

STRUCTURAL EVOLUTION IN IRON OXIDE TABLETS AT VIBRATION TESTING FOR CATALYTIC CONVERTERS

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Abstract. This paper presents structural evolution in iron oxide tablets at vibration testing for catalytic converters. The raw tablets composed from a mixture of cordierite powder with nanostructured iron oxide powders (pure and K-doped) and PVP binder. The analysis of the structural integrity of the raw tablets before vibration testing is evidenced by metallographic microscopic highlight the incidence of cracks. The raw tablets were mechanical vibration tested under normal operating conditions within the vibration damper to determine the structural integrity of the tablets. The mechanical vibration behavior of the tablets is essential in the development of new catalyst based on iron oxide nanoparticles for the reduction of gaseous pollutants from internal combustion engines.

Keywords: cordierite; iron oxide; potassium-doped iron oxide; raw tablets; vibration testing.

1. INTRODUCTION

So far, from the analysis of the research results, there is no data on the development of raw tablets from cordierite powder, iron oxide powder and binder, polyvinylpyrrolidone and their vibration testing. Frequently employed catalysts for the catalytic reduction of exhaust gases are precious metals, metal oxides and mixed metal oxides [1-5].

Nanostructured metal oxide-based catalysts for NH₃-SCR are the most efficient, while the use of Pt-based catalysts has been rather limited because their optimal temperature range is small [6]. Due to their excellent activity, the selectivity and stability of V₂O₅-WO₃/TiO₂ catalysts have been intensively studied [6]. The disadvantages are high activity for unwanted SO₂ oxidation, high V toxicity and inefficiency at low and high temperatures [7]. For the SCR process, the most widely used catalyst is V₂O₅ dispersed on TiO₂ anatase support and WO₃ (and/or MoO₃) support. Generally, the total surface area of catalysts is 50–100 m²/g, containing 0.5-3% V₂O₅ and 5-10% MoO₃ or WO₃. IR and Raman studies show that V, W, Mo are present on the surfaces of these catalysts [8]. Iron oxide, as a catalyst, has been intensively studied recently due to its characteristics, namely, low toxicity and thermal stability [9]. Shen et al [10] synthesized iron-doped Mn-Ce/TiO₂ (Fe-Mn-Ce/TiO₂) catalysts for low-temperature selective catalytic reduction (SCR) of NO with NH₃ by the sol-gel method. The results showed that this conversion of NO on Fe-Mn-Ce/TiO₂ was markedly improved after iron doping compared to that on Mn-Ce/TiO₂. Fe-Mn-Ce/TiO₂ with Fe/Ti molar ratio = 0.1 showed the highest activity. The results revealed that 96.8% NO conversion

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was obtained on Fe (0.1)-Mn-Ce/TiO₂. Fe-Mn-Ce/TiO₂ showed much higher resistance to H₂O and SO₂ than that of Mn-Ce/TiO₂. The properties of the catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption, temperature programmed desorption (NH₃-TPD and NO_x-TPD) and X-ray photoelectron spectroscopy (XPS) techniques. BET, NH₃-TPD and NO_x-TPD results showed that the specific surface area and NH₃ and NO_x adsorption capacity of the catalysts increased with Fe doping. From the XPS analysis, it was found that the valence state of Fe on the surface of the catalysts was in the Fe³⁺ state. Fe doping improved the dispersion and oxidation state of Mn and Ce on the surface of the catalysts. It was found that the oxygen concentrations on the surface of the catalysts increased after iron doping. Fe-Mn-Ce/TiO₂ is a promising catalyst for low temperature SCR (Selective Catalytic Reduction) of NO with NH₃ in the presence of H₂O and SO₂.

Other researchers, such as Azalim with co-workers [11] have used cordierite honeycomb. Thus, in the work *Washcoating of cordierite honeycomb with Ce-Zr-Mn mixed oxides for VOC catalytic oxidation*, the authors [11], used a commercial honeycomb monolith made of cordierite with a cell density 200 cpsi and square channels, then the honeycomb was cut to obtain cylindrical samples with a diameter of 10 mm and a length of 30 mm. The samples were then immersed in concentrated nitric acid (65%) for 1 day at 25°C to remove soluble impurities and to prepare the surface before coating. The resulting monoliths were washed thoroughly with distilled water and then dried for 12 h at 120°C in air and immersed in repeated cycles in the prepared soil. Channel stripping was carried out under a weak argon flow. Before being subjected to calcination, the resulting monoliths were left for 12 h at room temperature.

Gomez together with his collaborators [12] elaborated a Co₃O₄ catalyst by the polymerization-combustion technique from Co(NO₃)₂·6H₂O (99.9%) and citric acid monohydrate (99.99%), which was utilized as the active phase on a cordierite support. The honeycomb cordierite monolith exhibits a cell density of 400 cells in-2 (D = 12 mm, L = 8 mm). A stoichiometric amount of precursor salt (0.01 mol) was added to 20 mL of absolute ethanol in a glass vessel equipped with magnetic stirring (150 rpm), reflux system and temperature control. After total dissolution was reached, citric acid was added in a molar ratio of 0.5:1 to the total concentration of the dissolving metal cation. The starting solution (0.5 M) was kept under reflux at 120°C for 12 hours until a viscous liquid was formed, which was then impregnated on to the cordierite. After washing, the monolith was heated at 150°C under air flow in a furnace until the solvent evaporated completely and calcined at 500°C under oxygen flow for 4 hours to remove the residues. After several impregnation cycles, the excess material was removed using an ultrasonic cleaner.

Bo and his collaborators [13] used a commercial honeycomb cordierite monolith with a cell density of 300 psi and square channels (150 mm × 150 mm section and 350 mm length) as a substrate. Before impregnation, the monolith was pretreated to remove soluble impurities by immersion in distilled water for 12 h, oven dried at 80°C for 5 hours and, calcined at 300°C for 3 hours. To obtain the titania sol, tetrabutyl titanate was used as precursor, which was dissolved in ethanol and added dropwise to deionized water together with inhibitors and catalysts under constant stirring at 300 rpm in a three-necked flask at room temperature for 2 hours. While until now the research focus on wet method for impregnation of cordierite we propose the iron oxide-impregnated cordierite catalyst, starting from powders, to be used for the catalytic reduction of gaseous pollutants.

2. MATERIALS AND METHODS

2.1. MATERIALS

For this study, cordierite powder, polyvinylpyrrolidone and iron oxide nanostructured powders pure and doped were used to obtain the raw tablets.

2.2. PREPARATION OF RAW TABLETS

The pressing of the powders into raw tablets for vibration testing was carried out in two steps:

- the mixture of cordierite powders, pure iron oxide powders elaborated by hydrolytic synthesis at 65°C and binder (PVP-polyvinylpyrrolidone) was placed in a metal mold.
- pressed in such a way as to fill the useful volume of the mold; The pressure of 7 bar was applied for tablets with a diameter of 0.6 mm and a thickness of 0.3 mm.

The parameters used to obtain C1, C2, C3 tablets are shown in Table 1.

Table 1. The main parameters and the conditions for the obtaining of tablets.

Tablet code	Cordierite powder	Iron oxide powder/ processing conditions	Binder	P(bar)
C1	2MgO ₂ Al ₂ O ₃ .5SiO ₂	Fe ₂ O ₃ / hydrolytic synthesis 65 ⁰ C /0,1 M Fe ³⁺ ; pH=11; 300 ⁰ C	PVP	7
C2		Fe ₂ O ₃ / hydrolytic synthesis 85 ⁰ C /0,1 M Fe ³⁺ ; pH=11; 300 ⁰ C		
C3		Fe ₂ O ₃ / microwave /0,1 M Fe ³⁺ ; pH=11; 300 ⁰ C		
C4		Potassium-doped Fe ₂ O ₃ / hydrolytic synthesis by co-precipitation 65 ⁰ C/0,1 M Fe ³⁺ ; /0,025M KCl, pH=11; 300 ⁰ C		
C5		Potassium-doped Fe ₂ O ₃ / hydrolytic synthesis by co-precipitation 85 ⁰ C/0,1 M Fe ³⁺ ; /0,025 M KCl,pH=11; 300 ⁰ C		
C6		Potassium-doped Fe ₂ O ₃ / microwave /0,1 M Fe ³⁺ ; 0,025 M KCl pH=11; 300 ⁰ C		

The tablets were examined under an Olympus BX51M metallographic microscope before vibration testing for structural integrity. Evaluation of the degradation potential of oxide raw tablets is useful to analyze whether there is potential for disruption of the catalytic support when used for a catalytic drum, correlated with the degradation effect of vibration. Vibration testing of oxide raw tablets consists of testing of normal operating conditions on the catalytic converter housing. To determine the test conditions, the vibration frequency was measured at the converter housing under normal engine operating conditions. The measurement of the response was performed using a piezoelectric accelerometer attached to the housing by a magnet (Fig. 1).

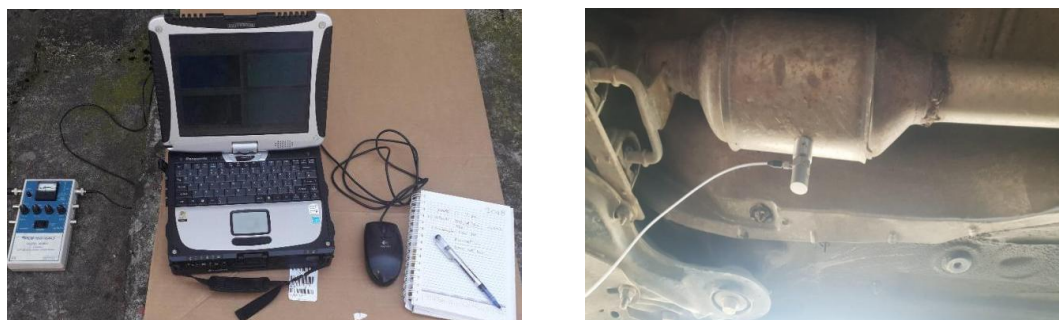


Figure 1 a) Overview of the piezoelectric accelerometer attached to the catalytic converter housing and b) the soundbook MK2 portable universal noise and vibration analyzer.

3. RESULTS AND DISCUSSION

3.1. RESULTS

3.3.1. Determination of structural integrity

Figs. 2-7 illustrate that microscopic examination revealed that homogeneous tablets were made using the experimental conditions presented above.

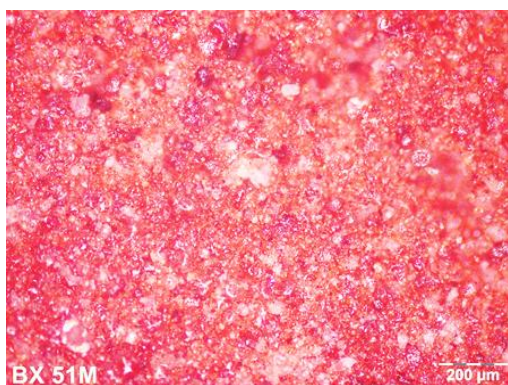


Figure 2. Surface microstructure of C1, M 100X

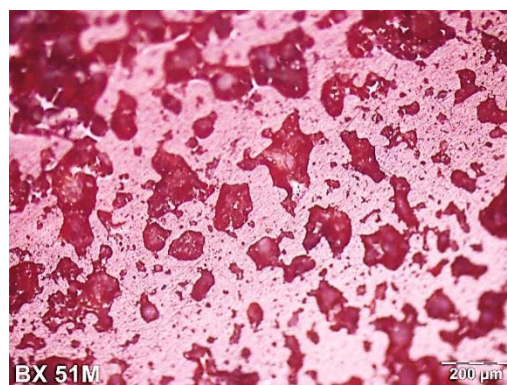


Figure 3. Surface microstructure of C2, M 100X

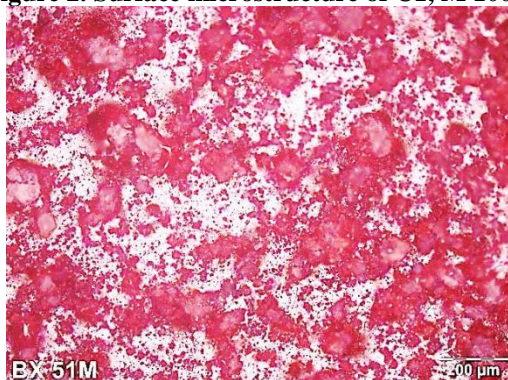


Figure 4. Surface microstructure of C3, M 100X

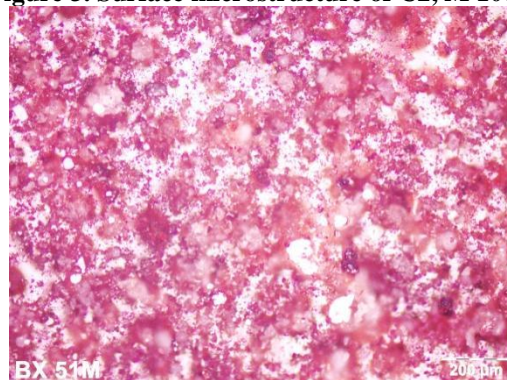


Figure 5. Surface microstructure of C4, M 100X

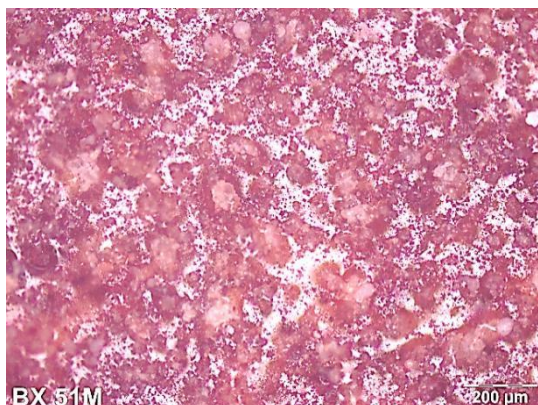


Figure 6. Surface microstructure of C5, M 100X

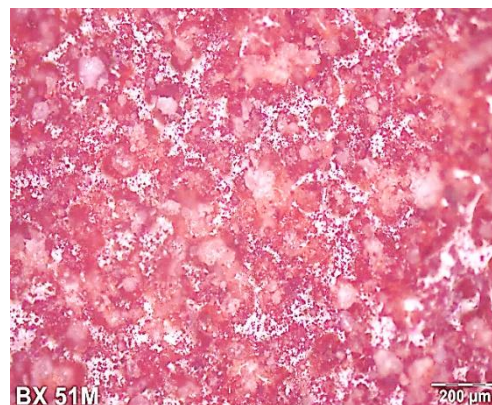


Figure 7. Surface microstructure of C6, M 100X

3.3.2 Vibration testing

Since a car's exhaust system is fitted with a vibration damper, the frequency of mechanical vibrations in the exhaust system will have the same value whether the engine is running at idle or full speed. The frequency spectra determined by the Soundbook MK2 handheld universal noise and vibration analyzer with piezoelectric accelerometer transducer allow the determination of the excitation frequencies due to engine operation and the resonance frequencies of mechanical vibrations at the converter housing. The motor excitation frequencies are a function of motor speed and can be calculated using the relation:

$$f = \left(\frac{\text{no. rot/min}}{60} \cdot 4 \right) : 2$$

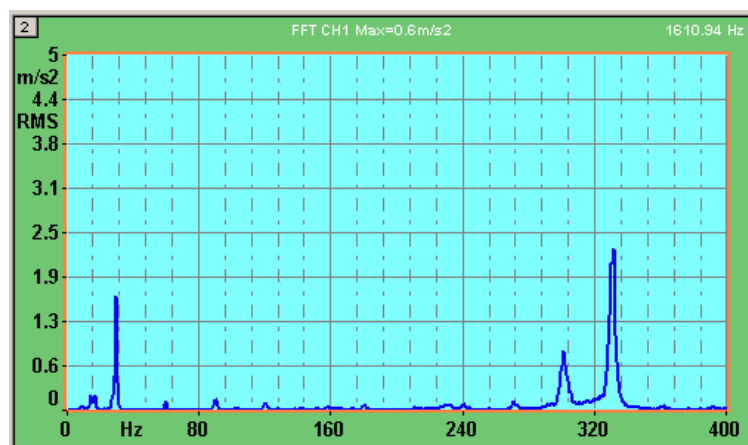


Figure 8. Frequency analysis of measured vibrations on the catalytic converter housing at 1000 rpm

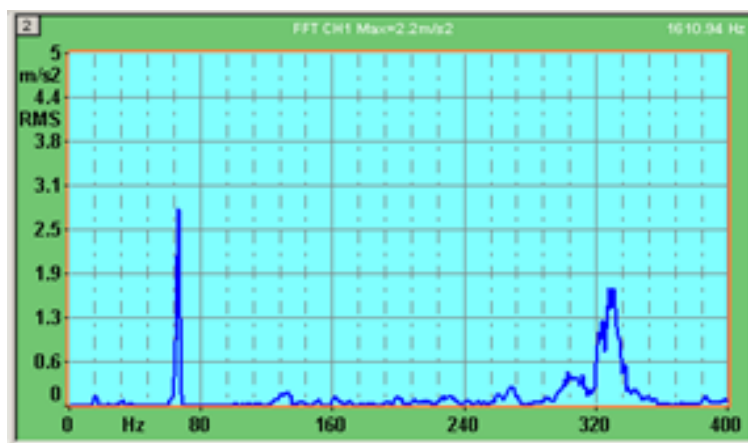


Figure 9. Frequency analysis of vibrations measured on converter housing at 2000 rpm

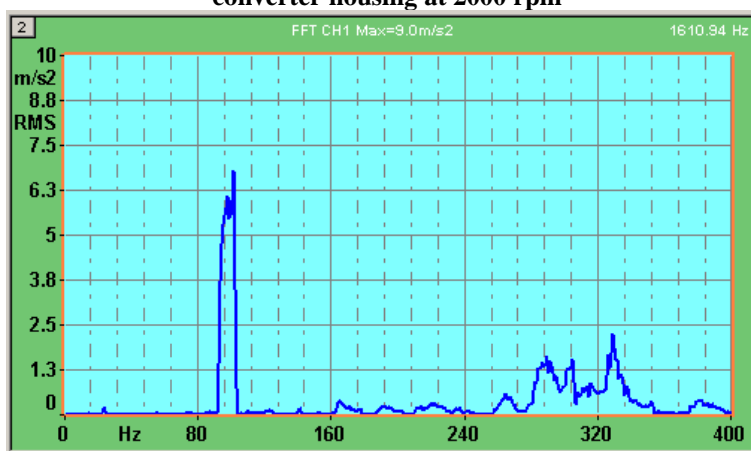


Figure 10 Frequency analysis of vibrations measured on converter housing at 3000 rpm

Measurements were taken at 1000 rpm, 2000 rpm and 3000 rpm and the results were processed, then by applying FFT (Fast Fourier Transform), which converts a signal into individual spectral components and thus provides frequency information about the signal [14]. From the analysis of the frequency spectra, two characteristic peaks/peaks are highlighted, thus the first peak/peak is located in the area, where the excitation frequency occurs, and the second peak/peak located in the area of 320 Hz frequency. Analyzing the three spectra, is observed that a direct link is maintained between the excitation frequency determined by relation (1) and the motor configuration. Thus, it is found that the value for 320 Hz does not change, this being the resonant frequency of the catalytic assembly. From measurements at 1000 rpm, 2000 rpm and 3000 rpm, it was determined that resonance vibrations at the casing occur in the range 300–330 Hz (Figs. 8–10). After establishing the resonance frequency at the catalytic converter housing, vibration tests were carried out on oxide raw tablets using mechanical excitation at these frequency values with the equipment. The structural integrity of the oxide raw tablets was monitored.

The tablets were vibration tested to see if they would withstand normal operating conditions inside the vibration damper. Tests were performed under operating conditions on the catalytic converter housing for the pressed tablets.

From the excitation diagrams (Figs. 11 and 12) the acceleration at resonance frequency ($a_{rms}=62.8 \text{ m/s}^2$ $a_{rms}=15.7 \text{ m/s}^2$) was determined. These values are higher than those determined on the catalytic converter support.

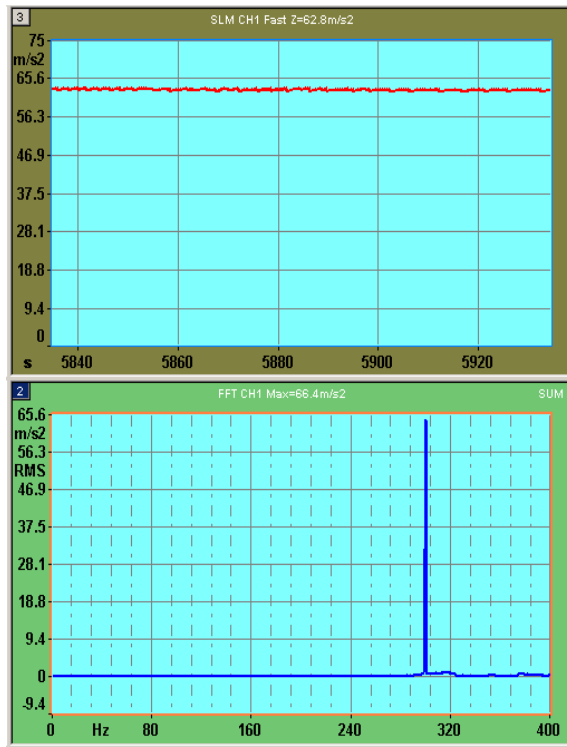


Figure 11. Excitation diagram
300 Hz, $a_{\text{rms}}=62,8 \text{ m/s}^2$

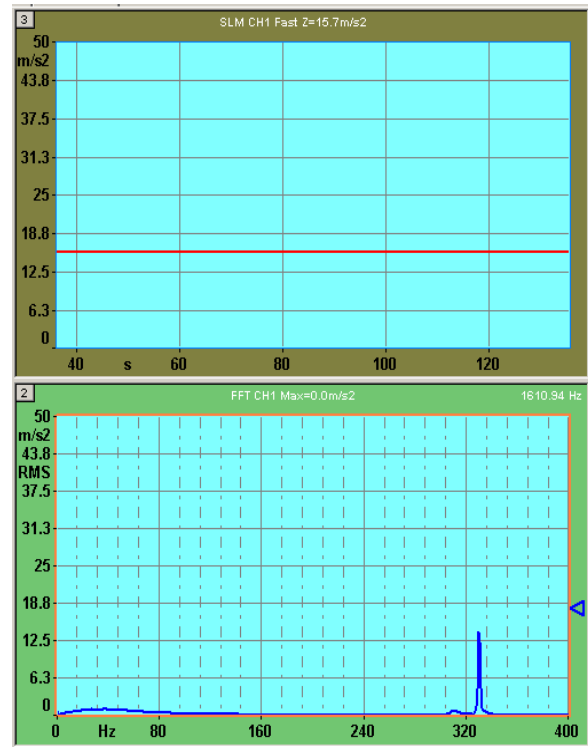


Figure 12. Excitation diagram
330Hz, $a_{\text{rms}}=15,7 \text{ m/s}^2$

After vibration testing, the tablets were subjected to metallographic examination to determine whether structural integrity was maintained after the test, at different magnifications.

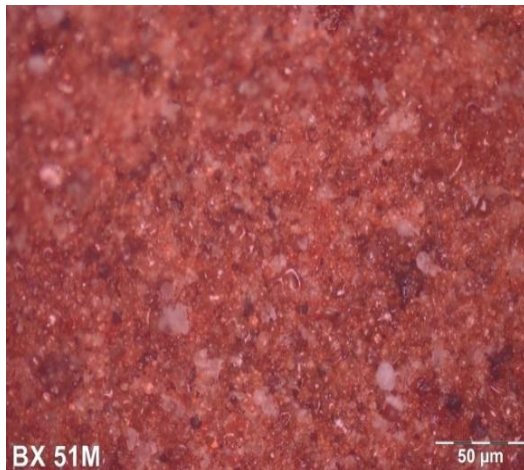


Figure 13. Surface microstructure of C1 after vibration testing: 4h, 300Hz, 62.8 m/s^2 , M 500X

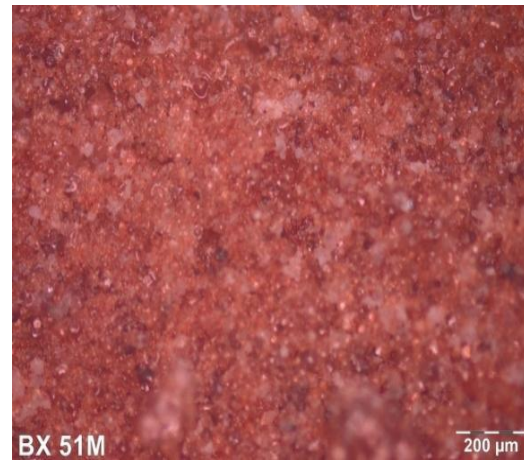


Figure 14. Surface microstructure of C1 after vibration testing: 4h, 330Hz, 15.7 m/s^2 , M 100X

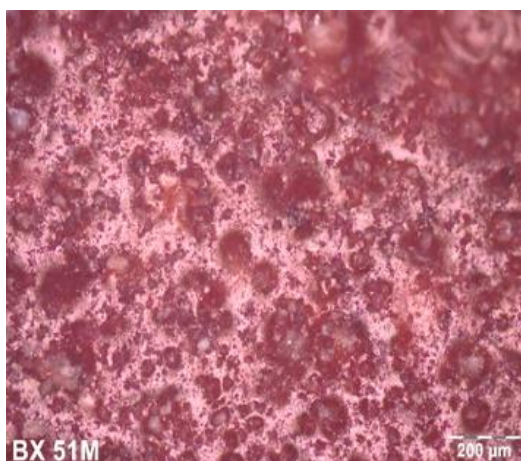


Figure 15. Surface microstructure of C2 after vibration testing: 4h, 300Hz, 62.8 m/s² M 100X

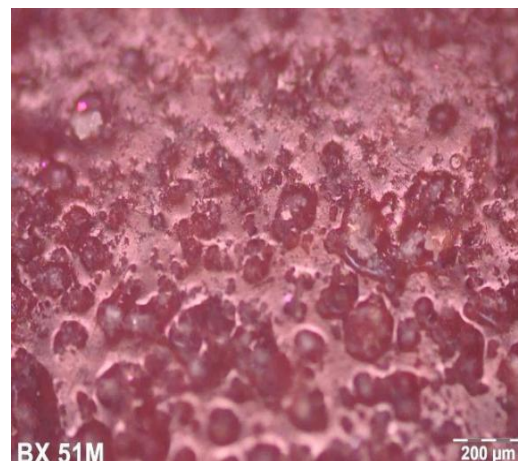


Figure 16. Surface microstructure of C2 after vibration testing: 4h, 330Hz, 15.7 m/s² M 100X

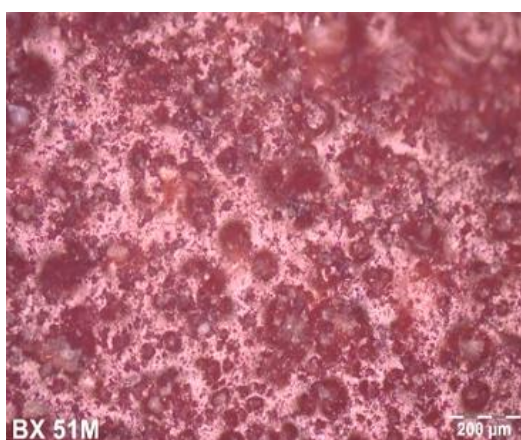


Figure 18. Surface microstructure of C6 after vibration testing: 4h, 300Hz, 62.8 m/s² M 100X



Figure 19. Surface microstructure of C3 after vibration testing: 4h, 330Hz, 15.7 m/s² M 100X

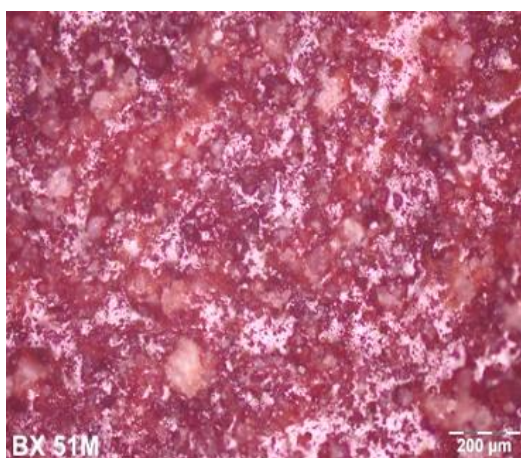


Figure 22. Surface microstructure of C5 after vibration testing: 4h, 300Hz, 62.8 m/s² M 100X

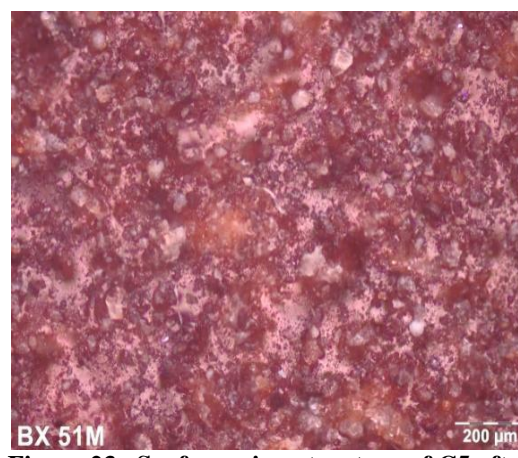


Figure 23. Surface microstructure of C5 after vibration testing: 4h, 330Hz, 15.7 m/s² M 100X

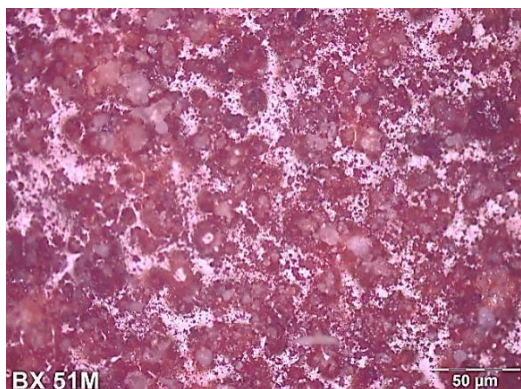


Figure 24 Surface microstructure of C6 after vibration testing: 4h, 300Hz, 62,8 m/s², M 500X



Figure 25 Surface microstructure of C6 after vibration testing: 4h, 330Hz, 15.7 m/s², M 100X

The analysis of the optical micrographs shows that there are no fissures, which confirms that the production parameters, shown in table 1, are optimal for homogeneous raw tablets (Figs.14-25).

4. CONCLUSIONS

The resonant frequency at the catalytic converter housing induced by the presence of the vibration damper was in the range 300-330 Hz. No cracks were found in the raw oxide pellets subjected to vibration testing from the structural integrity analysis. The conditions for obtaining oxide raw tablets for use in catalytic converters are: cordierite powder, binder (PVP), pure nanostructured iron oxide powders doped with K. The resonant frequency corresponds to an engine speed of ~9600 rpm, outside the operating range of internal combustion engines conventionally used in the automotive industry.

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