

## NEW MATERIALS OF CONSTRUCTION FOR HEAT ENGINES IN HIGH TEMPERATURE SERVICE.

By

**B.L. Majumder, M.Sc., A.M. Inst. F.**

### ABSTRACT.

The demand for materials that will withstand the high stresses in rapidly rotating parts of the gas turbines and jet propulsion engines for their efficient operation at a high gas temperature has resulted in the development of several ceramic materials for such applications. The study of their properties at elevated temperatures has provided encouraging data for the design of gas turbine blades. The ceramic materials retain their strength at elevated temperatures and many of them resist oxidation; they are, however, more susceptible to failure from thermal shock than the metallic alloys. Various compositions have recently been studied to improve their resistance to thermal shock.

The progress in the development of gas turbines, jet engines etc. has been very slow as only a few alloys can satisfy the service requirements at an operating temperatures of 600°C. and their strengths, in general, rapidly decrease above this temperature. This limitation has directed the attention to the refractory properties of ceramic materials and other less familiar compounds such as carbides for applications in gas turbines enabling them to be operated at high gas temperature with increased efficiency and also making them last longer at present temperatures. Above 600°C., the ceramic materials have certain inherent advantages over the metals and metallic alloys: their high melting points, low bulk density, high strength-density ratio and chemical inertness naturally lend themselves for use as a blading material. This short paper seeks to examine some of these materials and their expected behaviour under peculiar service conditions of high stresses at extreme temperatures.

The search for special ceramics with unusual mechanical and thermal properties has led to the judicious selection of little-known oxide type and carbide type systems as possible fields of such study and throughout these development the approach and technique of crystal chemistry<sup>1</sup>

TABLE I  
Properties of Several Ceramic Materials

Material	Powder density g.p.c.c.	Melting point, °C.	Tensile strength (tons per sq. in.) of sintered article determined at	
			room temp.	1000°C.
Alumina	4.00	2050	15.73	14.65
Zircon .. ..	4.72	2430*	5.20	3.88
Zirconia	5.70	2700	8.00	3.02
Beryllia .. ..	3.03	2570	6.11	2.77
Sillimanite .. ..	2.80	1810	5.38	8.48
Boron Carbide	2.51	2350	10.25	7.10
Titanium Carbide ..	4.91	3140	—	7.95
Zirconium Carbide ..	6.22	3800	13.85	6.45
Magnesia .. ..	3.55	2135	7.90	5.15
NBS 4811	3.00	x	..	8.15

\* melts incongruently

has been very prominent. The properties of few of these bodies are quoted in Table I from sources and before discussing their use and performance in gas turbines, it may be of interest to consider the methods of precision fabricating the airfoil shape of their blades with necessary twist and surface smoothness. The choice of a technique for fabricating them partly determines the degree of porosity which, in turn, affects the physical properties of the fired body. The ease of fabrication has again a bearing on their application as part of limitations of the structural alloys is in the operations required to make and shape them.

The raw materials are of highest purity and after suitable physical treatment for imparting the necessary plasticity or green strength, the turbine components may be produced by conventional methods like slip casting or extrusion and sintered by firing to a temperature the melting point of the raw materials. These methods, however, do not give the desired density and consequently the complexity of shapes such as turbine blades, bushings, nozzles, etc., are made by hydrostatically pressing the finely ground powders. Such dry pressing of carbides, borides, nitrides, etc., is, however, difficult because of their high compressive strength and poor flow characteristics<sup>2</sup>. It has often proved satisfactory to press what would be equivalent to ingots and then to machine the pressed compact by surface grinding, turning and contour forming, making allowance for shrinkage. The sintering of these articles presents further problems as the furnace temperature in excess of 2000 °C. has to be maintained for several hours<sup>3</sup> with provisions for precise atmosphere control<sup>4</sup>. Attempts to sinter a mixture of TiC and TiN even by heating for one hour at 2000°C. In a vacuum of 2.5 microns of Hg pressure resulted in only partial sintering of the compact. This may be overcome either by utilising the thermal conductivity of the carbides<sup>5</sup> when a heavy current passing through the cold compact raises its temperature by the resistance effect or by hot pressing them with small amount of cobalt, nickel or their oxides at temperatures high enough to melt the metal binder. The process achieves sintering at lower temperatures and produces a dense body, pressed to close tolerances of  $\pm 0.002$ " without warpage or shrinkage from heating. However, the presence of relatively low melting metallic phase may become plastic at elevated temperatures; attempts<sup>6</sup> have, therefore, been made to remove this by heating in vacuum to such high temperature that all the binder metal distills out.

The main requirements of the blades<sup>7</sup> attached to the rotor as regards high mechanical strength both at room and elevated temperatures is due to the centrifugal force and as this is directly proportional to their weights, the low specific gravity of the ceramic materials is an advantage and the required strength is considerably lower than the metallic ones. Thus, under normal operating conditions, stresses in the neighbourhood of 11 tons/sq. in. produced in a metal turbine blade<sup>8</sup> will be equivalent to a stress of 3 to 4 tons/sq. in. for a low density ceramic blade. Figure I shows the variation of tensile strengths of several ceramic materials with increase of temperature and for a direct comparison of these values with those of best known alloys, the strengths have been plotted on strength-density ratio. The ceramic materials do not exhibit appreciable reduction in strength until about 1100°C. while the strength of sillimanite is maximum at 1000 °C owing to its phase changes on heating.<sup>9</sup>

The compressive strengths of the ceramic materials are of the order of 10 times their tensile strength and, therefore, in good design ceramic parts are either prestressed in compression or subjected to compressive loads, e.g. when it is desired to join a ceramic part to a metal section, the former should be used for male coupling and the metal for the female. Prestressing offers further possibilities of reducing the effects of thermal and mechanical shocks, since failures from such shocks are basically tensile in nature. Full use of this advantage has been proposed in the so-called 'inverted' turbine<sup>10</sup> where the moving blades are mounted internally on an external rotating drum so that the forces acting on the blades produced only a bending and compressive stress.

Further, as the efficiencies of the engines are dependent on the maintenance and dimensional accuracy of the components during service, the rate of deformation or creep of the ceramic materials under purely tensile stress at elevated temperature has recently been studied. Stress-rupture strength expressing the life of the materials in hours at a certain stress and temperature

or dead loads supported by them indicate<sup>11</sup> that the ceramic materials exhibit greater strength (on strength-density ratio) at 1000°C. than any heat resisting alloys.

In addition to the centrifugal stress, turbine blades are subjected, within seconds, to a very high temperature gradient—for example, by sudden starting up or shutting down as a result of failure of fuel supply. The temperature may fluctuate from that of the cold and even moisture-laden air to that of the combustion gases at 800° to 1000°C. and as a result of the cumulative effects of such thermal shocks turbine blades fail by fracture through the materials, or in some cases failure may result from the action of centrifugal stress and mechanical shock after the material had been weakened by the effects of thermal shocks.

While the tensile strengths of the ceramic materials at elevated temperatures are definitely promising, their susceptibility to fracture by thermal stress constitute a major problem and may seriously limit the potentiality of these materials in this sphere. High strengths, high thermal conductivities, low elastic constants and low thermal expansion contribute to good thermal stress resistance and attempts to obtain these desirable properties in ceramic materials have developed new types of materials and methods of fabrication, e.g. the blades<sup>12</sup> are composed of layers of different porosity—this being achieved by the incorporation of varying quantities of combustibles in an alumina body. The relationships are not, however, constant but vary with temperature. The thermal stress resistance of magnesia, alumina and zirconia first decreased with increasing temperature<sup>13</sup> until minima were reached and then increased owing to the increased plasticity of the oxides at that temperature.

Several pure oxide ceramics are potentially suitable<sup>14</sup> for gas turbines provided they run under such operating conditions as to minimise thermal shock, e.g. some protection may be assured, in the event of fuel stoppage, by automatic introduction of fuel from an auxiliary source. The new series of carbide-base compositions combine the thermal shock resistance of the alloys with the high temperature strength of ceramics. During the war the Germans developed silicon carbide bodies for use as stator blades where the conditions are less drastic. The refractory carbides and nitrides crystallising with the face-centred cubic structure are the highest melting materials known—the bonds between their cations and the interstitial carbon or nitrogen ions are remarkably strong. They are, however, susceptible to oxidation in varying degrees, particularly at elevated temperatures and at a gas temperature of 1100 °C. the oxidation rates of some carbide bodies are so high that the life of a turbine blade would be limited to about 10 hours. The resistance to oxidation may be improved by the application of a suitable glaze or the incorporation of other basic materials in the compositions so that a different oxide more resistant to oxidation by diffusion processes can be formed<sup>15</sup>. The glazing of carbide bodies gives a very desirable smooth finish on the blade and increases their tensile strengths considerably. The addition of a small percentage of columbium and tantalum carbides<sup>16</sup> or about 5% chromium<sup>17</sup> to TiC greatly increases its resistance to oxidation at high temperature.

The metals have been incorporated in ceramics for combining the most valuable properties of the metals and ceramics in a single body<sup>18, 19</sup>; but these composite 'cermet' bodies have an inherent disadvantage in that their density is higher and corrosion resistance lower than the oxide materials. The metals can be added to ceramic materials in various ways: metallic salts can be mixed with plastic ceramic material and the product then fired, or ceramic and metal powders can be mixed, pressed and fired<sup>20</sup>. Their structure and properties depend on the techniques employed in fabrication; and sintering mechanism has been studied<sup>21</sup> in establishing conditions which yield optimum properties. The American TP-1 compressor stator blade provides an example of infiltrating porous compacts<sup>22</sup> of pressed and sintered iron powder. The artefact is machined to exact dimensions and infiltrated with a copper alloy to 100% density, and lastly heat treated to develop the required ultimate strength. The technique has been slightly modified for metallic stator blades.

The first attempts to use oxide-metal combination for gas turbine blades originated in Germany during the war when various mixtures of 40—70% alumina with iron powder

(called Dug) were developed. From the mechanical strength point of view, alumina is one of the most attractive engineering materials and the Swiss high-temperature alloy SAP—sintered aluminium powder—is another example. It contains 10–20 % of alumina, the balance being aluminium powder, and displays remarkable physical properties at and even above 500°C. . . cermets containing 70 %  $\text{Al}_2\text{O}_3$ , 30 % Cr, 3–5 % Fe and 2–3 % W have adequate strength<sup>23</sup> for use in jet engines at temperatures upto 980°C or even higher; the strength is not seriously affected when this is heated in air for 100 hours at 1500°C and it has better thermal shock resistance than alumina. Experiments are also in progress on boride-metal and nitride-metal combinations. Thus, oxidation and physical properties of TiC—base<sup>24</sup> and B4C—base<sup>25</sup> cermets containing various metallic constituents have been considered as another series of promising materials for rotor blades.

A low value of thermal conductivity may, on the other hand, be advantageous when ceramic blades are fixed in a metal since less heat will be conducted through them. Besides, in certain applications like rocket nozzles etc. where the heat transfer coefficient is higher and body dimensions greater, thermal conductivity is of little importance<sup>26</sup> for any improvement in thermal shock resistance. In such cases improvements may be attained by lowering the coefficients of thermal expansion and modulus of elasticity<sup>27</sup>. There are indications that moduli of elasticity of ceramic materials maintain a nearly constant ratio with the tensile strength at the same temperature<sup>28</sup> and consequently attempts to improve the materials by altering their elastic properties are not likely to solve the problem.

Thermal expansion properties<sup>29</sup> of several ceramic materials have been compared with those of two alloys. Fused silica and cordierite bodies were investigated for rotor and blade units because of their low thermal expansion. However, owing to the low refractoriness and possibility of divitrification, fused silica assembly may be used only upto a maximum operating temperature of 1000°C and may find stationary application where the temperature conditions are not so severe. As the cordierite porcelain first tried in the combustion chamber cracked during the initial heating, it has not been tested in actual gas turbine. Zircon<sup>30</sup> has been developed mainly because of its high refractoriness and low coefficient of expansion.

The application of ceramic coatings is becoming established for jet engine components and high temperature exhaust systems for piston engines to extend their service lives. Steel sheet (0.002 in.) having a thin coating (0.005 in.) has flexibility comparable to that of tin foil and can be warped on to the blast tubes of jet engines; the thickness of the coatings is about 0.001–0.003 in. in normal American practice<sup>31</sup>. The coating may be applied on the metal surface by spraying like enamelling, or alternatively by deposition of refractory material from the vapour phase<sup>32</sup>. These coatings resist chemical or physical changes normally occurring in the presence of flaming gas temperatures; the metal exhaust systems are thus protected against any deterioration by oxidation, absorption of carbon with consequent surface embrittlement and corrosive effects of lead bromide vapour<sup>33</sup> (formed by the interaction of tetra-ethyl lead and ethylene dibromide, which are active additives in lead petrol). Further, the successful performance of ceramic coated stainless steel under the ravages of jet engines environment would not only save nickel but may improve thermal characteristics. The temperatures at which the coatings can be used, however, have a potential limit in that the firing temperature must increase with increased refractoriness but obviously cannot exceed the melting point of the base metal.

High temperature enamels have also been developed<sup>34</sup> for protecting the tungsten metal from oxidation. Zirocon was chosen as the base material for this enamel because of its suitable thermal behaviour, resistance to slags and immunity to reaction with carbon monoxide. The excellent tensile strength and high melting point of the tungsten metal may thus be effectively used for high temperature engineering work.

A number of ceramic materials have shown better performance and tensile properties at elevated temperatures than the performance ceiling of the metallic alloys; however, there are better chances for the success<sup>35</sup> of ceramic component in designs embodying ceramic stator blades

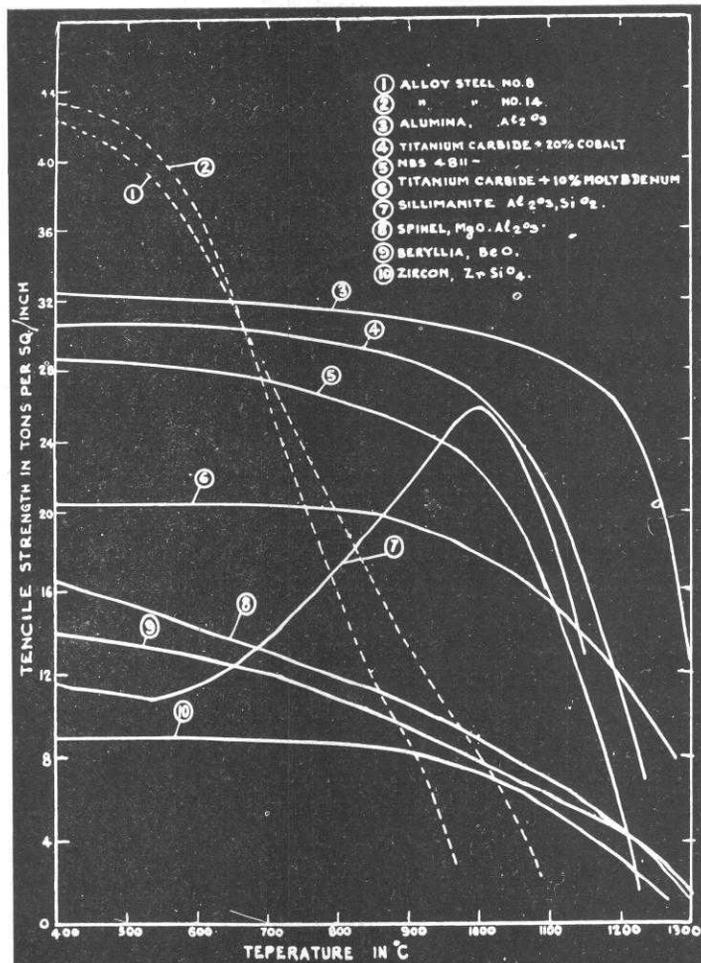


FIG. 1.  
TENSILE STRENGTH OF STEEL AND CERAMIC MATERIALS AT  
ELEVATED TEMPERATURE  
(EQUIVALENT STRENGTH OF CERAMIC MATERIALS AT DENSITY EQUAL  
TO THAT OF METALLIC ALLOY BEING 8.3)

than those in which ceramic rotors are used. Such application in an aircraft engine will greatly reduce the weight and cost, but high inlet gas temperature may not be permissible.

In service tests the life of a number of turbine wheels either completely or partly fitted with ceramic blades has been found to be short, primarily because of their lack of ductility and unforeseen fabrication difficulties. The ceramic blade root is fastened into the slot of the metal disk and the resultant concentrated stress at the root<sup>36</sup> has in many cases been the cause of failure. It appears that the best performance from the ceramic materials may be obtained by making such changes in design or operational adjustments in gas turbine as to incorporate their advantages.

It is impossible as yet to predict the types of material that will ultimately prove satisfactory for gas turbines and similar applications. It seems fairly certain, however, that no one material or combination will prove to be suitable for all such applications and the choice will depend on the purpose for which the turbine is designed. For example, in military aircraft the aim is to improve the thermal efficiency by raising the gas temperature from the present limit of about 850°C to an interim target of 1200°C and ultimately to 1500°C, while at the other end of the scale, stationary power producing installations will probably derive greater benefit in the first instance from extending the operational life to 100,000 hours.

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