Design and Development of Advanced Ceramic Fibers, Interfaces, and Interphases in Composites

PHYSICAL AND CHEMICAL PROPERTIES OF SILICON CARBIDE FIBERS

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ABSTRACT

SiC fibres are more and more used as commercial applications are growing. An overview of some characterisation is proposed and especially concerning their morphologies and environmental considerations. A comparison is done between SiC whiskers and different SiC fibres made from polymers. Then in order to make a first basic evaluation concerning exposition for workers, some measurements were done in order to try to evaluate risks when workers handle SiC fibres. Results are presented.

INTRODUCTION

ACGIH's 2003 publication CAS 409-21-2 studies the dangerousness of Silicon carbide. According to this document, an important distinction is to be made between:

-The so-called "Nonfibrous forms of SiC", sometimes referred to as "angular" particles, the toxicity of which is considered as very low in human and experimental animals.

-The so-called "Fibrous form of SiC" (including whiskers), classified as A1- Suspected human carcinogen. The feared mechanism is linked to the penetration and the persistence of these respirable elements in the lungs, suspected to cause lung and pleural carcinogenicity. As a consequence, the ACGIH proposes a TLV-TWA limit of 0.1 Respirable Fiber per cube centimeter, a Respirable Fiber being defined as a particle with a diameter lower than 3µm, a length greater than 5µm and an "aspect ratio Length/Diameter" greater than 3.

Besides, the Ceramic Matrix Composites (CMC) enters a production phase, especially for applications in aeronautics. The reinforcement of the most advanced CMC consists of long continuous silicon carbide fibers, marketed under the names Nicalon®, Tyranno®, etc.

Our company Safran implements such continuous fibers for the production of CMC parts. This paper studies the Hi Nicalon Type S® fiber produced by NGS Advanced Fibers in Japan, which is becoming the standard for CMC for aeronautics. It is compared to the particles and the medical scenarios summarized in the ACGIH publication.

EXPERIMENTAL

Last generation of continuous SiC fibers are known to have very good mechanical performances up to 1400°C [1] (Figure 1).

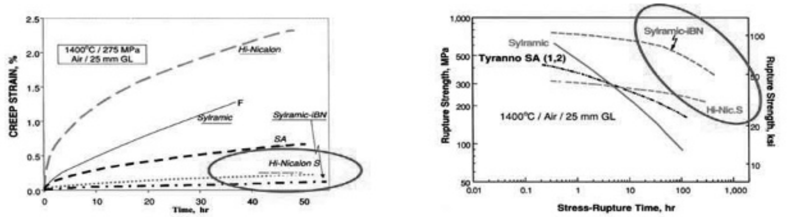

Figure 1.Creep strain versus temperature at 1400°C and rupture strength versus Rupture time at 1400°C for various continuous SiC fibers.

Now, Hi-Nicalon type S® is entering into mass production and is becoming the standard as it can reach the demand on high temperature CMC capabilities.

Figure 2 illustrates Hi Nicalon Type S® fibers used for CMC reinforcement do not fall within the definition of Respirable Fibers (Ø<3µm, L>5µm, L/Ø >3) due to their length (continuous) and their diameter (6 to 22µm).

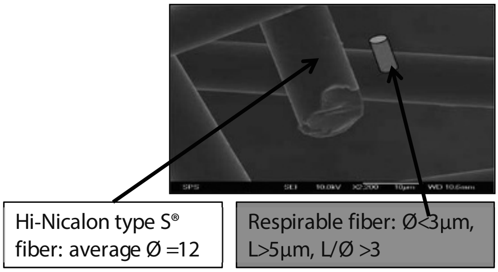

Figure 2. Morphological comparison between continuous SiC fibers and respirable Fibers.

SEM Studies of Fractural behavior of Hi Nicalon type S® due to hardened handling was done as followed: a) friction on a metallic bar, b) knot to rupture and c) cut with metallic scissors. SEM observations (figure 3) show for each case the same consequences: cut filaments are mostly with initial diameters around 12µm, particles are granular with irregular shapes and small metallic particles are present due to erosion from the metallic bar or the scissors.

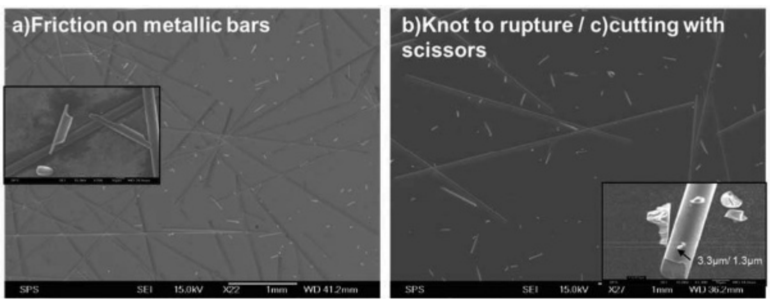

Figure 3. SEM observations after hardened handling: a) friction on a metallic bar, b) knot to rupture and c) cut with metallic scissors.

Controls of dust exposition for workers who handle this continuous fiber were done in order to get a first basis evaluation. Controls were implemented at different stages of manufacturing of CMC derived from Nicalon and Hi-Nicalon type S fibers: cut of sized cloth, control on desized cloth, cut of desized cloth, preparation of samples for fiber reception controls, loading of SiC textile in a CVI furnace, cut of polymerized composite with diamond saw, demolding and cleaning molds after resin polymerization, tensile test on composite, Geometric control of composite parts. Sampling have been made on workers and at 3 m of working area:

control of dust exposition by gravimetric result according to NFX 43-257 show a dust exposition far below threshold limits (table 1), contrast phase optical microscope results (XP-X43-269) show % respirable fiber far below threshold limit (table 2) and SEM results according to ISO –DIS- 14-966 (table 3) show a maximum of one respirable fiber possibly coming from SiC fibers (chemical nature not distinguishable: SiC, SiO2, etc ?)

Table 1:Control of dust exposition: Gravimetric results according to NFX43-257

Operation	mg/m^3 On worker (TLV-TWA<10mg/m3 - 8h exposition)	At 3 meters from working area
Cut of sized Nicalon and Hi Nicalon's cloth	< 0,06	< 0,06
Control on desized Nicalon and Hi Nicalon's cloth	< 0,06	< 0,06
Cut of desized Nicalon and Hi Nicalon's cloth	< 0,06	< 0,06
Preparation of samples for reception controls on Nicalon and Hi Nicalon's fibres	< 0,06	< 0,06
Loading of textile textures in a CVI furnace	< 0,06	< 0,06
Cut of polymerized composite with diamond saw	< 0,06	< 0,06
Demolding and cleaning molds after SiCN resin polymerization	< 0,06	< 0,06
Tensile Test on composite	< 0,06	< 0,06
Geometric control of composite parts	< 0,06	< 0,06

Table 2. Contrast Phase Optical Microscope results (XP-X43-269)

Measurements on 100 fields in C.P.O.M. (no chemical identification at this stage)	On worker (<0,1fibre/cm^3 sur 8h)	At emission source
Cut of sized Nicalon and Hi Nicalon's cloth	<0,001 fibre/cm^3	<0,001 fibre/cm^3
Control of desized Nicalon and Hi Nicalon's cloth	0,002 fibre/cm^3	0,001 fibre/cm^3
Cut of desized Nicalon and Hi Nicalon's cloth	< 0,001 fibre/cm^3	0,002 fibre/cm^3
Preparation of samples for reception controls on Nicalon and Hi Nicalon's fibres	Not done	<0,004 fibre/cm^3
Loading of textile textures in a CVI ovens	< 0,002 fibre/cm^3	Not done
Cut of polymerized composite with diamond scie	Not done	0,004 fibre/cm^3
Demolding and cleaning of molds after resin polymerization	0,003 fibre/cm^3	0,008 fibre/cm^3
Tensile Test on composite	0,003 fibre/cm^3	0,003 fibre/cm^3
Geometric control of composite parts	< 0,001 fibre/cm^3	<0,001 fibre/cm^3

Table 3.SEM results according ISO –DIS- 14-966

Measurements on 150 SEM fields (magnification x 5000)	At emission source
Cut of sized Nicalon and Hi Nicalon's cloth	0 fibre
Control of desized Nicalon and Hi Nicalon's cloth	0 fibre
Cut of desized Nicalon and Hi Nicalon's cloth	0 fibre
Preparation of samples for reception controls on Nicalon and Hi Nicalon's fibres	0 fibre
Cut of polymerized composite with diamond saw	1 fibre Si 9µm x 0,5µm 1 fibre SiN 6µm x 0,3µm → from matrix
Demolding and cleaning of molds after SICN resin polymerization	0 fibre
Tensile Test on composite	0 fibre
Geometric control of composite parts	0 fibre

→ **A maximum of one respirable fiber possibly coming from SiC fibers ⇨ chemical nature not distinguishable : SiC, SiO_2, etc. ?)**

CONCLUSIONS

Due to their length (continuous) and their diameter (6 to 22µm), the Hi Nicalon Type S® fibers used for CMC reinforcement do not fall within the definition of Respirable Fibers.

Under tests of wearing or fracturing, the Hi Nicalon Type S® fibers have tended to break preferentially in angular particle, and not in Respirable Fibers.The exposure of workers has been characterized by atmosphere samplings at several steps of implementation of the Hi Nicalon Type S® fibers (handling, cutting, machining, etc.). Dust exposures are far below regulation threshold limits and often near to detection limits. Among other fragments, a maximum of one Respirable Fiber potentially coming from the continuous fibers was found (chemical nature not distinguishable: SiC, SiO_2, …?).

REFERENCES

[1] James A. DiCarlo and Hee-Mann Yun, Handbook of Ceramic Composites, 2- Non oxyde (Silicon Carbide) Fibers