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Some Aspects of German Work on High Temperature Materials.

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE.

Some Aspects of German Work on High Temperature Materials.

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Interview with Dr. Max Bentele head of Predevelopment Department at Hirth Motoren (Stuttgart).

He took part in the great conference of scientists and engineers held in Berlin on 29th November, 1944. At that conference high temperature materials for jet aircraft were discussed.

Reports by the following authors were read and discussed under the chairmanship of Prof. Bollenrath on 29/30-11-44 at Jena.

(a) Schelp	-	Berlin
(b) Oestrich	-	Berlin/Spandau
(c) E. Schmidt	-	Braunsweig
(d) Sorensen	-	Augsburg
(e) Rath	-	Hermsdorf
(f) Dirkusen	-	Braunsweig
(g) V. Lutz	-	" (leader of discussion)

The following products were also discussed.

(a) Quartzglas
(b) Artostan (Hescho). Kleine Warmedehnung
Feuerfest bis 1800°C.
(c) Tonerde (Degussa)
(d) Siliziumlnarbid (Staatl. Porzellanmanufaktur)
(e) Calit (Hescho) hohe Zugfestigkeit
grosse Wärmedehnung

It was agreed that extensive research should be made on the use of ceramics, in the first place for stator blades. Bentele did not concur with this view and thought that they could be used equally well for rotor blade. He pointed out that rotor blades had only one fixed point and could be made to operate in compression; while stator blades had two fixed points, are subjected to bending stresses and to extensive vibration.

A conference was held at Jena a month later, and the following men were present:-

Dr. Miller (Staatliche Porzellanmanufaktur, Berlin).
Dr. Stuchart (enamel specialist)
Dr. Bentele (Hirth Motoren Co.).

It was decided to start work with the following materials:-

(a) Al_2O_3 + Fe, and materials such as "Ardostan", "Cali developed by Hescho.

(b) SiC + other materials (carbon, Al_2O_3), e.g. SiC + C & Fe.

(c) Quartz.

Work was also to be done on the coating of metal blades.

Regarding SiC it was considered that since it has a higher conductivity than Al_2O_3 it would have a better thermal shock resistance. It can be mixed with other materials, including carbon (which has a low specific gravity); but since carbon is readily attacked by oxygen at high temperatures, it was thought that a protective coating would be necessary for this type of mixture. An important point raised by Dr. Müller was that a heating period of two weeks was necessary in order to sinter SiC properly. It was decided to cooperate with the Osram-Siemens Co. on the joining of ceramics to steel.

Bentele thought that values for static and dynamic strength tests should be obtained on these materials before work was done on them in his pre-development department. Having obtained these figures he would then be in a position to design a turbine in which the material was used to the best advantage. When tests resembling actual service conditions were done on ceramic blades, he found that cracks tended to form at the trailing edge. Blades with little difference in thickness between leading and trailing edges would be better from this point of view, and a compromise had therefore to be reached between aerodynamic considerations and resistance to cracking. At 800 to 1,000°C and 2 to 3 Km.* strength" (corresponding for steel to 26 Kg/sq.mm) was required.

* The material should be capable of suspending vertically a length 2 to 3 Km long of itself without breaking.

Points in favour of the use of quartz are as follows:-

(a) It is a reliable material, the properties of which are well known.

(b) It is easily welded.

(c) It has a good resistance to thermal shock.

It was pointed out also that the existing test results were by no means final (see report on visit to M.A.N. Augsburg).

Bentele said that the method of fixing of these blades had to provide a certain degree of free movement, in order to increase the damping capacity of the structure. He was occupied with the design of this.

Bentele had also designed hollow air cooled metal blades made from steel C.M.V.-Spezial (cromadur) - a material which had the highest nitrogen content (0.28%) ever met with in German steels. The process for deep drawing these blades is illustrated in (x) in the attached picture reproduced from a Hirth-Motoren report.

Interview with Richard Walther, 9 Weilheimer Strasse Sternberg (26,27,29,30, September, 1945).

Richard Walther[@] was visited at his private laboratory at Starnberg. He was an old man and had worked for many years on carbides, high temperature metals and ceramics. He had set up a firm for manufacturing carbide tools - Montenwerke Walter, Tübinger - and was responsible for about 200 patents, most of which had been exploited by Krupps. The laboratory at Starnberg was extremely well equipped, and was undamaged.

(a) Carbides

He had found that tentalum carbide was the most resistant to oxidation of all metallic materials. At a temperature as high as 2,000°C. there was no appreciable oxidation. Another carbide of interest was beryllium carbide, which was a very stable compound of metallic character. Walther suggested that an alloy of tantalum and beryllium carbides could be developed as a super high temperature metallic material.

(b) Chromium-cobalt alloy

He had developed an alloy with very good resistance to oxidation and good welding properties, having the following composition:-

55% Co   41.5% Cr   3 to 5% Si   0.5% C.

At high temperatures it forms a hard dense form of Cr_2O_3 and SiO_2 on the surface, similar to crystoballite. By replacing the Si with Zr he thinks that the strength at high temperatures could be increased. Formation of ZrO_2 with Cr_2O_3 may also give better scaling resistance than the SiO_2 - Cr_2O_3 film. He has not however tried introducing zirconium because of the shortage of that metal.

@ Richard Walther died on 11th Nov.1945.

(e) Ceramics

Walther has worked with about a hundred different mixtures of oxides, including the formation of spinels, and has tested them for hardness, melting point, recrystallisation temperature, and resistance to thermal shock. The two best compositions were

A. $ZrO_2 . Al_2O_3$ + 5% Kaolin

B. $BeO . Al_2O_3$

The Brinell hardness of these two materials was about 800 kg/mm.sq. while that of the others was about 200 to 600 kg/mm.sq. These materials have a high thermal shock resistance and in this respect are as good as quartz. Their strength at high temperatures is several times greater. Shrinkage during sintering was about 13% for material A and about 16% for material B, while the other mixtures tried by Walther had a shrinkage greater than 20%.

Walther has not been using the slip casting method for preparing these ceramics as he considers it no good for this purpose, since in the first stage of drying cracks may occur which, though unnoticeable at first, may grow larger during sintering and become dangerous. He therefore preferred a dry method, and pressed them under a pressure of 3,000 Kg/sq.cm. The compressed pieces were sintered at about 1,700°C. for several hours. When the composition corresponds to a spinel formula the temperature was much lower, and 1,200°C was sufficient to cause the reaction. After this reaction, heating up to a higher temperature for a longer time has no effect on the physical properties of the specimen. Shrinkage occurs while the reaction is taking place.

The oxides used in the preparation of spinels must be amorphous in form, and not crystalline. For example fine corundum will not form a spinel with any other oxide. Ryschkewitsch agreed with this.

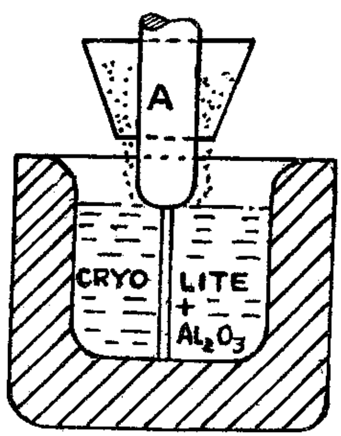
(d) Scaling apparatus

The apparatus consists of a small furnace inside which is a disc of refractory material, mounted horizontally on a vertical axle. In this disc are ten holes, in which the specimens are fixed. The disc is rotated mechanically, and the flame from the burner falls on each specimen in turn. Every eight hours the specimens were brushed free from scale, and weighed. This method is exceedingly simple and gives a useful comparative result, one set of specimens being used as a control.

(e) Preparation of metals (Th, Zr, W, Ti, Cr, V, Co, Ni, Fe).

The method involves the production of aluminium vapour, which is used to reduce the oxide of the metal concerned. The apparatus is sketched diagrammatically in Figure . Current is passed between the thick graphite rod electrode and the graphite crucible. The crucible is charged with a mixture of cryolite and aluminium oxide. The thin graphite extension of the electrode A becomes very hot, melting the cryolite. Round the tip of A, the alumina is reduced by carbon from the electrode, and owing to the high local temperature forms aluminium vapour. The ore of the required metal is introduced round A, falls into the area of aluminium vapour and is reduced. The molten metal thus produced falls into the molten salt, and collects at the bottom of the crucible. The metal is free from oxygen, having however a small carbon content which comes from the crucible.

A



Interview with Dr. Schütte of M.A.N. Augsburg

Dr. Schütte was assistant to Professor Sorensen. The following materials were developed for use in gas turbines:-

(a) For turbine blade (solid) - Tinidur

(b) For combustion chambers - B.V.T. 90(0.18 C, 0.935 Si, 0.55 Mu, 1.43 Cr, 91.1 Mo, 0.55V).

The B.V.T. alloy was chromised before use, where the maximum depth of chromium diffusion was 1 mm. with 30% Cr on the surface diminishing to 1.43% Cr. which is the original content of chromium in the steel.

This method of protection gave satisfactory protection against scaling at temperatures up to 650°C.

Aluminium oxide blades made by Dr. Ryskewitch to the design shown in fig.   were tested at M.A.N. in an engine. Porcelain blades prepared by Dr. Rath of Hescho Hernsdorf were also given engine tests. The results given by alumina blades were poor on account of cracks and those of porcelain were encouraging, although the strength of porcelain at 900°C was the same as that of alumina at 1,400°C. Dr. Rath was also thinking of making blades from a mixture of porcelain and silicon carbide. The quartz disc and blade assemblies has been made. The results were not very satisfactory because of the low strength of quartz at 1,000°C. which is about 1 Km. This value was not final, however, and it was decided to make a new design of quartz assembly. Quartz blades were made from natural quartz crystals, and the disc from silica sand. It is believed that quartz is good for a bonding material for various mixtures of ceramics and carbides. The main programme for developing ceramics for turbine blades was centred at M.A.N. They had on order a high frequency accoustic apparatus for testing the soundness of ceramic components.

It was proposed to make hollow water cooled blades for rotors (Prof. E. Schmidt's design) and ceramics for stator blades working at 1,100°C. Meyer Hartwig from Hesho had developed a method of bonding alumina to steel by sintering a layer of iron powder between them. He was alsq working on the preparation of a rod of aluminium oxide and iron powder in such a way that the composition varies uniformly from 100% Al_2O_3 at one end to 100% Fe at the other.

Interrogation of Dr. Eugen Ryschkewitsch, at Kempten on 30/9/45 - 3/10/45 and Dr. R. Kieffe (Reutte)

Heater elements for 1400 - 1700°C

Dr. Ryschkewitsch, with Dr. Schwartzknopf, designed graphite heater elements.

One type consisted of a graphite rod sealed inside a gas-tight alumina tube with a mixture of Al_2O_3 + Fe, and provided with copper leads at the end. The sealing mixture was graded from 100% Al_2O_3 at the joint with the tube to 100% Fe at the joint with the copper connector. A horizontal furnace using this type of element is at the Metallwerke Plansee. The working temperature of the furnace was 1,600°C, and once heated, the furnace was never allowed to cool. After long heating of these elements in a horizontal furnace, they showed some sagging.

A firm at Duisberg used graphite grog in a vertical alumina tube, the ends of the tube being sealed temporarily. As the graphite was burnt away, more could be added, while the furnace was in operation.

Dr. Kieffe worked with Konopicki,, of the Austrian-American Magnesite Co. at Radentheim, on a heating element made from a gas-tight sillimanite tube surrounding a molybdenum rod. The end of the tube was covered with copper caps, sealed to the tube with silver chloride, and water cooled. The furnace worked satisfactorily at 1,400°C.

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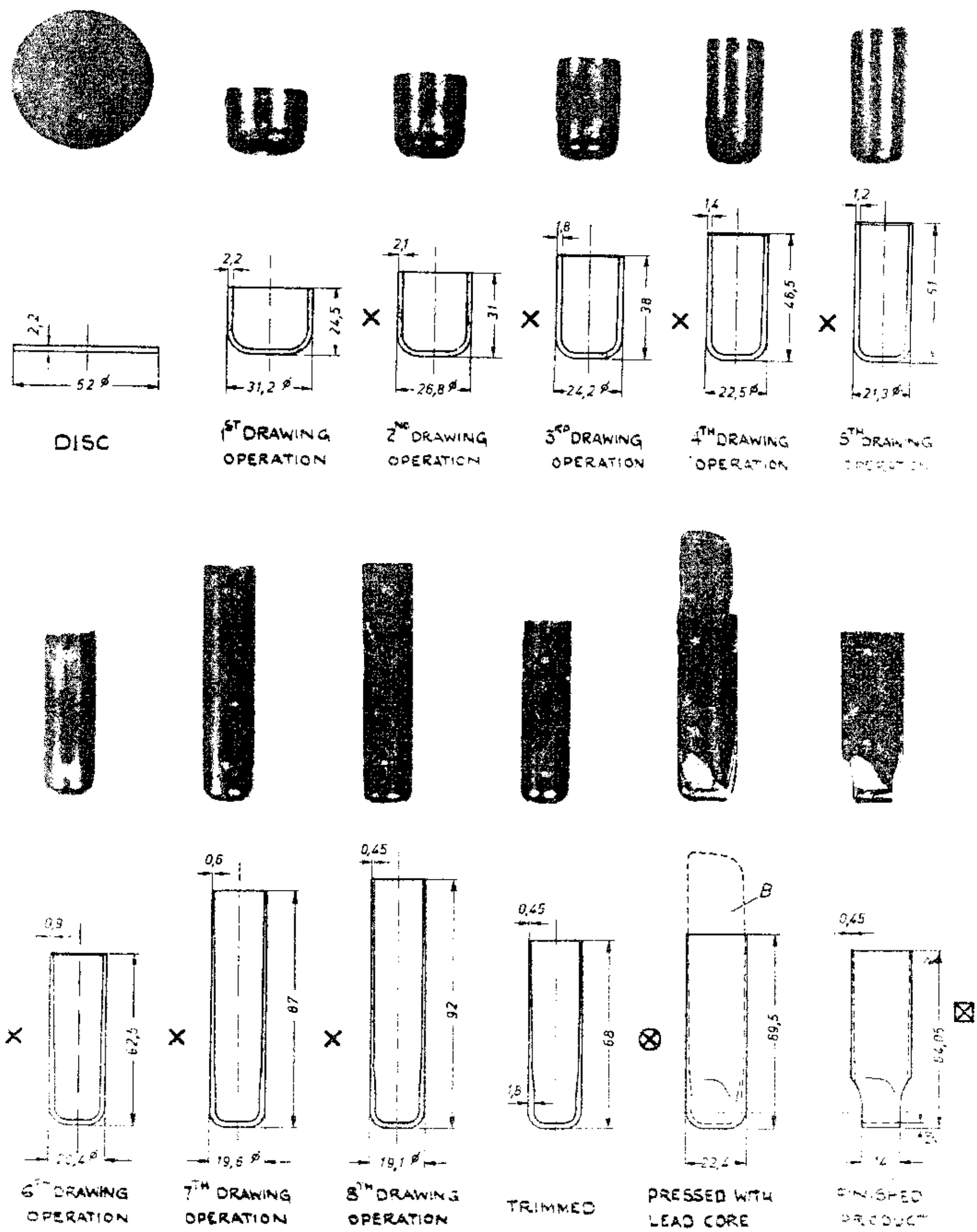
PROCESSING OF TURBINE BLADES.

STEEL: CMV-SPEZIAL (CROMADUR), KRUPP ESSEN,

CHEM. COMPOSITION: 0·11 % C, 13 % Cr, 17 % Mn, 0·8 % V, 0·28 % N_2



X = HEAT TREATED AT 1050°C QUENCHED IN WATER
⊗ = " " " 1100°C " "
⊠ = ANNEALED 800°C 2 HRS. COOLED IN AIR

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