A study about the contribution of the α-β phase transition of quartz to thermal cycle damage of a refractory used in fluidized catalytic cracking units

(Estudo da contribuição da transição de fase α-β do quartzo para o dano por ciclo térmico em um refratário empregado em UFCC)

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Abstract

The deterioration of refractories used in fluidized catalytic cracking units (FCC-units) is responsible for high costs of maintenance for the petrochemical industry. This is commonly associated with coke deposition during the production of light hydrocarbons. However, other mechanisms responsible for causing damage may also occur, such as the generation of cracks by expansive phase transition. The aim of the work herein was to study the contribution of the α-β phase transition of quartz particles to the deterioration of a commercial aluminosilicate refractory used in a riser by the means of slow thermal cycles. Such damage may occur if the working temperature of the equipment fluctuates around the α-β transition temperature (573 °C). The current study considered the material with and without coke impregnation to evaluate the combined effect of coke presence and phase transition. To evaluate the damage, it was used the Young's modulus as a function of temperature by applying the Impulse Excitation Technique under controlled atmosphere. An equipment recently developed by the authors research group was applied. Specimens were prepared and submitted to slow thermal cycles of temperatures up to 500 °C and up to 700 °C, with a heating rate of 2 °C/min. Part of the specimens was previously impregnated with coke by a reactor using propen. To complete the evaluation, characterization by X-ray diffraction, as well as by dilatometry and scanning electron microscopy were performed. The findings of this study showed that the presence of quartz particles determine the thermo-mechanical behaviour of the material, as well as the thermocycling damage resistance. In spite of the fact that the α-β phase transition stiffens the material during the heating stage, it increases the damage by slow thermal cycling. The coke impregnation increases the resistance to slow thermal cycles, however it decreases the resistance to the damage evolution.

Keywords: refractory castables, phase transition, quartz, slow thermal cycling damage, coke impregnation, FCC-unit, impulse excitation technique, Young's modulus, damping.

Resumo

A deterioração de refratários utilizados em unidades fluidizadas de craqueamento catalítico (UFCC) é responsável por altos custos de manutenção para a indústria petroquímica. Esse fenômeno é comumente associado à deposição de coque durante a produção de hidrocarbonetos. Entretanto, outros mecanismos causadores de dano podem ocorrer, como a geração de defeitos por transição de fase expansiva. O objetivo deste trabalho foi estudar a contribuição da transição de fase α-β de partículas de quartzo para a deterioração de um refratário comercial sílico-aluminoso empregado em riser de UFCC, por meio de ciclos térmicos lentos. Este dano pode ocorrer caso a temperatura de operação do equipamento oscile ao redor da temperatura da transição α-β (573 °C). Este estudo foi realizado no material com e sem coque impregnado, visando avaliar o efeito conjunto da presença do coque e da transformação de fase. Para a avaliação do dano empregou-se a medida do módulo de Young em função da temperatura através da Técnica de Excitação por Impulso em atmosfera controlada. Para tal, utilizou-se um equipamento recentemente desenvolvido no grupo de pesquisa dos autores. Foram preparados corpos de prova do material e estes foram submetidos a ciclos térmicos lentos com temperaturas máximas de 500 °C e 700 °C com taxa de aquecimento de 2 °C/min. Uma parcela destes corpos foi previamente impregnada por coque em reator de propeno. Complementarmente, ensaios de difração de raios X, de dilatometria e a observação com microscopia eletrônica foram realizados. Comprovou-se que as partículas de quartzo são determinantes para o comportamento termomecânico do material e para a resistência ao dano por ciclagem térmica. A transição de fase α-β, embora enrijeça o material no aquecimento, intensifica o dano por ciclo térmico lento. A impregnação pelo coque aumenta a resistência a ciclos térmicos lentos, porém reduz a resistência à evolução do dano.

Palavras-chave: *concreto refratário, transformação de fase, quartzo, dano por ciclo térmico lento, impregnação por coque, UFCC, técnica de excitação por impulso, módulo de Young, amortecimento.*

INTRODUCTION

Fluidized catalytic cracking units (FCC-units) are large-scale equipment made of three main parts – riser, reactor and regenerator – that operate between 550 and 800 °C [1]. Changes in temperature and coke impregnation mainly occur

in the riser region. It presents the highest susceptibility to the damage of the refractory lining and it ultimately determines the equipment life span.

Refractory materials used in FCC-units cannot be sintered *in situ* because of the low working temperature, differently to what occurs, for instance, to the refractories that are used in the siderurgy. Considering this, and aiming mechanical resistance, the selection of refractories to be used in such process deserve special attention, as it is the case of the refractory castables binded by hydratable phases in the green-body state.

To begin with, it is possible to find many advantages in the utilization of refractories rich in silica and in phases that contain silica, justifying why those refractories are used in FCC-units. For instance, the mullite phase presents low thermal expansion coefficient and low thermal conductivity, when compared to alumina. Those factors allow a more efficient thermal isolation, energetic gains and less susceptibility to thermal shock damage. Nevertheless, the initial mineralogical composition of aluminosilicate refractories may present quartz particles that, despite being a source of silica when it comes to the formation of refractory phases (such as mullite), can also be deleterious to their mechanical properties. That can be explained by the fact that only in high temperatures, such as those found in siderurgy and cement industry, quartz particles can benefit the formation of the other phases. It is important to note, though, that not all aluminosilicate refractories contain particles of quartz in their mineralogical composition.

The disadvantages brought by the presence of quartz particles in refractories is due to the polymorphic α-β phase transition, which takes place under about 573 ºC. The α quartz reversibly transforms itself into β quartz and in this process there is a volumetric expansion of approximately 0.45% [2]. This expansion can cause structural damage to the material, mainly if it has not been sintered. In fact, the damage could even occur to the quartz particles themselves. Fig. 1 shows the percentage of volumetric change for the
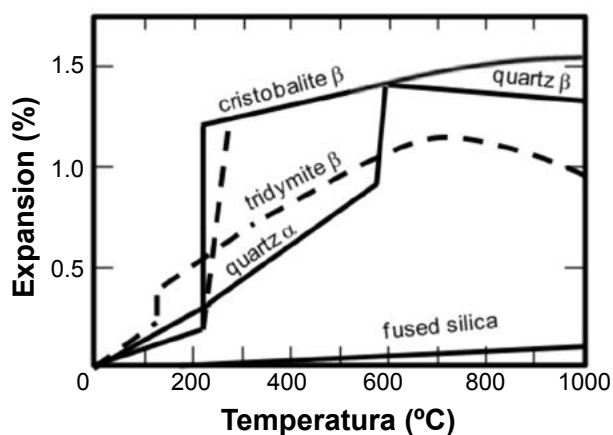
diverse types of silica crystals as a function of temperature [3].

When an aluminosilicate refractory castable containing quartz particles is applied as the lining of a FCC-unit (that operates on a temperature ranging from 550 to 800 ºC), it is subjected to thermal cycles that include the α-β transition temperature. In addition, because of the low processing temperature, sintering does not occur and this material can only count on the mechanical resistance coming from its particles packing, the interlocking of one particle to another. Furthermore, its microstructure can have phases of different thermal expansion coefficients. The confluence of all the factors above allow to predict the occurrence of a significant damage caused by thermal cycles, even when at a slow rate.

Therefore, the current work aims to evaluate the slow thermal cycle damage that may occur on a commercial aluminosilicate refractory containing particles of quartz, as well as the effect of the coke impregnation in the refractory. That could be seen as a step towards the validation of a new hypothesis proposed by this study, that the damage is majorly caused by the deposition of coke concurrent to the cyclic occurrence of the expansive α-β phase transition of quartz. In real working conditions, the formation of coke is continuous. In that circumstance, the coke would fill the new cracks or micro cracks caused or expanded by the α-β transition of quartz particles. This process, that generates flaws and its coke filling, could also explain the expansion and spalling observed in post-mortem analysis of FCC-units refractory lining.

Degradation mechanisms caused by coke

Refractory linings applied in the riser are highly susceptible to coke impregnation. It is even possible to say that, as long as there is enough porosity for the impregnation to occur, it will indeed happen regardless of the type of refractory being used. According to Xu and Brown [4], if the refractory presents a significant amount of iron oxide phase, this could be converted into catalytic sites for the formation of coke. In that case, the carbon monoxide is adsorbed by the catalyst surface, reacting with the carbon monoxide present in the gas. The surface of metallic iron present as reinforcement fibers is also appointed as potential catalytic site [5, 6]. In reality, it is not only the iron monoxide or the metallic iron that will help the formation of coke; the refractory, as a whole, may favour that too. For that to occur, there will only be needed acid sites, such as Brosted and/or Lewis [7-9], which are present in alumina [10, 11]. In that case, the main reagent is not the carbon monoxide, but the aromatic compounds originated from the petrochemical refining process.

At the end of each operational campaign in FCC-units, it is possible to observe the detachment of the refractory, spalling and cracking on a large scale [12, 13], which are usually associated with the inevitable coke impregnation. Many possible explanations regarding the role played by

Figure 1: Expansion of diverse quartz crystals as a function of temperature [3].
[Figura 1: Expansão de diversos cristais de quartzo em função da temperatura [3].]

the coke when it comes to the occurrence of flaws have been raised [1, 13, 14], however, there are only a few clarifying conclusions. The continuous coke deposition on the refractory could be the origin of a hydrostatic pressure from the pores to the matrix, causing the cracks. Considering the occurrence of cracks, the refractories would become weaker, being more susceptible to damage due to thermal shocks and thermal cycles. Those flaws could also be responsible for stress concentration, which could also facilitate the damage increase. Nevertheless, studies previously carried out [14] did not find enough evidences to prove that coke would be responsible for the damage in the refractory lining. What was in fact verified was that the concentration of coke increases the brittleness of the refractory [15], which could increase the chances of cracking and catastrophic propagation, when submitted to mechanical stresses. It should be noticed, though, that this finding does not necessary mean that the coke deposition, when seen on its own, is the responsible for causing the damage. It means, however, that it does modify the material properties.

MATERIALS AND METHODS

Preparing and coking the specimens

The material studied in the work herein, designated as CR4, is a class C anti-erosive commercial refractory. That refractory is one of ultra-low cement type (0.2% < CaO < 1.0%), containing in his chemical composition 50% of SiO_2. When preparing the specimens, the material, which was purchased under a particulate and dry condition, was homogenized by a mixer, and the batches for this weighted 2.5 kg. Following that, the mixture was made at constant rotation speed, with the addition of 8.5% of water under a constant stirring that lasted for 5 min. Prismatic specimens were molded into the dimensions of 150 mm x 25 mm x 25 mm using a metallic mold and a vibrating table. The molded specimens were cured for 48 h in a vapor-saturated chamber at 20 ºC, and dried for another 24 h in an oven at 110 °C. Finally, a set of specimens was calcined for 120 h at 540 °C and the other set was submitted to a coking process in a pilot reactor of the CENPES-Petrobras Laboratory. The coking process consisted of exposing the specimens to a propene atmosphere for 120 h, under 2 bar and 540 °C. The coking process is equivalent to a thermal treatment of calcination, once it eliminates the chemical bonded water from the hydratable phases.

Characterization of phases using X-ray diffraction

The mineralogical phases of the CR4 castable were characterized via X-ray diffraction. For that, a Bruker D8 Focus equipment with a Cu X-ray tube and a Ni filter was used. The equipment was operated under 40 kV and 40 mA. The used range of 2θ was from 5° to 80°, with a speed of 2°min^{-1}. Samples of the particulate material were analysed as received.

Microstructural characterization

The occurrence of quartz particles and their detachment of the matrix were verified via scanning electron microscopy on fracture surfaces of the specimens in a FEI-INSPECT S50 equipment, with EDS and EBSD.

Dilatometry

To be able to choose the maximum temperatures for the thermal cycles, it was necessary to do a dilatometry experiment using the Netzsch 421 equipment, which is appropriate for determining refractoriness-under-load and creep of refractory materials. The compression pre-load of the experiment was 0.02 MPa and the heating rate was 3 °C/min. A cylinder-like specimen was tested, whose dimensions were 50 mm of height and 50 mm of external diameter. The specimen had a longitudinal through hole of 12 mm in diameter. This specimen was pre-calcined at 540 ºC for 120 h.

Measurement of Young's modulus as a function of temperature

The measurement of Young's modulus and the damping of vibration throughout five slow thermal cycles were done to evaluate the damage and the thermo-mechanical behaviour. The Impulse Excitation Technique [16] and the logarithm decrement method were respectively used [17]. In the case of the specimens with coke impregnation, thermal cycles were carried out in an argon atmosphere. In what regards the Impulse Excitation Technique, the specimen is supported on wires in the nodal lines of the
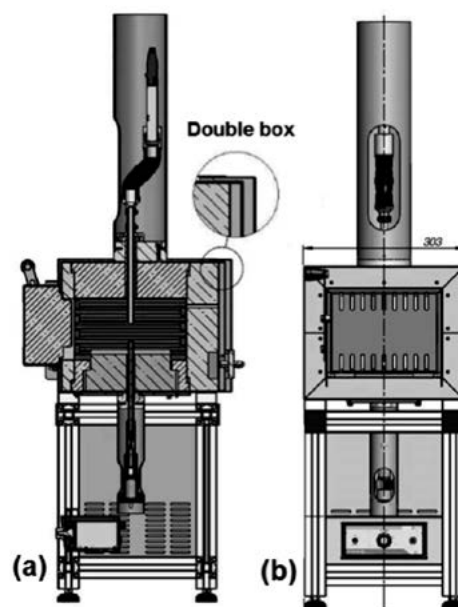

Figure 2: Side view (a) and front view (b) of the instrumented muffle mechanical project.
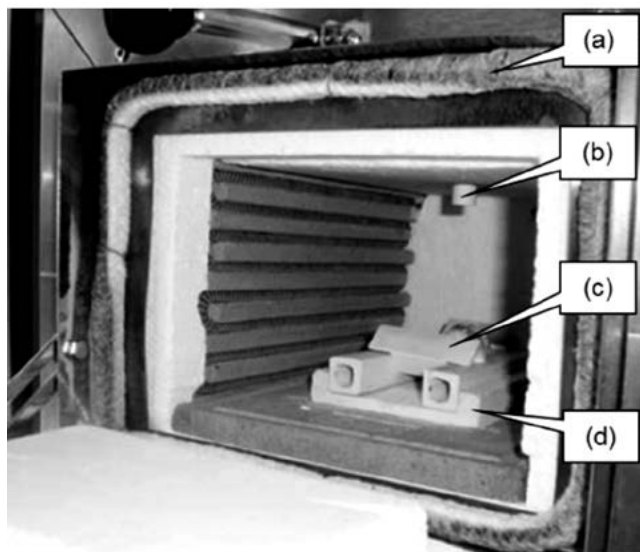*[Figura 2: Vista lateral (a) e frontal (b) do projeto mecânico do forno instrumentado.]*

Figure 3: Instrumented muffle chamber view: (a) gasket for sealing, (b) wave guide for capturing acoustic response, (c) dense alumina support and (d) refractory material base.
[Figura 3: Vista da câmara do forno instrumentado: (a) gaxeta para vedação, (b) guia de onda para captura da resposta acústica, (c) suporte de alumina densa e (d) base de material refratário.]

flexional vibration mode and receives a gentle mechanical impulse, which causes an acoustic response. This acoustic response, when properly processed by software, reveals the natural vibration frequencies of the specimen and their attenuation rates. After determining those frequencies, the attenuation rates, the dimensions and the specimen weight, it is possible to calculate the Young's modulus, by using equations of Picket [18], and the damping, by using the logarithmic decrement method [17]. To perform those characterizations, the Sonelastic® equipment (ATCP Physical Engineering, Ribeirão Preto, Brazil) was used in association with an instrumented furnace developed by the research group (GEMM). The instrumented furnace was developed from a commercial muffle that had been automated in order to allow specimen excitation and the capture of acoustic response. The muffle was also prepared to control the atmosphere aiming to avoid oxidation of coke impregnated specimens. According to Figs. 2 and 3, a system was built containing an air cooled waveguide integrated with a directional microphone on the top part of the muffle chamber. In the bottom part of the muffle a refractory insert and an air cooled electromagnetic impulse device was accommodated. To isolate the muffle chamber, it was necessary to install a stainless steel intermediate box, a ceramic gasket and a lock on the door. Special specimen supports were also developed, one of them having platinum wires for operation temperatures up to 800 °C, and the other with dense alumina components for temperatures up to 1150 °C. The atmosphere control was done by flowing argon through the chamber. For that, two entries immediately located behind the specimen support were installed.

Slow thermal cycles

Two types of slow thermal cycles have been carried out. The first type was carried out from room temperature up to 500 °C, and the second one, from room temperature up to 700 °C. Both heating steps were followed by cooling. The maximum temperatures were established in such a manner that the α-β phase transition of quartz would take place only in the thermal cycles up to 700 °C. Each cycle consisted of heating up firstly to the plateau of 100 °C. Such temperature remained constant for 30 min, thereafter heated up again up to its maximum plateau, remaining constant for another 30 min. Subsequently, it was cooled back down to the plateau of 100 °C and stayed there for another 30 min. In all cases, the temperature variation rate was 2 °C/min. The thermal cycle damage evaluation used as a reference the Young's modulus value taken at the end of the 100 °C plateaus. The specimens that have not been impregnated were submitted to thermal cycles in air and the impregnated ones, in argon.

RESULTS AND DISCUSSIONS

Characterization of phases and microstructure

Fig. 4 presents the X-ray diffraction pattern of the received material, in its particulate and dried form. The diffraction pattern indicates the presence of quartz as well as of mullite, cristobalite, corundum and kyanite [19].
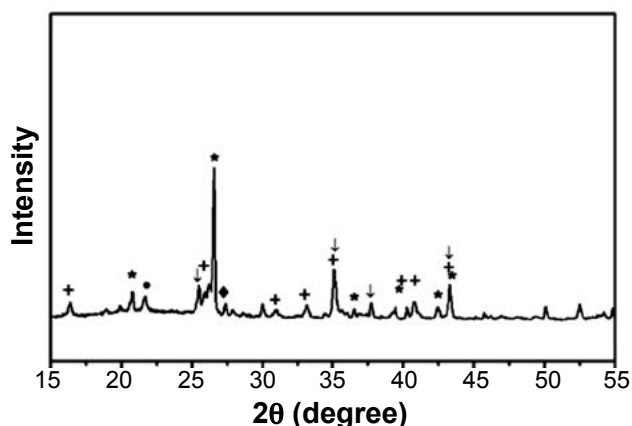

Figure 4: X-ray diffraction pattern of the material as received. +: Mullite; *: Quartz; ●: Cristobalite; ♦: Kyanite; ↓: Corundum.
*[Figura 4: Difratograma de raios X do material como recebido. +: Mulita; *: Quartzo; ●: Cristobalita; ♦: Cianita; ↓: Corindon.]*

Fig. 5 presents a micrograph showing a cracked particle of quartz that has been detached from the matrix measuring approximately 0.1 mm in the calcined refractory material, after thermal shocks [20].

Dilatometry and the maximum temperature of the cycles

The dilatometry during the heating of CR4, which was previously calcined at 540 ºC for 120 h, is presented in Fig. 6.
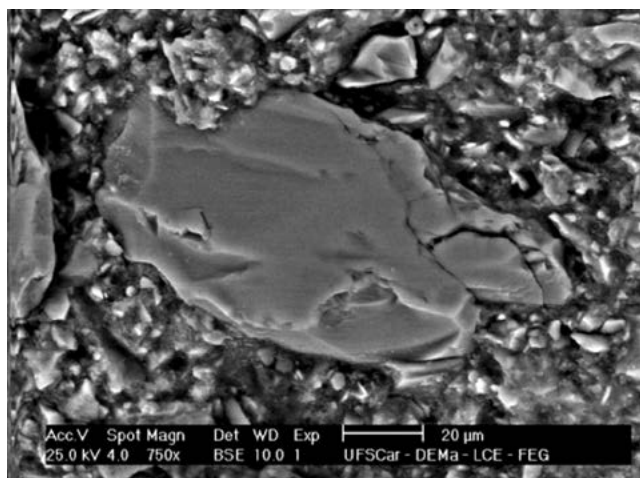
Figure 5: Micrograph obtained by SEM, in BSE mode, showing a particle of quartz in the refractory material measuring approximately 0.1 mm [20].
[Figura 5: Micrografia obtida por MEV, em modo BSE, mostrando uma partícula de quartzo no material refratário com comprimento aproximado de 0,1 mm [20].]
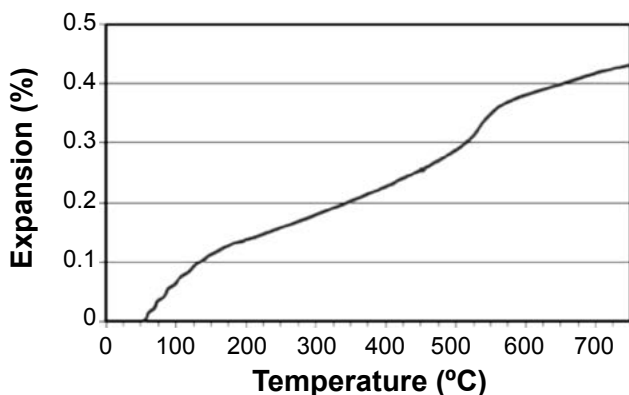

Figure 6: Dilatometry curve during the heating of CR4, which has been previously calcined at 540 ºC, for 120 h.
[Figura 6: Curva de dilatometria de aquecimento do CR4 previamente calcinado a 540 ºC por 120 h.]

The maximum temperatures chosen for the characterization of Young's modulus as a function of temperature of CR4 were based on that result.

By observing Fig. 6, it is possible to notice a change on the expansion rate between 520 ºC and 575 ºC. This alteration is attributed to the polymorphic transformation of quartz, which occurs at 573 ºC. Considering this, the characterization of Young's modulus as a function of temperature was carried out up to the maximum temperatures of 500 ºC and 700 ºC. Therefore, in the thermal cycles up to 500 °C, it is not expected the occurrence of an α-β phase transition. On the other hand, in the cycles up to 700 °C, it is expected that the phase transition should occur and throughout the whole of the specimen.

Thermo-mechanical behaviour

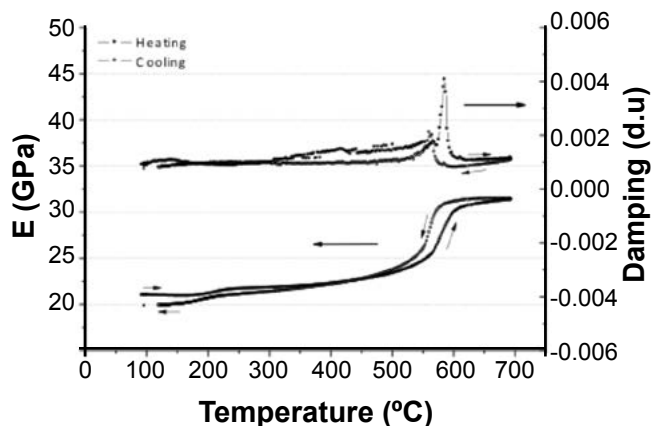Fig. 7 shows the change in Young's modulus values and

Figure 7: Young's modulus and damping of the material that has not been impregnated with coke as a function of the temperature throughout the second thermal cycle up to 700 °C in air.
[Figura 7: Módulo de Young do material sem impregnação com coque em função da temperatura ao longo do 2° ciclo térmico de até 700 °C ao ar.]

in the damping of a specimen without coke as a function of temperature throughout the second thermal cycle up to 700 °C in air. During heating, the damping presents a peak at 585 °C and during cooling, at 560 °C. Simultaneously to the peaks of damping, it takes place a reversible alteration of around 50% at the Young's modulus. It is attributed as a cause to such damping peaks and material stiffness during heating the expansive α-β phase transition of the particles of quartz, which occurred at around 573 °C. The increase in the Young's modulus along the temperature increase is characteristic of materials with particles or aggregates partially or fully detached, however with the thermal expansion coefficient higher than the matrix one. Considering the increase in temperature, such particles or aggregates tend to occupy the same or even bigger space to the cavity that they find themselves in, what contributes to material stiffness [21]. Nevertheless, this process induces
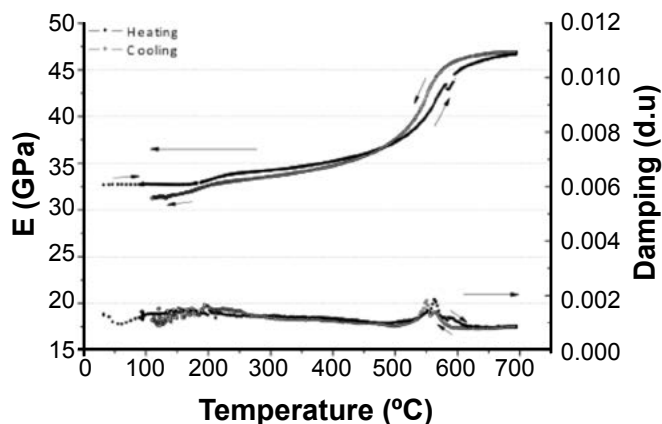

Figure 8: Young's modulus and damping for the coke impregnated material as a function of temperature along the second thermal cycle up to 700 °C in argon atmosphere.
[Figura 8: Módulo de Young do material impregnado com coque em função da temperatura ao longo do 2° ciclo térmico de até 700 °C em atmosfera de argônio.]

the generation and propagation of cracks and micro cracks, causing additional damage.

Fig. 8 shows the Young's modulus and the damping of the coke impregnated material, during the second thermal cycle up to 700 °C in argon atmosphere. During heating, the damping presents a peak at 565 °C and during cooling, at 550 °C, at the same temperature range as the material without coke. Such peaks are present in the same temperature range for all thermal cycles up to 700 °C, regardless of the coke impregnation. The percentage of Young's modulus increase is equally similar, in that case of approximately 50%. However, Young's modulus change for the impregnated material is more subtle and the damping peaks less intense. Nevertheless, considering both cycles presented in Fig. 8 and in Fig. 7, Young's modulus presents a smaller value to what it initially shows due to the damage caused to the material along the cycle. The coke impregnation fills the pores and cracks, what have caused the increase in Young's modulus and the decrease in the amplitude of damping peaks [14].

Figs. 9 and 10 show the Young's modulus and damping increase for the specimens without coke impregnation and with coke impregnation, respectively, as a function of temperature along the second thermal cycle up to 500 °C. As the maximum temperature goes below the α-β phase transition, localized alterations in the Young's modulus value are not detected.

Even when not occurring the α-β transition during thermal cycles up to 500 °C, certain damage does occur due to the thermal cycle (the Young's modulus value after thermal cycle is lower than the value before the cycle). That probably happens due to the anisotropic expansion and mismatch in the expansion coefficient of phases and that has caused the material stiffness as well as the generation and propagation of cracks.

The drop of Young's modulus as a function of slow thermal cycles

Figs. 11 and 12 show the percentage of decrease of Young's modulus as a function of thermal cycles up to 500 °C and up to 700 °C, for both impregnated and not impregnated materials.

In Fig. 11 the percentage of drop considers the Young's modulus values measured after the pre-calcination, prior to the first slow thermal cycle (see the section on experimental procedure). When considering the material without impregnation, the drop in Young's modulus was 35% after the first cycle up to 700 °C, but 15% after the first cycle up to 500 °C. On the other hand, considering the coke impregnated material, the drop was 18% after the first cycle up to 700 °C, whilst it was 8% after the first cycle up to 500 °C. Therefore,
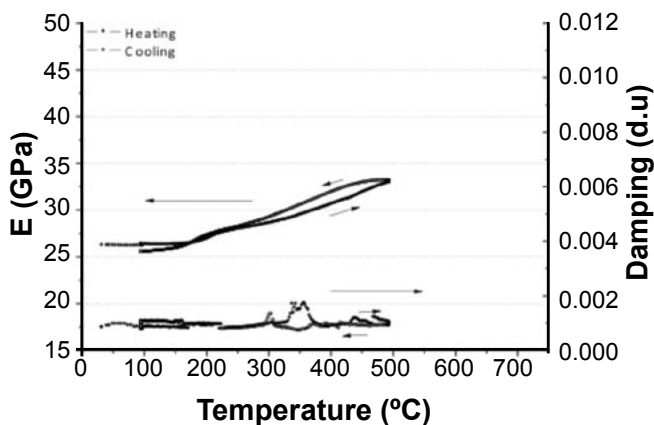
Figure 9: Young's modulus and damping for the material without coke impregnation as a function of temperature along the second thermal cycle up to 500 °C in air.
[Figura 9: Módulo de Young do material sem impregnação com coque em função da temperatura ao longo do 2° ciclo térmico de até 500 °C ao ar.]
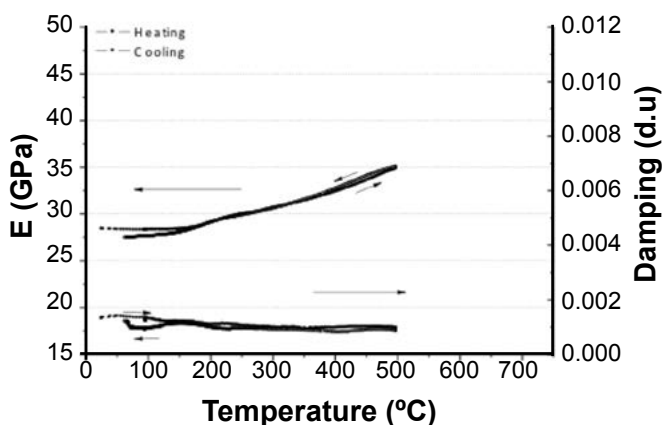
Figure 10: Young's modulus and damping for the coke impregnated material as a function of temperature along the second thermal cycle up to 500 °C in argon atmosphere.
[Figura 10: Módulo de Young do material impregnado com coque em função da temperatura ao longo do 2° ciclo térmico de até 500 °C em atmosfera inerte.]
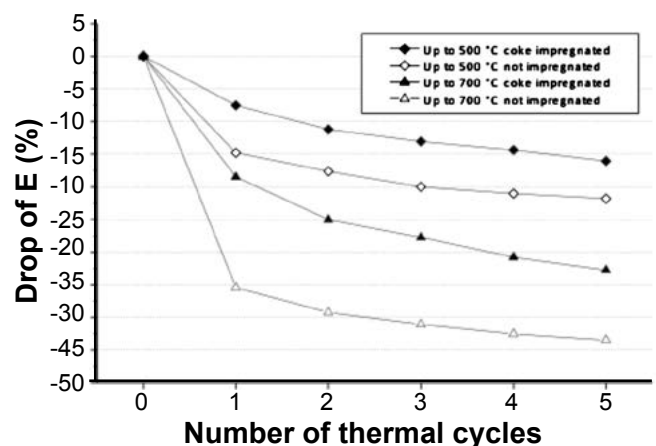
Figure 11: Young's modulus drop percentage as a function of the number of slow thermal cycles considering their values prior to the first thermal cycle.
[Figura 11: Percentual de queda do módulo de Young em função dos ciclos térmicos lentos referenciados aos valores iniciais do módulo, antes do primeiro ciclo térmico.]
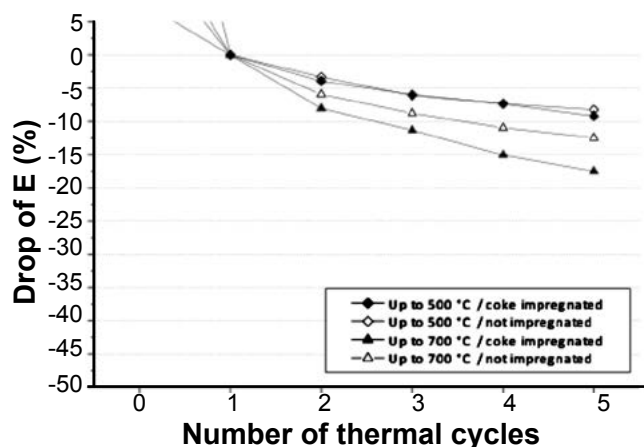
Figure 12: Percentage of drop of Young's modulus as a function of the number of slow thermal cycles, considering their values after the first thermal cycle.
[Figura 12: Percentual de queda do módulo de Young em função dos ciclos térmicos lentos referenciados aos valores do módulo após o primeiro ciclo térmico.]

in the slow thermal cycles up to 700 °C, the damage, and consequently the drop in Young's, has at least doubled when compared to the values in cycles up to 500 °C. However, the maximum temperature increase of 200 °C in the cycles is not enough to explain the damage increase without considering a noteworthy contribution of the expansive α-β phase transition of particles of quartz. It can be observed in Fig. 11 that the damage on the impregnated materials is significantly lower than on the materials without coke after five cycles, mainly due to the first cycle drop. It also indicates that the presence of coke has contributed to the materials resistance to the slow thermal cycle, at least for the experimental conditions and temperatures involved in this study.

In Fig. 12, the percentage of drop considers the Young's modulus values measured after the first slow thermal cycle as reference. It is noticeable that the damage change due to cycles up to 500 °C has no influence of coke impregnation. Nevertheless, in the case of cycles of up 700 °C, the coke impregnation has contributed to increase the damage. It is important to note that, when considering the castables submitted to thermal cycles of a maximum temperature of 700 ºC, the drop percentage rate for E (slope of E(%)) is higher for the impregnated castable. In sum, even considering that the impregnated matrix is mechanically more resistant to support the quartz expansion after the first thermal cycle, in a matrix with average Young's modulus 20% higher than the not impregnated matrix, the deterioration advances on a higher rate for the impregnated castable than it does for the one without impregnation.

It is important to mention that in real working conditions of an FCC-unit, the combination of coke and quartz actions may be intensified by the continuous coke impregnation to which the material is submitted. That would probably fill all news gaps that would have occurred due to damage. This cyclic process of generation of flaws and of coke filling can explain the expansion and the spalling of the refractory

material during operation. Normally, such damages have been mostly associated with coke impregnation. In that case, experiments in which the impregnation would have alternated with slow thermal cycles up to 700 °C could have deepen the understanding of the possible interaction between the coke impregnation and the expansive α-β phase transition to explain the occurrence of damages on FCC-unit linings.

CONCLUSIONS

The particles of quartz present in the CR4 refractory material have played a crucial role in its thermo mechanical behaviour. That is due to the expansive α-β phase transition of quartz, occurring at 573 °C. During heating, that phase transition reversibly stiffens the material, increasing the Young's modulus in approximately 50%. Additionally it doubles the slow thermal cycle damage. That when compared to the drop in Young's modulus caused by cycles up to 500 °C with the one caused by cycles up to 700 °C, the coke impregnation increases the damage resistance during the first slow thermal cycle, reducing however that resistance in subsequent cycles.

ACKNOWLEDGMENTS

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