ARTIFICIAL AND NATURAL HIGH-TEMPERATURE COMPOSITES

W. BUNK, Dr.rer.nat.
Direktor, Institut für Werkstoff-Forschung,
505 Porz-Wahn, Linder Höhe, West-Germany.

Abstract

Composites will probably replace conventional superalloys as turbine blades in jet engines allowing higher temperatures of combustion and therefore resulting in higher efficiency.
Examples of such composites as materials for engine design will be discussed. New processing methods (high energy rate forming and directional casting) and some recent results will be described.

1. Introduction

1.1. Definition

Artificial composites are defined as materials which are formed by fibres embedded in a matallic matrix, for example steelwires in aluminium.

On the other hand we call a composite "natural" if it is formed by directional solidification of an eutectic melt. That means a natural composite is a metallurgical conglomeration consisting out of two or more components forming a multiphase composite.

For the characterization of "artificial" or "natural" we can use the thermodynamical equilibrium. In the first case the artificial composite does not exist in equilibrium whereas in case of the directional solidification of an eutectic melt the system is always in equilibrium. For this reason the directional solidified eutectic alloys are qualified especially for permanent application at high and highest temperatures because these composites have a high thermodynamical stability.

For the so defined artificial composites it is necessary to create a barrier layer between matrix and fiber in order to obtain a kind of limited pseudo-stability.

1.2. Motivation

Materials for turbine blades, Ni- and C-base superalloys, are used at the present time up to 0.8 of the homologous melting temperature, that means close to the natural melting point where the material transfers to the liquid state and therefore becomes useless.

The technological development of the last years in the field of turbine blades, as an example for high temperature materials, was done mainly by the designers who invented very useful cooling technics. But even this possibility is almost exhausted today.

The challenge for materials engineering is to develop a new generation of high temperature materials which are qualified for long life application at temperatures higher than 1 000°C. In searching for such new materials the scientists came across the eutectics. In the first moment this seems unreasonable because an eutectic always solidifies at much lower temperature than the individual starting components. However, important is the fact that an eutectic is always in thermodynamical equilibrium. But also, one does not give up the artificial high temperature materials, and there are just now again a number of scientists who believe that this research direction will be successful. - Let us wait and see which concept will win the race. But there is one point in which all scientists agree: The next generation of high temperature materials will certainly be composites.

2. Artificial "In Situ" - Composites

By "artificial" we mean that the fibers are produced separately and that they have to be embedded afterwards in a matrix to form a composite. An example is aluminium reinforced with boron fibers: Long boron fibers produced by deposition from the gas phase on a tungsten core are connected with aluminium foils by diffusion-bonding or the aluminium matrix is added by plasma spraying.

Analogous to these developments in the last years on high strength composites for application at low temperatures our own work is concentrated on high temperature composites.

First of all it is important to create an improved high temperature fiber material and then combine it powder metallurgically by hot pressing using a high speed hammer (HERF) with a suitable superalloy matrix. At present I can only talk about the experiemnts to produce the fiber material.

The application of such a metallic fiber material has the advantage over ceramic fibers because the difference in the thermal expansion coefficient between matrix and fiber is small. A high resistance against thermal cycling is expected in that way. We do not work with pure, metallic tungsten but with tungsten + 20 % ZrO_2 for a further increase in high temperature strength. It is known that pure or alloyed tungsten looses the excellent high temperature strength at very high temperatures by recrystallization. Our task was to increase the recrystallization temperature by adding the ceramic ZrO_2- particles preventing dislocation annihilation and grain boundary movement. Hereby a diffusion of the nickel from the superalloy matrix of the subsequent composite into the fibers and with this their destruction will be avoided. This problem was solved by using the high speed hammer, (Dynapak) (see fig.1). This slide shows the principle of the high speed deformation. With the aid of the hammer and the high deformation speed the original spherical ZrO_2- particles are transformed to short fibers by the sudden extrusion. We succeeded to produce at 2500°C and a press ratio of 20 : 1, short fibers with an aspect ratio of about 50 : 1. Even during the next step in the process, namely round forging which followed the high speed deformation, we stayed below the recrystallization temperature. Hereby a further extension of the fibers and the formation of a fiber-like matrix structure resulted. To obtain this, one has to stay below the recrystallization temperature. On the other hand it is necessary to keep a certain minimum temperature during the forging because otherwise the oxides will break. The degree of reduction and the intermediate annealing temperature have to be chosen in such a way that the material remains always below the recrystallization threshold.

Fig. 2 shows the extension of the original spherical ZrO_2 - particles to short fibers by the extrusion with the high speed hammer at 2 500 °C.

The artificial composite consisting out of a superalloy matrix and the tungsten wires with their "In Situ" - ZrO_2 - short-fibers is to begin with not in a thermodynamical equilibrium with respect to the interface matrix-fiber like this is always the case for the directional solidified eutectic alloys. To avoid or to drastically reduce the diffusion of nickel from the matrix into the tungsten wires it is effective to provide the wires with a protective layer as a diffusion barrier. This is done preferentially by cold-cathode-sputtering or other methods.

3. Natural "In Situ" - Composites: Directional Solidified Alloys

3.1. General Remarks

During the last thirty years it was possible to increase the application temperatures for gas turbines each year about 7°C because of the good teamwork of metallurgists, materials scientists, and engineers. This remarkable development is expressed in Fig. 3 by the rise of the curve after the introduction of the vacuum-melting. Although the formerly pure empirical development of the manifold superalloys on Ni- and C-basis was replaced by a computer assisted optimization of the alloying elements with higher concentrations a natural limit was reached in the seventies. All experts agree that it will not continue in this way forever, and that a new generation of materials has to be developed to satisfy the demands of the industry for a higher efficiency of the gasturbine.

From the physical metallurgy viewpoint it was essentially the γ'-phase Ni_3Al which helped the Ni -base superalloys on their victory if one considers the vacuum melting and the inv. casting method as two necessary but important conditions. The γ'-age-hardening has a metastable character like all other agehardening processes: After long times at temperatures of 850 - 900°C the decrease of the high temperature strength is remarkable. The addition of dispersions, as we will see later on in an example, resulted in an improvement at high temperatures but could not solve the problem of the high temperature materials because of concomitant deformation - and annealing - mechanisms. During the search for such materials one started to remember that materials exist, were in thermodynamical equilibrium and which also maintained their properties close up to their melting points. This required thermodynamical stability is a property of the eutectics. This venture with the eutectics started a true renaissance of classical work on the heterogeneous equilibria of high melting elements.

3.2. Heterogeneous Equilibria

First it appears unreasonable to consider the eutectics with their melting points always lower than the participarting elements. But meanwhile one was already thinking in terms of composites and was realizing the potential of unexplored possibilities in this border area between metal and nonmetal. The metal, like nickel or cobalt, has the invaluable advantage of a good corrosion resistance and ductility whereas the crucial point of desired properties of nonmetals, like ceramics, is the extreme high strength at high temperatures. The unique chance opened up to combine the ductile and corrosion resistant metallic matrix with the strong ceramic parts into one natural composite. It is a gift of nature that the strengthening phase grows generally without difficulties as single crystal or whisker from the directional solidified melt if the optimum growth conditions are obeyed. Then we have a material with parallel fibers but almost without grain boundaries which is especially useful for high temperature application. The most important production method for a natural composite is directional solidification. The desired microstructure is obtained by preservation of a planar solidification front (Fig.4) and a material produced in such a way can be still applied at >90 % of its homologous melting temperature.

The cooling has to be done with a suitable medium, for example with water or liquid metal, and has to be very drastically (Fig.5) that means a steep temperature gradient of about 100°C/cm should be obeyed. Equipments with such facilities for induction heating of melts and subsequent cooling were long known from the growth of single crystals and from zone melting. Thus, it was natural to use this knowledge.

If a crucible is lowered in such a furnace then a microstructure is created which is shown in Fig.5: At the beginning an irregular microstructure is produced within the nucleation zone, the desired directional microstructure within the equilibrium zone, and at the end again an irregular microstructure. The connection between the directional solidification of eutectic alloys and the thermodynamical phase diagram is shown in Fig.6: Hereby, a system with symmetrical constitution is desired, that means similar high melting temperature and volume fraction for both phases and approximately the same slope of the liquidus line in the area of the eutectic point.

"Eutectic" means in Greek: fine microstructure. An example of such a fine microstructure of an eutectic after directional solidification is shown in Fig.7. In this case we see the binary eutectic Ni_3Al-Ni_3Ta, that means intermetallic compounds, to the left parallel and to the right perpendicular to the growing direction. An example of a binary eutectic with a metallic matrix and a compound as strengthening fiber is shown in Fig.8. The character of the strengthening by whiskers is demonstrated especially clearly in a binary metal-metal system: Fig.9: the nickel matrix is partly dissolved chemically, the tungsten whiskers are visible in the scanning electron micrograph as strictly directed needles protruding from the nickel matrix. One can see that the diameter of the single crystal tungsten fibers as well as their distance is only a few μ. It is difficult to visualize how such a fine distribution of these thin fibers can be produced otherwise than by this "natural" metallurgical method. This is another characteristic feature of the directional solidified eutectics which makes this technique superior to all others.

3.3. Processing Technique

What are now the "tricks" of the technique? I mentioned already that one was recalling the experience with zone melting, in which a small melted zone is running over the length of the solid specimen by moving an induction coil. In the present case of the directional solidification we have a relative movement of the melt and the heating and cooling devices. As a rule the crucible is moved, like it was shown in a previous sketch, from top to the bottom through a steep temperature gradient. This can result in a satisfactory alignment of the composite microstructure even for complex target shapes like for turbine blades (Fig.10).

And what is the most important point during pulling the melt through the steep temperature gradient? It is easy to recognise that the pulling speed that means the solidification rate has a strong influence on the quality of the alignment of the microstructure and therefore on the properties of the composite (Fig.11). The desired directional microstructure is produced in a better perfection if the heat flow is directed only to the bottom and not to the sides. In addition a planar solidification front is necessary; depending on the system this planar front is easy or more difficult to realize. For a realization the proper ratio of temperature gradient to pulling speed has to be determined and obeyed during the experiment.

3.4. The Cobalt-Chromium-Carbide System

After illustrating the experimental conditions and showing some results on simple binary model-systems I would like to come to a multi-phase system which was investigated at our laboratory recently. Although as a material the ternary system Cobalt-Chromium-Carbide is applicable more to stationary gas turbines than to aeroplane turbines, this system is best suited to show the problems of the directional solidifications, both theoretically as well as experimentally. The experiments were performed with a temperature gradient of 280°C/cm and solidification rates between 0.6 and 20 cm/h. The directional solidified rods had a diameter of 0.5 and a length of 30 cm. Fig.12 shows the melt equilibria and experimental alloys on the quasi-binary section. Besides the eutectic composition also alloys with lower and higher concentrations were investigated.

The result of an experiment with a solidification rate of 2 cm/h is shown in Fig.13: the Co-Cr-matrix was partly dissolved chemically, the scanning electron micrograph reveals long fibers of Cr-carbide having a relative uniform fineness but forming sometimes dendritic branches. Fig.14 shows in a cross-section that the carbide fibers have mostly a hexagonal shape. The volume fraction of the carbide fibers is about 32 % for the alloy with 42 % Cr and 2.6 % C and the diameter of the fibers is about 2 μ.

The investigation of the mechanical properties showed that the tensile strength at room temperature had the value of 1000 MN/m^2, elongation to fracture was 1,5 %. A separation of the carbide fibers from the matrix was not observed in these tests.

3.5. The System CoTaC and γ'-δ

Aside from the alloy CoCrC which is still very interesting for the stationary gas turbines the interest has concentrated at the moment on two more systems which are especially useful for aeroplane turbines. These are first of all the CoTaC-alloys with approximately 13 wt.-% fibers of the ceramic monocarbide TaC in a Co,Cr-matrix to which nickel and other elements are added to remove the allotropy of the cobalt lattice. And there are secondly the γ'-δ alloys Ni_3Al-Ni_3Nb.

In the following part a report is given about the two most favourable systems for application as turbine blade materials in contrast to the Co-CrC-system. Both systems fulfill the conditions of a melting point above 1200°C, a better high temperature creep resistance than the superalloys, and a sufficient high temperature corrosion resistance even if the protective layer is damaged. The fatigue strength is especially good. With respect to thermal shock resistance only insufficient results are existing. To obtain reasonable properties the CoTaC contains considerable amounts of chromium and portions of aluminium and titanium contributing to the strength and high temperature corrosion resistance. The lamellar pseudo-binary eutectic γ' - (Ni_3Al-Ni_3Nb) consists of two intermetallic phases; one of which, namely Ni_3Al, is ductile. It is a disadvantage of this system that its composition cannot be varied in contrast to CoTaC.

3.6. Mechanical Properties

3.6.1. Tensile Strength and Elongation

The available data from the literature are summarized in Table 15; While CoCrC and γ'-δ, probable because of their high content (30 vol.-%) of ceramic strengthening component, are fairly brittle at room temperature. CoTaC shows a high ductility like corresponding stress-strain curves of compact materials, for example mild steel. At 1000-1100°C both composites show a sufficient ductility of a few percent elongation.

3.6.2. Impact Strength

Taking into account the anisotropy of the properties CoTaC shows a good impact strength perpendicular to the fiber direction. On the other hand the results published up to now indicate that the impact strength of the other directional solidified eutectics mentioned here is still disappointing low.

3.6.3. Creep Resistance

This property of the material for a possible application in turbine blades i the most important one for the construction engineer for turbines. The available data for the 1000 hour creep strength are plotted in Fig.16 for temperatures up to 1100°C.

It is remarkable that at high temperatures all composites are superior to the best superalloy MAR-M 200. The curves for COTAC and γ'-δ show the following difference: the former is lower but intersects the latter at about 1100°C and shows afterwards higher creep strength values.

In the next years the decision has to be made between CoTaC and γ'-δ if not at all other systems with better properties will be invented.

3.6.4. Fatigue Properties

It is not surprising that all directional solidified eutectics which are discussed here show very good fatigue properties, particulary because the fibers or lamella act as crack stopper.

3.6.5. Thermal stability

From the facts mentioned so far it is obvious that the directional solidified eutectics have a good compatibility between matrix and strengthening component because of their "natural" character. They are approximately in a thermodynamical equilibrium and therefore thermally stable. The situation is changing slightly if additional elements are added to harden the matrix. As a handicap internal stresses appear if the phases have different thermal expansion coefficients. One has to fear that thereby the values for thermal fatigue will be lowered. In this area intense research work should be done in the next years.

3.6.6. Hot Gas Corrosion

All turbine blade materials have to be protected by surface layers against hot gas corrosion. Fortunately, the growing oxide layer on the surface is thicker than the diameter of the fibers in composites with monocarbides, thereby protecting the refractory carbide fibers automatically.

A chronium-aluminium layer can protect all mentioned eutectics sufficiently against hot gas corrosion.

3.6.7. Conclusion Remarks on Directional Solidified Eutectics

In summarizing all the properties of the directional solidified eutectics one can conclude that these composites might be the next generation of high temperature materials for the hottest parts of the gas turbine. But certainly plenty of research and development work has to be still performed to improve the creep resistance and thermal fatigue.

Also nondestructive testing methods have to be developed.

How far the development of the directional solidified eutectics is at the present time can be best seen by the following fact: The U.S. goverment has started this year the financial support of a large development program on industrial processing techniques whereby the CoTaC and the γ'-δ system play the most important role.

4. Materials Development oriented towards Construction Parts

A typical example of the consequence of a fruitful cooperation between materials engineers and construction engineers is a modern jet engine. By the time the demands of the engine producers for further improvements could not be satisfied by the cast turbine blades out of superalloys, because the material was at "the end" at approximately 0.8 homologous temperature that means at 80 % of its melting temperature in spite of optimum protection layers, new cooling devices were developed.

This grandoise contribution of the construction engineers was pressing oncemore the maximum permissible temperatures remarkable higher. Fig.17 shows the concept for convention-film and transpiration cooling respectively. In near future the construction engineers and the technical development will demand materials of the next generation. Very probably these will be composites.

In the development of "artificial" composites with diffusion barriers between matrix and fibers the possibility of using optional concentrations and structural arrangements of the strengthening fibers corresponding to the desired load characteristics of the construction part will be utilized.

The directional solidified eutectics have to be processed in such a way that the arrangement of the fibers or plate-like whiskers is adapted extensively to the requirements of the construction part configuration. Although this will be very difficult, one has the expectation to overcome these difficulties with construction parts designed to the properties of materials. This optimism is based on the first positive experimental results and emphasizes the importance of team work between physical metallurgists and construction engineers.

Both kinds of composites have to allow the application of additional cooling.

5. Practical Examples, Forescast on Future Application Possibilities

The aeroplane turbine is a very good example to demonstrate the state of the development with respect to application possibilities of advanced materials, especially composites with metal and polymer matrix. Without exaggeration one can say that the key for the development of efficient thermal engines lies in the development of suitable materials. In case of the thermal engine the application temperature is proportional to the efficiency. It is the task of the materials engineer to produce materials which possess sufficient technological properties at high temperatures, namely besides other creep strength and low specific weight. A schematical drawing of a turbine is shown in Fig.18. Three different temperature regions can be separated. The opinion of some experts about the most favourable materials for the different stages of the engine is tabulated in Fig.19. It looks like the answer of the materials engineer to the demand for higher application temperatures are composites. For the compressor as well as for the turbine one thinks of composites.

In spite of the catastrophe at Rolls-Royce one thinks of polymer composites for the compressor, but certainly with a better impact strength against FOD. For the turbine itself only composites with metallic matrix are eligible. One tries to optimize the conventional titanium alloys and is testing composites with titanium matrix and protected boron fibers as strengthening components. Composites with Al-matrix are less taken into account than composites with To-matrix because of the danger of FOD. But also these composites have to be protected at the blade edges with resistant metal inserts. Fig.20 shows to the right a conventional forged compressor blade of the first stage of the compressor. To the left a blade out of the titanium alloy Ti-6Al-4V is shown which has 50 % reinforcement with boron fibers protected by SiC. Immediately one can notice the difference: Because of the much higher rigidity of the reinforced blade the stiffening ring can be omitted after 2/3 of the height and the blade has a thinner wall thickness. By these both steps the weight is reduced by approximately 30 %.

At present the compressor blades of the second stage (500-650^{o}C) are made out of nickel alloys. A forecast shows that at the end of the seventies powdermetallurgically produced, high temperature strength titanium alloys with finely distributed particles for additional strengthening might be available. If this is the case then the gain in weight would be about 50%. Disks of the second stage and of the turbine will be produced in future to an increasing extend powder metallurgically utilizing prealloyed powder, that means the vacuum melt will be pulverized in an inert gas stream. The material sintered in this way exhibits at room temperature about twice the starting strength and a higher fatigue strength than the cast alloy. At the high temperatures of over 800^{o}C the sintered material is softer than the cast material and at temperatures above 1000^{o}C it is superplastic because of its fine grain size. This property can be utilized in the production of disks.

Fig.21 demonstrates what kind of influence efficient coatings can have on the life time of turbine blade materials under service condition. It can be seen that the superalloys can be protected sufficient against oxidation by multiple coatings.

To summarize the state of R and D in the field of materials for high temperature performance all signs point in direction of composites tailored to the needs of engine engineers be ing candidate materials of the next generation.

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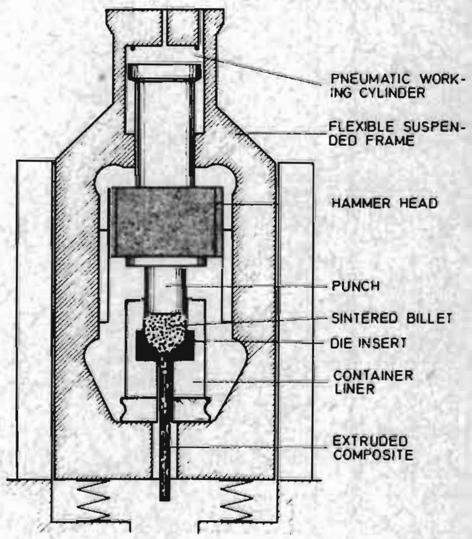

Fig. 1: Dynapak HERF extrusion machine

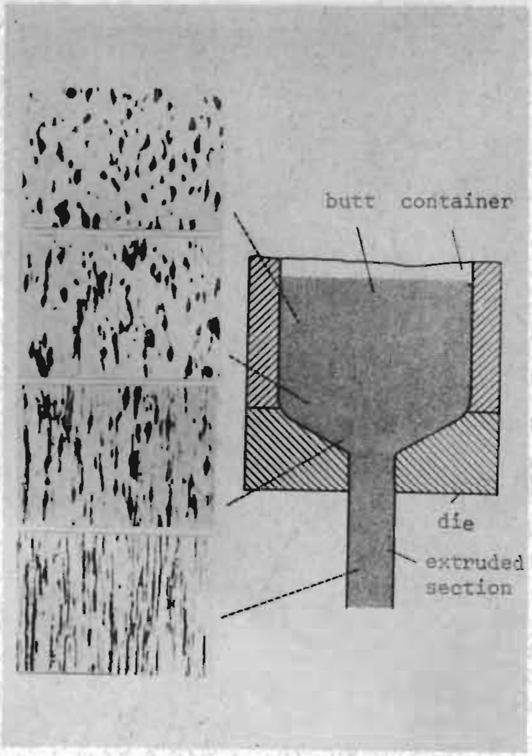

Fig. 2: Extrusion by HERF

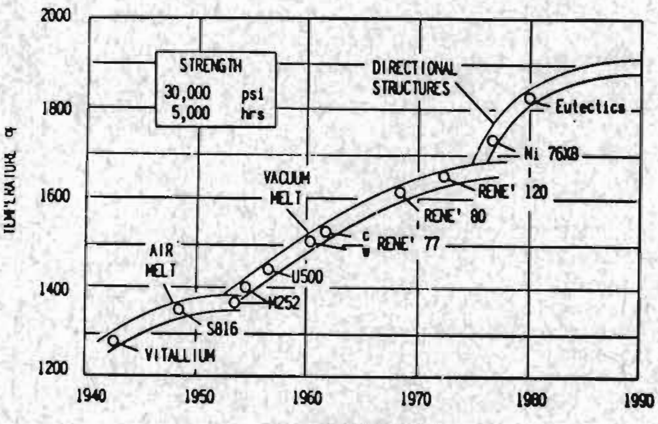

Fig. 3: Progress in turbine blade materials

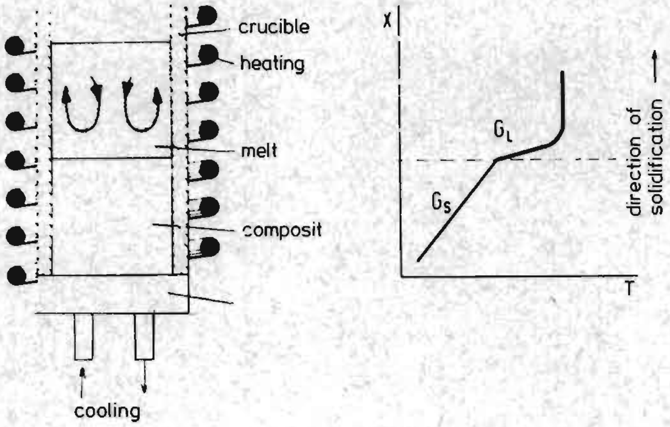

Fig. 4: Principle of directional solidification (Sahm)

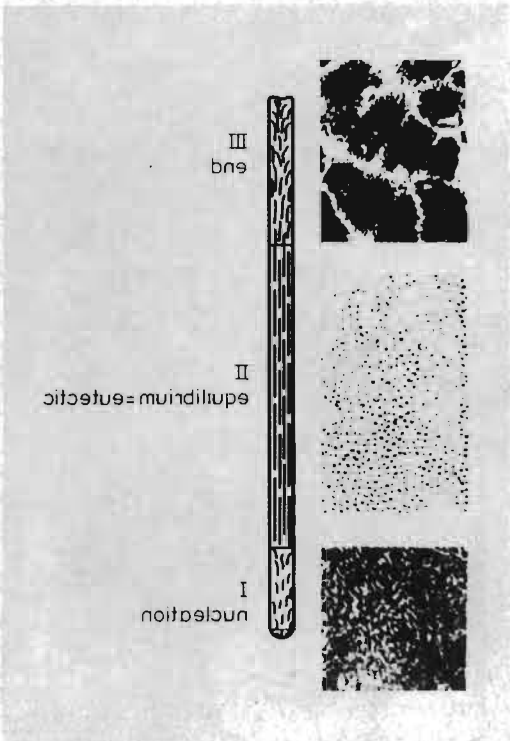

Fig. 5: Processing of d.s. eutectics (Sahm)

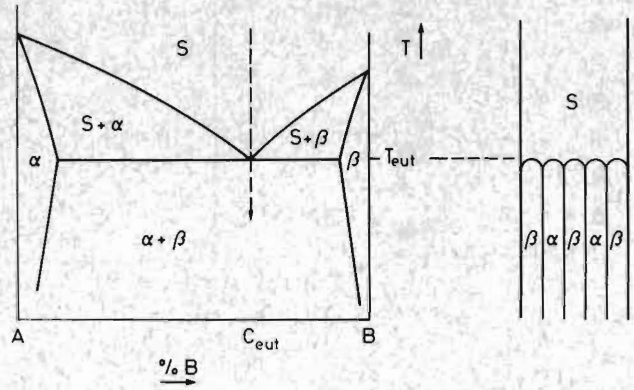

Fig. 6: Eutectic Solidification

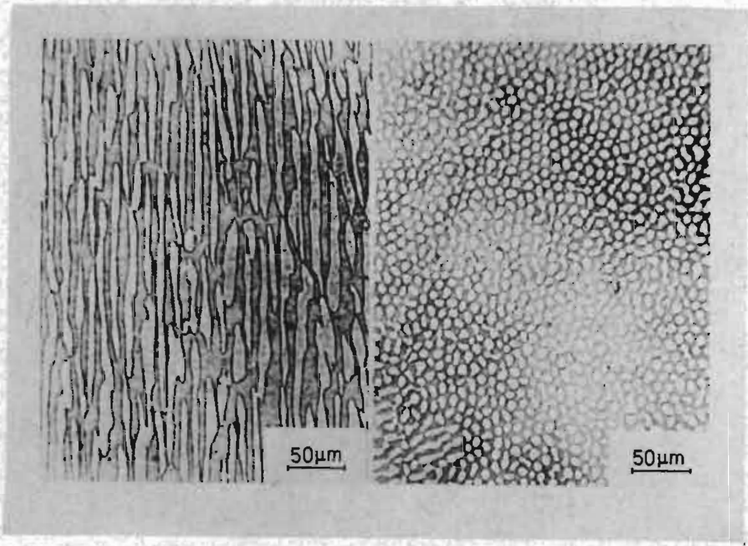

Fig. 7: Structure of d.s. eutectic Ni_3Al-Ni_3Ta

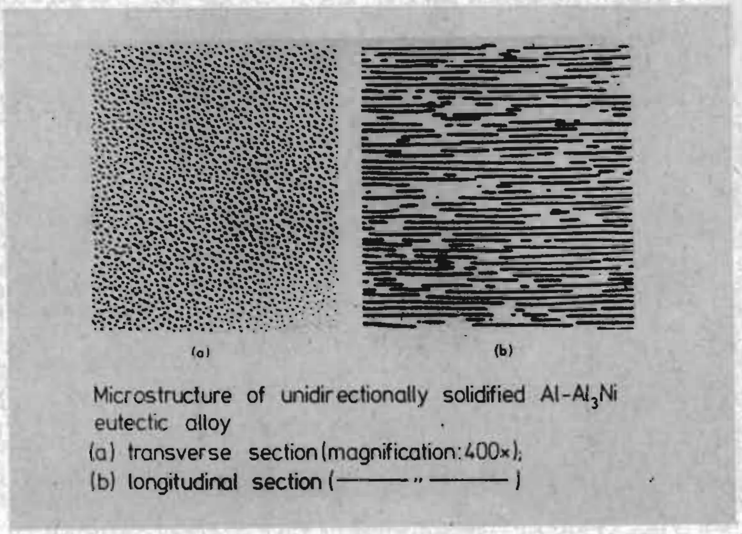

Fig. 8: Microstructure of unidirectionally solidified $Al-Al_3Ni$ eutectic alloy
a) transverse section (magnification:400x);
b) longitudinal section (" ")

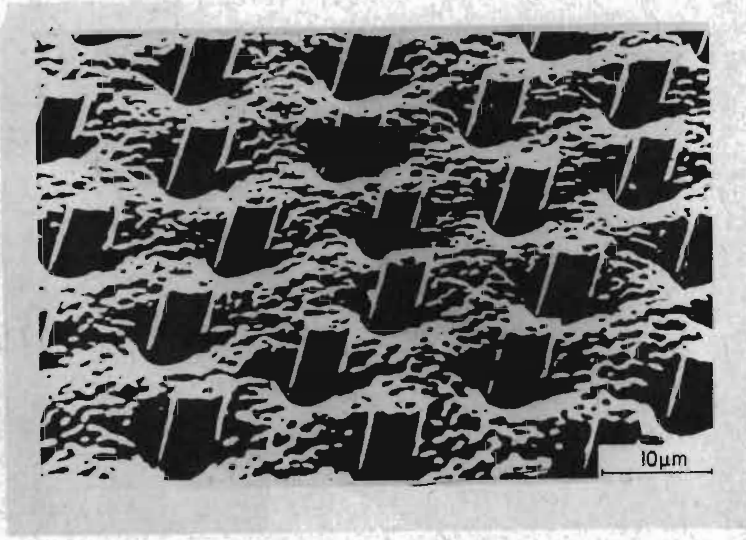

Fig. 9: Tungsten whiskers in nickel matrix

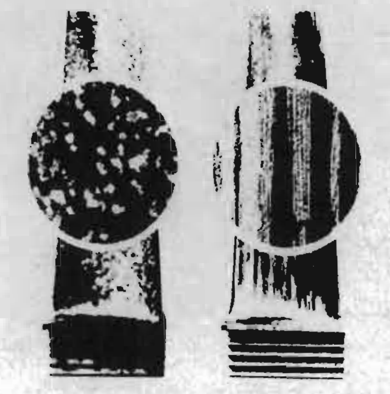

Fig. 10: Random grain structure; Columnar grain structure

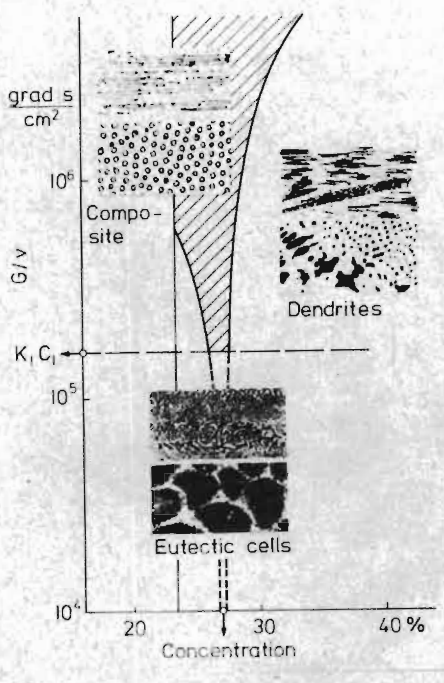

Fig. 11: Temperature gradient G and process velocity v of directional solidification (Sahm)

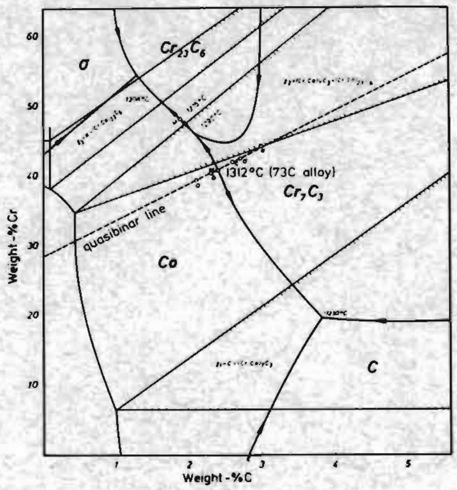

Fig. 12: Detail of ternary system Co-Cr-C

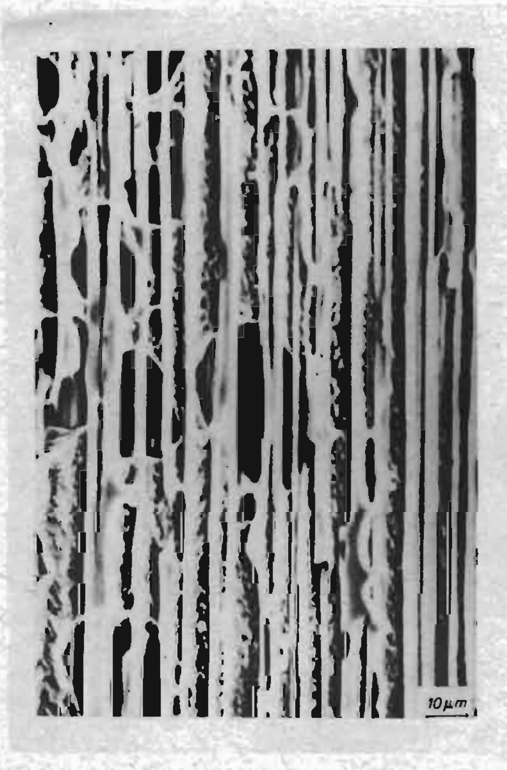

Fig. 13: Longitudinal section of Co-Cr-C eutectic composite

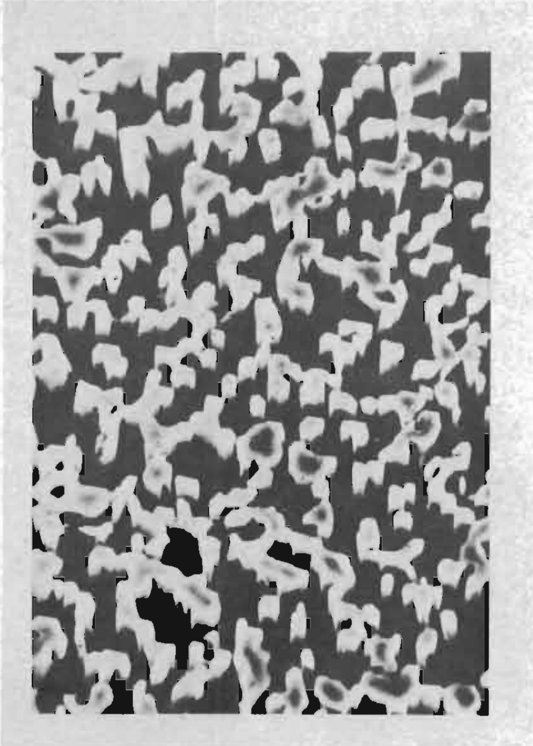

Fig. 14: Cross section of Co-Cr-C eutectic composi...

system		$CoCr-Cr_7C_3$	Co-TaC	Ni_3Al-Ni_3Nb
melting temperature [°C]		1300	1350	1280
UTS [MN/m²]	20-25°C	ca. 1000	ca. 1000	ca. 1200
	1000-1100°C	ca. 300	ca. 420	ca 740
elongation [%]	20-25°C	ca. 1.5	ca 30	ca 0.6
	1000-1100°C	ca. 1.5	4	3-10

Fig. 15: Mechanical properties of eutectic composites at room temp. and 1000-1100°C (after lit.)

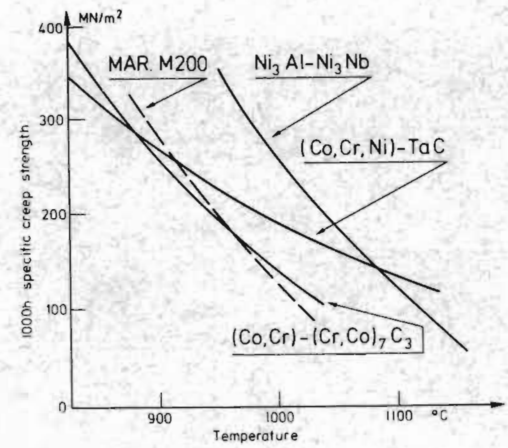

Fig. 16: 1000 h specific creep strength (El Gammal)

Fig. 17: Advanced cooling concepts

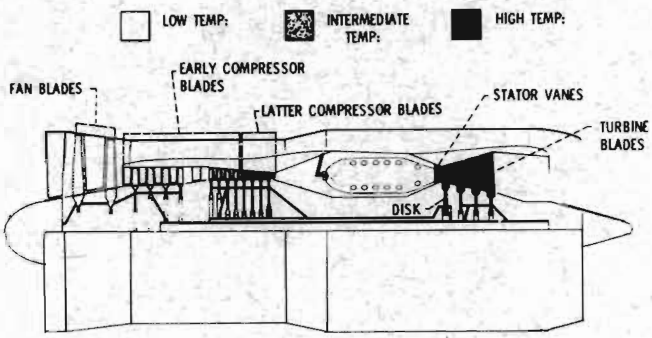

Fig. 18: Schematic sketch of jet engine

component	material	advances
fan blades	polymer composit	weight reduction at 300°C
compressor blades	Ti-alloys Ti-composites	substitution of Ni-alloys by half at 650°C
turbine blades	superalloy matrix composites	temperature raise to 1200°C

Fig. 19: Projected improvements in engine materials [NASA SP-292-1971]

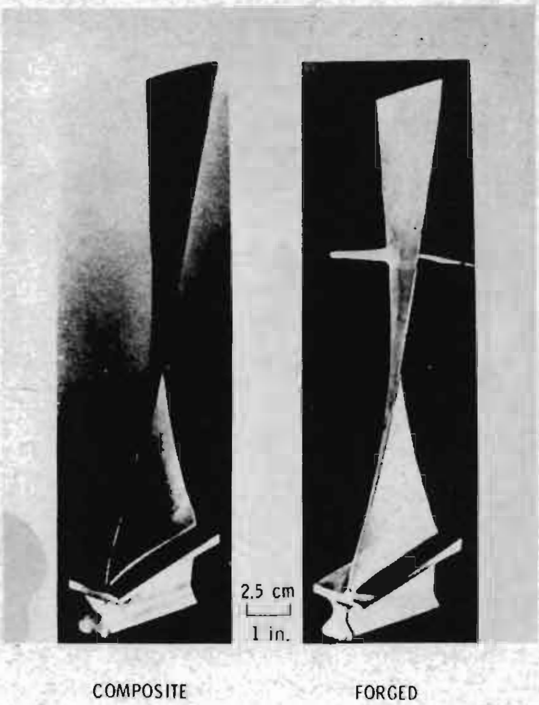

Fig. 20: Composite and forged titanium alloy blades

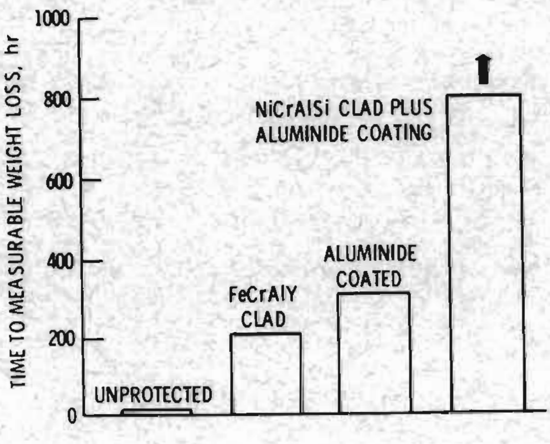

Fig. 21: Effectiveness of oxidation protection systems for alloy IN-100 in Mach I burner test. (Cycle: Ih at 1093°C; 3min at room temp.) [NASA]