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Cost effective Manufacturing Methods for structural Ceramic Matrix Composite (CMC) Components

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BREAK

ABSTRACT

MAN Technologie AG has been engaged in the field of ceramic matrix composites (C/SiC, SiC/SiC) for approximately 10 years. Two manufacturing methods have been developed with respect to economical series production:

- Chemical Vapour Infiltration Process (CVI) with temperature and pressure gradients
- Liquid Polymer Impregnation (LPI) and Pyrolysis

The advantage of these methods is an essential reduction of process time compared to the conventional isothermal-isobaric CVI method, with equivalent material performance. The main material characterization data, such as strength/strain, thermal shock, dynamic fatigue and high temperature behaviour are described. Several components under development or in low volume preseries production are presented.

1. INTRODUCTION

MAN Technologie has been involved in the field of "Ceramic Matrix Composites" (CMC) since 1984 and participates in several national and international ceramic programs, in addition to its own internally funded R & D activities. We develop CMC components for spacecraft, aircraft, missiles and chemical equipment application, including ceramic fasteners [1-3].

Due to the material´s special mechanical and physical behaviour, CMC can be regarded as a viable structural material, as well as for extreme hot structures and those exposed to aggressive chemicals. The application of such ceramic components will lead to an increase in system efficiency. To create the opportunity for market penetration by ceramic components, in addition to technical aspects, acceptable costs are important in volume production. Therefore in our company cost effective CMC manufacturing methods have been developed and installed, i.e. either rapid manufacturing, or low cost investment.

2. MANUFACTURING METHODS AT MAN TECHNOLOGIE

Sol-gel, gradient-CVI, and liquid polymer impregnation are the processes in use. Process selection depends on the respective requirements of the structure or part in question, taking into account operational demands, design rules, manufacturing needs and limits, plus cost.

2.1 The Chemical Vapour Infiltration (CVI) Process

Cost was the dominat driver for the industrial development of the temperature and pressure gradient-CVI for the manufacture of high performance C/SiC and SiC/SiC. In contrast, high costs are associated with the more conventional isothermal/isobaric CVI process, due to very long manufacturing times [4] and development cycles. The development of the gradient-CVI process [5] led to complete technical success, e.g. for highly loaded hot structures, and is now being employed for the low volume production of machinery parts. In fact, considerable cost advantage has been

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attained with this process. It turned out, however, that this advantage is clearly reduced for complex, highly integrated components as well as low volume production. The essential purpose of the CVI process with a temperature and pressure gradient is to drastically reduce the time required for densification of the fibrous preforms. This is accomplished by the following procedures:

The pressure gradient between upstream (gas inlet) and downstream (gas exhaust) side of the preform allows for an increased mass transport of deposition gas through the fibrous structure, as it leads to a forced convection with a rapid exchange of feed gas and reacted gas. The preform is to be mounted into a device in a way that it seals off both the upstream and downstream sides to build up the pressure gradient with the gas flow, which consists of methyltrichlorosilane as SiC precursor in hydrogen carrier gas.

The temperature gradient controls the local distribution of the deposition within the preform. At the beginning of the infiltration process, the down-stream side of the preform body is typically heated to 1450 K for the SiC matrix process whereas the upstream side is cooled to a temperature low enough that SiC deposition does not occur. This means that the densification of the fibrous structure by SiC matrix growth proceeds from the rear to the front side relative to the gas flow direction and thus allows for a permanently open access for the feed gas through-out the densification process, until the growth front reaches the upstream surface. Progress of the growth front is driven by the increase in thermal conductivity caused by filling of the pores with SiC matrix.

In comparison to the isothermal/isobaric CVI process, gradient-CVI exhibits two essential differences: a markedly higher gas flow, plus a raised deposition temperature. Both of these features involve a remarkably higher deposition rate which would soon cause clogging of the surface near pores and exclude complete densification when applied to the isothermal/isobaric process. This higher useful deposition rate reduces the time required for densification of a given thickness by at least one order of magnitude. In order to obtain further cost reduction, stabilized, selfsupporting preforms are preferably utilized. The preform consists of locally bonded woven fabrics and is made using the tape winding or laminate moulding process. The adhesive is an organic or organosilicon resin system, which is subsequently transformed into solid carbon or SiC by pyrolysis.

2.2 The Liquid Polymer Impregnation (LPI) Process

For parts of high complexity, such as a space craft heat shield panel (Fig. 8), the LPI process is preferable, as it permits manufacture of such a part with integral-laminated reinforcement, at a cost level comparable to that for regularly shaped gradient-CVI parts. The LPI process applied by MAN Technologie and described here, is based on the utilization of woven fabrics of carbon fibers, with parts formed by wet lamination. The carbon fibers are coated with carbon by CVD. The matrix precursor consists of a blend of different silicon-bearing polymers, adjusted for proper viscosity, wetting, and ceramic yield. The ceramic product is obtained by a pyrolysis step in inert gas atmosphere.

In order to reduce matrix shrinkage during pyrolysis, a submicron SiC powder is added. Thus a solid residue of 80 % by weight is achieved in the very first impregnation cycle. This residue mainly consists of amorphous SiC. Due to the volume shrinkage of the polymer during its conversion to ceramic, cracks and pores are formed. These are refilled by repeated impregnation and pyrolysis cycles. Usually three re-impregnation cycles in a vacuum chamber are sufficient for the densification and the required material properties. For the re-impregnation steps, the same precursor blend as for the first cycle is used, but without the SiC filler.

3. MATERIAL PROPERTIES

3.1 Specific material data

The ongoing development activities in the field of fibre reinforced ceramics are based on the concept of creating a relatively ductile ceramic material, compared with existing brittle monolithic ceramics.

CMC at present normally consists of carbon or SiC fibre in a SiC matrix. The main advantages of the following material properties relating to its ductile behaviour are:

a) High Elongation under Tensile Stress

The high elongation is caused by partial debonding and slipping of fibres in the matrix, and finally by pullout of the fibres (figure 1) under tensile stresses. The condition reponsible for this effect is a relatively weak bond (created by a carbon coating on the fibre surface) between fibre and matrix, which deflects matrix cracks along the fibre surface.

b) Thermal Shock Resistance

One of the most important properties of CMC is its very good resistance to thermal cycling. During a cycling test up to about 1100°C (see figure 2), monolithic ceramics are totally split within 10 cycles, whereas the CMC material withstands 1000 cycles without any damage.

c) Fatigue Resistance

Fatigue tests with tension-compression loads at room temperature show a very flat decrease in slope of the Wöhler fatigue curve. This means that several million load cycles at stress levels relatively close to the ultimate strength can be applied (see figure 3).

In figure 4, the main mechanical and physical material data for C/SiC and SiC/SiC at room temperature are presented. This table gives an indication of the general levels of the different material properties with respect to the present CVI and LPI technology-standards.

3.2 Thermal Behaviour

Besides application in corrosive environments, CMC is expected to be used for structural components at temperature of 1000°C and above. In this case temperature dependent behaviour of CMC is to be considered. Thermal resistance of the different CMC types is dependent on the respective manufacturing method.

The LPI derived C/SiC can be used preferably for short duration applications. Figure 5 shows the residual properties after 30 min aging at 1600°C in air, vacuum and argon respectively relative to the data in figure 4. After longer aging periods above 1300°C the strength and strain to failure of LPI-C/SiC is markedly reduced, e.g. after 10 h at 1400°C, or 1 h at 1600°C, to about 50 % of original tensile strength. This is due to the degradation of the amorphous polymer derived matrix by decay of the material structure.

CVI-SiC/SiC made with Tyranno fibres also shows a strength degradation at elevated temperatures (> 1000°C), but in this case due to the strength loss of the polymer derived amorphous SiC fibre [6].

CVI-C/SiC provides a long term stability in inert atmosphere. After preliminary tests up to 100 h at 1400°C and 10 h at 1600°C, no strength reduction occured. However, for application in an oxidative atmosphere, oxidation protection is required, since the oxidation of carbon fibre begins in the range of 500°C. The effectiveness of our oxidation protection has been demonstrated by cycling tests up to 100 h at 1400°C in air, yielding a residual strength of 80 %.

4. REQUIREMENTS

For the applications referred in the Introduction, different categories of requirement exist.

- High temperature / very short duration:
  Applicable requirements for possible missile components are in the range of 1700 °C, with an operational time of several seconds.

- High temperature / short duration:
  The requirements for space craft reentry vehicle components are 1500 °C and more, with an operational time up to several hours.

- High temperature / medium duration:
  A temperature range of 1200 °C and more for several hundred hours is typical for hot military jet engine components.

- High temperature / long duration:
  Hot components in civil jet engines have to resist a temperature above 1400 °C for 10,000 to 20,000 hours, whereas for stationary turbines the required life time is 100,000 to 200,000 hours.

5. COMPONENTS PRODUCED TO DATE

The following photographs illustrate selected CMC parts developed by MAN Technologie.

5.1 Air Intake Ramp

Within the German Hypersonic Technology Program, a prototype air intake ramp using a modular design concept has been built with CVI-C/SiC elements [7]. This ramp has been tested under conditions corresponding to loads at Mach 2.9 and Mach 5.6 respectively, e.g. test temperature 1250°C, in full compliance with the mission profile, without any damage occurring (Figure 6).

5.2 Combustion Chamber Liner

A CVI-SiC/SiC tube, representative of a combustion chamber component, has been tested in a small gas turbine for 50 hours with cyclic load end peak temperatures up to 1500°C, without any damage (figure 7).

5.3 Heat Shield Panel

Within the framework of an European Space Agency (ESA) development program, C/SiC heat shield panels for a reentry capsule have been manufactured via the LPI process (figure 8). Panel-segments have been tested under simulated reentry conditions, i.e. exposed to four high temperature cycles at a maximum temperature of 1560°C and 6 min exposure time per cycle. The parts were subjected to very high temperature gradients and transients, which did not cause any damage [8].

5.4 Sealing Ring

Highly loaded sealing rings (20,000 min^{-1}, 65 bar) produced in CVI-SiC/SiC show very low wear and are currently running in series chemical pumps in service up to 10,000 hours (figure 9).

6. CONCLUSIONS

The material and component tests illustrate that CMC is a real potential candidate for structural components in hot and corrosive environments.

For relatively "cold" parts (up to about 400 °C) the currently existing material is already in use for serial components, mainly for chemical equipement.

The present material also has sufficient temperature resistance for high temperature/short term applications such as spacecraft and missile components.

Further development activities are necessary to improve the oxidation protection of the underlying CMC material. High temperature, medium duration loaded components in military jet engines can be achieved with CMC parts improved in this manner.

For high temperature/long duration applications, e.g. civil jet engines, the existing carbon containing CMC cannot be protected sufficiently, since unavoidable surface damage will lead to corrosion and strength reduction. Such severe requirements can only be fulfilled by new oxidation resistant fibres with an adequate surface treatment, combined with the oxidation resistant SiC matrix produced via the gas infiltration process.

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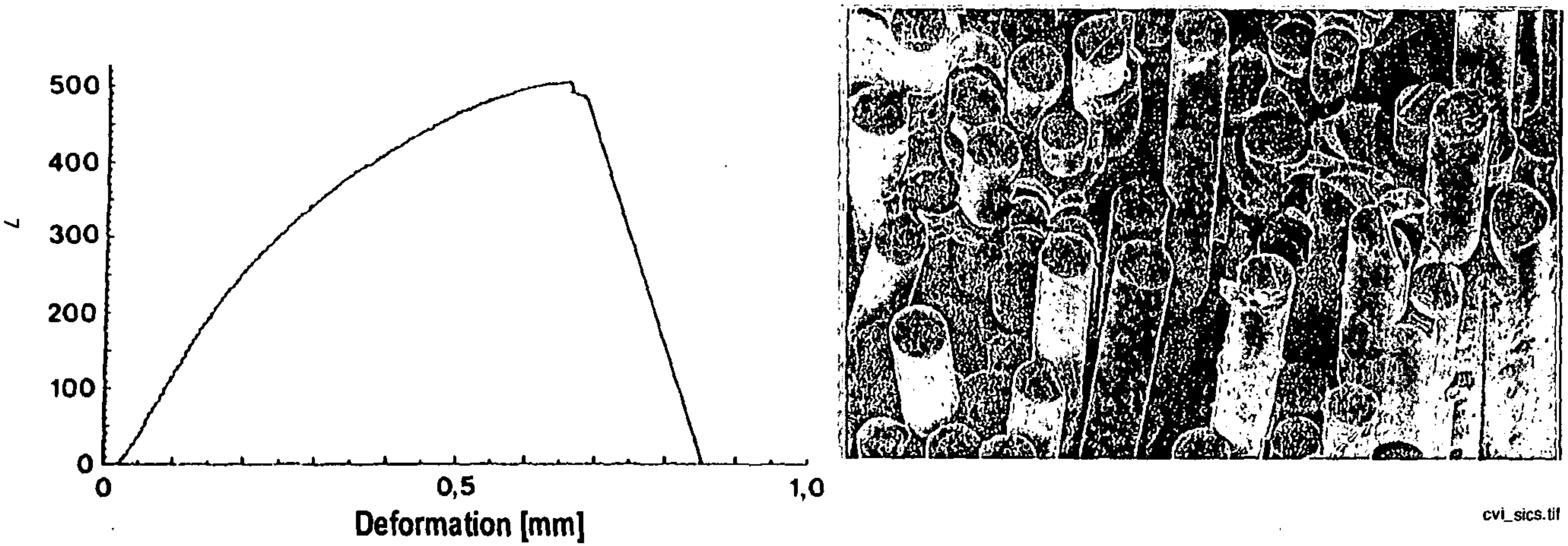
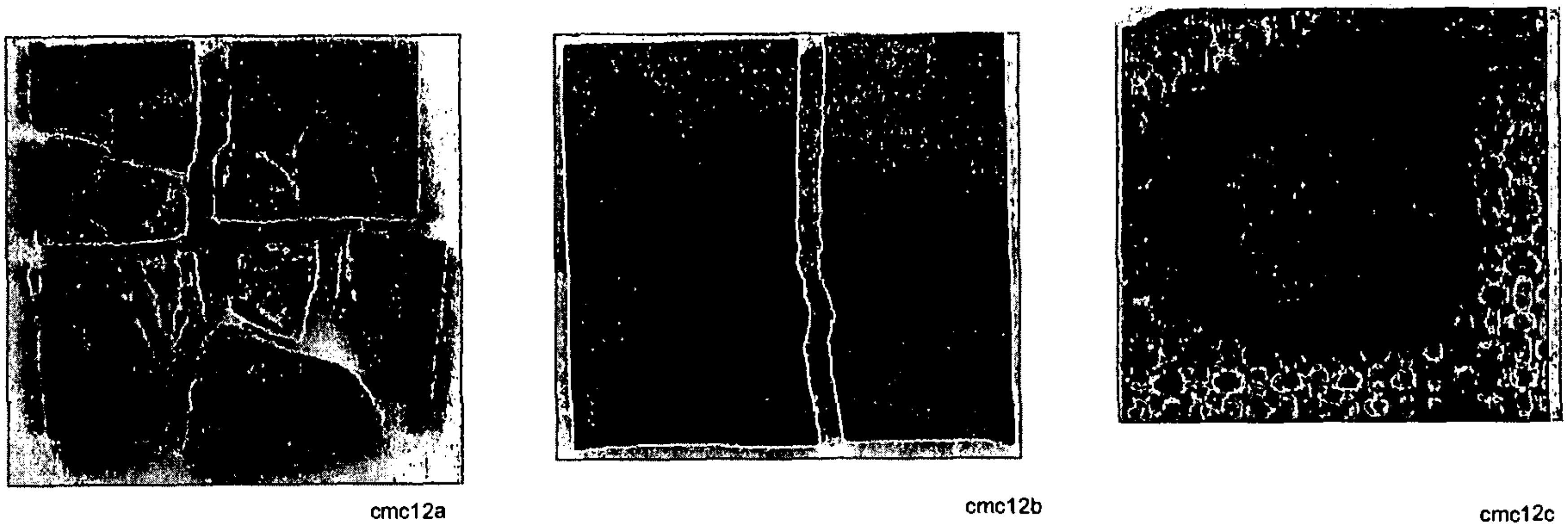


Fig. 1: „Pull out Effect“ CVI-SiC/SiC



after 3 cycles

after 10 cycles

1 000 cycles without fracture

	ZrO_2	SiSiC	SiC/SiC
Heating Time:		20 sec	5 sec
Cooling Time		10 sec	10 sec
Max. Temperature:		1000°C	1 100 °C

Fig. 2: Thermal Shock Test

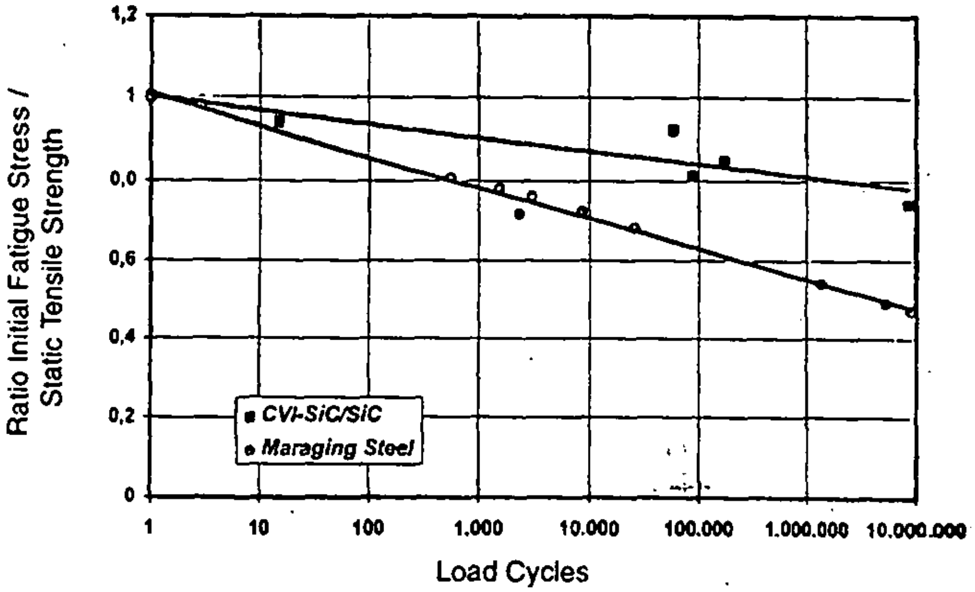


Fig. 3: Tension-Compression Fatigue Test
(Wöhler Fatigue Curve)

		Gradient CVI SiC/SiC	Gradient CVI C/SiC	LPI C/SiC
Fiber Fraction	Vol%	42 - 47	42 - 47	42 - 44
Density	g/cm^3	2,3 - 2,5	2,1 - 2,2	1,7 - 1,8
Porosity	%	10 - 15	10 - 15	15 - 20
Tensile Strength	MPa	280 - 340	300- 320	240 - 270
Strain	%	0,5 - 0,7	0,6 - 0,9	0,8 - 1,1
E-Modulus	GPa	190 - 210	90 - 100	60 - 80
Flex. Strength	MPa	450 - 550	450 - 500	330 - 370
Compr.Strength	MPa	600 - 650	450 - 570	430 - 450
ILS	Mpa	45 - 48	44 - 48	35
CTE	$10^{-6}K^{-1}$ $\parallel$	4	3	3
	$\perp$	4	5	4

Fig. 4: Mechanical and Physical Data

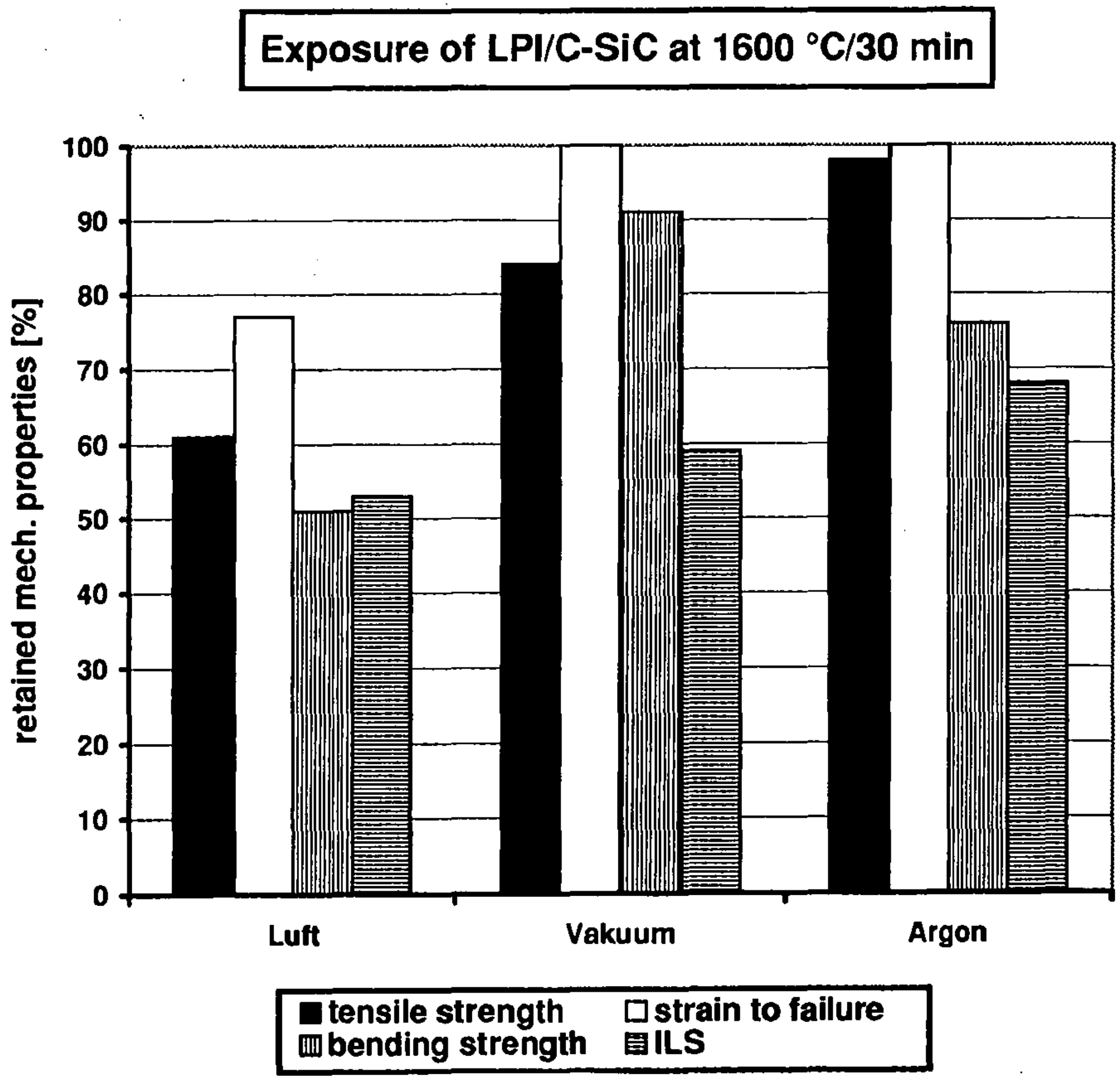


Fig. 5: Residual Properties of LPI-C/SiC after Thermal Ageing at 1600°C, 30 min (relevant for re-entry cycle with safety margin), average of three samples for each value

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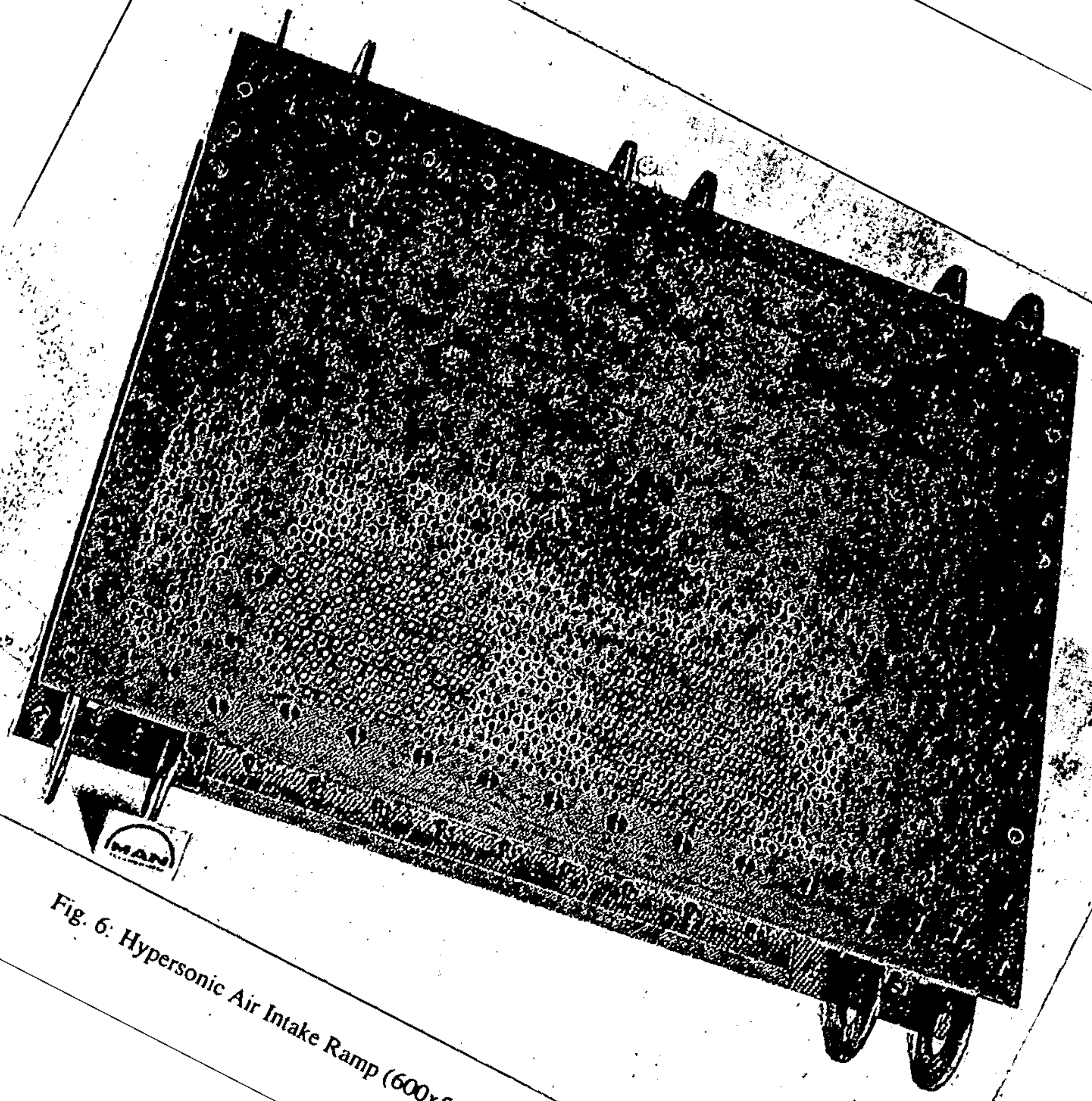

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Fig. 6: Hypersonic Air Intake Ramp (600x500x80 mm)

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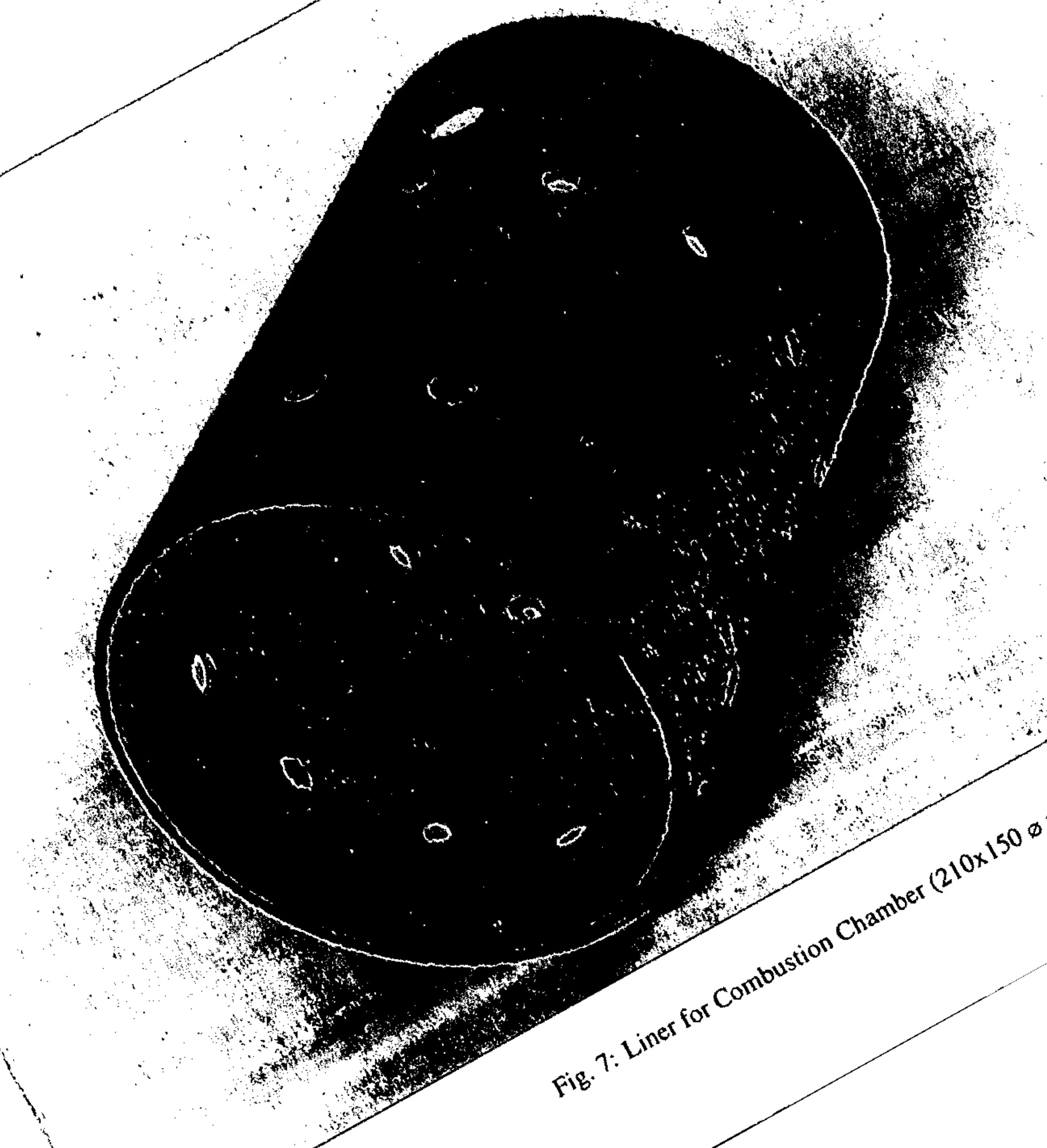

Fig. 7: Liner for Combustion Chamber (210x150 ø mm)

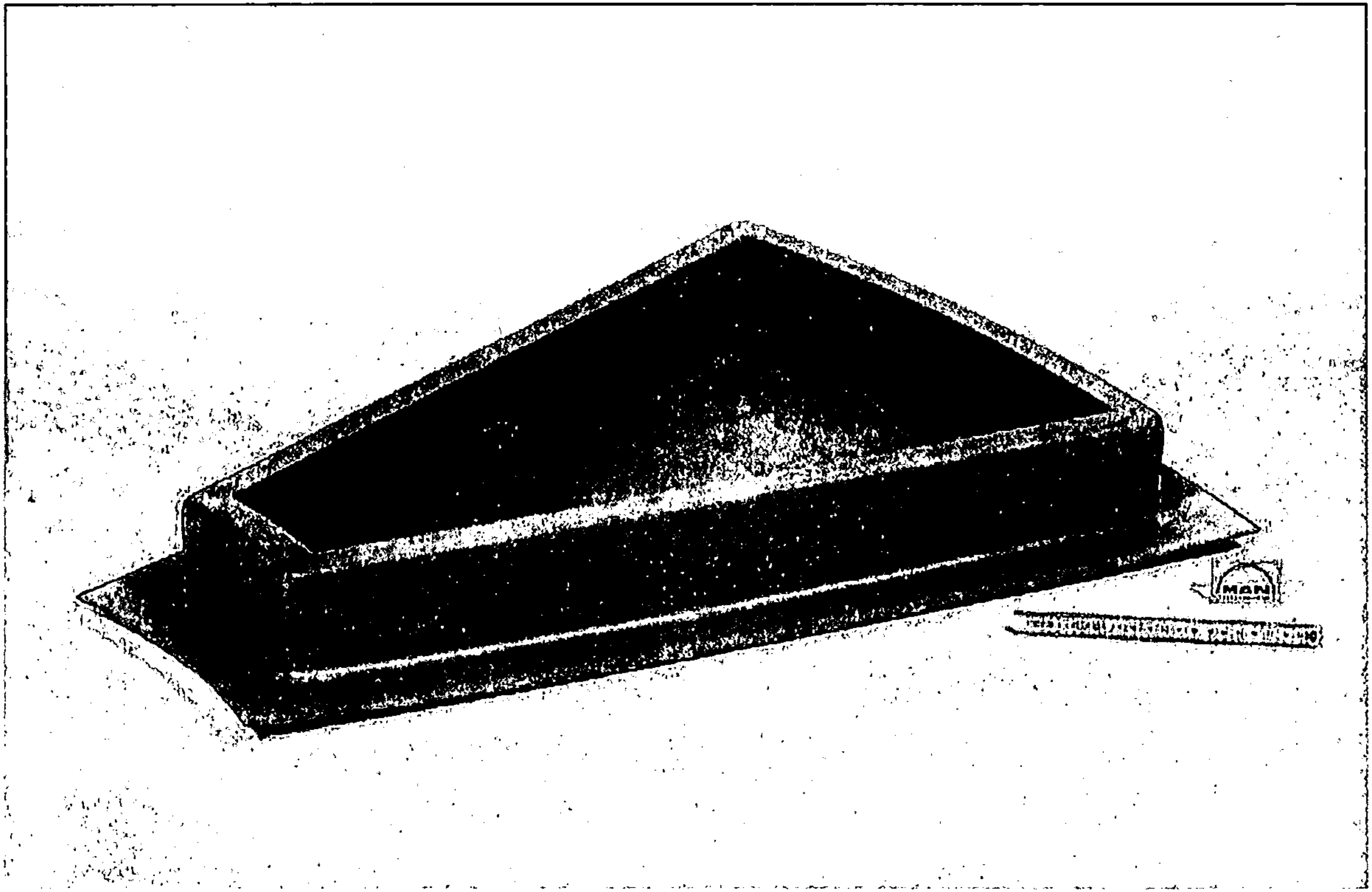

Fig. 8: Heat Shield Panel (700x560x80 mm)

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Fig. 9: Sealing Ring (150 ⌀ mm)