FOREWORD

ABSTRACT

This final report of a program of research on growth and deformation processes in spinel includes a description of an R. F. plasma growth facility and its operation. The main conclusion from the growth experiments is that the instability of spinel at its melting point precludes the growth of large stoichiometric single crystals by direct fusion. Alternative techniques are discussed.

The effect of heat treatment on the microindentation behavior and room temperature compressive strength of alumina-rich spinel single crystals is discussed. Some high temperature strength data on alumina-rich spinel are included.

Publication of this technical documentary report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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ILLUSTRATIONS

INTRODUCTION

This report describes the concluding phases of research carried out under Contract AF 33(616)-7820. It has been concerned with growth of spinel single crystals, with characterizations of their defects, and with studies of strength and deformation in such crystals. The initial phases of this investigation have already been described in Technical Documentary Report No. ASD-TDR-62-1086 dated February, 1963. At that juncture, it had been determined that stoichiometric $MgAl_2O_4$ single crystals of acceptable size and perfection could not be readily grown by conventional Verneuil techniques employing oxy-hydrogen flames as the heat source. Consequently, an R. F. plasma heat source (offering higher working temperatures and selective control over the atmospheric environment in which the crystal grows) was selected for further study of the growth of spinel boules, and an appropriate apparatus had been designed and was being constructed. One section of this report describes that apparatus, discusses its operation and performance, and summarizes the results of many crystal growth experiments which have been carried out with it.

Some small transparent boules of fairly high quality have been infrequently obtained, but evidence pointing to chemical instability of $MgAl_2O_4$ at (and above) its melting point casts much doubt on the feasibility of growing high quality stoichiometric boules of useful size by any direct fusion technique, regardless of heat source. Therefore consideration has been given to other alternative methods for crystal synthesis, with emphasis on those taking place at lower temperatures.

Alumina-rich spinel boules can be grown with relative ease and both laboratory-grown and commercially obtained crystals with an approximate $MgO:2.9 Al_2O_3$ ratio have been employed in studies of variations in microindentation surface hardness and room temperature compressive strength as functions of heat treatment. Exsolution of excess alumina as $\alpha-Al_2O_3$ platelets oriented epitaxially on $\{111\}$ planes within the spinel as a result of heat treatment materially alter the microstructure, and significantly change surface hardness and strength. Both annealing and hardening (embrittling) effects are observed, the former in the 700 - 1000°C range, the latter in the 1000 - 1400°C range. High temperature compression studies of spinel

demonstrated plasticity related to movement on multiple (111) [110] slip systems. Chemical and thermal etching methods, partially successful in revealing dislocation concentrations and subgrain boundary configurations in spinel, have been developed, and have been employed in correlating strength and deformation behavior with structure and orientation of spinel crystal specimens.

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R. F. PLASMA CRYSTAL GROWTH FACILITY

Apparatus

Equipment designed and constructed at N. C. State for crystal growth research using the inductively coupled thermal plasma heat source originally developed by Reed[1] is illustrated in Figures 1 and 2, which show front and side views respectively. All controls, including those of the Lepel T-10-3MC power supply are accessible from the front, and view ports permitting direct observation of the plasma and the growing crystal are located in front and side panels. The viewports, composed of two 1/8 inch thick, dark grey Plexiglass sheets (uncooled in these photographs, now fully water cooled), filter enough of the intense radiant energy from the plasma to permit safe, comfortable viewing for reasonable time periods without auxiliary dark safety goggles.

The entire side panel may be swung away on hinges, permitting convenient access to the coil, lower portions of the torch, furnace, and accessory items. The "hot chamber" is water cooled, and for safety purposes, is ventilated with a forced draft suction system exhausting outside the building.

Since both the power supply and the plasma facility are critically dependent upon a reliable supply of cooling water, a recirculating system was constructed to provide an adequate flow of water at a constant 45 psi, the temperature of water supplied to the facility is thermostatically controlled at $90^\circ F$. This slightly higher than ambient setting is utilized to eliminate any danger of moisture condensation and subsequent arc-over within the water-cooled, high-voltage, high-frequency power supply.

A schematic view of the principal components of the facility is shown in Figure 3. The principle of operation is straightforward: (a) The intensely hot plasma (estimated 6000° – $15,000^\circ C)[2]$ is generated within the torch by eddy currents induced within ionized argon gas (which may be selectively admixed with modifying gases) by an R. F. field maintained within the load coil by alternating current supplied by the Lepel unit (frequency approximately 3.45 MC); (b) heat from the stable, floating electrodeless plasma melts (and even vaporizes) small particles of feed material being carried along from the vibratory feeder by the innermost stream of gas entering the torch; (c) heat from the plasma also initially melts the tip of a seed crystal brought

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Figure 1.   Front view of R. F. plasma
crystal growth facility.
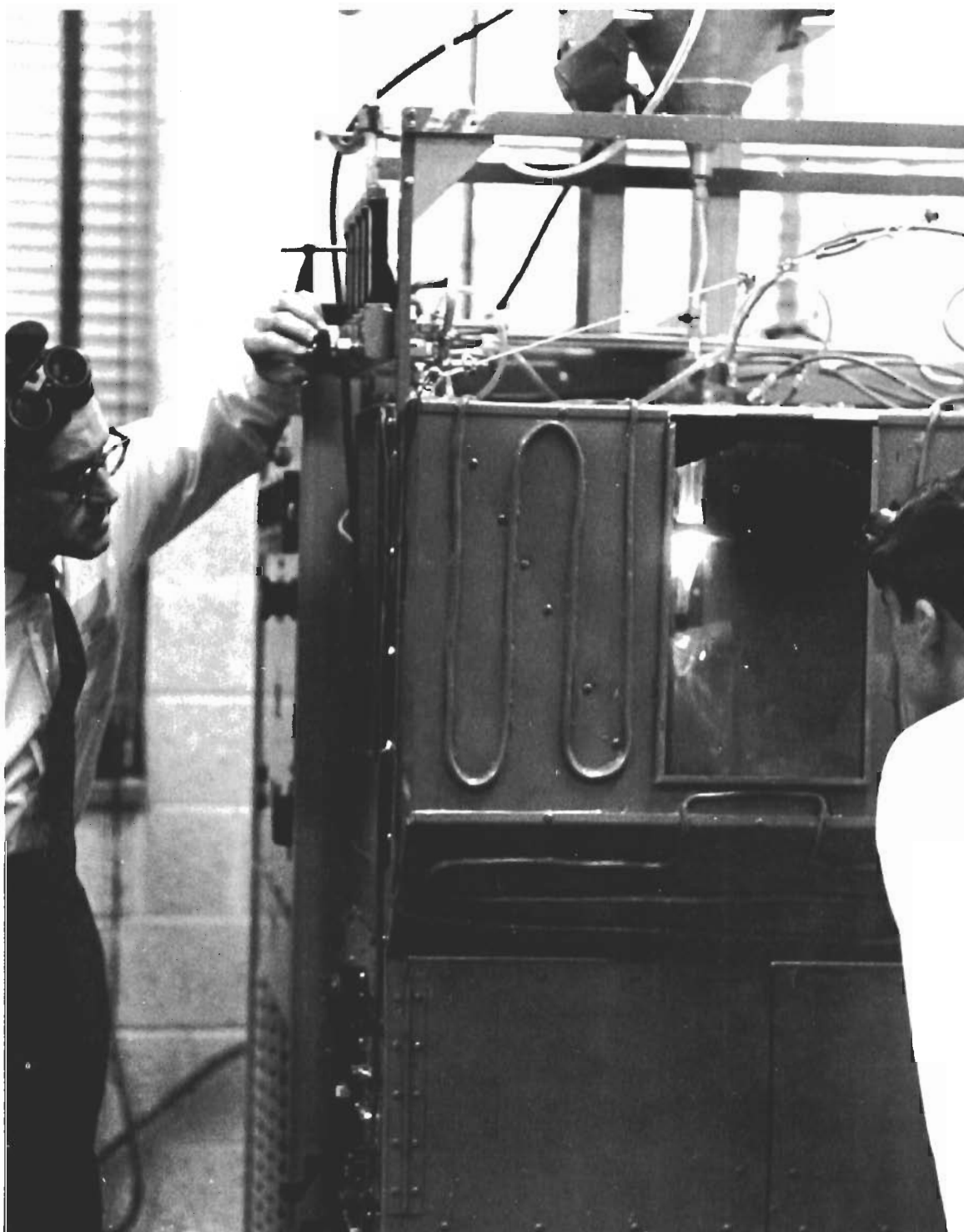
Figure 2. Side view of R. F. plasma
crystal growth facility.
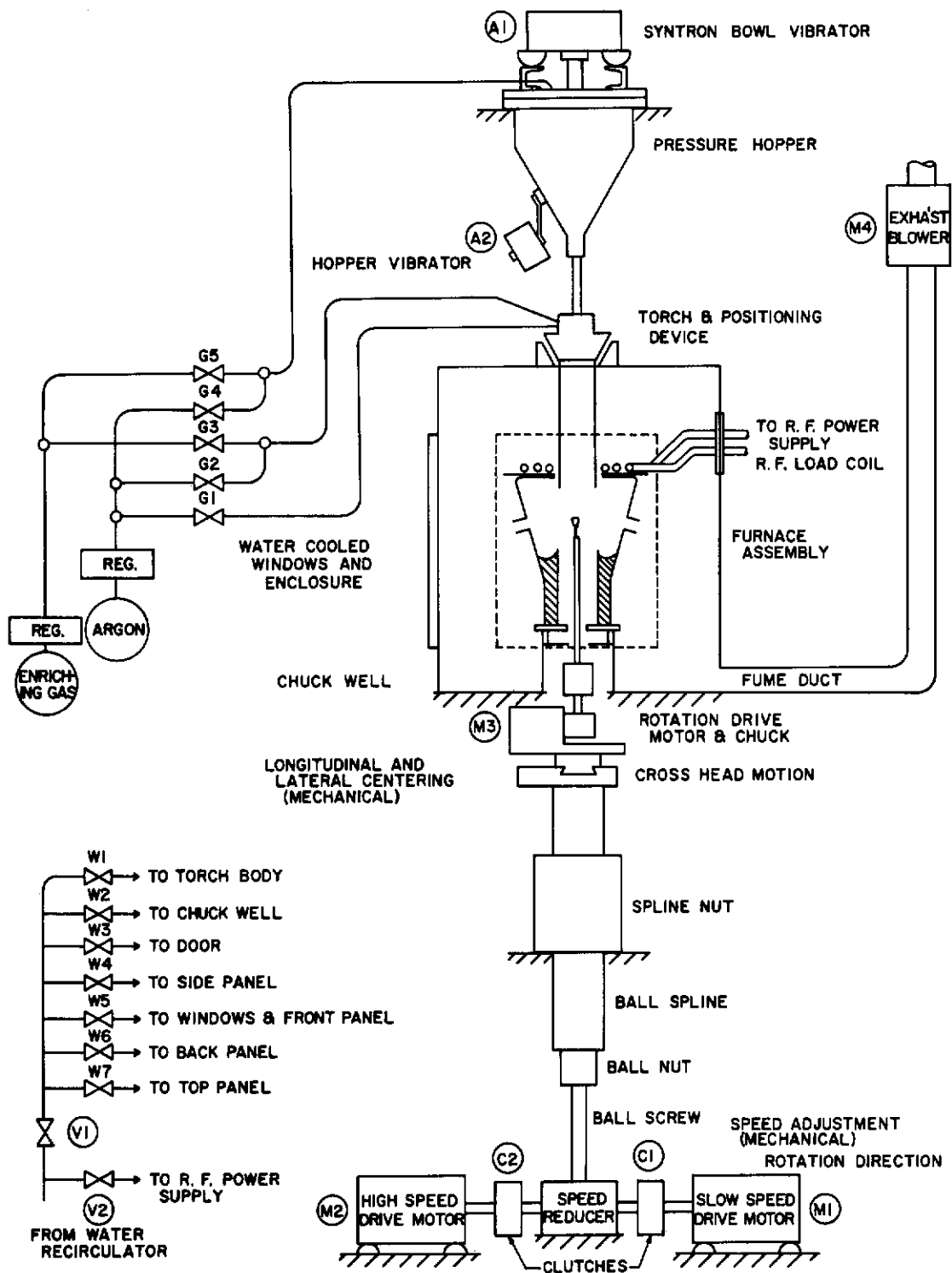
Figure 3. Schematic drawing of R. F. plasma
crystal growth facility.

up into position and rotated by electro-mechanical devices, and thereafter, maintains a molten layer over the surface of the growing boule.

During growth, the seed and its increasingly longer boule are gradually withdrawn so that the molten cap remains essentially stationary with respect to the heat source. Molten particles are added to the liquid layer from above as crystallized material is removed from below. Feed and withdrawal rates must be capable of being sensitively controlled over wide ranges. Adjustments in one must be made with respect to the other, and in addition, must be conditioned by the particular heat flux-temperature conditions which prevail.

In most respects, the function of the facility is directly related to that already described for traditional Verneuil oxy-hydrogen crystal furnaces.[3] The principal difference is to be found in the character of the heat source employed, and in the wide range of non-combustive atmospheres that can be attained by using the plasma source.

Four modes of semi-automatic vertical motion, plus rotation at 9 RPM about the vertical axis are provided. In addition, two rectilinear modes of lateral translation of the seed and candle are provided through cable-connected manual drives.

The basic machinery for the semi-automatic motions consists of two reversible motors, two electric clutches and a common speed-reducing gear box. A ball-screw ball-spline assembly converts the rotary motion from the gear train into vertical motion of the seed crystal. With appropriate switches controlling the electric clutches, either motor (a constant speed reversable one yielding a fast traverse of 3 in/min., up or down; the other slow and manually variable and reversable, yielding growing speeds ranging from 0 - 3.6 in/hr.) may be connected to the speed reducer.

Details of the vibratory feeder - pressure hopper assembly and of the R. F. plasma torch have been previously illustrated in Figures 12 and 16[*] respectively, of Reference 4. Control

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[*]Illustrations for Figures 16 and 17 of Reference 4 were erroneously exchanged during printing. The correct caption (Fig. 16) appears on p. 45, the corresponding drawing appears on p. 46 (Fig. 17).

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circuits for the electromechanical system are schematically il-
lustrated in Figure 4a; nomenclature for the various components
is given in Figure 4b. A transparent enclosure-furnace assembly
utilized for crystal growth experiments in the R. F. plasma fa-
cility is illustrated in Figure 5.

Experimental Procedures for Crystal Growth

Experimental procedures which have been found most favorable
for growth of single crystal spinel are dependent upon the desired
environmental conditions, and upon many interrelated parameters
in the system, e.g. heat flux, plasma flame stoichiometry, boule
size, feed rate, and/or withdrawal rate. Each experiment requires
these four steps: (1) set up and load, (2) initiate, stabilize
and invert the plasma, (3) insert and melt the tip of the seed
crystal and initiate growth, and (4) cool and shut down.

The required set up time often equals or surpases the time
of the run, because it is frequently necessary to clean up, re-
place damaged fused quartz components, replenish gas supplies,
change feed materials, select and position a new seed, and/or align
the components of the apparatus. A typical sequence is outlined
below. Fresh tanks of argon and other additive gases are secured
to the manifolds, and the line pressure is set at 15 psi. During
the required 40 minute warm up period the power supply is water
cooled and its heat losses bring the cooling water in the reser-
voir of the recirculating unit to equlibrium at $90^{\circ}F$.

When the set-up is complete and components of the facility
fully warmed up, a plasma is initiated by drawing an arc (initial
source of electrons and argon ions) from the 1/16" diameter tanta-
lum starting electrode, which is then quickly withdrawn upward
through the torch body as soon as power couples spontaneously into
the ionized gas to create a stable, teardrop-shaped plasma. Typ-
ical starting conditions are: plate 24%, grid 52%, (gas input 1)
argon at 10.0 liters/min., (gas input 2) argon at 10.5 liters/min.
Immediately after the plasma initiates, the protective outer vor-
tex of cooling argon (input gas 1) is increased to about 27.0
liters/min. and the grid current is rebalanced at 10% of plate
current to prolong the life of the oscillator tube.

Once the plasma is stabilized, the exhaust draft fan is
started and all systems are rechecked to insure stable, safe op-
eration. An eccentrically located plasma, inadequate gas flow in
the torch, inadequate flow of cooling water, or an unbalanced grid

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current, to cite some examples, can endanger the life of the equipment or can cause an electrical overload and/or safety circuit abort; either eventuality proves disastrous to a growing boule.

Rotation of seed and candle is started, and the seed is mechanically raised from its initial position low in the furnace to a point where the tip of the seed just melts. This position, usually 1/2 to 1 inch above the furnace tube, and approximately the same distance below the visible tip of the plasma, is the "seat of crystallization;" ideally, the shallow melt can be maintained at this level as fresh material is added at the top, and crystal pulled away beneath. Next, the center gas flow (input 3) which carries entrained feed material is set at approximately 1 liter/min. and the gas sustaining the plasma (input 2) is reduced to 7.5 liters/min. Under these conditions the center gas velocity will penetrate the dense plasma (inverted condition) and introduce the fine particles of feed, otherwise the feed would bypass the plasma and not penetrate its sheath of electrons.

Finally, actual growth is initiated by turning on and adjusting the vibratory feeder. Dynamic factors cause the particles, initially introduced from a 1 mm. bore, to disperse to the much larger growth surface ($\approx$ 10 mm.). An inverted plasma is much more efficient in its ability to heat particles to the melt temperature and keep them axially collimated and directed toward the growth surface. Vaporization of the feed particles also tends to lessen their concentration at the growth surface. The total heat flux and this local concentration of molten feed material in the critical growth zone are perhaps the most important factors which determine the growth rate and overall quality of the boule.

Enclosing the plasma and boule is a modified wide mouthed Erhlenmeyer flask of fused quartz which serves to eliminate random effects attributable to cross drafts caused by the exhaust system; its neck also contains and supports the tubular annealing furnace. The flask was modified by cutting an axial hole for the plasma torch and by adding two ducts to act as relief ports. The inverted flask shape is very favorable for dissipating intense radiant and convective energy from the plasma. Other containment shapes, e.g., cylinders, did not perform as well, but caused overheating of torch components. Excessive back pressures were encountered if relief ports were not incorporated; the cooling gas vortex sweeps down around the plasma and exits primarily through these ports.

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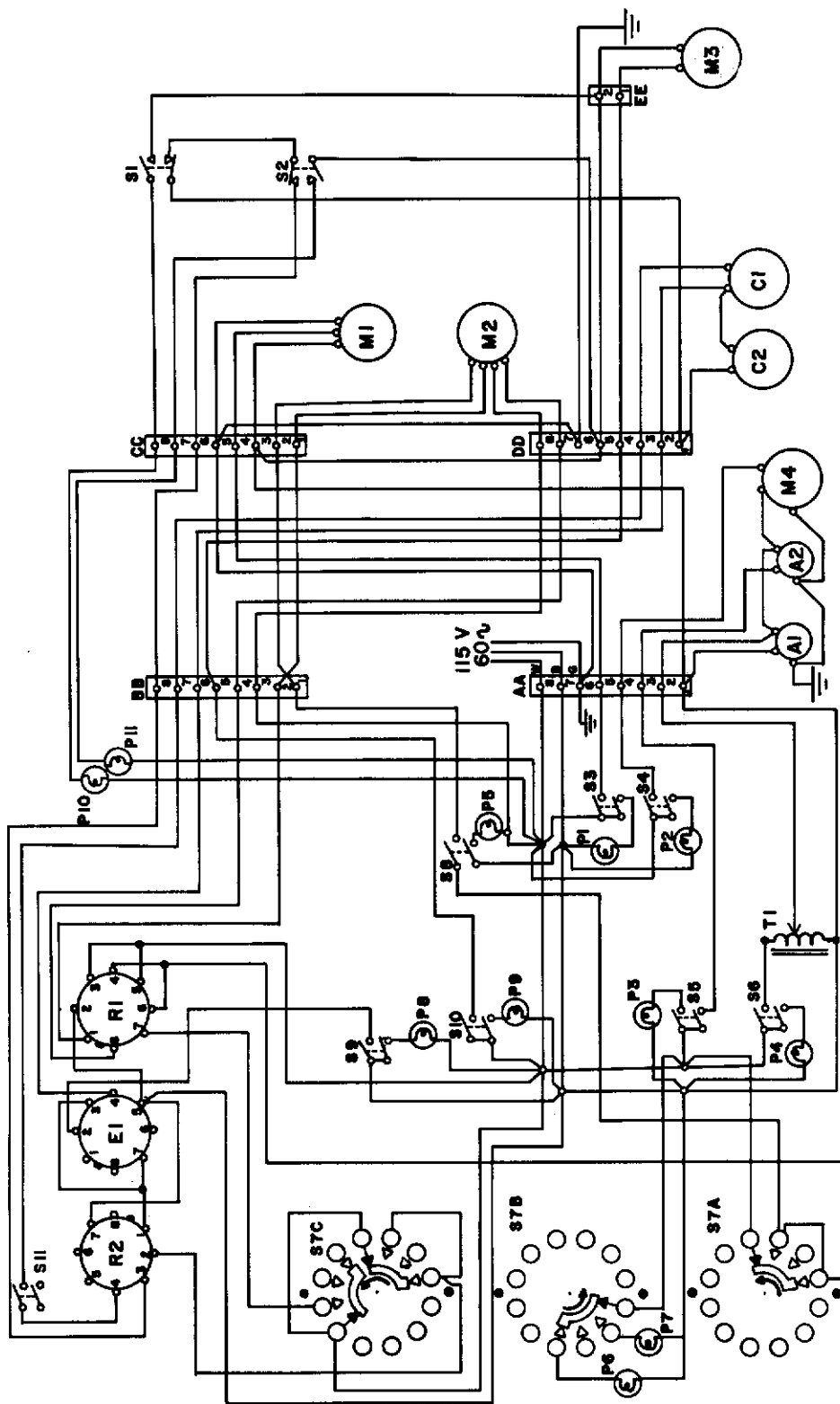
Figure 4a. Wiring diagram for electromechanical systems of the R. F. plasma crystal growth facility.

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VIBRATORS

AI-BOWL
A2-HOPPER

CLUTCHES

CI-SLOW DRIVE
C2-FAST DRIVE

POWER SUPPLY

EI-CLUTCH POWER

MOTORS

MI-SLOW DRIVE
M2-FAST DRIVE
M3-ROTATION
M4-EXHAUST

PILOT LIGHTS

PI-SLOW DRIVE MOTOR
P2-EXAUST BLOWER
P3-HOPPER VIBRATOR
P4-BOWL VIBRATOR
P5-FAST DRIVE MOTOR
P6-UP   ) FAST DRIVE
P7-DOWN)
P8-CLUTCH POWER
P9-ROTATION MOTOR
PIO-UPPER LIMIT
PII-LOWER LIMIT

RELAYS

RI-DPDT
R2-DPDT

SWITCHES

SI-UPPER LIMIT
S2-LOWER LIMIT
S3-SLOW DRIVE MOTOR
S4-EXHAUST BLOWER
S5-HOPPER VIBRATOR
S6-BOWL VIBRATOR
S7-FAST DR. SELECTOR
S8-FAST DRIVE MOTOR
S9-CLUTCH POWER
SIO-ROTATION MOTOR
SII-SLOW DRIVE CLUTCH

TRANSFORMERS

TI-FEED RATE

Figure 4b.   Nomenclature for electromechanical systems
of the R. F. plasma crystal growth facility.

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TO RF GENERATOR

PLASMA TORCH

LOAD COIL AND
CONCENTRATOR

TRANSPARENT
FUSED QUARTZ
FURNACE ENCLOSURE
(MODIFIED 2000 cc
EHRLENMEYER FLASK)

BOULE AND SEED

RELIEF PORTS

GRANULAR
INSULATION

ALUMINA FURNACE
TUBE WITH AUXILIARY
HEATER WINDINGS

FIBROUS INSULATION

FUSED QUARTZ
SUPPORT PLATE

FUSED QUARTZ SUPPORTS

FUSED QUARTZ
FLAME DEFLECTORS

ADAPTOR FLANGE

WATER COOLED
CHUCK HOUSING

Figure 5.   Detail of furnace for R. F. plasma
crystal growth facility.

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Incandescent gases from the plasma stream downward over the boule in almost laminar flow, and also heat the annealing furnace. At the base, the hot gas is deflected by fused quartz plates and discs which protect the positioning devices beneath the floor of the housing; the spent gases dissipate their heat within the water-cooled housing and finally are carried out of the housing by the exhaust blower. The furnace assembly is supported by another fused quartz disc resting on three fused quartz cylinders positioned on triangulated metal posts. During cooling, with the plasma operating at low power levels with reduced gas velocities, it is necessary to plug the relief ports with fiberfrax to eliminate chilling drafts resulting from thermally-induced chimney effects and/or cross-currents caused by the exhaust blower.

As Figure 5 illustrates, auxiliary heat input from an electrical resistance winding (Pt 40% Rh) during the annealing phase of crystal growth had been planned, but to date all experiments have been carried out without the winding to permit evaluation of heat distributions and stability of the 99.5% alumina tube (McDanel AP-35) under exposure to the intense radiation from the plasma. It has been learned that experiments at the General Electric Research Laboratory with si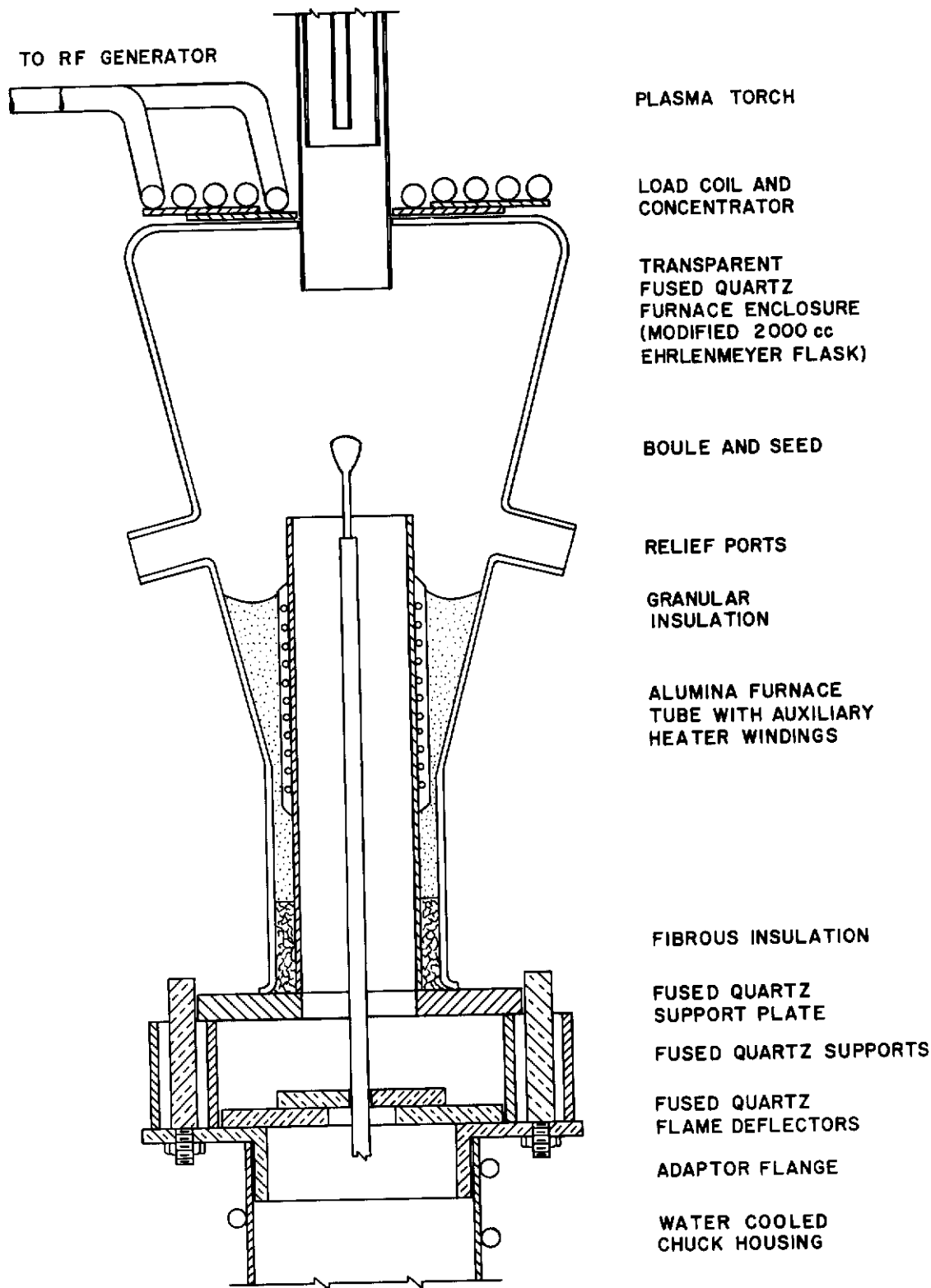milar resistance windings were not satisfactory; the electrically conductive plasma was able to penetrate the ceramic furnace tube and short out to ground through the windings (presumably because the tube was heated well above the temperature at which the ceramic could function as an effective insulator). At General Electric, a combustion-heated annealing furnace has been substituted for the resistance-wound construction.[*]

Materials

An ideal feed material for crystal growth by flame fusion should be extremely pure, and it must be easy to feed at a controlled, variable rate into a gas stream; when injected into the flame, it should melt readily, but not disperse excessively. For oxy-hydrogen fueled Verneuil crystal furnaces, the classic ideal is "sapphire boule powder," an alumina derived from aluminum alum by gentle calcination; it is fairly free-flowing with a relatively low angle of repose. Such materials have very small ultimate

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[*]Personal Communication, E. M. Clausen, General Electric Research Laboratories, April, 1964.

particle sizes, so they melt quickly, but they are agglomerated
in light, floccy masses, which enhance the flow behavior during
feeding.

Spinel of very high purity has also been prepared in a com-
parable manner, by gentle calcination of coprecipitated $Al(OH)_3 \cdot$
$Mg(OH)_2 \cdot x \, H_2O$.[4] It occurs as soft, very friable agglomerates,
and its ultimate particle size is only 40 mμ. Unfortunately, it
differs from sapphire boule powder by having a very high angle
of repose ($> 70^o$). It is very difficult to dispense reliably
from any sort of vibratory feeder (including those with mesh
bottoms); once out of the feeder proper, it is likely to pile up
on hopper walls (60° surface, teflon coated) or to bridge up in
tube bores or torch tips. Apart from greater difficulty in
maintaining consistent feed rates as compared with sapphire feed
material, this coprecipitated and calcined spinel behaved satis-
factorily at high temperatures during crystal growth experiments
in the Verneuil furnace. However, it was entirely too fine for
use in the R. F. plasma facility; the particles had too little
density (and hence momentum) to be able to penetrate the plasma.
Most of the oncoming feed bounced upward off the "hard" plasma,
and thereafter went around it in a dispersive pattern; little or
none actually arrived at the growth face of the seed crystal.

Arc-fused spinel obtained from Muscle Shoals Electrochemical
Corporation (low-soda grade, 99[+]% purity, described on pp. 198,
201 of Ref. 5) has proven to be the most satisfactory material
tested to date in terms of consistency of feed. When calcined to
remove carbon (residual from the arc electrodes) and thereafter
kept free from moisture adsorbed from the atmosphere, the minus
200-, plus 270- mesh fraction feeds satisfactorily, melts well,
and is not excessively dispersed during its passage through and/
or around the plasma. In terms of composition and purity, this
material is not ideal for crystal growth, but it is illustrative
of the coarser, denser physical form required for experimentation
in the R. F. plasma facility.[*] It should be noted that finer

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[*]Arc-melted material of the very high purity desired for
crystal growth is not readily available, and is not likely to be
because of contamination sources inherent in melting and subsequent
crushing. A more likely source of dense stoichiometric spinel ca-
pable of being crushed to yield moderate particle sizings is at-
tainable by hot pressing high purity fine grained spinel obtained
by coprecipitation.[6] To retain the initial high purity of the
hot pressed compact, special crushing and leaching techniques
would be required.

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fractions (minus 270- or minus 325- mesh) of the arc-fused material display very high angles of repose, and are more difficult to feed.

Results of Crystal Growth Experiments

In using the oxy-hydrogen fueled Verneuil torch and apparatus described in Reference 3, the chief experimental difficulty encountered in growing stoichiometric spinel was in maintaining a sufficiently high heat flux to maintain a proper melt at 2135°C without having to employ excessively high gas velocities. At lower temperatures (1950 - 2050°C) where alumina-rich spinels, sapphires, and rubies are readily grown, this problem is much less severe. Very careful manipulation of oxygen and hydrogen flow rates to achieve an optimum stoichiometry were required for spinel. In general, such adjustments fell within the range of uncertainity of the flow meters employed; they were best accomplished by optimizing temperature as determined by a Latronics Color-ratio pyrometer focused directly on the liquid layer of the growing boule.

A second experimental difficulty is related to the choice of proper seed materials. No suitable single crystals of stoichiometric spinel are available as seed stock. The spinel-alumina eutectic at about 1950°C seriously interferes with the use of easily-obtained sapphire seed crystals. Magnesia crystals are refractory enough, and are available, but are not structurally compatible with spinel.[7, 8] Therefore, polycrystalline spinel "slivers" cut from a thin walled crucible have been employed most reliably as "seeds", although they are far from ideal for the purpose. If a polycrystalline column about 0.1 x 0.1 x 1.3 inches is ground to an approximate 60° tapered point and aligned in an alumina candle, it is not too difficult to initiate a transparent melt on the tip, from which a single crystal is presumed to nucleate. Obviously, multiple nucleations are fairly likely; a true single crystal seed would be much preferred on theoretical grounds.

Entirely apart from fundamental considerations, the use of polycrystalline seed stock has one final and frustrating experimental drawback. During growth, each portion of the seed is at some very high temperature, ranging downward from the melting point, 2135°C (or just below), at the base of the boule to perhaps 1800°C at its junction with the candle. The strength of the slender seed at such temperatures is low, probably not more

than a few hundred psi at slow strain rates.[9] As the experiment
progresses, the stress imposed on the seed by the growing boule
increases, and plastic deformation is likely to be induced by
eccentricities in the mass of the rotating boule, or by spurious
vibrations. A number of experiments have been terminated ab-
rubtly by a failure of the polycrystalline seed just beneath the
boule; the white-hot boule drops from the furnace and cracks
under the suddenly imposed thermal stress.

Figure 6 shows fracture surfaces of one such accidentally
cracked boule grown on a polycrystalline seed in the oxy-hydro-
gen furnace. It can be noted in the right hand fragment that
the transparency initially developed was not maintained as the
boule grew larger, but became interspersed with progressively
more bubbly and/or translucent regions. This point is discussed
in further detail in a later section.

Many of the experiments carried out in the R. F. plasma
facility have been single-variable studies concerned principally
with working out a particular problem of feed behavior, of plas-
ma inversion, etc., such that crystal growth per se frequently
was only a secondary objective, or was being used to monitor the
influence of the variable under study. As these various problems
have been worked out one by one, it has been possible to carry
out full-fledged crystal growing experiments under well con-
trolled conditions. In these cases, the principal factor which
is likely to determine the success of an experiment is the diag-
nostic judgement of the operator(s), a problem already discussed
in Reference 3. In most respects, the growth of good quality
crystals in the R. F. plasma facility is dependent on attaining
much the same conditions one strives for in the oxy-hydrogen
furnace, so that criteria upon which operator judgement is based
are not too different between the two units, although the pro-
cedures involved in implementing a corrective change in condi-
tions may be quite unlike.

In the early stages of growth in the R. F. plasma, clear
transparent boules of spinel can be grown on polycrystalline
seeds using minus 200-mesh arc-fused spinel as feed material;
one such boule is illustrated in Figure 7. Blockage of a feed
tube above the torch terminated this particular run so that the
boule was not able to attain a larger size. It was cooled to
about $1600^{\circ}C$ by gradual withdrawal into the furnace with the
plasma source operating at reduced power, and thereafter, when
the plasma had been extinguished, at the natural furnace cooling
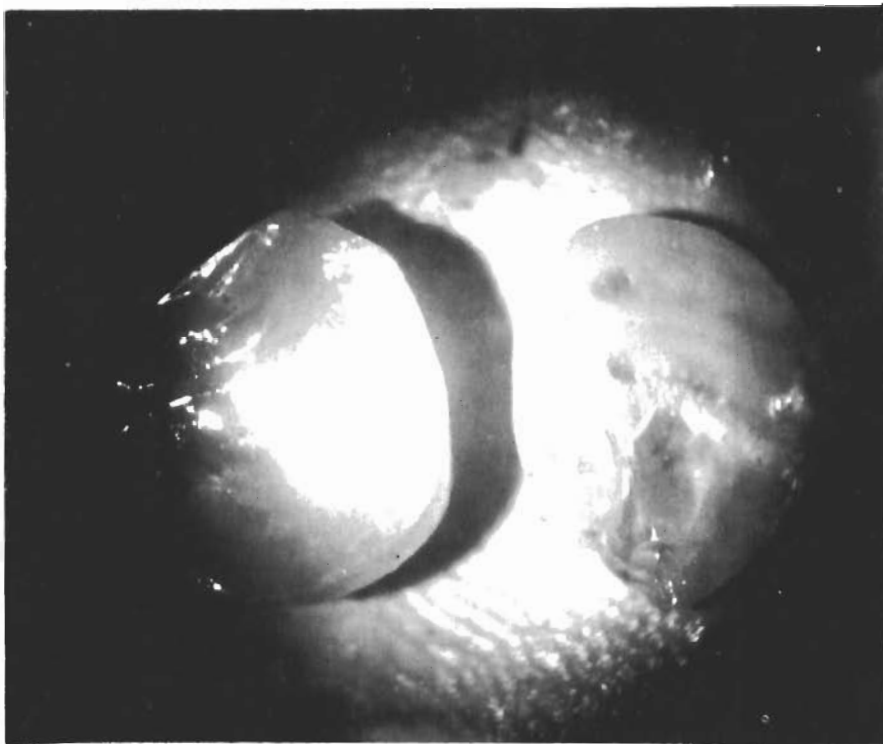rate. Although it is relatively free of flaws and macroscopic

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Figure 6.   Two halves of cracked stoichiometric spinel boule
grown in oxy-hydrogen fueled Verneuil furnace.

fractures, Laue back reflection X-ray photograms indicated a considerable amount of lattice distortion, and a substantial incidence of subgrains.

If sapphire seed crystals are utilized, the growing spinel crystal takes on a morphology which is quite reminiscent of sapphire boules grown upon similarly oriented seeds. This effect is illustrated in Figure 8; the spinel crystal shown in 8a was grown on a $0°$ sapphire seed (c-axis coincident with rod axis) and has the slender, axially symmetrical, columnar growth habit characteristic of this orientation. The epitaxy existing between Al_2O_3 {0001} and spinel {111} is such that the growth direction for spinel should be $<111>$. The crystal illustrated in Figure 8b was grown on a $90°$ sapphire seed, and quickly developed the broad growth surface and blocky shape associated with $90°$ sapphire boules. Either $<110>$ or $<112>$ growth directions are likely for spinel under these conditions, this particular one grew approximately along $<110>$. As previously mentioned, sapphire seeds are not very satisfactory for growing spinel. A fluid, bubbly, and very mobile liquid droplet (presumed to be the spinel-alumina eutectic) was usually formed just beneath the boule and thereafter migrated about over the seed and lower portions of the boule. Such seeds were prone to severe thinning just below the boule and frequently failed because of thermochemical corrosion.

A particularly baffling problem relating to bubbling in R. F. plasma-grown spinel crystals is also evidenced by the illustrations in Figure 8. The bubbling usually does not appear until growth has been completed and cooling has been initiated; what had appeared to be transparent crystal covered with a shallow melt begins to bubble, even to the point of frothing! The phenomenon continued with further cooling until the melt was completely solidified, and perhaps even after solidification. Development of bubbles during or just after growth was more severe when the basic plasma gas (argon) was enriched with oxygen, and was reduced in extent when a dilute hydrogen - helium mixture were substituted. The phenomenon has been consistently observed, even in pure argon, and even when special precautions had been taken to eliminate extraneous gas sources from the system, including carbonaceous residues from
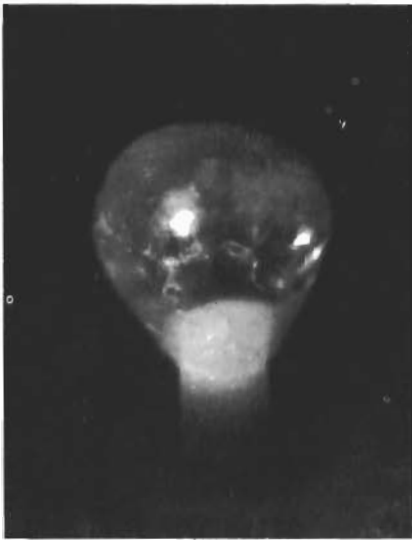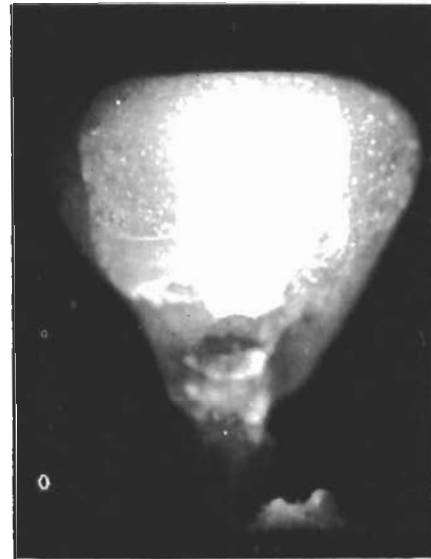
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Figure 7. Two views of a spinel boule grown in the
R. F. plasma crystal growth facility uti-
lizing a polycrystalline seed and minus
200-mesh arc-fused spinel feed material.

(a) 0° Sapphire Seed   (b) 90° Sapphire Seed

Figure 8. Spinel boules grown in the R. F. plasma
crystal growth facility utilizing sin-
gle crystal sapphire as seed material.

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feed materials.[*]

One may analyze the possible causes for the bubbling phenomenon in this way:

(a) The bubbles are created during the early stages of cooling by the evolution of a gas phase less soluble in the crystalline state than in the melt.

(b) The source of the gas creating the bubbles could be extraneous, e.g., air entrained in and near the plasma might be heated enough to cause O_2 and N_2 to react, forming NO_2. However, high flow rates of relatively cool, un-ionized argon surrounding the plasma within its fused quartz enclosure should provide a protective blanket, making this possibility fairly unlikely.

(c) Spinel itself could be disproportionating, yielding a vapor phase, presumably MgO.[11] The vapor pressure of MgO is known to be relatively high at these temperatures, and the stoichiometry of spinel does change when processed in the plasma (see later discussion). However, it is not easy to explain why the bubbles only appear after cooling has begun if MgO is the culprit; $MgO_{(vapor)}$ should be even less soluble in a spinel melt than in a spinel crystal, and it should evaporate more readily from free surfaces than from within the interior.

(d) The possibility of adsorption of argon in the spinel melt during growth and its subsequent release during cooling must be considered. The plasma itself provides a rich source of energetic argon atoms and ions; furthermore, some interaction of the plasma environment with the spinel is suggested by the luminous glow which persists just at the surface of the boule during growth. The marked lattice distortion of particles

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[*]Bubbling in plasma-grown crystals has also been observed by Clausen and Rutter[10] at General Electric Research Laboratory; they attributed bubbling in Al_2O_3 boules to evaporation of impurities initially present in the feed. It should be noted that the bubbling they reported occurred during growth (a phenomenon we have also encountered) whereas our present concern is with bubbling which appears during cooling of an essentially transparent boule.
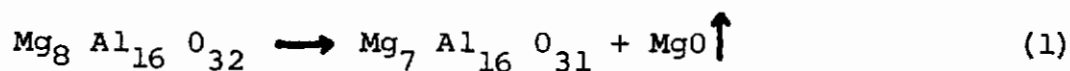
heated in the plasma and quench-cooled thereafter (see later discussion) also could be indicative of some interaction with argon at the high temperatures attained.

(e) Vacancy clusters (aggregations of individual lattice vacancies) might form, grow, and attain "bubble" size at temperatures near the melting point.

Of the several possibilities, argon absorption-desorption and/or vacancy clustering have been considered most likely; they have been studied in some detail, and are discussed below.

Even in this era of noble gas chemistry,[12] one does not suggest lightly that argon has entered into reactions with spinel, nor accept the hypothesis without strong proof. A series of tests were carried out in an attempt to determine the presence or absence of argon. Minus 200-mesh samples of (a) unaltered feed material (b) feed material quenched after a single pass through an argon plasma, and (c) a boule grown from the feed material in argon were subjected to heating to $900^{\circ}C$ in a fused quartz container in vacuo (continuously pumped); periodically gas samples were transferred to a Consolidated Electrodynamics Type 21-620 mass spectrometer, and were analyzed over the range mass 12 to mass 44. Up to $900^{\circ}C$, release of argon (mass 40) was not experimentally evident. It should be pointed out, however, that had argon been frozen in at $2135^{\circ}C$ (the melting point for spinel); the limiting temperature in the mass spectrometer experiments (only $900^{\circ}C$) might well have failed to release detectable amounts. The gases which were detected in decreasing order had masses of 28, 18, and 12; CO was the principal gas present. Since the fused silica bulb had been blown offhand with a gas fueled torch, the container, rather than the samples, could well have been the source of the CO. Thus the experiments to date are inconclusive as to whether or not argon reacts with spinel during processing in the R. F. plasma at temperatures near the $2135^{\circ}C$ melting point. In the absence of any strong proof that argon did contribute to bubbling, some other explanation for the phenomenon is required. Vacancy clustering, discussed below, offers the most satisfactory argument.

As a consequence of evaporation of MgO from spinel, the spinel stoichiometry becomes alumina-rich, with cation vacancies being created in the structure:

$$Mg_8 \, Al_{16} \, O_{32} \longrightarrow Mg_7 \, Al_{16} \, O_{31} + MgO\uparrow \qquad (1)$$

$$Mg_7 Al_{16} O_{31} \longrightarrow 31/32 \left[(Mg_{7.4} Al_{0.4} \square_{0.2}) Al_{16} O_{32} \right] \quad (2)$$
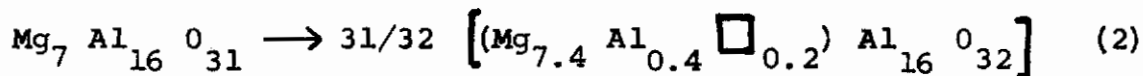
where $\square$ = vacant tetrahedral site.

Attributable to nonstoichiometry, these tetrahedral site vacancies exist in the growing crystal along with thermally-induced anion-cation vacancy pairs of Schottky type. As evidenced by its smaller lattice parameter, the material in the boule has contracted. The required shrinkage could have been accomplished by the evolution of vacancies in clustered form. Formation of such vacancy clusters and their migration toward free surfaces during cooling thus offers a fairly tenable explanation for the bubbling phenomenon under discussion.

Confirmatory evidence for this vacancy cluster hypothesis of bubble formation has come from observations of spontaneous bubble generation in spinel at elevated temperatures. The specimens in this case were polished portions of spontaneously fractured boules of nominally stoichiometric composition grown at the Raytheon Company* which were being employed as controls in a study of plastically deformed crystals being thermally etched in vacuo. During careful microscopic examination of polished surfaces following heat treatment, it was noted that sub-surface bubbles had begun to form as low as 1700°C, and that they gradually increased in size with subsequent treatments at temperatures up to 1800°C. These temperatures are sufficiently high to cause MgO evaporation in vacuo, and it is now thought that the vacancies left behind were clustering to create the microscopically (ultimately macroscopic), bubbles within the crystals.

Lattice constants obtained from X-ray diffraction patterns of (a) feed material (arc-fused MgO-rich spinel) prior to passage through the plasma; (b) the same material after a single pass through the plasma and (c) a crushed specimen taken from a boule grown in the plasma from this feed material are listed in Table 1. The unaltered feed material showed an average unit cell size, a_o, of 8.083Å, as compared with an average of 8.066Å for the ASTM X-ray standard for spinel (card 5-672). After a single pass through the plasma, the lattice constant had

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*Specimens were made available by Stanley I. Warshaw, of the Raytheon Company, whose contributions and helpful discussions are gratefully acknowledged.

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TABLE 1. CHANGES IN THE SPINEL LATTICE CONSTANT RESULTING FROM PLASMA TREATMENT

hkl	$\sqrt{\dfrac{1}{n}}$	STANDARD VALUES		FEED		SPHEROIDS		CRYSTAL	
		d spacing, Å	lattice constant, Å	d spacing, Å	lattice constant, Å	d spacing, Å	lattice constant, Å	d spacing, Å	lattice constant, Å
111	.577*	4.67**	8.093***	4.6707****	8.093	4.6465	8.052	4.6465	8.052
220	.353	2.858	8.096	2.8666	8.120	2.8577	8.095	2.8400	8.045
311	.302	2.436	8.066	2.4422	8.086	2.4422	8.086	2.4169	8.022
222	.289	2.333	8.072	2.3382	8.090	2.3382	8.090		
400	.250	2.021	8.084	2.0230	8.092	2.0187	8.074	2.0018	8.007
422	.204	1.649	8.083	1.6529	8.102	1.6502	8.089	1.6340	8.009
511	.193	1.555	8.056	1.5559	8.062	1.5559	8.062	1.5371	7.964
440	.177	1.429	8.073	1.4289	8.073	1.4289	8.073	1.4192	8.018
531	.170	1.366	8.035	1.3697	8.057	1.3662	8.036	1.3542	7.966
620	.159	1.278	8.037	1.2809	8.056	1.2780	8.038		
533	.153	1.232	8.052	1.2356	8.076	1.2329	8.058	1.2210	7.980
622	.151	1.218	8.066	1.2197	8.077				
444	.145	1.1662	8.042	1.1703	8.071	1.1703	8.071	1.1543	7.961
711	.140	1.1312	8.080	1.1346	8.104			1.1230	8.021
Average			8.066		8.083		8.069		8.002

*n = $h^2 + k^2 + l^2$

**d spacing according to Swanson and Fuyat, NBS Circular 539, Vol. II, p. 35, 1953.

***lattice constants calculated from d spacings ($d = a_o \sqrt{\dfrac{1}{n}}$).

****d spacings according to Geological Survey Circular 29 equivalents.

decreased still more, to 8.002Å. Such a decrease in lattice
parameter is indicative of a progressive loss of MgO, yielding
an alumina-rich spinel solid solution.[8]

Figure 9 shows intensity versus diffraction angle 2θ as
determined in separate studies made with a scintillation counter-
goniometer X-ray diffractometer for the lines which show broad-
ening as a function of plasma treatment. Loss of free MgO, con-
traction of the lattice, and distortion of lattice spacings as a
result of plasma porcessing are clearly evident.

Broadening of the lines, particularly (440) and (511) in
Figure 9b, is thought to be indicative of a tetragonal distortion
of the spinel structure. These particles were heated and cooled
almost instantaneously in their brief passage through the in-
tensely hot plasma, so that the distorted structure may be an
unstable, non-equilibrium one.

The detrimental role played during crystal growth by the
instability of spinel at its melting point is clearly indicated
by these results. Since loss of MgO and consequent contraction
of the spinel lattice appear to depend upon the length of time
of exposure at temperature, it follows that the composition, and
hence the lattice parameter, of spinel in a crystal will vary
according to its particular position in the boule, as well as
according to the size of the boule (i.e. to the total time re-
quired to grow).

If such gradients in lattice spacing do exist, it is appar-
ent that strains of increasing magnitude will be developed as
the size of the boule is increased; such strains are now con-
sidered the probable cause of the spontaneous fractures occuring
during growth and/or annealing which many investigators have
noted as being so characteristic of stoichiometric spinel.[3, 13]
Along this same line of reasoning, it seems quite probable that
the overfeeding technique reported by Lefever[14] (which builds up
a polycrystalline jacket around a single crystal core of stoi-
chiometric spinel) contributes to successful growth as much by
acting as a barrier capable of preventing MgO losses by evapora-
tion, hence stabilizing the composition, as it does by insulating
against thermal shock fractures.

In concluding this section on crystal growth, some final
points are worthy of comment which stand out from our overall
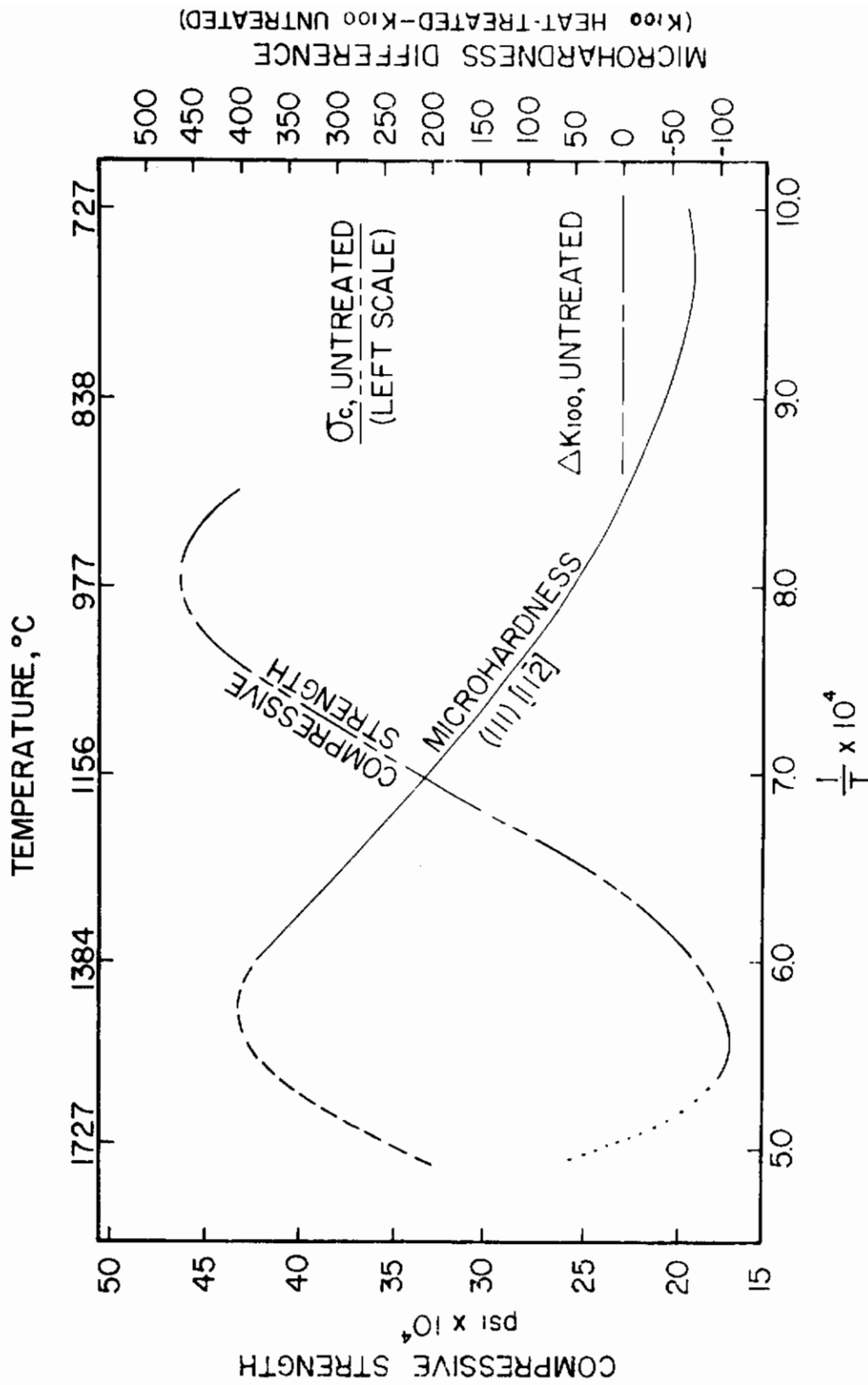experience, and some future directions for research on growth of

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Figure 9. Intensity versus diffraction angle, 2θ, for (a) arc-fused MgO-rich spinel feed material, (b) the same feed material after a single pass through the plasma, and (c) a crushed specimen taken from a boule grown in the plasma utilizing this feed material.

spinel are reviewed. The evaporative losses and structural changes which occur in $MgAl_2O_4$ at or near its melting point are thought to be particularly detrimental to the growth of large whole boules of accurate cation stoichiometry and high quality by flame fusion processes. There is but little difference to be found between oxy-hydrogen and R. F. plasma heat sources insofar as instability is concerned; the basic problem is that feed particles and the boule itself must be maintained at temperatures near the melting point for relatively long periods of time, during which the spinel progressively changes.

Another basic difficulty with any flame fusion process relates to its need for very uniform deposition through a dynamic gas transfer medium of properly heated feed particles within a rather localized space-temperature zone. This need, together with the purity levels required for high quality crystals, places very stringent demands on the electromechanical feeding device, even with free flowing material. These requirements also complicate torch design and heat transfer. The high angles of repose and packing tendencies characteristic of spinel feed materials further compound the problem, so that, of the many experimental problems, material feed has been the most difficult to get, and keep, under control.

We have come to the conclusion that flame fusion (regardless of heat source) and indeed, any other method requiring the material to be kept at its melting point, is not likely to yield good single crystals of stoichiometric spinel of a sort useful in studies of mechanical properties. Therefore, it is our opinion that future research on spinel crystal growth should be directed toward methods which can operate at lower temperatures.

Such methods fall into two basic types, i.e., (a) growth by crystallization from vapor deposits or by pyrolysis, or (b) growth by crystallization from a fluxed melt (including hydrothermal "melts" fluxed with H_2O). A recent example of the former is found in the work by Schaffer[15] on growth of Al_2O_3 single crystals by vapor deposition. In adapting the method to spinel, it would be necessary to achieve equal activities of both cation species in the vapor phase at the deposition temperature. The work of Austerman[16] on flux-grown BeO single crystals may be cited as an example of the second type of moderate-temperature process.

The Czochralski[17] method of crystal growth is considered to be particularly favorable for attaining the sizes, shapes, and

freedom from defects desired in boules for mechanical property studies; its success is attested by its wide use in growing silicon and germanium crystals for semi-conductor applications. For spinel, the Czochralski technique is not thought to be applicable for direct growth from a pure spinel melt, first, because of the instabilities of spinel at such temperatures, and second, because of the difficulty in finding a non-reacting crucible which will contain the spinel melt. Experiments already have eliminated graphite, molybdenum, tungsten, and tantalum in vacuo or inert gases; iridium is perhaps the only likely candidate, and its chances of success are considered marginal. On the other hand, Czochralski pulling of spinel crystals from fluxed melts (at temperatures far below the melting point of spinel) does appear to offer a promising direction for continuing research (already underway on a limited scale with University funding).*

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*While traveling in England (June, 1964), one of us (W. W. Kriegel) has learned that Dr. E. A. D. White, Hirst Research Center, General Electric Company, Wembley, has been growing spinels by pulling from a fluxed melt. Complete information is not available at the time of writing.

MECHANICAL PROPERTIES

The microhardness and compressive strength of alumina-rich spinel single crystals have been studied as a function of the state of exsolution of the excess alumina.[18] When the boule is quickly cooled from the molten state at the conclusion of growth the excess alumina remains in metastable solid solution. If the boule subsequently is heat treated at temperatures above 1000°C the excess alumina precipitates in the form of epitaxially oriented α-Al_2O_3 platelets which have their basal planes coincident with the (111) planes of the spinel matrix. As the exsolution progresses over the range 1000 - 1400°C the Knoop microhardness increases; the temperature time-atmosphere-hardness relationship determined in these studies is statistically different for indentations normal to [112] and [110] directions, respectively, on (111) planes in spinel.

Over the range 700 - 1000°C, the hardness studies suggest an annealing effect attributable to the thermally activated dissipation of surface cold work resulting from cutting and polishing, and of internal strains residual in boules quenched from the growth temperature.

In metals, hardening of this sort is usually associated with concomitant strengthening, but a parallel study of compressive strength at room temperature for heat treated spinel crystals indicated that, at room temperature, microhardness and strength are _inversely_ related (Fig. 10). Both properties responded to annealing in the 700 - 1000°C range, but in opposite ways. By comparison to untreated material, annealing produced a 6% decrease in microhardness and a 34% increase in compressive strength (to 436,000 psi). At higher temperature, e.g., 1400°C, hardness had increased 31% above that of the untreated control ($K_{100} \approx 1135$), but the strength had fallen by 50%, reaching a minimum of about 156,000 psi (~56%) at 1520°C.

At a higher test temperature, 1000°C, the compressive strength of [110] -oriented spinel crystals which had been heat treated was quite different from that measured in room temperature tests. The average compressive strength of the samples which had been heat treated at 1021°C was 183,000 psi (in comparison to room temperature data, this represents a reduction in strength of 56%) while samples heat treated at 1357°C decreased to 150,000 psi, a reduction of only 7% from the room temperature strength value. A tentative explanation for this

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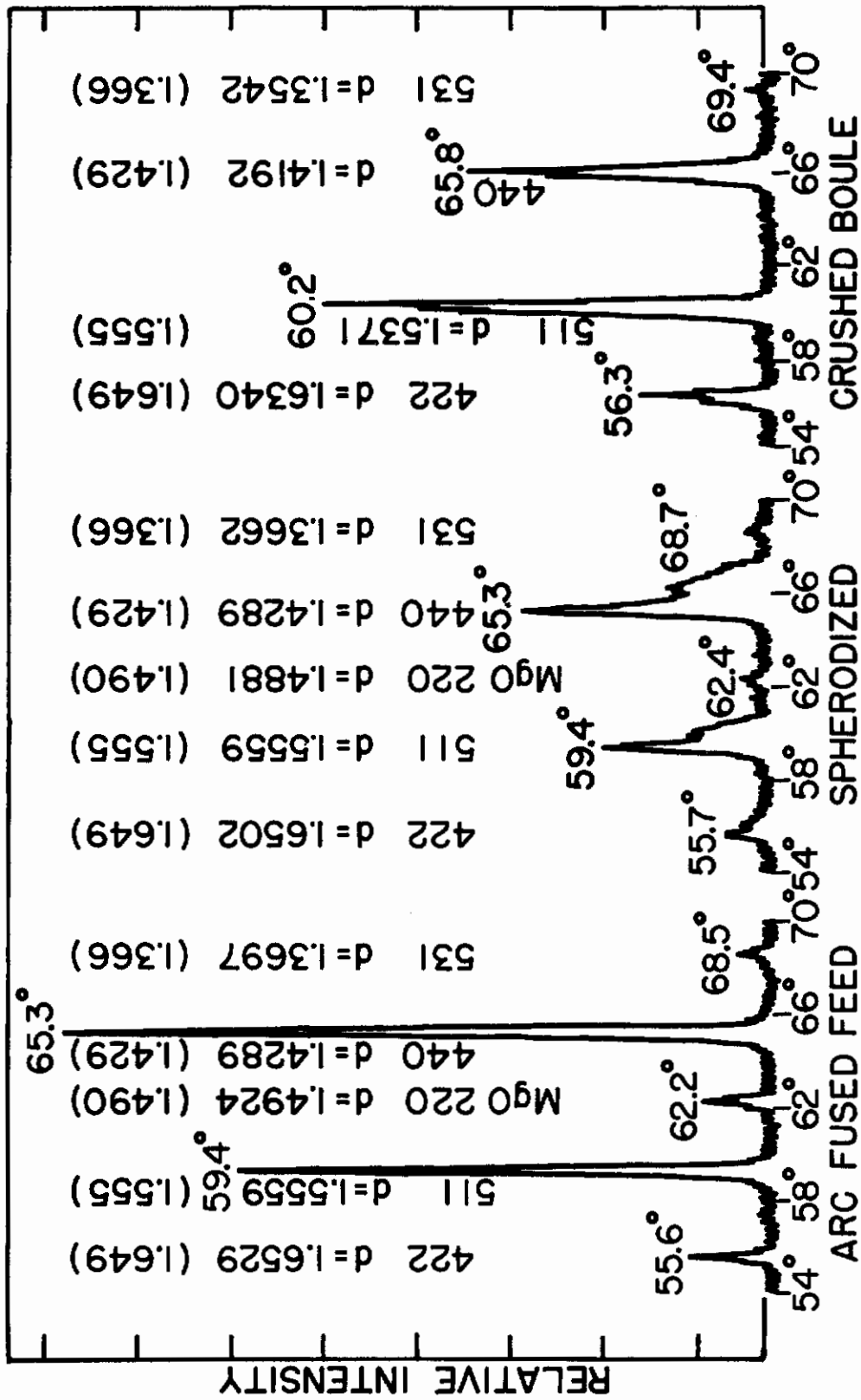
Figure 10. Predicted variations in microhardness and compressive strength as functions of temperature for heat-treated alumina-rich spinel single crystals.

RELATIVE INTENSITY

CRUSHED BOULE

531 d=1.35542 (1.366)

d=1.4192 (1.429)

440 69.4°

65.8°

70°

66°

62°

511 d=1.5371 (1.555)

60.2°

422 d=1.6340 (1.649)

58°

56.3°

54°

SPHERODIZED

531 d=1.3662 (1.366)

68.7°

70°

440 d=1.4289 (1.429)

65.3°

66°

MgO 220 d=1.4881 (1.490)

62.4°

62°

511 d=1.5559 (1.555)

59.4°

58°

422 d=1.6502 (1.649)

55.7°

54°

ARC FUSED FEED

531 d=1.3697 (1.366)

68.5°

70°

66°

440 d=1.4289 (1.429)

65.3°

MgO 220 d=1.4924 (1.490)

62.2°

62°

511 d=1.5559 (1.555)

59.4°

58°

422 d=1.6529 (1.649)

55.6°

54°

phenomenon is that the limited mobility at 1000°C of dislocations in previously annealed spinel resulted in some slip on the two intersecting (111) planes oriented to receive equal levels of resolved shear stress. Intersections and pile ups of dislocations on these two planes during the initial portions of plastic strain led to crack formation, thus inducing brittle failure at very small strains and low stress levels.[19, 20, 21] In the case of two phase samples which had been heat treated at 1357°C, dislocations were pinned by the precipitate and thus were not mobile enough to induce a comparable reduction in strength through dislocation interactions. It should be noted that most of the internal strain attributable to thermal expansion mismatch between alumina and spinel, so detrimental to room temperature strength in heat treated specimens, will have been relieved during heating to test temperature, hence it is not a particularly significant factor in strength at 1000°C.

At 1500°C, spinel crystals oriented so that [110] was the load axis underwent considerable deformation, displaying upper and lower yield points and a significant amount of work hardening (Fig. 11). The flow stress was strongly dependent on strain rate.

At still higher temperatures (1800°C), single crystal spinel specimens tested on spinel anvils initially began to deform, but work-hardened, raising the flow stress. Thereafter, most of the applied stress went into deforming the dense polycrystalline anvil blocks, not the test specimen; these tests consequently were inconclusive. No non-reactive anvil material with sufficiently high compressive strength has been found to permit unambiguous strength and flow measurements in spinel crystals at these higher temperatures. However, at low crosshead strain rates (≤ 0.02 in/min.) and at stress levels up to 3,800 psi, tungsten anvils have been successfully employed in deforming spinel crystals at 1800°C.

Specimens deformed at 1500°C and above changed shape in an unusual and characteristic way: the {110} column face paralleling the <110> load axis became significantly broader due to intersecting slip on the two families of {111} slip planes which received equal levels of resolved shear stress in this orientation. The orthogonal {100} column face broadened slightly due to intersecting slip occurring in {111} planes between the two slip systems operative on {111} (i.e., utilizing the two <110> Burgers vectors which have components in the shear direction).[22]
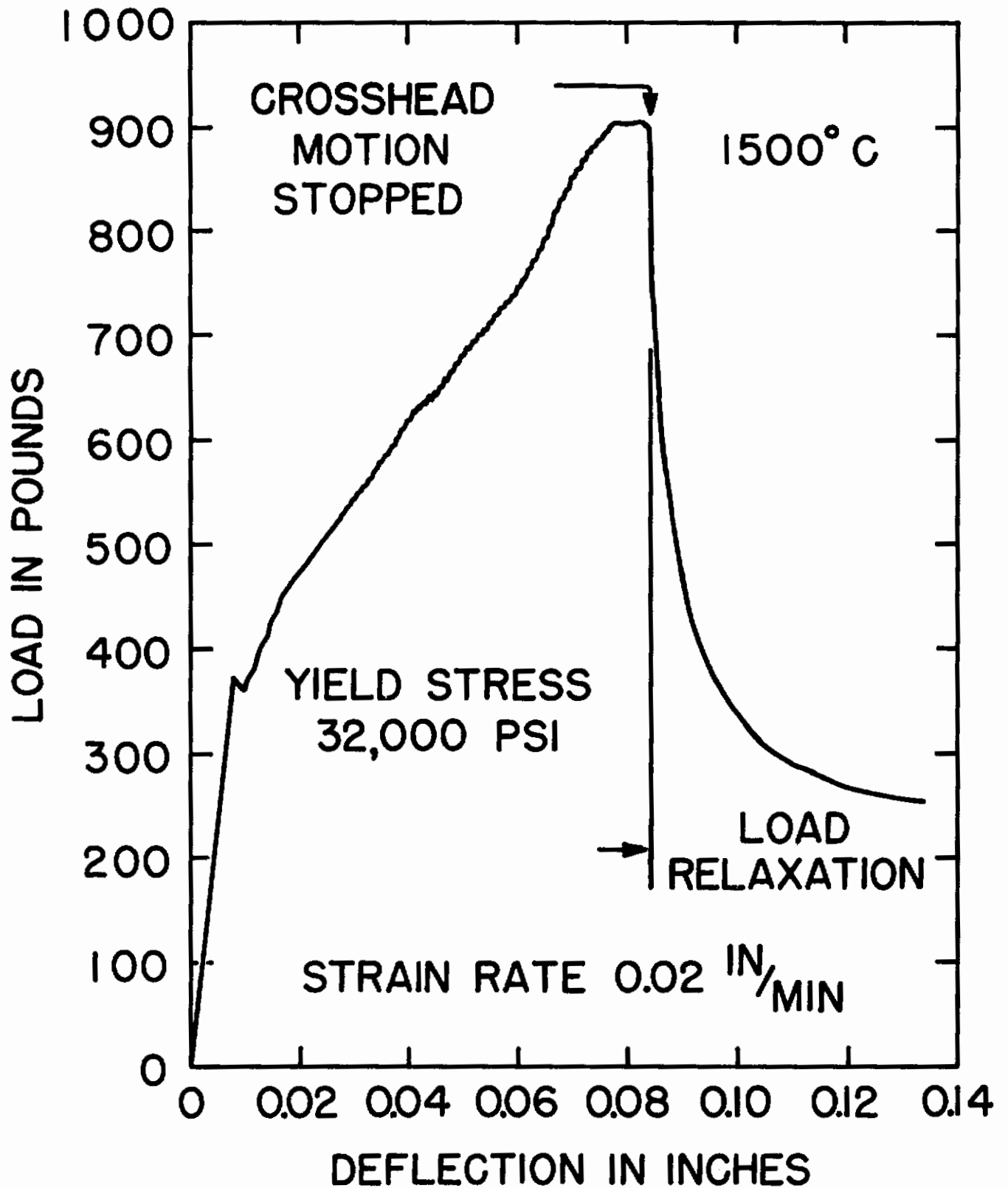
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Figure 11.   Load versus deflection for alumina-rich
             spinel single crystal with a [110] load
             axis tested at 1500°C.

At 1800°C, a specimen deformed 4.4% along the $\langle 110 \rangle$ load axis had broadened 4.9% in the $\langle 100 \rangle$ direction on the orthogonal $\{110\}$ face, but had increased by only 0.5% in the $\langle 110 \rangle$ direction on the $\{100\}$ face. With extensive flow, a third deformation type appeared: the upper portion of the $\{100\}$ face became visibly offset from the lower. This phenomenon is related to the usual immobility of dislocations on vertically oriented sets of $\{111\}$ planes which were subjected to normal rather than shear forces along the one operable $\langle 110 \rangle$ Burgers vector; such a situation favors a special type of deformation called kinking, which probably accounts for the observed behavior.[23, 24]

The extremely stable spinel compound is almost immune to chemical attack; hence the usual chemical etch pit reagents and techniques employed for studies of dislocation concentrations and interactions in other oxides have not been applicable. In the course of this investigation many reagents have been tried, with at best only partial success. An etchant (H_2SO_4 at 200°C for periods of about one hour) which reveals dislocation termini and subgrain boundaries was developed,[25] but it proved to be effective only on $\{111\}$ planes, and thus it has not been of much value in seeking evidences of slip bands on $\{110\}$ or of kinking on $\{100\}$ faces of specimens extensively deformed in compression at high temperatures.

Attempts at thermal etching _in vacuo_ also failed to reveal the specific evidences of plastic flow being sought, but they did bring out another significant fact. Regions which had been extensively deformed at high temperature did _not_ develop an exsolved alumina second phase, whereas unstressed control specimens (or even portions of the same crystal specimen which had been protected from extensive deformation by the clamping effects of end restraint) did show marked exsolution after the thermal etch treatment.

Excess alumina in solid solution in spinel is thought to be the "impurity" which contributed to upper-lower yield points in stress-strain plots obtained at 1500°C (Fig. 11). A strong interaction between alumina impurities and mobile dislocations is also evidenced by the reluctance of extensively deformed regions to revert to the thermodynamically stable two phase state. It is not clear pending further study whether deformation might stabilize the spinel-alumina solid solution by providing favorable sites for Al^{+++} in the strained regions surrounding dislocations, or in a less likely alternative, whether Al^{+++} might be

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swept out of the strained area by moving dislocations, thus reducing the alumina content of the solid solution below the level at which exsolution can occur.

The strain-stabilization phenomenon is of interest from a purely scientific standpoint, but in addition, it carries one very practical implication: plastic straining (hot working) might afford a novel means of stabilizing alumina-rich spinel solid solutions against subsequent thermally-induced exsolution of the embrittling second phase, thus avoiding the severe strength losses which have been observed at room temperature in heat-treated crystals containing exsolved α-Al_2O_3.

SUMMARY

The construction of an R. F. plasma crystal growth facility has been described, and its operation in studies of growth of stoichiometric $MgAl_2O_4$ crystals at $2135^{\circ}C$ has been discussed in detail. Despite some encouraging results and some near-successes, it has become apparent that the R. F. plasma heat source is in itself not an answer to the problem of growing spinel single crystals of stoichiometric composition. An analysis of what happens to the feed material and to the beginning boule strongly suggests that instability of the compound $MgAl_2O_4$ at its melting point makes direct fusion synthesis of high quality stoichiometric spinel crystals fairly unlikely regardless of the means employed. Other alternative avenues to successful growth of spinel single crystals at lower temperatures, e.g., Czochralski pulling from a flux-melt, have been suggested.

The mechanical strength and microhardness of spinel single crystals having alumina-rich stoichiometry have been extensively studied as a function of the state of exsolution of excess alumina. A boule quenched from the growth temperature retains the excess alumina in solid solution, but when subsequently heat treated at temperatures higher than $900 - 1000^{\circ}C$, the metastable solid solution reverts to the stable two phase system spinel-alumina. The second phase exsolves in the form of epitaxially oriented α-Al_2O_3 platelets contiguous on their (0001) planes with (111) planes in the spinel host crystal. As exsolution progresses over the range $1000 - 1400^{\circ}C$ the surface microhardness increases; the temperature-hardness relationship is statistically different in [112] and [110] directions on (111) spinel planes studied by Knoop microindentation.

The room temperature compressive strength follows an _inverse_ path in comparison to hardness as a function of heat treatment: annealing causes an increase in strength, and exsolution of alumina at higher temperatures embrittles the crystal and materially weakens it. Annealed spinel crystals averaged 436,000 psi, those heat treated at $1500^{\circ}C$ only 156,000 psi, whereas untreated control specimens were tested at 336,000 psi.

Crystals tested in compression at $1000^{\circ}C$ were nominally brittle, but had lost the sensitivity to weakening attributable to exsolution in prior heat treatment. Previously annealed crystals suffered a 56% loss in strength over room temperature

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values due to crack initiation resulting from dislocation inter-
actions during straining. Those tested at 1500°C and higher
were extensively deformed in truly plastic fashion, with evi-
dences of intersecting slip within slip planes and interpene-
trating slip between slip planes.

These several observations of strength and flow at elevated
temperatures in spinel single crystals clearly demonstrate the
plastic deformation of spinel. The operation of multiple (111)
[110] slip systems in spinel (at least four in the least favor-
able [110] load axis orientation) has been observed, and the
likelihood of a kinking contribution to deformation in this
same orientation has been demonstrated.

Finally, it has been noted that after extensive deforma-
tion at high temperature, exsolution of excess alumina from spi-
nel was not induced in the strained region of the crystal speci-
men by subsequent heat treatment, although it did develop in
less-strained regions of the same crystal and in unstrained con-
trols. Entirely apart from the scientific interest in inter-
actions between mobile dislocations and alumina "impurities,"
the strain-stabilization phenomenon is worthy of practical in-
terest as a possible means of stabilizing the mechanically
strong spinel solid solution by appropriate hot work, thus a-
voiding embrittlement and loss of strength due to exsolution.

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