur.

Figure 17. Examples of the microstructure resulting from (a) 1 wt% additional YF_3 , and (b) 2.5 wt% additional YF_3 , using a withdrawal rate of 3.6 centimeters per hour for each

Figure 18. Micrograph showing the formation of tantalum beads along the zirconia phase in the eutectic ceramic containing 1 wt% additional YF_3

In addition to the YF_3 experiments, two experiments were run which contained additions of tantalum and vanadium respectively. As the phenomenon of metal beading along the zirconia phase had been previously noted, it was decided to try to impregnate the ceramic with additional metal particles. It was hoped that these metals would experience the same behavior, and thus allow for further study of the phenomenon. If a metal addition to the ceramic matrix could be controlled in such a manner, the results could be quite interesting. A ductile metal addition to the ceramic which does not overly disrupt the microstructure could prove to be a significant toughening mechanism.

Both the tantalum and the vanadium were added at very small levels to the initial ceramic powders, on the order of 50 ppm or so. Small levels were chosen in order to avoid the formation of larger metal conglomerations or possibly dendrites within the ceramic. These samples were solidified at 3.6 centimeters per hour. A conscious effort was being made in the later experiments to keep solidification rates in the 3.6 to 7.2 centimeters per hour range. This was done to minimize the amount of time the tantalum crucibles spent in the hot zone, as well as providing the smallest effective eutectic spacing. Rates faster than 7.2 cm/hr did not seem to decrease spacing significantly.

Once the finished products were mounted and polished, they were examined underneath the SEM for traces of the metal beading phenomenon. No evidence could be found. The microstructures of both samples did not depart significantly from those seen in previous

experiments. Both samples exhibited the traditional appearance of occasional tantalum impurities, but no beading. Photomicrograph examples of the results of these experiments can be seen in Figure 19. Quite possibly the metal additions were on too small a level to be detected. EDS measurements of each sample detected no trace of the impurity additions. However, the results did seem to prove the inability to produce the beading effect whenever desired.

E. High Purity Experiments

Because the addition of impurity getters did not seem to work, and impurity additions appeared to degrade microstructures, the use of high purity powders became the next logical step. A tantalum crucible was packed with high purity powder carefully weighed out at the eutectic composition. The sample was withdrawn at 1.8 cm/hr and solidified under the same conditions as the previous runs. The results from this experiment appeared very promising.

Examination of the sample revealed a large area of colony free growth. This occurred in the middle of the sample. The area also appeared to exhibit much more directional growth than previously seen. Instead of the zirconia rods appearing as spheres, indicating radial growth, in the longitudinal cut of this sample the zirconia appeared more lamellar in nature. Figure 20 shows a representation of this behavior. Occasionally within the sample, tantalum contamination was seen, especially in the form of tantalum dendrites. The occurrence of these contaminants appeared significantly reduced, however.

(a)

(b)

Figure 19. Photomicrographs depicting the results of the (a) tantalum and (b) vanadium additions to the ceramic using withdrawal rates of 3.6 centimeters per hour for each

Figure 20. Micrograph showing the lamellar nature and lack of colony formation experienced by the high purity ceramic withdrawn at a rate of 1.8 centimeters per hour

Within the sample, a definite segregation effect was noticed as well. At the bottom of the sample, a region of zirconia dendrites existed, while at the top was an area rich in alumina dendrites. The zirconia dendrites were noted to be growing at specific angles to the withdrawal axis. Near the edge of the crucible, the greatest amount of deflection from the growth axis existed. The zirconia dendrites here grew at 45 degree angles to the longitudinal axis of the ceramic and the space between dendrites was large. Closer to the center of the sample, however, the dendrites grew nearly parallel with the longitudinal axis and there spacing was much finer. The zirconia dendrites also grew to a specific distance within the sample, then halted. At that point, a region of uniform eutectic microstructure commenced. Then, at the very end of the solidification process, alumina dendrites manifested themselves. Figure 21 depicts this segregation behavior. Reasons behind this segregation will be explained in further detail in the discussion section.

F. Addition of Scandium

As directionality was still of concern for nearly all of the samples, an experiment concerning control of the heat flow was proposed. Since, zirconia dendrites were already observed to grow at close angles to the withdrawal axis, perhaps metal dendrites could be grown in a similar manner. Being metal and aligned with the growth axis, they would act as heat sinks for the solidifying ceramic. This would allow for an ease in the dissipation of the latent heat of fusion

Figure 21. Longitudinal section micrographs of the high purity powder experiment: (a) zirconia dendrites at bottom of sample, (b) colony free middle of sample

(c)

Figure 21 cont. Longitudinal section micrographs of the high purity powder experiment: (c) alumina dendrites at top of sample

and could possibly increase directionality.

For this experiment, scandium metal was chosen. The metal needed to melt at a lower temperature than the ceramic system, so that the ceramic eutectic growth would precede the metal. This way the metal would be forced to fill the gaps between the solidifying colonies of eutectic, rather than vice versa. This would cut down on the coarsened region at the colony boundaries. In addition to this, the metal needed to be relatively nonreactive with the ceramic. The formation of volatile oxides would be very detrimental to the goals of this experiment.

Scandium metal was added to the aluminum-zirconium system at a level of 20 volume percent. This was hoped to be enough metal so that the formation of dendrites would be possible. The sample was solidified as before, using a rate of 3.6 cm/hr. Upon removal from the furnace, the ceramic appeared to have solidified well, and initially appeared to exhibit directionality. Closer examination using the SEM revealed that good directionality did indeed exist, but without the presence of the metal phase.

No metal phases were present anywhere within the sample. Colony growth was extremely prevalent, and the colonies were aligned quite nicely along the growth axis. The addition of scandium may have contributed favorably to this alignment. However, the scandium appeared to have gone into solution in the ceramic, probably within the alumina matrix existing between the colonies. Micrographs showing these microstructures appear in Figure 22.

(a)

(b)

Figure 22. Micrograph a and b depict colony formation and the resulting microstructure due to the addition of 20 vol.% scandium solidified using a withdrawal rate of 1.8 centimeters per hour

VI. DISCUSSION

A. Microstructural Features

In the lower purity experiments, a rod type of eutectic structure formed almost exclusively. These zirconia rods in an alumina matrix solidified in evenly spaced, well aligned groups within the colonies. The colonies themselves, however, lacked significant directionality within the ceramic. Growth of the colonies appeared to be radially outward toward the crucible walls, rather than along the axis of withdrawal. At the colony boundaries, a coarsening effect was noted. As the boundaries of different colonies approach each other, the microstructural growth direction turns almost toward to the crucible walls, and subsequently the solidification rate slows. This allows a much coarser microstructure to form.

In some cases, where grains were present within the samples, the rods appeared in specific orientations that repeated periodically, as in Figure 9a. This seems to suggest some type of crystallographic dependence exists which can act to control rod formation. As discovered in the literature review, when a seed sapphire crystal oriented in the $[1120]$ direction was used to start growth in the alumina-zirconia ceramic, a well aligned rod structure prevailed. Perhaps, within these grains, the zirconia rods are exhibiting the same behavior.

Lamellar structures have been produced in the alumina-zirconia system, but not through these most recent experiments. Only in the colony-free portion of the high purity sample did there appear to be any

lamellar behavior. At a eutectic composition, the volume fraction of zirconia is between 34 and 35 percent. This value range is above the approximated 32% limit set for rod formation. The existing 2-3% difference is probably outweighed when surface energy considerations are examined. Also, the theoretical volume fraction can be smaller if the composition is slightly off eutectic.

It has been previously hypothesized that impurities aid rod formation. Certain experiments involving metal systems [7] have shown that when zone refined materials were directionally solidified, lamellar eutectic growth resulted. When minute levels of impurities were added, however, the resulting eutectic growth was rod-type. This behavior is thought to stem directly from the formation of colonies. The colonies resulting from the presence of impurities have curved boundaries by nature. These boundaries have multiple crystallographic orientations which tend to promote rod eutectic growth, since the rods already experience multiple orientations due to their circular cross section. Lamellae have preferred crystallographic planes, and therefore do not lend themselves well to growth when a curved interface is involved.

B. Eutectic and Colony Spacing

The eutectic spacing in the directionally solidified samples was quantitatively measured with respect to growth rate. The eutectic spacing plot from Figure 12, reproduced here as Figure 23 with additional data from other investigations, shows that overall size of

Figure 23. Eutectic spacing versus velocity for the alumina-zirconia and other systems

microstructural features does diminish with increasing rate. However, a leveling off of this trend is noticed between the rates of 2.0 and 200 microns per second mark for the eutectic composition. A leveling trend was not apparent when colony spacing was measured with respect to growth rate as shown in the combined plot of Figure 24. Previous experiments by Borodin et al [18] appear in Figure 24 as well. Within the experimental errors, all data show a decrease in colony spacing with increasing growth rate. The colony spacing, λ_c , is found to be approximately inversely proportional to $V^{1/2}$, thus showing a scaling law of $V\lambda_c^2 = \text{constant}$.

C. Comparison With Theory

If we examine the results for the eutectic composition ceramic, then the eutectic spacing appears to level off as the velocity is increased. In contrast, the data of Brandt and Stubican initially show a much smaller decrease in spacing with velocity, but the spacing decreases sharply as the velocity is increased. When all current data are examined together, then a decrease in eutectic spacing with velocity is observed. Although there is significant scatter, the results do indicate the spacing varies inversely with the square root of the velocity, as predicted by the JH model.

Jackson and Hunt did neglect all kinetic effects at the interface in order to simplify the solution to the model. This assumption seems to be valid for most metals systems, but might not be so for ceramics. Because ceramic melts contain groups of ions, solidification kinetics

Figure 24. Combined representation of colony spacing versus velocity

become more complex than those of simple metal systems. Diffusion of these clusters away from the interface, orientation, and subsequent growth is assumably much more difficult to achieve in these systems. Furthermore, the aluminum phase is faceted so that kinetic effects could be important. As growth velocity increases, the importance of the kinetics involved in solidification increase as well. For the alumina-zirconia system, the kinetic effects at the interface may no longer be negligible at high velocities. Thus the JH model needs to be modified to include the interface kinetics effect.

Originally the Jackson and Hunt model is based on the equation for the average undercooling at an interface, which is:

$$\Delta T = m[C_E - C(x)] + a/r(x)$$

where m is the liquidus slope, C_E is the eutectic composition, $C(x)$ and $r(x)$ are the composition and radius of curvature at point x on the interface, and a is a constant defined by the Gibbs-Thompson relationship. This equation has been expanded by Jackson and Hunt for the eutectic system and takes the form of:

$$\Delta T/m = V\lambda Q^L + a^L/\lambda$$

In this equation, λ is the eutectic spacing and Q^L is a constant expressed as:

$$Q^L = P(1 + \zeta)^2 C_0 / \zeta D$$

where P is a constant depending upon lamellar spacings, D is the liquid diffusion coefficient, ζ is an α to β phase spacing ratio, and C_0 is the difference between the compositions of the two phases in the solid. Also present in this equation is a^L which can be expressed as follows:

$$a^L = 2(1 + \zeta) \left[\frac{\left(\frac{T_E}{L} \right)_\alpha \sigma_\alpha \sin \theta_\alpha}{m_\alpha} + \frac{\left(\frac{T_E}{L} \right)_\beta \sigma_\beta \sin \theta_\beta}{m_\beta} \right]$$

where T_E is the melting temperature, L is the latent heat of fusion, σ_α and σ_β are surface energy terms, the θ 's represent the contact angles of the respective phases, and $m_{\alpha,\beta}$ are the liquidus slopes of the α and β phases. The full model is described in further detail in reference [8].

Because the JH equation may not accurately describe the behavior in the alumina-zirconia system, a term allowing for the kinetic effects present at the solidifying interface was then added. Tiller [29] had examined the possible kinetic term effects on solidification for faceted interfaces and derived a theoretical expression for the kinetic undercooling, based upon the nucleation model for growth, as:

$$\Delta T_{\text{kin}} = 2\alpha / 3 \ln(\lambda^2/a)$$

in which α is a constant defined as:

$$\alpha = \pi h \gamma^2 / 3 \Delta S_f k T$$

where h is the ledge height, γ is a surface energy term, S_f refers to the entropy of fusion per unit volume, k is Boltzmann's constant, and T is the melting temperature. This equation is also in terms of λ which once again represents the eutectic spacing, and the parameter a which is defined as:

$$a = (\pi^{1/2} \beta_2 \Delta S_f h / V_0)^{2/3}$$

where β_2 depends upon jump frequencies, and V_0 is a constant approximately equal to 10^{27} . This term was added to the overall undercooling equation and resulted in:

$$\frac{\Delta T}{m} = \lambda v_Q^L + \frac{a^L}{\lambda} + \frac{2\alpha}{3m \left[\ln \left(\frac{\lambda^2}{a} \right) \right]^2}$$

Taking this equation and finding its minimum by differentiating with respect to λ results in:

$$0 = v_Q^L - \frac{a^L}{\lambda^2} - \frac{4\alpha}{3m \lambda \left[\ln \left(\frac{\lambda^2}{a} \right) \right]^2}$$

Now by rearranging and solving in terms of $V\lambda^2$, the final equation looks like this:

$$V\lambda^2 = \frac{a^L}{Q^L} + \frac{4\alpha}{3m\lambda Q^L \left[\ln\left(\frac{\lambda^2}{a}\right) \right]^2}$$

When appropriate constants are applied to this equation, the kinetic term does cause a slight deviation from the predicted JH behavior. However, the behavior predicted by this new model is on a much smaller scale and is negligible for the growth velocities examined.

D. Heat Flow in Ceramics

The deviation of results in the alumina-zirconia system from the theoretical model might also exist due to the failure to remove heat from the solidifying ceramic. If the latent heat cannot be removed, the actual growth rate of the interface may lag behind the imposed growth rate. For the alumina-zirconia system, after some critical speed, a limit of the steady state removal of heat may occur. This limit for the heat removal from the ceramic, would then in turn impose a limit to the actual growth speed of the interface. The result would be a lower end limit to the microstructural eutectic spacing. This would again suggest that for the application of Jackson and Hunt's theory, the spacing needs to be correlated with the interface velocity and not with the withdrawal velocity.

As was noted in the experiments, the solidified ceramic did not demonstrate the desired directionality as well. The growth of the microstructure seemed to be of a radial nature. This behavior can be attributed to heat flow difficulties within the ceramic. Because the solid ceramic acts as a thermal insulator, the heat rejected by the advancing growth front is drawn radially outward toward the metal crucible walls. It has been suggested by Brandon and Derby [28], that infrared transmission through the ceramic is an important method of heat dissipation. If many colonies/grain boundaries exist, possible channels for the conduction of infrared heat are effectively blocked. This causes problems for the heat flow away from the solidifying interface. They also suggested that severe deflection of the solid/liquid interface occurs near the crucible walls, thus further enhancing radial growth within the ceramic.

Thicker walled crucibles could be used to alleviate this problem. If the majority of the heat flow was taking place out to the crucible walls and down, it is thought that these types of crucibles might help improve directionality. Also, a longer crucible with a smaller diameter would result in growth patterns with less deflection away from the withdrawal axis, merely due to the increase in the ratio of length to diameter. This would therefore effectively reduce the radial growth within the sample. When taller crucibles with smaller diameters were employed in these experiments, they did appear to aid the solidification process somewhat. Samples from these experiments showed a larger

degree of directionality. But it was not until the high purity powder experiments that the effect was really noticed.

E. Segregation and Solidification

With some of the eutectic composition samples, especially the high purity sample, a definite segregation effect was noticed. Zirconia dendrites were seen at the bottom of the samples while alumina dendrites pervaded the top. Figure 21 depicts this phenomenon. This behavior might arise from the difference between the liquid densities of the alumina and zirconia. It has been noted that zirconia is more dense than alumina in the solid phase with a reported density of 5.89 g/cm³ compared to alumina's density of 3.96 g/cm³. This difference is assumed to carry over into the liquid. Segregation might occur if gravitational effects overcame the natural convection effect produced by the RF field. This appears unlikely as the microstructures depicted in Figure 21 strongly resemble those seen in cast metal systems where convection is present. Also, this effect was noted only at slower rates where convection effects become important.

The reason behind the observed microstructure lies in the placement of the coupled zone. As these samples began solidifying, the zirconia-rich region at the bottom of the crucible was outside the coupled zone, thus yielding the zirconia dendrites. Then, as the amount of zirconia was depleted, the system was driven back to a coupled growth state. At the end of the solidification process, an alumina-rich liquid remained, and produced the alumina dendrites.

Another possible explanation lies in the mobility of aluminum and zirconium ions in the liquid state. The molten state of this ceramic does not appear to be too viscous in nature. Therefore difficulty in diffusing the solute might be encountered. It is hypothesized that the $+4$ Zr ion would necessarily attract two oxygen ions, and this trio forced to move en masse through the liquid since it could not be readily incorporated into the solid. At the same time, the Al $+3$ ion might simply only attract one oxygen ion and thus form a more mobile ion pair. Due to this behavior, perhaps the zirconia cannot readily diffuse away from the advancing interface, and the system experiences a zirconia buildup. This results in the zirconia dendrites. This causes the sample to become alumina-rich and because of its higher mobility, solidifies at the end of the ceramic growth process as alumina dendrites.

The fact that ceramic melts contain ions rather than simple atoms, may have additional effects on the solidification behavior of the system. The kinetics involved in correctly orienting and attaching entire molecules probably cannot be ignored in this case.

F. Colony Formation

Extensive colony growth appeared in most of the ceramic directional solidification experiments. Obviously, a steady planar front was never achieved. All of the samples, save the one solidified at 7.2 cm/hr, were very close to the eutectic composition, so the formation of a boundary layer of solute at the solid/liquid interface should not be

a consideration. The colony growth most likely resulted from contamination of the melt with impurities.

In the theory section, it was stated that impurities have been reported to cause colony growth in other systems. In the alumina-zirconia system, even small amounts of impurities play a significant role. Due to the more viscous nature of ceramic melts, the impurities experience difficulties in diffusing away from the solid interface, thus allowing for an impurity concentration buildup. This yields the constitutional supercooling condition mentioned previously, which results in colony formation.

It does appear that colony growth can be controlled through the use of higher purity starting materials. In the directional solidification sample which used the higher grade purity powders, a large region of colony free growth was observed. The middle region of the ceramic sample appeared to have achieved some sort of steady state growth, producing no discernable microstructural fanning or colony boundaries. In fact, when the colonies were removed from the sample, directional growth was also enhanced. From this behavior, it appears that in order to eliminate colony growth from directionally solidified ceramic materials, care should be taken to insure that a high purity melt is maintained.

G. Metal/Ceramic Experiments

Several experiments were attempted in which various metals were added to the alumina-zirconia eutectic system. Metals can

greatly improve the ductility of ceramics and thus improve their toughness. Because both tantalum and rhenium were previously seen to exist relatively inertly within the ceramic, tantalum, vanadium, and scandium were added to the system. The tantalum and vanadium were added to attempt to reproduce the tantalum beading effect resulting in an earlier experiment. The scandium was added to aid in heat flow away from the solidifying ceramic through the formation of metal dendrites within a ceramic matrix.

The tantalum beading effect was unable to be reproduced. The tantalum and vanadium additions were perhaps on too small of a scale to produce visible results. Unfortunately the effect seems to occur randomly and only in conjunction with a finely dispersed tantalum phase. The effect was never associated with the appearance of larger conglomerations of tantalum within the ceramic. Only a tiny amount of tantalum was able to experience the beading behavior.

The scandium metal addition at a 20 volume percent level to the ceramic eutectic did not produce the desired dendritic effect. It did, however, seem to increase the directionality of the colonies present. Colony growth was much less radial, and elongated groupings parallel to the withdrawal axis prevailed. The scandium appeared to dissolve into the alumina matrix present between the colonies, assisting with heat flow even without forming metal dendrite heat sinks. The mere presence of metal particles within the ceramic probably allowed for better thermal conductivity in the solid.

VII. CONCLUSION

It is possible to produce alumina-zirconia ceramic samples through existing solidification techniques. The resulting microstructures typically consist of rods of zirconia in an alumina matrix, although a lamellar structure has been noted in some cases. In nearly all cases, colony growth was present which may possibly result from grain size, repeated nucleation events, and lamellar oscillations. In the same vein, it appears that the amount of impurities within the system might be the underlying cause for the colony growth. Colony growth was diminished through impurity control as the higher purity samples exhibited colony free behavior. In addition to colony formations, faceted alumina dendrites or nonfaceted zirconia dendrites may result in the ceramic if the sample is solidified out of the coupled zone. In all cases, for larger-sized Bridgman samples, a lower limit in the eutectic spacing was noted. The solidification model which includes the kinetic effect has been developed, although the effect appears to be negligible under present experimental conditions. A spacing limit might also occur due to the result of heat flow problems. Heat flow out of the ceramic is difficult to control, often causing radial and not axial growth. This behavior is exaggerated in the presence of impurities. Thus, higher purity powders should always be used. Higher purity samples, in addition to yielding a more microstructurally uniform ceramic, also show increased directionality.

In the future, the kinetic model needs to be examined in more detail, and further research needs to be accomplished in the area of

molten ceramics. Once better system constants are in place, the kinetic model will give a better indication of the behavior in the alumina-zirconia system. In addition, further work is necessary in the area of heat flow in solidifying ceramics. Experiments using thicker walled crucibles need to be attempted in order to improve microstructure unidirectionality. Also, performing comparative quench experiments at different velocities should prove whether or not heat flow is a controlling factor in ceramic solidification.

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