BEYOND SUPERALLOYS: The Goals, the Materials and Some Reality

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Unusual national and international attention is now being focused on materials, - their science, their technology, their engineering. "Materials" are being challenged to give society great benefits new in areas such superconductivity, information and computers, and the transportation field. It seems to materials engineers as if they had been suddenly "discovered", and investors are told of immemse potential businesses in new materials, such as ceramics.

The field of high-temperature materials applies to one of the top two United States leading high technology turbines for aircraft engines and businesses, - that of gas industrial energy; it is in the forefront of this wave. atmosphere is being charged by issue ofunusually challenging goals for the performance of military aircraft gas turbine engines. A "quantum leap" forward is being sought. As a result, agencies which sponsor major research programs in materials identified revolutionary objectives for materials properties for building these engines in late 1984.

These objectives appear to add up to something doubling of both temperature and strength-to-weight capability in the forseeable future. This breaks property requirements which require, at the very least. significantly increased absolute mechanical strength. materials densities which appear to eliminate materials more dense than alluminum and titanium, and surface stability to allow the materials to operate in atmospheres which could be oxidizing, neutral. or reducing. The goals also intrinsic use of combinations of very dissimilar reactive materials in untried chemical combinations. All this is to be at temperatures which approach double current practice.

MATERIALS GOALS

The materials goals follow from the engineering objective, which is to increase significantly the thrust-to-weight ratio of military engines. These goals, as apparent by early 1985 were:

- o Design and build engines with a minimal turbine inlet temperature of about 4000F (2200C)
- Design the engine(s) with very little cooling of hot-stage materials.
- O Utilize materials with a maximum density of about Superalloys 1988
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o Maximize energy from the fuel by combustion at stoichiometric conditions.

These goals are supported by extensive R&D programs which started in 1985 and in years thereafter at universities and other laboratories which invent materials for engines. The materials systems defined for study often are specified on the basis of very simple properties such as melting point, density, or modulus. Step-wise developments in conventional materials, such as superalloys, appear to be a thing of the past.

GOALS MODIFIED

After about three years the goals appear to have been somewhat modified. A temperature range of 3000-4000F is now being mentioned and a partial use of materials with greater density than 5g/cc is suggested as allowed, although this author has heard of no change in cooling or stoichiometric However, these objectives to a materials combustion goals. engineer still mean operation at 1.5 to 1.8 times present materials temperature, replacement of much of the nickel, cobalt, and the iron-base alloys now used, for very rejection of refractory metals (except, perhaps, minor portions of total engine weight through a trade-off with vey light-weight materials). Further, many more engine will approach actual combustion construction materials if the cooling, and temperature due to restricted stoichiometric combustion goal is retained, a now notexisting-in-nature class of materials,-resistant to both oxidizing and deducing conditions, will be needed.

The materials classes proposed for this job can be identified as follows:

- o Ceramics and ceramic alloys
- o Ceramic/ceramic composites
- o Composites containing carbon (graphite fibers)
- o Intermetallic compounds and IMC composites
- o Metal-matrix composites

In addition, refractory metals are still mentioned, and, as implied above, superalloys exist in place as the standard, although both of these systems have densities far above 5g/cc.

WHAT DO THE GOALS MEAN?

It is appropriate to take a broad, engineering-like perspective of the stated goals, particularly since they are so far beyond current capability.

Temperature. Figure 1 places in perspective the regime of temperatures serviced to man. Importantly, it has taken 84 years to advance from about 500F to 2000F in turbine materials,— the last 20 years at about 15F per year. Now the objective is to reach specific bulk materials temperature of the 3000-4000F range in perhaps 10-15 years from 2000F,— a rate of about 100F per year.

Cooling. Figure 2 shows advances achieved in turbine engine performance from cooling alone in the last 20 years. It has exceeded advances through improved metallurgical invention.

Density. Figure 3 gives a simple listing of materials available based on a density consideration. It also lists the fracture toughness of the materials classes, showing that the elimination of metallic systems eliminates the toughness contribution common to date.

Stoichiometry. Stoichiometric combustion means complete burning of all the fuel hydrocarbons to a perfect neutralized balance of oxidizing and reducing components in the gas stream at 4000F. (4000F is about the stoichiometric combustion temperature for JP-5). If the gas stream becomes even slightly reducing, materials will be destroyed very If reducing-resistant materials are used, even rapidly. slight oxidation destroys them. Figure 4 shows the root section of a turbine bucket when a combuster went out of control allowing reducing conditions to exist. Over 100 blades like this one were burned off in 45 seconds. Immense energy was released, - a catastrophy. The slightest variation from stoichiometry in any system will produce this type of failure.

ARE THESE THE ONLY GOALS?

It is absolutely vital to remember that the above-stated "goals" are actually only a kind of ambient condition goal for materials, secondary to the design/engineering physical "requirements" to make the machine go:

- o *Strength*. The materials must be (at least) as strong as superalloys.
- o *Toughness*. The materials must be capable of sustained exposure to a wide variety of stress and temperature conditions, which absolutely require that the materials demonstrate a significant level of toughness,— at least a large portion of that available in superalloys.
- o **Surface Stability**. Surface recession rates allowing the small, thin, materials parts to retain their load-bearing capability for, at the very least, 100-200 hours are requisite, with thousands desirable.
- o *Other Properties*. The above still does not face many other essentials,-HCF resistance, CTE (∠) needs, retained structural stability, corrosion resistance, and the like.

GOALS IN RETROSPECT

Even this brief consideration of the materials property goals put forth in 1984, resulting in a number of now massive developmental programs, raises several questions.

o Since the temperature and density goals eliminate metals and ductile IMC's, have the toughness requirements for future machines been very significantly reduced to compensate?

- o Since stoichiometry is wanted (and oxidation resistance essential) is any class of materials with this combination of properties known?
- o Why has development toward still more effective cooling stopped?

EVALUATION OF THE MATERIALS

While a number of major efforts were put in place to study or develop new materials based on empirical logic, several parallel programs were initiated to evaluate simply the basic physical/chemical properties of existing materials candidates. It is the interest here to cover, with high brevity, the salient features of several evaluations.

Existing Solid Materials. A broad survey comparing solid materials on the basis of density and (real or estimated) Youngs Modulus was compiled by Fleischer. A portion of his results are shown in Figure 5. It is quickly obvious that (on the basis of density and modulus only) carbon/graphite, carbides and oxides dominate the available materials. Metals are far behind. This is a shopping list. Fleischer did not pretend to consider toughness, chemical reactivity and the like.

Preliminary Evaluation. Hillig then attempted to apply a first level of reality to the (apparent) range of candidates. He considered not only density and modulus, but projected potential candidates for very-high temperature service on the basis of structural and surface stability (phase changes and vapor pressure), and mechanical behavior through estimates of creep performance. Directing the study into the composite area, he considered materials interaction as well. Hillig then attempted a balanced evaluation to identify possible composite systems. Examples of this approach as his recommendations are shown in Figure 6.

Creep Evaluation. This author attempted an engineering evaluation of creep by calculation intended to show whether any material exists capable of withstanding continued mechanical load of a usuable level at the original goal of 4000F (Figure 7).

Findings from this study are that the only material capable of usuable mechanical stress in turbines at 4000F is carbon/graphite. However, this is based on a single set of data of questionable character. Further, as discussed more below, graphite will burn explosively at 4000F in air, and toughness is almost non-existant.

Oxides exist at and have some strength at 4000F, but those found so far with calculable properties creep too rapidly. Further, the study suggests that diffusion is an underused technique for estimating creep.

Surface Stability. In Hillig's study, he evaluated the vaporization effects on surface recession rate of the now fairly obvious groups of "high-temperature" materials, with the results shown in Figure 8. The conclusion from this solid work also is clear, that non-oxide systems either

vaporize or oxidize too rapidly at the (original) goal of 4000F to be useful. Only oxide-type materials appear to have potential,— and that does not yet appear to have developed much depth. In any case, materials which do not satisfy the demands of this measurement should not be under study.

DISCUSSION AND SITUATIONS ANALYSIS

Materials Science and Engineering (MSE): The New Atmosphere After years of being inventive followers, materials engineers and scientists are suddenly in the limelight. MSE is regarded as one of the most important high-tech industries of the future. This new atmosphere appears due to two major factors,-several spectacular developments in materials, and continued public emphasis, through both technical and non-technical news media of the (apparent) incredible future of "materials".

The technical developments are real. The public relations emphasis, however, is quite misleading. Growth of ceramics to a \$300 *billion* business by the year 2000 has been trumpeted for about 5-6 years. The fact is, that no turbines, aircraft or industrial, yet use ceramics, and the potential of other than trial demonstrations by the year 2000 is a myth.

Still, every materials magazine leads with articles on ceramics, composites and graphite, which, through exciting illustrations about *potential*, create an atmosphere that suggest such materials are just a half step away, - although prudent consideration of actual properties shows that they are many, years off, if at all. The situation is discussed in detail by TW Eagers, who tends to conclude that the real need is for common-sense attention toward quantities of economical advanced materials for clearly identified societial benefit, not curiosities. His article is needed reading.

Materials for Advanced Turbine Engines: The Cited Goals As discussed previously, the goals presented to the technical community initially appear only in part to be "workable". Achnowledging this, recently the goals have been modified somewhat. For instance, the temperature goal has been stated now to be 3000-4000F instead of absolute 4000F. It is extremely important to realize that this relaxation may mean that stoichiometric combustion is not longer a hard requirement. The goals for combustion appear now to be "near-stoichiometric". If true, this is most fortunate, since it rescues design of advanced engines out of the realm of absolute impossibility, from the materials existance view, and suggests something might be available.

However, it still leaves a rather incredible hurdle, - that of changing the key hot-stage engine components from a superalloy technology to a ceramics/composites/graphitic technology. It seems assumed that the toughness problem will be eliminated.

Materials for Advanced Engines: The Candidates
Let us explore the potential materials on the assumption
that they must be higher melting than superalloys. In order
to be concise, this is done by a chart which generally
categorizes the possible materials groups. There are no
others. See Table I. The advanced engine goals are
included but so are a few basic engineering requirements.

While there are eight items total on this chart, it is imperative to understand that, of the eight, two items are essential, regardless of goals. If the material does not have (1) strength and (2) environmental resistance or a rational, reasonable potential of obtaining both of these, further attention is a waste of time. The field considered here is very complex and the chart is heavily subjective, due to the cryptic nature of this presentation. However, this writer has some points to offer believed critically important.

- 1. Graphite and Graphite Fibers will be consumed in oxidation at a rate controlled only by ability to bring the reacting constituents together. Carbon is a fuel. Protection is conceivable, for a few seconds or minutes, but reaction thermodynamics has always shown very clearly that dynamic structural use at very high temperature is impossible.
- 2. Monolithic Covalent Ceramics. Despite millions expended, solving or bypassing the critical flaw size problem in these brittle materials has not been done, and the fracture toughness needs are not satisfied. Potentially, very tiny, high-cost parts may be possible to 2700F, the service limit of silica, the generated oxide protective film.
- 3. Composites. The millions poured into ceramics before, are now pouring into composites, because "fiber pull-out" demonstrates a slight increase in toughness over ceramics (still far below engine requirements) and also because of the tailored property potential, a real plus. Like ceramics, oxidation service is limited to 2700F.
- 4. Unalloyed Oxides and Oxide/Oxide Composites. The surface stability column in Table I shows that only these materials have potential to exist in the 3000-4000F range. The oxides are mechanically weak, but also largely unexplored.

From this, it is apparent that oxide ceramics, which have not been favored with any developmental attention, have the only real potential for 3000-4000F service. Further, the word *potential* used here is relative and subjective.

OXIDES FOR VERY HIGH TEMPERATURE SERVICE

To explore whether oxides have some real potential, a carefully plannedbody of work is needed. Some suggestions, and support comments follow.

- 1. At present, oxide ceramics of the alumina-chromia type are operating in the hot agressive atmosphere of military and all other engines to about 2100F; here they service in non-loading-bearing application as 1-5 mil protective coatings.
- 2. Oxides, and probably oxide/oxide composites, can be generally expected to have stability in oxidizing environment up to temperatures where they sublimate, disproportionate, or otherwise self-destruct.
- 3. Oxides are weak in creep and are generally brittle. Strengthening is a major objective.
- 4. Results of studies on oxides also will be applicable to other systems, all of which must have oxides to protect them.

ADVANCED AIR COOLING

The original goals specified "reduced cooling" at 4000F. With modified goals, it is now reduced cooling at 3000instructive to 4000F. It is observe the circumstance, and review this goal. Advances in gas turbine engine temperatures over the last 30 years have been due cooling and materials advances with cooling both to providing about 60% of the advance. At present, materials real surfaces at about 2100F. gas stream temperature of above 3000F can be achieved for short periods This is a 1000F gas temperature capability when needed. above blade metal due to cooling. A cooling breakthrough, increasing cooling effectiveness by say 40% would put engine 3700F, - probably temperatures around as close stoichiometry as practical.

SUPERALLOYS

Discarded as having no further potential by the original and revised advanced engine goals, it is important to understand that significant advances in superalloy capabilities are still occuring as industrial programs tail down. With their proven toughness, creep strength, and oxidation resistance, this is a vital signal. Five years later, superalloys are not done; they are not dead; they are very much alive.

FINAL OBSERVATIONS

The total situation, of course, is much more complex than can be shown in this short discussion. Recent changes in HPTE materials are laudable, -but this writer believes more changes are needed. A danger exists that development efforts will fall so far short (ceramics already) that the materials community will loose credibility. All participants want and expect challenging goals, sometimes impossible to fully attain, - but goals must be rational and supportable by sound engineering.

This writer recommends the following:

- O Development programs on highly advanced superalloys should be strongly supported, and integrated with new advanced cooling programs.
- o Very advanced work, towards bulk material temperature in the 3000-3500F range should center on oxides and oxide systems.
- o The very extensive developmental programs in composites containing ceramics, graphites or IMC's should be faced with a specific goal in toughness at a level designers state is acceptable. If the goal is not met in five more years, composites should be abandoned.

REFERENCES

- o Fleischer, R.L., High-Temperature, High-Strength Materials An Overview. J. Met., 37, no. 12, Dec. 1985, 16-20.
- o Hillig, W.B., Prospects for Ultra-High-Temperature Ceramic Composites. Tailoring Multiphase and Composite Ceramics, R.E. Tressler, et al., eds., Plenum, 1986, 697-712.
- o Eagar, Thomas, W., The Promise of New Materials Real or Imaginary? J. Metals 39, No. 4, April, 1987, p. 20-24.
- o Hertzberg, R.W., <u>Deformation and Fracture Mechanics of Engineering</u>
 Materials, John Wiley & Sons, New York, 1976.

TABLE I

Potential of Advanced Materials Classes to Meet
Materials and Engineering Goals for Advanced Engines

Materials Class		Materials Goals			Materials/Engineering Goals			
	T ₄ = 3-4000F	Stoich. Combus.	Density <5g/cc	Less Cooling	Creep Strength	Toughness	Surface Stability	Available & Economic
SUPERALLOYS	Poss.	No	No	No	Yes	Yes	Yes	Yes
OXIDES & OX/OX	Yes	No	Poss.	Yes	Poss.	Poss.	Yes	Yes
GRAPHITE COMPOSITES	Yes	No	Yes	Yes	Yes	No	No	Poss.
COMPOSITES (Ma	trix)							
Metal & IMC	No	No	No	?	Poss.	No	?	No
Ceramic	Yes	No	Yes	?	Poss.	No	No	No
0xide	Yes	No	Poss.	?	Poss.	?	Yes	No
YES - Has P	otential	POS	S. – Limite	ed Potential	NO	- No Potent	ial	

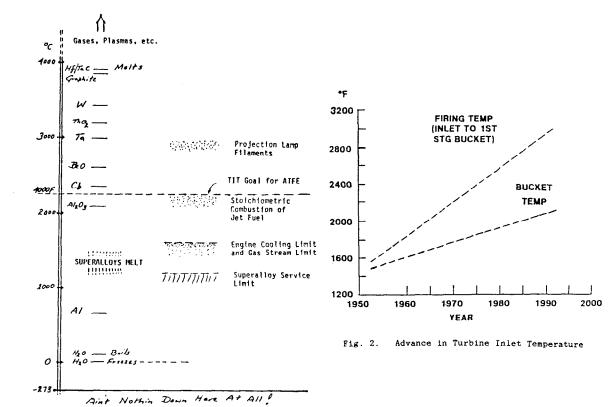


Fig. 1. Temperature and Its Relationship with Some Materials

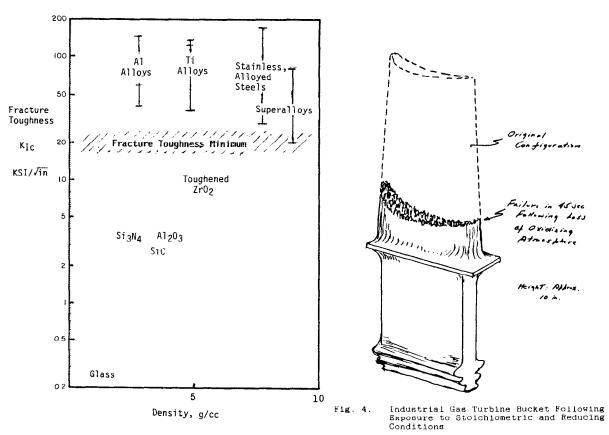


Fig. 3. Some Properties of Advanced Materials

Combined Criteria for Oxides

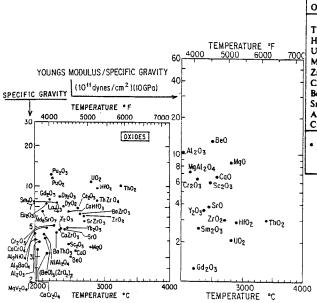


Fig. 5. Properties of Some Oxides (after Fleischer)

Oxide		Стеер					
	T _m	.85 <i>T</i> ,,	.7 <i>Tm</i>	Ε/ρ	Volatility	T _{min}	Rank
ThO,	3493	2970	2445	2290	2375	2290	3
HfO ₂	3117	2650	2180	2020°		2020	6
UO,	3113	2645	2180	2050		2050	5
MgO ₂	3098	2635	2170	2870	1825	1825	9
ZrO ₂	3037	2580	2125	2195	2775	2195(2125)	4
CaO	2882	2450	2015	2430	••	2430(2015)	1
BeO	2843	2415	1990	2710	2325	2325(1990)	2
SrO	2727	2320	1910	1750	2075	1750	10
Al ₂ O ₃	2327	1980	1630	2210		1980(1630)	7
CroOs	2300	1955	1610	2015		1955(1610)	8

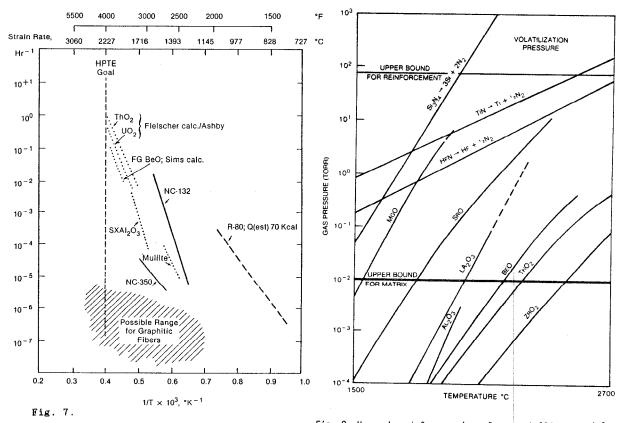
* Assumes E is the same as that reported for ZrO₂ Values in parentheses in T_{min} column refer to use as monolithics if that use results in a lower estimated use temperature.

Combined Criteria for Nonoxides

Mat'l	T _m	.7 <i>T</i> _	Ε/ρ	Volatility	Tmin	Rank
TaC	4258	2980	Fails		Fails	••
HfC	4163	2915	Fails		Fails	
NbC	3886	2720	2365		2365	6
C	3825	2670	3685	~3500	2670	2
ZrC	3803	2660	2715		2660	3
HſN	3660	2560			2560	(5)
TiC	3530	2470	3035		2470	4
HfB ₂	3523	2463	2345		2345	7
TaN	3360	2350	1855		1855	9
TaB ₂	3310	2315			2315	(8)
SiC	3100	NA	2850	2780	2780	1

Fig. 6.

Potential of Nonmetallic Materials for Composite Application (after Hillig)



Estimated Creep of Some Materials to 4000F

Fig. 8 Upper bound for service of non-metallic materials as defined by vaporization or dissociation (after Hillig).