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Moez Guellali, R. Oberacker, M.J. Hoffmann. Influence of heat treatment on microstructure and mechanical properties of CVI-CFC composites with medium and highly textured pyrocarbon matrices. *Composites Science and Technology*, 2009, 68 (5), pp.1115. <10.1016/j.compscitech.2007.07.013>. <hal-00545281>

HAL Id: hal-00545281

<https://hal.science/hal-00545281v1>

Submitted on 10 Dec 2010

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PII: S0266-3538(07)00285-0
DOI: [10.1016/j.compscitech.2007.07.013](https://doi.org/10.1016/j.compscitech.2007.07.013)
Reference: CSTE 3776

To appear in: *Composites Science and Technology*

Received Date: 4 April 2007
Revised Date: 9 July 2007
Accepted Date: 18 July 2007

Please cite this article as: Guellali, M., Oberacker, R., Hoffmann, M.J., Influence of heat treatment on microstructure and mechanical properties of CVI-CFC composites with medium and highly textured pyrocarbon matrices, *Composites Science and Technology* (2007), doi: [10.1016/j.compscitech.2007.07.013](https://doi.org/10.1016/j.compscitech.2007.07.013)



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Title: Influence of heat treatment on microstructure and mechanical properties of CVI–CFC composites with medium and highly textured pyrocarbon matrices

Moez Guellali *, Dr.–Ing.; R. Oberacker, Dr.–Ing.; M.J. Hoffmann.

Abstract: The Influence of heat treatment up to 2900°C on microstructure and mechanical properties of CVI-infiltrated carbon fiber felts with either medium (MT) or highly (HT) textured pyrocarbon matrices was studied by optical and scanning electron microscopy, X-ray diffraction, and three-point bending tests. The microstructural investigations of the HT-samples reveal a pronounced decrease of the interlayer spacing d_{002} with a simultaneous increase of the apparent layer stack height L_c with increasing heat treatment temperature. On the contrary, the d_{002} and L_c values of the MT-samples changed only slightly after heat treatment. But they exhibit distinct concentric cracks. The density of these cracks increases with increasing heat treatment temperature. The HT-samples show nearly no cracks after heat treatment.

Keywords: Heat treatment; Microstructure, mechanical properties; X–ray diffraction (XRD)

INTRODUCTION

The isothermal isobaric chemical vapor infiltration (I-CVI) process is widely used to manufacture complex carbon fiber reinforced carbon (CFC) parts for high tech applications like in aeronautical and aerospace industries [1]. The texture of the deposited pyrocarbon matrix can be varied between the isotropic nearly amorphous to the highly textured graphitic state by controlling the process parameters [2-3]. Moreover the microstructure of these pyrocarbon types can be influenced differently by heat treatment [4-5]. These microstructural changes should in turn influence the mechanical properties of the composites.

Despite the widely practice of the graphitization of CVI-CFC composites in the industry as a post treatment after the infiltration process, there are only few papers dealing with the influence of the heat treatment on the mechanical properties of the pyrolytic carbons and CFC composites. In 1966 Bokros et al. [6] already reported that the mechanical properties of pyrolytic carbons deposited in fluidized beds are strongly dependant on their different microstructures resulting from various deposition and annealing conditions. Granoff [7] studied the kinetics of graphitization of different textured CVI-CFC composites between 2300°C and 2660°C. Recently, Sauder et al. [8] studied the tensile properties of CVI carbon matrices at temperatures up to 2200°C. But they used CVI-CFC micro-composites because it is very difficult to produce CVI bulk materials with a pure low-, medium or high textured matrix at low deposition temperatures (1000°C-1200°C). Within the SFB 551 at the University of Karlsruhe we succeeded to produce bulk materials with nearly pure textured matrices at temperatures about 1100°C. The aim of this study is to characterize the influence of heat treatment on the microstructure and thus on the mechanical properties of these materials.

EXPERIMENTAL

The investigated samples are carbon fiber felts (CCKF 1001, Sintec, Germany) with an initial porosity of about 88 vol.% infiltrated by means of an I-CVI process. The infiltration was carried out in the group of Prof. Hüttinger at Institute for Chemical Technology of the University of Karlsruhe using pure methane as precursor gas, in a vertical gap reactor (Fig. 1). Further details on the infiltration procedure are given elsewhere [5, 9]. The PAN-fibers forming the felts have a typical mean diameter of 12 μm and are randomly oriented. This study focuses on the influence of the heat treatment on the deposited pyrocarbon forming the matrix of the samples and thus on their mechanical properties. Therefore the felt with its low fiber volume fraction and random orientation of the fibers is very beneficial. The infiltration conditions were adjusted to 1095°C/10kPa/0.1s/150h and 1070°C/30kPa/0.1s/120h in order to obtain bulk samples with either exclusively highly textured (HT) or medium textured (MT) pyrocarbon matrices (Fig. 1). The specimens were cut in two halves. The first half was used as a reference (named here as deposited) and the other half was treated at high temperature (2200°C or 2900°C) for 2h under helium atmosphere. The texture of the deposited pyrocarbons was determined on polished cross-sections under polarized light (PLM) using an OLYMPUS AX70 microscope according to their optical activity and the value of the extinction angle A_e as described by Bourrat et al. [10]. The corresponding pyrocarbon optical textures with a progressive anisotropy degree are defined as isotropic (ISO, $A_e < 4^\circ$), low textured or dark laminar (LT or DL, $4^\circ \leq A_e < 12^\circ$), medium textured or smooth laminar (MT or SL, $12^\circ \leq A_e < 18^\circ$), and highly textured or rough laminar (HT or RL, $A_e \geq 18^\circ$) [10-11]. X-ray diffraction measurements were carried out before and after heat treatment using a Siemens D500 diffractometer in order to characterize the influence of the

thermal post treatment on the texture of the samples. The interlayer spacing d_{002} and the apparent layer stack height L_c were calculated from the (002) diffraction peak using the Bragg and the modified Scherrer equation, respectively [12, 13].

Three-point bending tests were carried out in order to determine the mechanical properties of the composites. For this purpose rectangular bars of approximately $9 \times 4 \times 0.4 \text{ mm}^3$ were cut from the center of the samples using a diamond-wire saw. To avoid possible damaging of the samples (thickness $\leq 0.5 \text{ mm}$) their edges were not rounded as suggested in some ASTM standards for measuring strength of ceramics. The sample dimensions were measured using a micrometer screw. The tests were carried out according to DIN V ENV 658-3 on a universal testing machine (UTS, Germany). The specimens were placed on rollers, 3 mm in diameter. A span of 7 mm was used, so giving a span-to-height ratio of about 17. The tests were carried out with a constant cross head speed of 10 mm/min. At least twenty specimens were tested for each composite. The load and deflection values were recorded as a function of time. The nominal bending stress (σ) and the nominal outer fiber strain (ε) were calculated according to following equations [14]:

$$\sigma = \frac{3 \cdot F \cdot L}{2 \cdot b \cdot d^2} \quad (1)$$

$$\varepsilon = \frac{6 \cdot s \cdot d}{L^2} \cdot 100 \quad (2)$$

where F is the load (N), L is the span (mm), b is the specimen width (mm), d the specimen height (mm), and s is the displacement or deflection (mm).

In order to compare the quasi-ductile fracture behavior of the samples, a ductility factor F_D is introduced. It is calculated from the ratio of the secant modulus (E_{secant} : the slope of the line from the origin to the stress at failure in the stress-strain curve)

to the elastic modulus (E_{origin} : the slope of the linear part of the stress-strain curve) as it is described in figure 2 [5, 15-16].

The interpretation of the bending strength results was made with the help of the widely used Weibull distribution [17-18]. The Weibull parameters (m : shape parameter of the distribution and σ_0 : scale parameter, i.e. the strength at a failure probability of 63.21%) were calculated according to the literature [19].

After flexural testing, fracture surfaces were examined using a scanning electron microscope (SEM) 'LEO 440C' without depositing conductive layers.

RESULTS

Figure 3 shows the influence of the heat treatment on the crystallinity of the different textured pyrocarbon matrices. These results of the X-ray investigations show consistently with former works [4, 5] that highly textured (HT) pyrocarbon graphitizes very well. This is shown by the pronounced increase of the apparent layer stack height L_c and the decrease of interlayer spacing d_{002} with increasing heat treatment temperature. In fact, after the heat treatment at 2900°C the HT-samples show an interlayer spacing ranging between those of moderately annealed pyrolytic graphite (MAPG) and compression annealed pyrolytic graphite (CAPG) [20]. In contrast, the d_{002} and particularly the L_c values of the samples with medium textured (MT) pyrocarbon matrices changed only slightly after heat treatment confirming that the MT pyrocarbon graphitizes hardly even at very high temperatures [5].

Figure 4 and 5 show light optical micrographs of the examined composites before and after heat treatment at 2200°C and 2900°C. After heat treatment the MT-samples exhibit distinct concentric cracks around the fibers. The number as well as the width of these cracks increases remarkably between 2200°C and 2900°C

(Fig. 4). On the contrary, the HT-samples show no crack formation due to heat treatment (Fig. 5). This is confirmed by the results in figure 6 showing the change of the open porosity of the bulk samples as a function of the heat treatment temperature and the texture of the matrix. The MT-samples reveal a pronounced increase (about 1.4 %) of the open porosity after heat treatment at 2900°C.

In order to study the influence of these microstructural changes after heat treatment on the mechanical properties of the CVI-infiltrated carbon fiber felts, more than twenty bars were cut from the composite before and after the heat treatment process and were tested in a three-point bending mode. Nearly all the investigated samples exhibited a quasi-ductile fracture behavior reported in former works [15, 16].

Figure 7 shows the Weibull distributions of the flexural strengths of the investigated samples. In the case of the HT-samples with highly textured pyrocarbon matrices the flexural strength decreases distinctly with increasing heat treatment temperature. The scale parameter of the distribution (σ_0 : flexural strength with a failure probability of 63.21%) decreases about 20% and 40% after two hours heat treatment at 2200°C and 2900°C, respectively. On the opposite, the MT-samples with medium textured pyrocarbon matrices show a slight increase of the scale parameter, σ_0 , after heat treatment. But the curves are strongly overlapped showing that these changes are not statistically significant.

The influence of the heat treatment on the ductility of the CVI-infiltrated carbon felts with different textured pyrocarbon matrices is shown in figure 8. The mean strain at failure and the mean ductility factor of the HT-samples jumped from about 0.7% and 6%, respectively, before heat treatment up to 1.6% and 30% after a two hours heat treatment at 2900°C which indicates a remarkable increase of the quasi-ductility of these samples. On the contrary the MT-samples matrices show only slight changes

in the quasi-ductile fracture behavior after heat treatment. In fact only the mean strain at failure increases slightly with increasing heat treatment temperature.

DISCUSSION

Structural investigations and mechanical testing yielded complementary information about the correlation between the matrix microstructure before and after heat treatment, and the mechanical properties of the investigated composites. The results of the X-ray investigations confirm that the highly textured pyrocarbons graphitize very well while the medium textured pyrocarbons graphitize very hardly. In fact, with increasing heat treatment temperature the interlayer spacing between the graphene layers (d_{002}) within the matrix of the HT-samples decreases distinctly and the pyrocarbon “crystallites” (L_c) become thicker. Figure 9 shows SEM micrographs of the fracture surfaces after bending tests of the heat treated composites at 2900°C. An intensive fragmentation takes place within the highly textured matrix resulting in a very rough fracture surface. In contrast, the fracture surfaces of the medium textured carbon layers are much smoother. The zigzag shape of the fracture surface of the HT-samples proves that a multiple crack deflection took place at the interfaces of the “sublayers” within the highly textured pyrocarbon leading to energy dissipation and thus contributing to a toughness enhancement. These results correlate with the difference in the graphitizability between HT- and MT-pyrocarbons and explain the difference in the quasi-ductile fracture behavior between the HT- and MT-samples after heat treatment. The slight increase of the mean strain to failure of the MT-samples after heat treatment could be explained by the increase of the open porosity. In fact, the increase of the number and width of cracks acting like pores with different shapes and sizes leads to an enhancement of the interaction between

the induced crack during loading and the former cracks formed after heat treatment leading to crack branching and crack bridging and thus to a toughness increase [21]. The distinct decrease of the flexural strength of the HT-samples after heat treatment could be also explained with the distinct advance of the graphitization within the highly textured matrix. With increasing heat treatment temperature the graphene layers become better rearranged around the fiber forming more and more “sublayers”. During bending these sublayers can then easily slide on each other leading to a decrease of the flexural strength. We will expect the opposite tendency (increase of tensile strength) if the samples are tested in a tensile mode. This was confirmed in a study performed on CVD highly textured pyrocarbon samples. The results of this study will be submitted in another paper. In the case of the MT-samples the flexural strength does not change distinctly (overlap of the 95% confidence intervals in Fig. 7) after heat treatment. This correlates very well with their bad graphitization behavior proved by the X-ray investigations.

CONCLUSIONS

The results of the three-point bending tests carried out on CVI infiltrated carbon fiber felts with different textured pyrocarbon matrices before and after heat treatment reveal in the case of the HT-samples with highly textured pyrocarbon matrices a distinct increase of the ductility accompanied with a flexural strength decrease with increasing heat treatment temperature. On the opposite, the MT-samples with medium textured pyrocarbon matrices show no significant changes in the mechanical properties after heat treatment. These results could be very well correlated to the graphitization behaviors of different textured pyrocarbons forming the matrix of the investigated samples.

Acknowledgements

This research was performed in the Collaborative Research Center 551, Project Nr. D4. The financial support of the DFG is gratefully acknowledged. The authors thank K.J. Hüttinger for the infiltration of the samples, and all the people, who contributed to this work.

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Influence of heat treatment on microstructure and properties of different pyrocarbons

M. Guellali, R. Oberacker, M.J. Hoffmann

Figure captions

Fig. 1 Experimental setup and PLM micrographs of the investigated samples

Fig. 2 Definition of the ductility factor F_D

Fig. 3 Influence of heat treatment on the crystallinity of the different textured pyrocarbons

Fig. 4 PLM micrographs of the MT-samples showing the formation of concentric cracks within the matrix after heat treatment. The crack density increases with increasing heat treatment temperature

Fig. 5 PLM micrographs of the HT-samples before and after heat treatment

Fig. 6 Influence of the heat treatment on the open porosity of the MT- and HT-samples

Fig. 7 Weibull diagrams showing the influence of heat treatment on the flexural strength of the CVI-infiltrated carbon felts with different textured pyrocarbon matrices

Fig. 8 Influence of heat treatment on the ductility of the CVI-infiltrated carbon felts with different textured pyrocarbon matrices

Fig. 9 SEM micrographs of the fracture surfaces of HT- and MT-samples after heat treatment at 2900

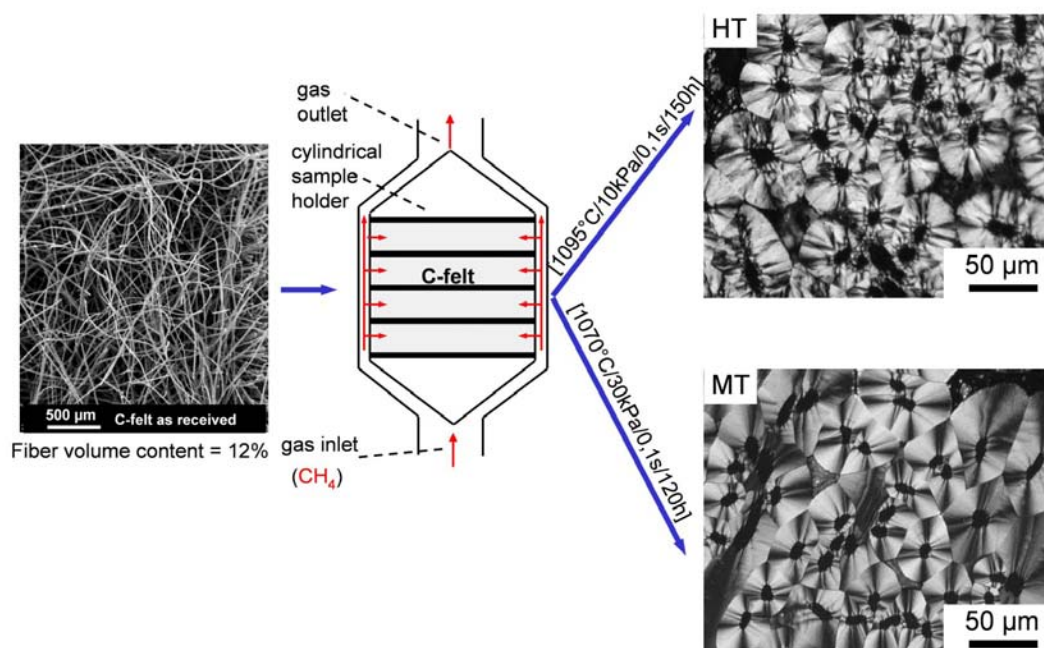


Fig 1

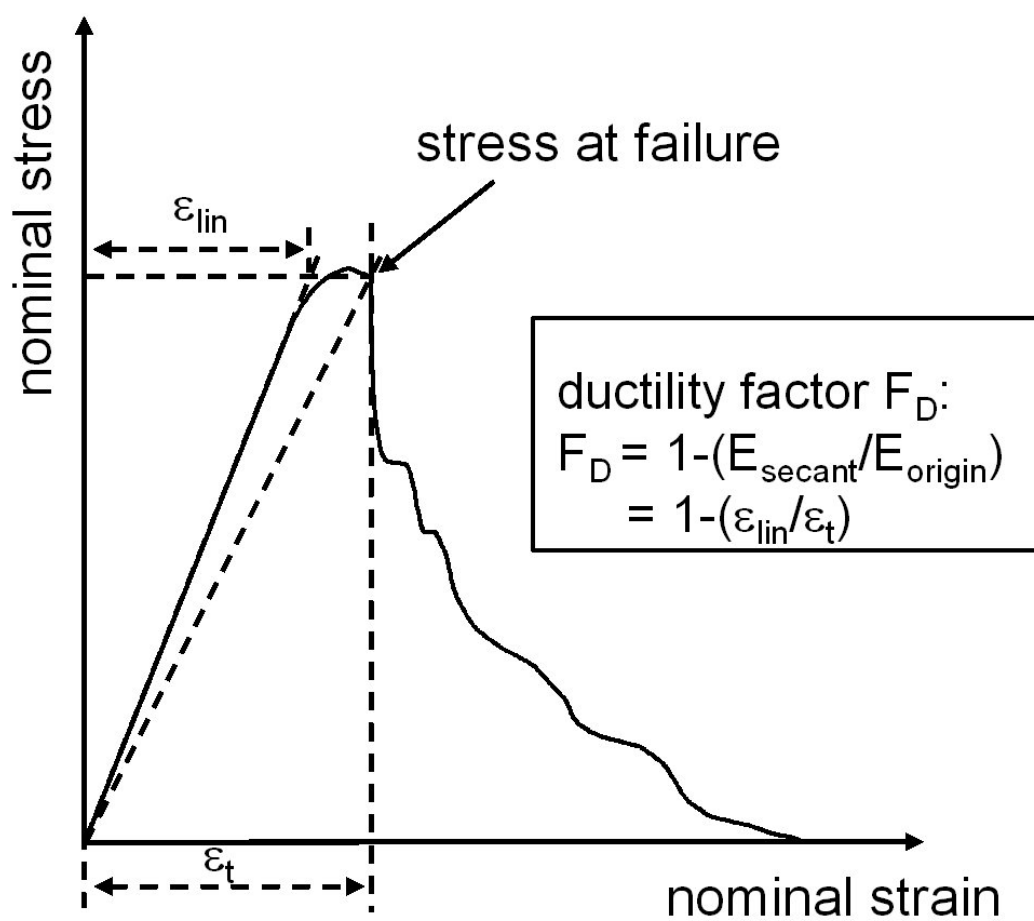


Fig 2

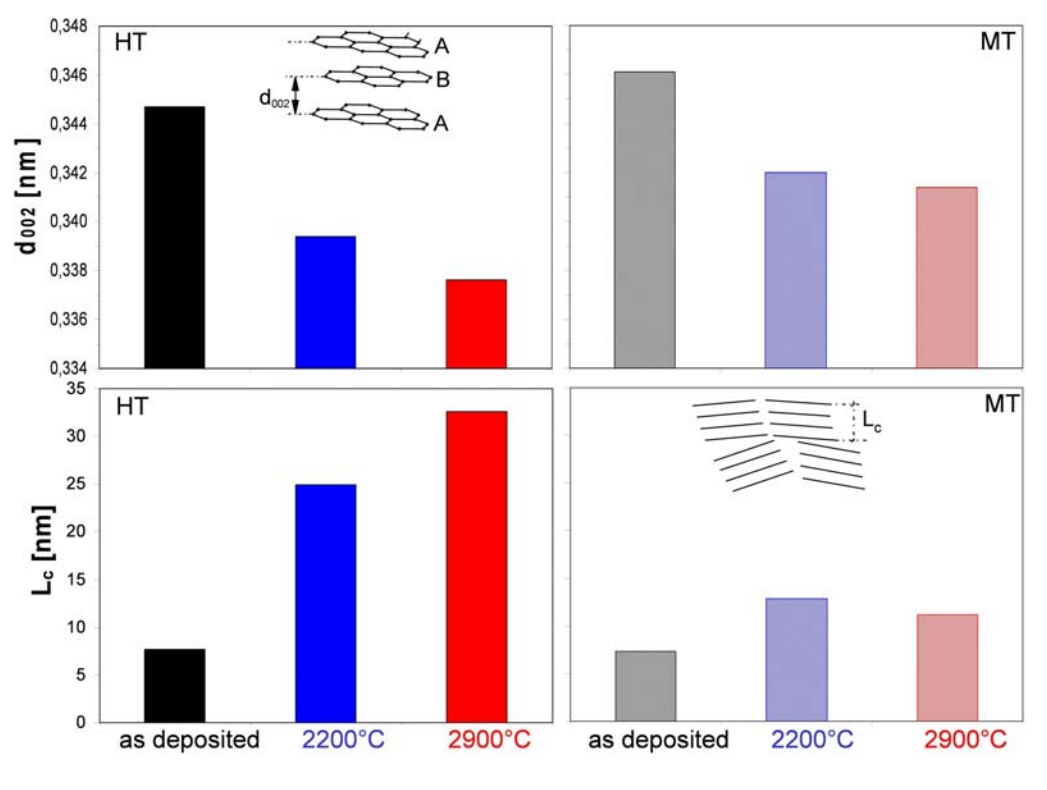


Fig 3

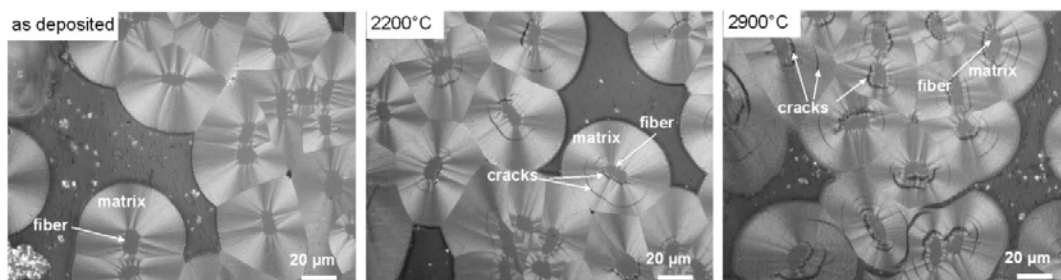


Fig 4

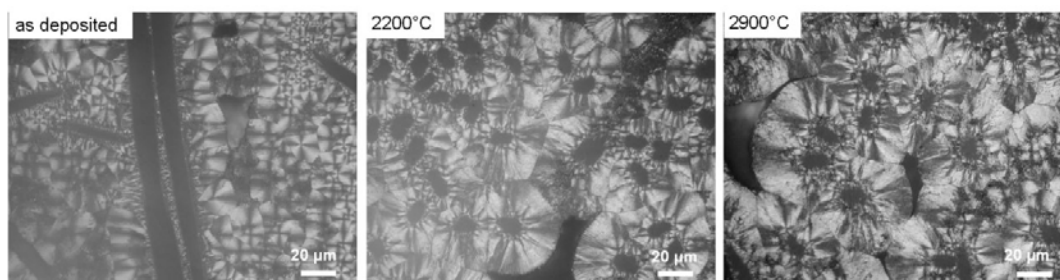


Fig 5

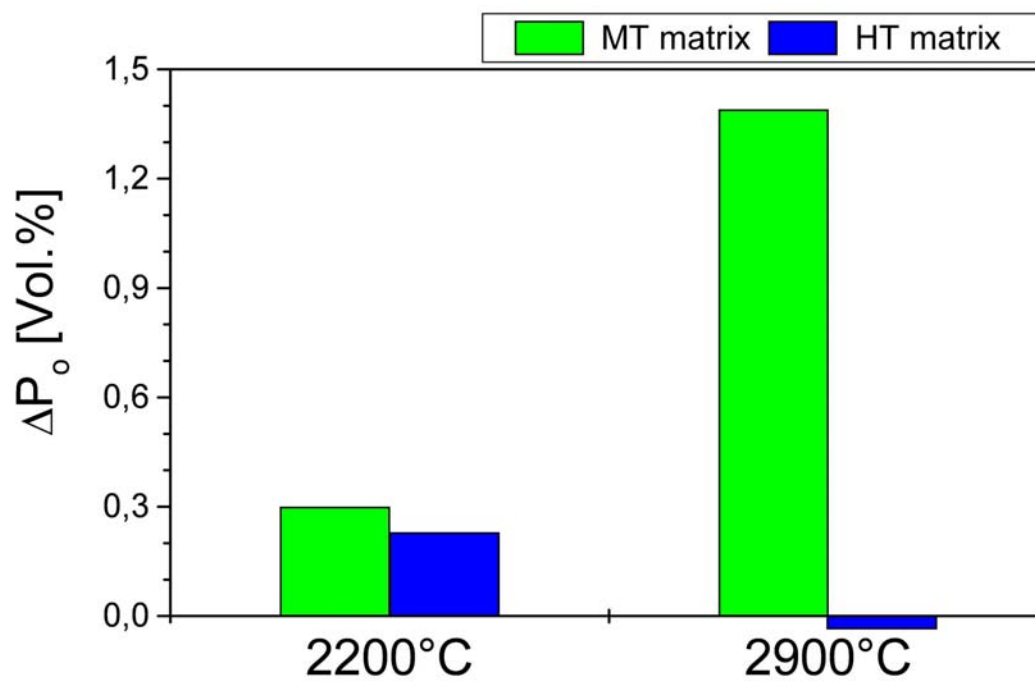


Fig 6

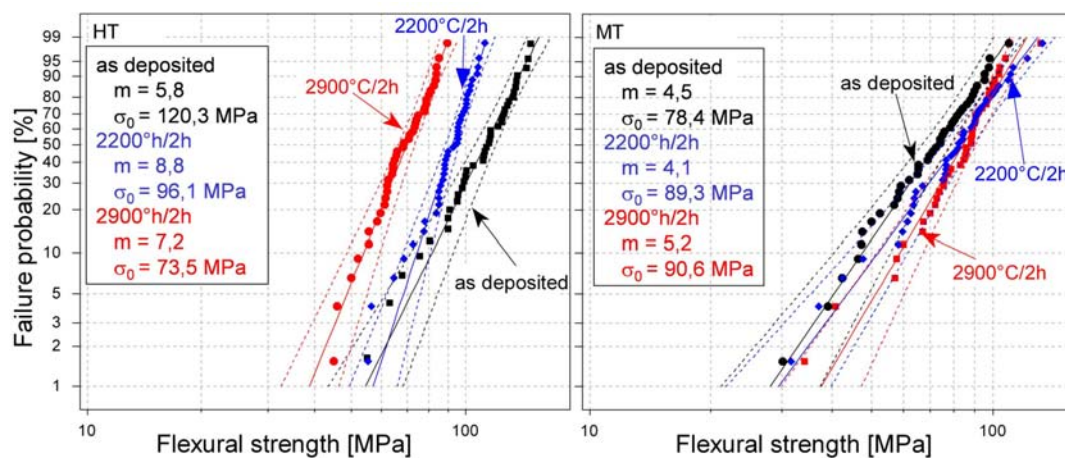


Fig 7

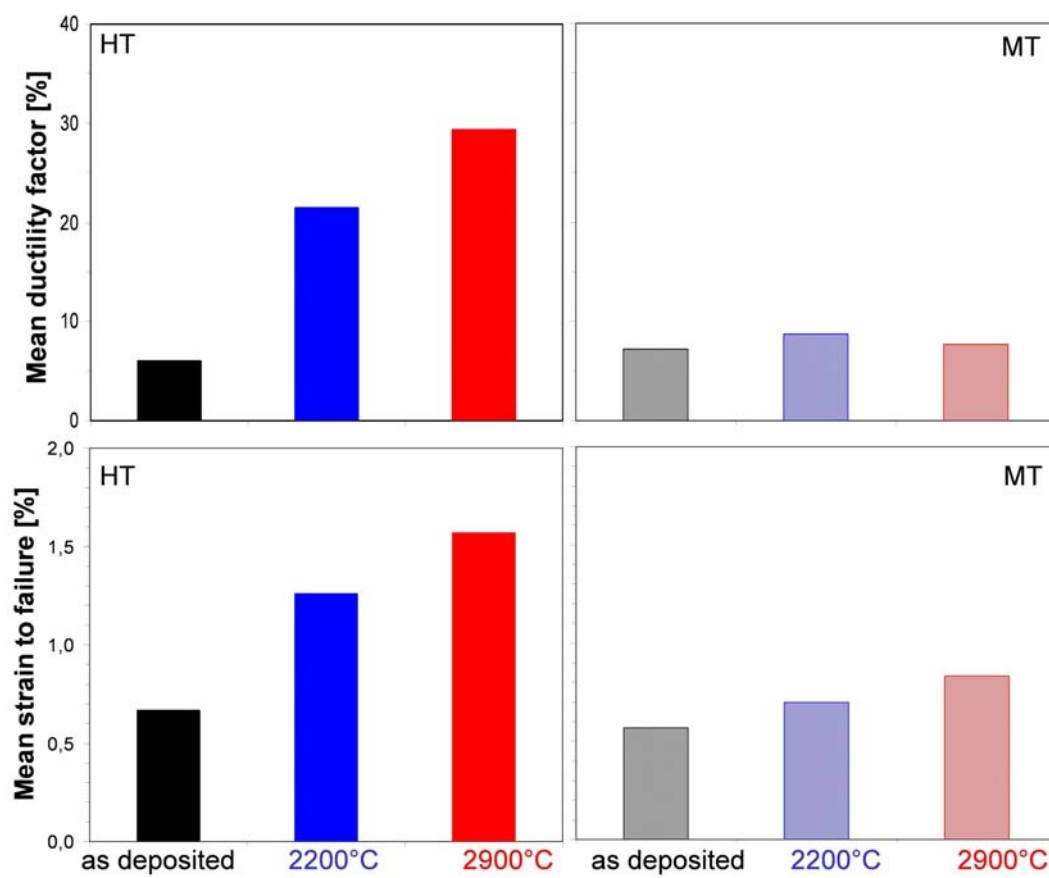


Fig 8

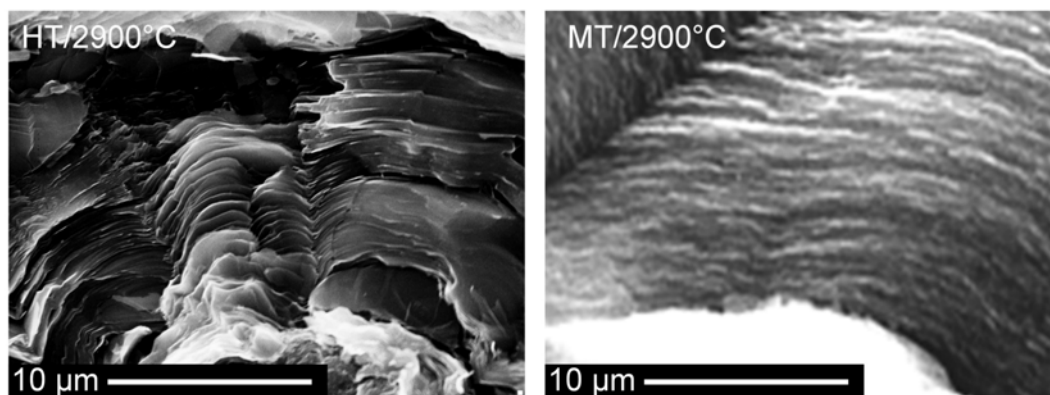


Fig 9