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FILE NO. XXXI-22

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RESTRICTED

REFRACTORIES IN TURBINE BLADES

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

CAVENDISH LABORATORIES.
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TELEPHONE: LANGHAM 1373.

DEBG/IB.

C.S.A.R.,
Royal Gun Powder Factory,
Powder Mill Lane,
Waltham Abbey.
For the attention of Mr. Verschoyle.

11th April, 1946.

Dear Mr. Verschoyle,

I have looked up the references that I quoted to you Tuesday with regard to refractory heat interchanger, and find that it is described in the supplement and miscellaneous sections of C.I.O.S. Report on "Refractories in Turbine Blades" item No. 1,18,21,25, file No. XXXI - 22.

Yours sincerely,

REFRACTORIES IN TURBINE BLADES PLUS MISCELLANEOUS APPLICATIONS

Reported by
S.S. KISTLER, T.I.I.C.

CIOS Target Numbers 1/331, 1/349
1/467, 18/63a, 21/23, 25/82, 27/205.
Radar
Armored Fighting Vehicles
Metallurgy
Aircraft
Instruments & Equipment

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

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INTRODUCTION

In the time available it has not been possible to cover all of the German refractory industry concerned with special high temperature refractories. Rather, it has been the objective of this investigation to cover the work done in several important companies on the adaptation of refractories to gas turbine blades. Two miscellaneous targets of opportunity are included.

COMBUSTION TURBINE BLADES.

In the design of gas turbines, the most important single factor controlling the efficiency is the temperature at which the gases enter the power turbine from the combustion chamber. Thermodynamic calculations show that the higher this initial temperature is the greater can be the fraction of the sensible heat of the entering gases converted to useful power. Such factors as the pressure used, the compression ratio, the interchange of heat between the exhaust gas and the entering air and the efficiency of the compressor are all important in determining overall efficiency, but the initial temperature is the single variable that establishes uniquely the maximum possible performance.

Normal flame temperatures are far too high for any of our present materials of construction, and consequently these materials become the most important limitation in combustion turbine design. Refractory lining of the combustion chamber or cooling of its walls is practical, so that the critical parts are the turbine blades in a reaction turbine or the nozzles and blades in an impulse turbine.

The practical utilization of the combustion turbine as an efficient prime mover has necessitated the development of turbine blades with high strength, high resistance to corrosion and low creep at high temperatures. Conventional alloys serve to 1000° F, while newly developed and expensive alloys have raised the permissible operating temperature to 1500° F with an accompanying large increase in efficiency. Due to the tendency of all metals to yield slowly under load at high temperatures, there is no bright prospect for again raising this top operating temperature by a substantial increment.

Whereas in America where the elements of these high temperature alloys were relatively abundant during the war, they were increasingly scarce, and almost unobtainable toward the end of the conflict, in Germany. This scarcity directed attention to the possibility of utilizing nonmetals in turbine construction.

CERAMICS FOR TURBINE BLADES

Several German organizations turned their attention to a study of ceramics for blades. In general porcelains and glasses have three main disadvantages. They are mechanically weak, they are brittle and they can be broken by steep temperature gradients (so called thermal shock). Their advantages are two, viz: they are inert to oxidation regardless of temperature and certain types show mechanical rigidity at temperatures well in excess of those attainable by metals.

Since at present there is no hope of producing a nonbrittle ceramic, attention was divided between compositions for high strength and thermal shock resistant compositions.

For strength, no ceramic has been produced to compete with sintered alumina. Its tensile strength is approximately 38,000 pounds per square inch at room temperature and decreases very little up to 1830° F. = ≈ 1000 Even at 2200° F the tensile strength is still 20,000 pounds per square inch. The compressive strength figures for room temperature and 2200° F are 450,000 and 4826 bar 70,000 pounds per square inch respectively. Due to the low specific gravity compared to metals, roughly one half, the centrifugal force on a blade of sintered alumina is only one-half of that on one of metal. In a centrifugal field of 10,000 gravity, roughly the order in practice, a three inch high blade would be stressed to 4,300 pounds per square inch at its base.

Since all ceramics are rigid and nonyielding, one of the primary problems involved is that of attachment of the ceramic blades to the metal turbine runner so that stresses will be uniformly distributed over the cross-section. The difficulty of attachment is further increased by the fact that ceramics and metals have, in general, quite different coefficients of thermal expansion.

The problems of attachment loomed so high to Prof. Schmidt that he abandoned the effort to use ceramic blades on the rotor and confined his attention to ceramic stator and water cooled rotor blades, although he did give some effort to the construction of a turbine in which the portion that is normally stator rotated while the normal rotor was stationary. In this way the rotating blades were put under compression instead of tension.

On the other hand, Siemens, Neuhaus, devised a blade design and mounting method that showed great promise, blades of sintered alumina in the first and only test tried attaining a speed of 30,000 r.p.m. on a radius of 40 cm before breakage occurred.

Sensitivity to a thermal gradient is increased by a high modulus of elasticity and by a high coefficient of thermal expansion, and decreased by high strength and by high thermal conductivity. For use in airplanes, a combustion turbine may be subjected to sudden and violent temperature changes as power is suddenly applied or cut off, and considerable attention was given to the development of ceramics that would be insensitive to such changes. Hescho experimented with a composition, Ardostan, with a thermal expansion only a sixth of that of sintered alumina and also with compositions containing silicon carbide for high thermal conductivity. Berlin Porcelain made very thermal-shock resistant blades of bonded silicon carbide, and Siemens achieved the same result by incorporating iron in sintered alumina.

None of the compositions that were developed for their resistance to sudden temperature change are as strong as sintered pure alumina, nor do they retain their strength as well to high temperatures. The selection of material for a specific application must, therefore, depend upon the relative importance of strength v. heat-shock resistance. From the narrow standpoint of turbine blade design and composition, the easiest solution lies in placing them under compression by the centrifugal force, in which case they can be made of materials resistant to thermal shock and will have adequate strength.

The above materials considered are highly crystalline. Glasses such as fused silica have been found entirely unsuitable due to their rapid devitrification at the desired temperatures, and to their tendency to creep.

LFA. BRAUMECHWEIG

The Herman Göhring Luftfahrtforschungsanstalt (LFA) was visited on June 20 to interrogate Professor Ernst Schmidt and Mr. Soehngen on their attempts to adapt ceramics to combustion turbine construction. Their sole interest was in the application of gas turbines to aircraft propulsion, and consequently some of their efforts were not well balanced. Apparently through their activities the following firms were stimulated to do work on the manufacture of ceramic blades:-

Hescho, Hermsdorf near Jena.
Stemag Berlin and Nuernberg.
Berlin Porcelain, Berlin and
    Selb bei Bayreuth.
Degussa, Stierstadt bei Frankfurt.
Siemens Neuhaus, bei Sonneberg.
Osram, Berlin.

The strongest blades that were offered to them were made by Degussa and Siemens from sintered alumina. Koppers also furnished strong blades of alumina containing 1 - 2% magnesia. The alumina was relatively sensitive to heat shock and consequently much of their attention was devoted to other products.

Four turbines were made or projected before the work was terminated. The first, T-1, was to have a rotating shell and stationary axis thus putting the rotating blades in compression. The parts were ordered but due to a low priority their delivery was greatly delayed and extensive work was done in the interim on water cooled blades. The results were so successful that T-1 was never completed, and T-2, a four stage unit with only one row of blades mounted, was built. This had a tip diameter of 12.6 inches and a speed of 660 feet per second. With the hot gas at 2200°F, the mild steel blades ran at 700-900°F. The air was compressed to four atmospheres and the exhaust was at half an atmosphere.

Various ceramics were tried for stator blades but failed at a temperature of ca 1470°F, apparently due to poor heat-shock resistance. Alumina-iron compositions were not tried. It was Prof. Schmidt's belief that 2200°F could be reached with proper root fixtures and a not too high rate of temperature change.

Turbine T-3 was to have all four stages mounted. It was never run.

Turbine T-4 was in the course of design. It was to have been built by MAN to operate at 2200° F and have water cooled blades. The output was to be 5000 kw.

A solid ceramic rotor was considered impractical.

Attempts to mount ceramic blades in metal footings followed four approaches. Pressed iron powder proved unsuccessful due to the different coefficients of expansion of the iron and ceramic. Silvered blades silver soldered into the footings failed due to fusion of the solder. Sprayed metal was too slow to build up. The best method found was to tamp iron powder around the blade set in a recess in a steel block. The recess was the same shape as the blade but a little larger. The powder was then sintered.

The interrogator was impressed by a lack of ingenuity in solving mounting problems.

For other pertinent reports see:

CIOS Report on Research and Development on Gas Turbines at LFA by H. Constant, MAP.

CIOS Report on The Development of Ceramic Materials for use in Gas Turbine Engines at LFA by F/L G.H. de Witt, RCAF.

Materials used or on hand for turbine blades with brief comments were:-

Steatite

At 1650°F the tensile strength is only 3000-4,500 pounds per square inch and its "Dauerfestigkeit" is small. It shows considerably more resistance to heat shock than sintered alumina, but shows a bad ageing effect involving grain growth and loss of strength.

Porcelain

Strength about that of Steatite. Not as good shock resistance, also ages.

Ardostan

High resistance to heat shock, due to very low coefficient of thermal expansion. No strength data or observations on ageing.

Calit

Relatively strong, tensile strength 18,000 pounds

Silicon Carbide

Products bonded with alumina, alumina plus silica, Calit and Kaolin plus additions experimented with, the last being best. Strength in cross bending 5,500 pounds per square inch, oxidation in 100 hours at 1830°F very slight. Heat shock resistance very good. Regarded as second best material for stator blades. Glazed blades from Berlin Porcelain, Selb, regarded as best.

Alumina plus Iron

Siemens, Stemag and Osram furnished this combination. Strength sufficient for startor blades. Optimum percentage of iron not yet determined, but probably lies between 30-50% by weight. Important to have very finely divided iron and to sinter at a high temperature. Most of the shrinkage during sintering occurs between 2560° and 2870°F. A fifty-fifty mixture sintered at 2870°F showed only 0.2% oxygen uptake on heating at 1830°F for ten hours.

The strength of a 30% Iron mixture was considerably increased by heating briefly to 3450°F. Cross bending ≈1900°C strength 22,000 pounds per square inch. On long time stressing the cross bending strength drops to 700-5,000 pounds per square inch, depending upon sintering temperature. At 1540°F the cross bending strength of an unidentified specimen was 37,000 pounds per square inch.

An iron alumina specimen can be heated to 1470°F and quenched in cold water without injury. A specimen was heated to 1470°F and quenched with a cold air blast forty times without harm. Quenching with a cold air blast is more severe than in cold water. This composition is regarded as the most promising for stator blades.

Further details on composition and tests were unavailable, due to the destruction of laboratory records by foreign laborers and U.S. soldiers.

MAN, Augsburg

From the interrogation of Professor Dr. Doug. Emil Sorensen of the Machinenfabrik Augsburg-Nürnberg A.G. by S.T. Robinson USNR and R.S. Sproule, RCAF, on June 23, 1945, CIOS Black List 5, the following account of the activities at this plant concerning refractory turbine blades was obtained.

The experiments, designed to find a suitable refractory for a temperature of 1470°F and a peripheral speed of 490 feet per second, extended over six years.

Sintered silicon carbide had attractive properties due to its strength at high temperatures, but it could not be molded to dimensions and grinding proved very difficult. For example, it required four hundred hours to remove 0.1 inch from the root of a sample blade. (Such inefficiency is almost unbelievable!) They did not try to cement the blades into a root fixture.

A whole runner, including blades, was made for them by Heraeus Glasschmelze of Hannau of fused quartz for RM 1200. It was eight inches in diameter and was designed to be held to steel shafts by a through bolt. Its resistance to thermal shock was not considered sufficient for aircraft applications. Also the tendency of the fused quartz to crystallize was regarded as a disadvantage.

Sorensen concentrated his attention on porcelanic materials fired at 1400°. The best found was a mixture of quartz, aluminum silicate and manganese dioxide or manganese silicate. All materials showed a serious drop in tensile strength above 1470°F. Room temperature strength of the materials studied varied between 5700 and 17,000 pounds per square inch.

No practical application of ceramics to gas turbines was made.

An appendix gives a list of laboratories and firms engaged in gas turbine research and development.

See also USTAF Tech. Intelligence Report No. A 422.

HESCHO, HERMSDORF near Jena

Dr. Fritz Obenaus, director of the porcelain works, Dr. Scheid, Technical Manager and Dr. Kaase, who is taking Dr. Rath's place were interrogated on their experimental work on the production of gas turbine blades. Found that Dr. Rath, their best authority and one of the best ceramists in Germany, had shortly before been evacuated to some unknown destination by the U.S.Army, apparently through the efforts of Mr. Brensford and Mr. Clark, who had spent two weeks in the plant. Their interest was in high frequency insulation. Dr. Rath was also a Privat Docent at the University of Breslau.

The compositions with which this company experimented for turbine blades were their trade named products Calit, Sicalit and Ardostan. The work on turbine blades had been under way only a short time and, therefore, meagre quantitative data were available.

Measurements were confined to tensile and cross bending strengths between room temperature and 1830°F. A good deal of effort was devoted to evaluation of the results in relation to the character of the fracture obtained. They feel that much can be learned on the quality of the particular article by examination of the fracture surfaces. Tensile measurement at elevated temperatures were slow due to the fact that the furnace takes only one specimen at a time, so that more attention was given to cross-bending in a furnace in which 18 specimens could be tested at one time, each being supported at the ends and independently loaded at the center by a link and ceramic rod passing through the bottom of the furnace and in turn being loaded by a lever and weight below. Due to the large spread in results with ceramic bodies, they took many measurements for a single value.

They had projected centrifugal tests on actual turbine blades, but had not yet started them.

Since the maximum firing temperature available was ca 2550°F, compositions with very high softening temperatures could not be produced.

The preferred methods of forming turbine blades were slip casting or pressing, prefiring to 1400°F, shaping the relatively soft article and then firing to ca 2500°F. They successfully extruded hollow blades.

Some data could not be found and it was assumed that Dr. Rath had taken it with him. Experiments were projected in which ageing effects, flow and breakage under long time stressing were to be studied.

Calit

The composition of Calit was given as:-

Soapstone	65.8%
Wildsteiner Ton	16.2%
Barium carbonate	10.8%
Magnesium "	7.2%
	100%

The most frequent tensile strength values range between 6000 and 9000 pounds per square inch at room temperature, with numerous single values both above and below. At 1830°F, the median is slightly higher.

In cross-bending the most frequent values center around 20,000 pounds per square inch at both room temperature and 1830°F.

Ardostan

The composition is:-

Kaolin	44%
Bentonite	4%
Silemanite	18%
Feldspar	10%
Soapstone	21%
Witterite	3%
	100%

The most outstanding feature of Ardostan is its exceptionally low coefficient of thermal expansion, $1.1 \times 10^{-6}/^{\circ}C$. It naturally makes Ardostan very insensitive to sudden changes of temperature. The low coefficient is due to the formation of cordierite on firing.

Tensile strength ranges around 6000-7000 pounds per square inch with no temperature dependence up to

1830°F.

The quality of the fracture was in general better than Calit.

Sicalit

Sicalit is Calit containing about 40% by weight of silicon carbide. It can be heated to redness in thin sections and plunged into cold water without harm. No measurement had been made on the rate of oxidation at elevated temperatures, nor had any attempt been made to glaze it.

The most frequent cross-bending strength values ranged between 22,000 and 28,000 pounds per square inch at temperatures between normal and 1830°F.

No tensile figures were available.

Other physical properties for the first two ceramics are:-

	Calit	Ardostan
Compressive strength	130,000 pi^2	48,000 pi^2
Modulus of elasticity	$17\text{x}10^6$	$14\text{x}10^6$
Specific heat	0.2	0.2
heat conductivity		
$\frac{\text{k. cal}}{\text{N m}^\circ\text{C}}$	1.9-2.2	1.7-2

SIEMENS, NEUHAUS bei SONNEBERG

Dr. Wm. Bussem, research director, Dr. Koenig, Works Manager and Dr. Hans Reusch were interrogated. Sintered alumina is a well established product with them (Sinterkorund). They were the first in Germany to undertake its manufacture commercially, and now make laboratory ware, fine tubes and rods for use in vacuum tubes, pyrometer tubes, spark plugs etc.

Preparation of the Slip.

Pure alumina of a grade for metal manufacture is purchased. The seller calcines it to a temperature unknown to Siemens. This calcination is important for the subsequent grinding and slip production. If the calcination temperature is too high, grinding is made difficult, apparently due to formation of too coarse crystals. If it is too low, the washing of the slip is difficult and the cast density is low.

There is evidence that the fine crystals are somewhat tabular.

Grinding is in an iron ball mill dry. It is continued until the bulk of the particles lie between 0.5 and 3 microns, with the most frequent particles 1 micron in diameter. The powder is then digested with 6% hydrochloric acid for 8 days at 122°F. The object is twofold, viz., to dissolve all iron and to etch the particles to condition them for the production of a good slip. If the concentration of hydrochloric acid is too high, subsequent washing becomes difficult.

To prepare the slip, the above slurry is diluted with water and washed by decantation until the hydrochloric acid content is reduced to 1.5%. The iron content is then approximately 0.3% $FeCl_3$. In this condition a good slip is readily formed without any organic or inorganic additions.

Casting is into plaster molds which remove some of the iron and alkali from the alumina. The remaining iron chloride and alkali volatilize on firing.

Very fine tubes and rods for the radio industry are extruded under a pressure of one ton per square inch. For this purpose, 3% gum tragacanth is added to the slip.

Firing

Firing is carried out in a gas fired tunnel kiln 43 feet long, 11 inches wide and 4 inches high. The temperature rises rapidly as the ware progresses through the kiln to a maximum of 3180 to 3270°F, depending on the size of the pieces being fired. Cooling starts immediately so that the ware is at the sintering temperature not more than half an hour, and the total cycle is complete in 40 hours.

The short time at top temperature is designed to prevent crystal growth. Their observations indicate that better physical and electrical properties result if the ultimate crystal size is held at a minimum. When the ware is fired in the tunnel kiln as above, microscopic measurement of the crystals gives dimensions of approximately 11x17 microns. Fired in a periodic kiln in which the ware is held at top temperature longer, the crystal dimensions were 23x27 microns.

In the tunnel kiln the linear shrinkage of the ware amounts to about 21 ± 1%. If, on the other hand, the alumina has been pressed at 4500 pounds per square inch instead of being cast, the shrinkage is 17%.

The top temperature to which it is necessary to fire alumina in order to get a well sintered product is largely dependent upon the particle size, and to a lesser extent on the size of the article being fired. With more coarsely ground alumina, the firing temperature may exceed 3450°F.

The tunnel kiln is of conventional design in which there is a heat recuperator consisting of parallel alloy steel tubes overlying the ware in the preheating zone and then passing over a baffle above the hottest zone before going to the burners. The tubes reach a temperature of ca 1800°F, and the temperature of the air entering the burners is 600-950°F.

Properties

Chemically, the sintered alumina is 99.6% Al_2O_3. The impurities consist of 0.1% Fe_2O_3, 0.1% MgO, 0.2% SiO_2 and a trace of calcium and alkali. For electrical purposes it is very important that the quantity of alkali be held very low.

The physical properties are:

density 3.8 - 3.9 g/cc.
porosity 1-4%
specific heat 0.20
thermal expansion 3.1×10^{-6} per °F. for 70-248°F
" " 4.3 " " " " 70-1690°
modulus of elasticity
single crystals 71×10^{6} pounds/sq. in.
polycrystalline 43 " " " "
(porcelain 14×10^{6} pounds/sq. in.)

tensile strength, room temperature	37,000	pounds/sq. in.
tensile strength at 1830°F	34,000	" "
cross-bending strength room temperature	49,000	" "
compressive " " "	430,000	" "
" " 1830°F	120,000	" "

(porcelain cross-bending strength 8,500 pounds/sq.in.)
heat conductivity = 21 kg. cal/hr m°C.
(porcelain = 3-4)
water absorption zero.

Siemens have a method of measuring heat shock resistance in which a differential temperature is established between periphery and center of an annulus of the material and gradually increased until rupture occurs. The temperature differential at rupture is numerically the heat shock resistance. By this method pure sintered alumina has a value of 90 whereas sintered alumina containing 2-3% SiO_2 has 130. The other physical properties of this product containing the silica are close to those of the pure alumina. It has, however, a greater tendency to flow under stress when hot than pure alumina, and is more readily attacked by PbO when used in spark plugs.

Pure sintered alumina shows no sign of a glass phase when examined in thin sections with polarized light.

The largest part of Siemens sintered alumina business is the manufacture of spark-plug bodies, of which they made 200,000 per month in 1944. They were cast to shape and were not ground after firing.

In their manufacture a defect often occurred in the nature of minute cracks on inside surfaces. The cause was traced to a grain orientation at the plaster surface. The oriented layer shrinks differently from the body of the insulator, causing cracks. An addition of 0.7%

MgF_2 to the slip prevents the cracks from forming. The explanation is not understood but it is surmised that the MgF_2 makes crystal growth more uniform in all directions. All of the fluorine evaporates from the mass on firing.

Turbine Blades

Preliminary work was done on the manufacture of sintered alumina turbine blades. The composition and technique of production was the same as for their other products. The picture shows one such blade.

Their method of mounting was clever and as a first attempt was very successful. As can be seen from the picture, a broad, thick base was cast on the blade, with two grooves in one side and one in the other. This base was silvered, heated to 800° to obtain adhesion and then copper plated to a thickness of one millimeter. The object of the heavy copper coating is to provide some cushioning between the sintered alumina base and the steel rotor, the copper being soft enough to flow and permit a better distribution of stresses. The blade is anchored in the runner by means of three round steel pins inserted into the three grooves in the base and matching grooves in the runner.

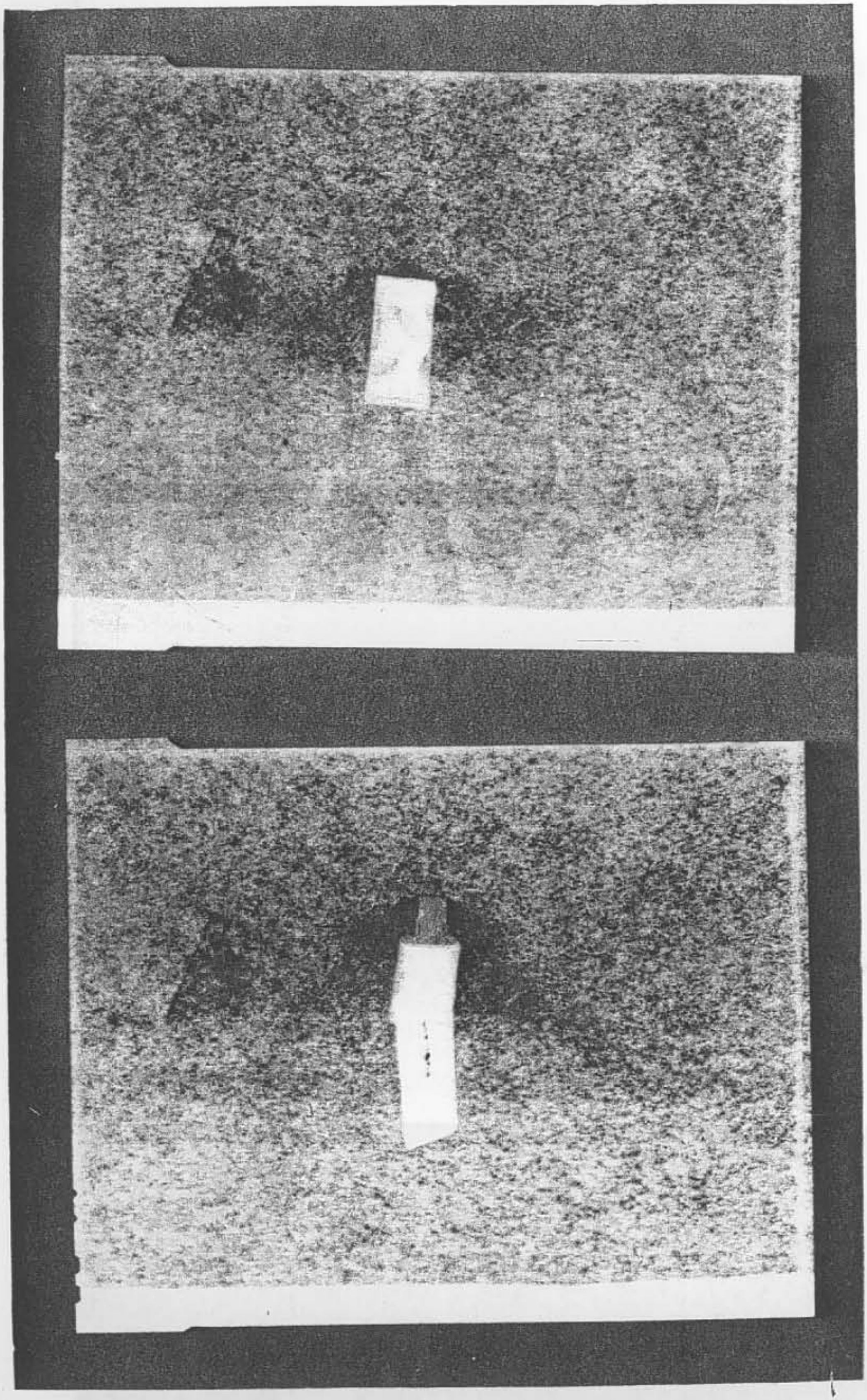
One experimental rotor 80 cm. in diameter was built up in this way and tested by slowly increasing the speed. No blades broke until 30,000 rpm was reached.

Sintered Iron-Alumina

In some former experiments searching for a good semiconductor, it was observed that when very fine carbonyl iron powder and alumina were sintered together, the conductivity suddenly increased tremendously as the iron content was increased above about 50% by weight. Reasoning that below this point the iron particles were sequestered within the alumina, it occurred to Siemens that iron-alumina mixtures might serve as turbine blade material, it having been observed that these compositions were very insensitive to sudden temperature changes.

Most of the work was done in Berlin and therefore relatively little data was available at Neuhaus. It appears, however, that the strength of such mixtures is good, being half of that of pure sintered alumina at 60% iron content, and that the impact strength is increased. They claimed not to have done any work on rate of oxidation of the mixtures. Sintering was done in an inert or reducing atmosphere.

10,000 volts/in.



The Siemens men appeared not to be as frank on iron-alumina as with the other matters, and it was sensed that they held back information that they could have given.

Sintered Rutile

Siemens made sintered pure rutile by the same process as alumina. The dielectric constant was 100, the loss angle $2x10^{-4}$ at one megacycle, and the dielectric strength was 10,000 volts/mm.

DEGUSSA, STIERSTADT

Dr. Gustav Jaeger was interrogated on July 9, 1945, concerning pure oxide refractories. The technique of producing them is similar to that used by Siemens, with enough differences to make a description desirable.

Preparation of the Slip

Calcined pure alumina is ground for 30-70 hours wet in an iron ball mill using steel balls. It is important that the alumina should be calcined. There is no upper temperature limit, and fused alumina can be used. Sixty to seventy percent of the particles are under five microns.

The resulting mud containing about 250 kg alumina in 1000 liters water is acidified with 20-40 kg concentrated hydrochloric acid and is heated by running in steam for about half an hour. The time is not important. Washing is by decantation two to three times. The cake is kept moist and may be stored indefinitely.

When ready to cast, the slip is made 0.5-1% acid with HCl, the concentration not being important. The workers think that more acid is required for small articles than for large. Casting is done in plaster. The distribution of grain size from the technical mills is about right for maximum density.

Reyschkewitz, when he was with Degussa, experimented with grinding to a maximum particle size of 1.5 micron in a dry ball mill by shaking with a frequency of 5-10 per second.

Large pieces, e.g., 25 x 6 x 2 cm can be slip cast. There is little danger of cracking during the drying, but the large pieces are apt to crack in firing because of the shrinkage of 18-20%.

The finished pieces are about 99% alumina, the remaining one percent being silica, soda, iron oxide and calcium oxide.

Firing

Firing is in a special surface combustion furnace of pure magnesia about 80 cm high and 35 cm diameter. It has been described by Reyschkewitz in Chemische Fabrik 1, 61 (1930); Feuerungstechnik 18, 173 (1930); Ceramic Oxide Single Material Systems, J. Springer, Berlin.

The temperature rises in ca 6 hours to 3420-3500° F, is held there about 3 hours, and cooling takes 6-10 hours. Since the operation of the furnaces is a bit capricious at these temperatures, the time that the maximum temperature is held is varied to compensate for different top temperatures. Also heavy pieces are fired longer than light.

Jaeger did not feel that there was serious danger from crystal growth, although it is important to have an atmosphere as free as possible from soda and oxygen to prevent recrystallization. The product contains up to 2% pores, which attempts to sinter in vacuum did not improve.

Products

Tubes, crucibles, rods, mortars, boats, dishes, thread guides, radio tube insulators, fine hones, grinding wheel truing discs and special bricks make up the bulk of their production, which amounted to approximately 1000 kg per month and was rising rapidly during the war. They have also learned to make wire drawing dies, but they were not yet in commercial production.

Sintered alumina can be used as a cutting tool for plastics, aluminum and copper alloys and even for iron. It is important to have the lathe very free from vibration. Cutting speeds are high and depth of cut small. Competition with sintered tungsten carbide would have to be on a price basis.

Sintered alumina makes excellent gauge blocks.

Degussa also makes sintered magnesium spinel, BeO, ZrO_2, ThO_2 and MgO. These special refractories represent only 10% of their business, of which BeO amounts to 6-7% leaving 3-4% for all others. They are all sintered at the same temperature as alumina. Pyrometer tubes 15 x 600 mm, crucibles and boats are the main items into which these other oxides go. Thoria and berylia can be made impervious. When magnesia is made, the iron is left in. It is always porous.

Physical Properties

A comparison of the compressive strengths of the various products at different temperatures is given below. The values are in thousands of pounds per square inch.

Temp.	Al_2O_3	BeO	ZrO_2	ThO_2	MgO Al_2O_3
20°C	425	114	300	213	270
200	327	100	270	170	241
400	255	87	249	127	206
600	198	74	220	93	170
800	156	60	192	64	135
1000	106	47	164	43	100
1200	67	53	114	21	43
1400	35	21	21	7	21
1600	7	8	-	-	-

The tensile strengths of three products are compared. The valves here are again in thousands of pounds per square inch.

Temp	Al_2O_3	BeO	$MgO \cdot Al_2O_3$
20°C	37	18.5	21.0
200	36	15.6	17.7
400	35	12.7	15.9
600	34.5	10.0	13.6
800	34	7.4	11.1
1000	32.2	4.7	
1200	18.5	1.8	5.3

The influence of the burning temperature on the shrinkage and modulus of elasticity of sintered alumina is given below:

Temp	Shrinkage	$E \times 10^{-6}$
1100°C	0.7%	1.7 pounds/sq. inch
1200	.8	2.1
1300	1.1	3.0
1400	1.9	4,3
1500	3.9	7.1
1600	7.4	12.
1700	12.3	30.
1800	19.0	50.
1900	19.0	50.

The strength of well sintered alumina is as high as that of single crystals, therefore when the sintered product is broken, the fracture goes through the crystals.

Degussa made turbine blades for both LFA and MAN of alumina. Believe that it is the best material for the purpose.

At 1000°C (1830°F) the creep strength after loading many weeks was found to be 15,600 pounds per square inch. The lack of resistance to thermal stress fatigue at low temperatures disappears with temperature rise due to slight plasticity. The ability to deform becomes noticeable at 1400°C (2550°F), although it is observable at room temperature.

For turbine blades a combination of alumina with silicon carbide or metals may be the answer. Silicon carbide does not react with it at 1900°C (3450°F).

Other references: Ordnance Target Report No.58 by Martin Fleishmann.

The following are all by Dr. Reyschkewitz:

Uber die Druckfestigkeit einiger oxidkeramischer Werkstoffe, Ber. Deutsch. Keram. Geo. 22, 54 (41).

Uber die Zerreisfestigkoit einiger oxidkeramiecher Werkstoffe, ibid 23, 243 (1942).

Torsionsmodul einiger keramischer Werkstoffe, ibid, in print.

Relation of tensile strength of ceramic materials to sintering temperature, ibid 25, 95 (1944).

Microscopic investigations of ceramic oxide materials, Hdbk. Mikroskopischer Arberts Methoden in der Technik, by Freund, Wetzlar.

Chemical Properties and corrosion Resistance --- Chem. Zeit. 64, 284 (1940).

Plastische Deformbarkeit Spröder Korper, Ber. d. Gastechn. Ges. 20, 166 (1942).

MISCELLANEOUS CERAMICS

Titanium Dioxide Dielectrics

While time was too limited to cover many of the ceramic specialities in Germany, opportunity permitted a visit to three plants manufacturing condenser dielectrics, and without making any pretence at covering the field thoroughly, a brief report on these is here included.

Hescho, Hermsdorf and Siemens, Neuhaus were visited for other purposes and a few details concerning the titania delectrics picked up, however, most of the information was obtained through Lutz & Co., in Lauf, since they were supposed to have carried the development of these bodies farthest.

Dr. Rother at Lutz is the experimental physicist who did the work. He claims to have made over 2,000 compositions from which the following have been selected. He wrote a prospectus containing much advertising glamor under the date July 15, 1945, parts of which will be translated below. Quotation marks will indicate direct quotation from the prospectus.

For communication purposes, the development of high dielectric constant refractories has been very important. The size of the oscillating circuits is greatly reduced, and the sharpness of the resonance peak is improved by the use of dielectrics with a high constant. Since the temperature stability of an oscillating circuit is influenced by the temperature coefficient of the dielectric constant and by the coefficient of expansion of copper, these two factors can be made to oppose each other so that the natural frequency of a circuit becomes relatively independent of temperature, a very important factor in Germany where extensive use of quartz crystals was not possible.

To recapitulate, the three important properties of a condenser dielectric are:-

A high dielectric constant, a controllable temperature coefficient, and a low dielectric loss.

"On the basis of the work of the author, it is now possible to achieve a high dielectric constant and a very small dielectric loss in the same mass. These products are as shown in Group one."

"An extremely high value of the dielectric constant has been achieved as shown in Group two. In the laboratory, dielectric constants as high as 2,000 have been reached. Values up to 500 are in production."

From personal interrogation it appears that the stability of the very high dielectric constant materials was not satisfactory. While certain specimens with constants as high as 2,000 were produced, reproductability was not achieved. Apparently firing conditions as well as composition are very important. Also, some of these materials have a tendency to change value with age. Theoretically, Rother predicts values as high as 8,000.

"In addition to the high dielectric constant of these new materials, which in Group one possess negative temperature coefficients, it is possible to vary this negative coefficient or even to make it positive".

Group 1.

New ceramic products with dielectric constants up to 100.

Composition 924

Rutile S 1053	69 parts
"Kronos" titania	10
Lanthanum oxyhydrate	10
Zirconium hydrate	10
Beryllium carbonate	1

Dielectric constant ca 90

Frequency, cycles	800	5000	10,000	300,000
Loss angle x 10^4	3	1.5	1.5	1

Temperature coefficient of the dielectric constant ca $-700 \times 10^{-6}/^{\circ}C$.

Composition 336

Rutiox	97 parts
Lanthanum oxyhydrate	1
Zirconium hydrate	2

Composition 336 (Cont:)

Dielectric constant	ca 105	
Frequency	1000	300,000
Loss angle x 10^4	7	0.5-1

Temperature coefficient same as 964.

Composition 267

Rutile	80.7 parts
Rutiox	9.5
Barium Carbonate	4.8
Zirconium hydrate	5

Dielectric constant ca 95
Loss angle x 10^4 at frequencies of 0.3-50 megs

room temperature	0.5
100° C.	5.0

Temperature coefficient of dielectric constant $-650 \times 10^{-6}/°$ C.

Group 2.

New ceramic products with dieletric constants over 100.

Composition 164

"Kronos" titania	70
Rutile S 1053	10
Titanium trioxide	13
Lanthanum oxyhydrate	7

Dielectric constant 405 at 800 cycles
Loss angle x .1360 at 800 cycles
Temperatufe coefficient of dieletric constant $- 1800 \times 10^{-6}/°C$

The dielectric constant appearw to have a branched dependence on frequency.

Rutile S 1053 above was obtained from I.G. In general, it is desirable to use a mixture of particle sizes, which explains the appearance of two grades of titanium dioxide in most of the formulas. It is important to produce a dielectric of maximum density, preferably with zero porosity.

The Kronos titania is a commercial form of anatase

The best results were obtained with very pure lanthanum containing less than one percent of didimium.

Dr. Rother suggests that some interesting ceramic bodies capable of producing phase shifts in high frequency radiations could be produced by welding together masses of high and low dielectric constant.

The general directions for the production of these ceramics are as follows:-

"The raw materials in the most finely divided form are mixed in a porcelain ball mill in approximately the proportions 1/3 each flint balls, powder and water.

"In general, the water amounts to approximately 2,5 litres for each 2 kilograms of powder. This is an approximate figure and the actual amount of water is regulated to give a satisfactory slurry. Grinding is continued for approximately 100 hours.

"At the end of grinding, the slurry is passed through a 140 mesh screen into a tank with propeller stirrer. It is kept in agitation to prevent segregation while it is being pumped from this tank to the filter press.

"The filter cake is ground in an edge mill and again passed through a screen to give a powder of suitable particle size for spreading in the desired forms.

"This powder, which must contain a certain amount of moisture, is then pressed into the desired shapes according to conventional ceramic technique. The burning can take place in a conventional ceramic tunnel kiln, the time varying from 10 to 75 hours depending on the shape and size of the pieces. The temperature used is between 2,500° and 2,550°F. The exact burning conditions depend upon the kiln and the shapes being fired.

"The finished pieces must frequently be given an electrically conducting metallic coating. The well known fired silver coating is satisfactory. A commercial silver preparation is applied by spraying or brushing, dried and the pieces heated for half an hour at approximately 800°C. For a heavier coat, this process can be repeated or more metal applied galvanically."

Paramagnetic Products

Lutz & Co., offered two types of ceramic bodies with increased magnetic permeability. The first is represented by a composition F.11. which consists of soapstone 15 parts, and magnetic iron oxide 85 parts.

"The masses with increased permeability are prepared exactly as described above. By firing in a reducing or an oxidising atmosphere, one can obtain either very low or very high electrical conductivity. For a reducing atmosphere, it is sufficient either to prevent access of air during the burning or to flush out the oven before burning with nitrogen".

The properties of F.11 dielectric are a magnetic pearmeability of 2.8, a magnetic loss angle of zero, an electrical loss angle of 0.06, and a dielectric constant of 5.2.

By using iron powder in the ceramic, permeabilities of 14 have been obtained, and higher are predicted. Dr. Rother believes that by combinations of magnetic pearmeability, dielectric constant and electrical conductivity, articles extremely useful for the high frequency industry can be produced.

For convenience of comparison with other available dielectrics in Germany, the following table of compositions being commercially produced by Hescho and Siemens is included. Siemens may have produced a series of dielectrics, but only the one listed came to our attention.

Dielectrics offered by Hescho and Siemens (not complete for Siemens).

		Dielectric Constant	Loss factor x 10^4 at frequency of 800	1000000	Temp coef. of D.K. x 10^6 at $f = 10^6$	Specific Resistance at 200°C
Hescho	Condensa	C. 80	30-120	5-10	-680 to -860	7×10^8
	"	F. 80	4-15	1.5-5	-680 to -860	4×10^9
	"	N. 40	30-65	5-20	-360 to -480	9×10^8
	Tempa	S. 14	3-50	0.5-1	+ 30 to + 90	2×10^{10}
	Tempa	T. 40	25-70	0.5-1.5	0 to -100	-
Siemens		100	-	2	-800	-

A V A (AERODYNAMISCHE VERSUCHSANSTALT), GOTTINGEN.

Dr. L. Ritz was interrogated on June 22 regarding his ceramic heat transfer device for returning some of the exhaust heat to the compressed gas before entering the combustion chamber. His exchanger is in the form of a porous disc or drum ground true so that as it rotates each element alternately passes between sets of ports, and has first hot exhaust gas from the turbine blow through it and then cold intake air drawn through. In this way by properly adjusting the rate of rotation to gas flow and temperature conditions a high percentage of heat transfer can be accomplished.

He has found that the thermal shock in going from the hot to the cold stream is not too great for ordinary porcelain. In order to achieve low weight and low pressure drop through the exchanger, he has made it a mass of parallel tubes of ca 1 mm diameter and wall thickness ca 0.15 mm. This was accomplished by layimg 1 mm rods of wood or plastic in a porcelain slip, spacing them suitably e.g., by means of cloth, drying, heating slowly to a preliminary burn of 800°C, grinding to shape, firing to a suitable final temperature, and finally lapping to dimensions. If wood was used, the ash was blown out to avoid contaminating the procelain during the final burh.

One method that he described for constructing the exchanger was to support the plastic rods in a web of nylon, running this through the slip and building up the body by lamination. The nylon is so strong that it requires only very thin webbing, which, when burned out does not leave large enough openings to short circuit the tubes.

Although the tube walls are very thin, the pressure drop between hot and cold ports is distributed between many walls and the strength is adequate.

One of the main difficulties in construction lies in grinding the surfaces true. The thin walls tend to chip and crack. He, therefore, prefers to grind after a prefire since the mass is then not so brittle as finally.

Ritz estimates the weight of such an exchanger for an aircraft turbine to run 0.1-0.15 kg per horse power, exclusive of housing.

For aircraft use a cylindrical design is preferred in which the exchanger surrounds and is coaxial with the turbine.

Ritz does not think much of Schmidt's water cooled blades, particularly for a reaction turbine. He believes that it is preferable to use an impulse type in which the expansion occurs in refractory nozzles and therefore the blades are not subjected to suh high temperatures and can be of metal. He described a two stage turbine, each with a single row of blades. His plan was to drive the compressor with one stage, have a heat exchanger between stages and take the power from the s econd stage. The two turbines would operate at independent speeds. His projected turbine for aircraft was to weigh 6500 kg, would devaop 15,000 hp at sea level and 5,000 hp at an altitude of 10 km. The efficiency would be 42-44%.

He has already obtained mozzles of an unknown ceramb composition from the Berlin Porcelain Co.

SUPPLEMENT

VISIT TO SWITZERLAND

Upon returning to London, considerable interest was shown in ceramic gas turbine blades, and it was urged that as complete a story as possible be secured. In view of the fact that the gas turbine for power purposes, other than airplane, has probably reached its highest development in Switzerland and that Brown Boveri also had a branch factory in Germany where, it was rumored, use was being made of Dr. Ritz heat recuperator, it was decided to visit Switzerland and try to cut short the labor of finishing the study.

Brown Boveri

Brown Boveri, Baden, Switzerland, was visited on August 24th by Prof. Stoughton and the author. Dr. Meyer and Mr. Thut were very hospitable and appeared to answer our questions frankly. They, very disappointingly, had only general information on what was done in Germany during the war. No exchange of knowledge had been permitted with their plant at Manheim. Dr. Meyer knew a little of the LFA, Braunschweig, work under Prof. Schmidt, but claimed to know nothing but what had appeared in the patent literature. They in Switzerland patented a blade, made by powder metallurgy technique, in which there is a gradation from pure metal at the bottom to ceramic at the top. He, however, held out little hope for success with ceramic blades for two reasons.

First, even in stationary applications there may be very sudden temperature changes as the power demand changes. He does not think that ceramics will stand the repeated shock.

Second, the vibration of the blades becomes a very important factor at certain speeds due to synchronization with the turbine speed or a multiple of it. A high damping coefficient is important, and that may be difficult to obtain with ceramics. To mount the blade in the runner so that the vibration does not develop some movement is difficult with steel and would be very much more difficult with ceramic both due to its mechanical properties and to the difference between the coefficients of thermal expansion. In high pressure steam turbines it is necessary to weld the blades into the runner.

Asked about the Ritz heat recuperator of tubular ceramic that was supposed to have been made in quantity by

Hesho, Hermsdorf, for Brown Bovari, Manheim, Dr. Meyer had heard nothing of it. He recognized the design as that of Lundstrom, who had used metal. He did not believe that the weight could be as low per kw output as Dr. Ritz claimed. One square meter of heat exchange surface in their present metal recuperators weighs 14 kg. From the curves efficiency vs. exchange area per kw and top temperature one much approach one square meter per kw to get satisfactory performance.

These curves showed very strikingly how both the recuperator efficiency and the overall efficiency go up steeply with rise in top temperature. They operate at a top temperature of 600°C, using an 18-8 steel containing tantalum and columbrium. They have not had alloys capable of operating at 800°C.

Escher Wyss, Zürich

This plant was visited on August 25 in company with Prof. Stoughton. Talked with Director Guyer and Dr. C. Keller, head of the experimental work. Dr. Keller knows Prof. Schmidt at Braunschweig personally but had only a vague knowledge of his work on ceramic turbine blades. Both he and Guyer knew of the work at MAN, but without detail. Neither felt that ceramic blades offer much promise due to the sensitivity to heat shock and to the supposition that if the temperatures are boosted very much there will be many new problems to solve connected with the construction of more heat resistant housings, heat exchangers, etc. They were frank to say that ultimately top temperatures may be boasted a good deal, but for the present they have chosen to use medium temperatures and gain satisfactory efficiencies by improvement in blade design, use of a closed system under pressure, and improvement in heat exchange efficiencies.

Due to the great importance of blade efficiencies, Dr. Keller thinks that it may be difficult to produce satisfactory ceramic blades. They are not so easily shaped to an exact pattern as metal.