

Original Article

Influence of cryogenic grinding surface on fatigue performance of carburised 27MnCr5



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ABSTRACT

Automotive transmission components are subjected to cyclic loads and, thus, must have a reliable fatigue performance. Since fatigue cracks nucleate at the surface, it is necessary to guarantee that its surface integrity accomplishes the required specifications. Typically, those components are finished by wet grinding after carburising heat treatment. However, there is an increasing demand to reduce pollutants and hazardous lubricants in the industry, and eco-friendly finishing operations have been highly encouraged. To this end, it is necessary to understand the effect of these novel finishing processes on surface integrity and, consequently, on fatigue behaviour. This study aims to assess the surface integrity and the fatigue performance of cryo-ground surfaces of 27MnCr5 steel, extensively used in fabricating shafts and gears for gearboxes. Fatigue specimens for pure torsion tests were initially case-hardened and afterwards finished using two different cryogenic grinding conditions applying liquid N₂ and, as a reference, using the conventional wet grinding process. First, the surface integrity was analysed in terms of texture, residual stresses, microstructure, and microhardness. Second, the batches of specimens were tested under pure torsion fatigue. Surface residual stress relaxation was also measured during fatigue tests. Finally, fracture surfaces were observed to identify crack initiation sites and establish correlations with the surface integrity. Specimens produced by cryogenic and conventional wet grinding did not show microstructural defects or hardness reductions in the carburised layer. All conditions induced compressive residual stresses, and they barely relaxed during fatigue tests. Compressive residual stresses induced by cryogenic grinding were 10-20% lower than those generated by conventional wet grinding. This decrease resulted in a minor reduction of the fatigue resistance (4-6%) compared to the wet grinding. Importantly, this study demonstrates that with a slight geometrical radio correction in the design of the mechanical components (around 2.2%), cryogenic grinding generates pieces with the same fatigue strength as conventional grinding. Therefore, it confirms that cryogenic

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cooling could be a potential solution to replace pollutant coolant/lubricant fluid in grinding operations.

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1. Introduction

Grinding has been widely used to achieve good surface quality and high dimensional accuracy on mechanical components [1]. However, this process requires complex cooling systems with big pumps and large quantities of liquid coolant. These requirements aggravate the manufacturing process in environmental and cost terms since the common coolant/lubricant utilised is based on cutting oils or synesthetic watermiscible emulsions [2]. These fluids create three main problems in grinding processes.

- The lubricant/coolant fluids are mixed with the swarf, and thus they require additional procedures to separate, clean and dry the sludge until recycled.
- These fluids need to be replaced after a time of use, creating pollutant fluids that require external treatment until their final disposal. Consequently, this treatment increases the production cost.
- 3. Due to the necessity of a large quantity of coolant/lubricant fluids, big pumps are required to recirculate the fluids, increasing energy consumption. According to some authors [3], pump energy consumption can be 45% of the total energy in the grinding process, which directly increases the cost of the ground components.

To reduce the above-mentioned environmental issues, sub-zero and cryogenic strategies have emerged as ecological solutions to improve grinding operations. These strategies use carbon dioxide (CO₂) [4] or liquid nitrogen (LN₂) [5] to replace traditional wet cooling. These fluids have a freezer quality due to the lower temperature achieved at atmospheric pressures (-78 to -195.8 °C). In sub-zero and cryogenic grinding processes, the cooling liquid directly impacts the grinding wheel freezing the grain of the wheel and reducing the temperature produced in the process [2,6,7]. Cryogenic fluids can also be mixed with a minimum quantity of lubricant (MQL) to reduce the joint wheel-workpiece friction [8].

The automotive industry is not an exception for the problems caused by conventional cooling systems used in grinding operations of mechanical components, such as shafts and gears of gearboxes. Particularly, shafts are subjected to cyclic in-service loads that cause bending and torsional fatigue [9]. To improve the fatigue performance of shafts made in steel, a carburisation treatment is applied, which increases the hardness near the surface as carbon content increases, leading to higher fatigue strength [10,11]. After carburising treatment, the final surface must be smooth to enhance fatigue performance, and this is obtained by conventional wet grinding. The environmental and economic issues abovementioned encourage the use of eco-friendly processes such as cryogenic grinding to finish shafts used in transmission components. Typically, the fatigue failure of a machined component nucleates near the surface as micro-failures [12,13] and consequently, the final surface integrity (microstructure, surface texture, residual stresses, and microhardness) induced by the finishing operation, such as grinding, will have a high impact on the fatigue performance [14]. The effect of surface texture/topography on the fatigue behaviour of the machined component has been analysed using Murakami's model or stress concentration factors [15,16]. Recently, Macek et al. [17] studied the fatigue behaviour of the 2017A-T4 alloy and proposed quantifying the surface topography of fractures in terms of S_a , S_z , and S_q . The research showed a correlation between surface roughness parameters in the fatigue tests.

Additionally, the same authors [18] studied the bending and torsion fatigue fractures of samples of S355J2 steel to determine the relationship between the loading course, fatigue life, and the characteristic features of their surface topographies. In this research, the authors also try to correlate fatigue specimens' surface topography with fractures' surface topography. Unfortunately, the research did not show a clear correlation between them because crack initiation could depend on additional parameters like punctual local valleys or residual stresses in the material. Although the effect of surface roughness on fatigue is relevant, this is negligible in the presence of high residual stresses [19,20] or when average roughness is below 0.4 μm [21]. For instance, Yang and Liu [22] found that the fatigue strength of Ti-6Al-4V samples increased when the compressive residual stress increased, although this improvement was not evident when residual stresses were relaxed. Hashimoto et al. [23] compared the relation of surface integrity between a hard turning and a grinding process over the rolling contact fatigue life of samples of AISI 52100 steel. The authors found hard-turned surfaces had lower roughness and thermal damage than ground surfaces, leading to improved fatigue life.

Therefore, evaluating the surface integrity characteristics of the novel cryogenic approaches and linking them to the final fatigue behaviour of the component is vital to validate the use of these ecological strategies in the industry. Beyond this scope, some studies have already analysed the surface integrity of several materials under specific sub-zero and cryogenic processes. These researchers have demonstrated that with CO_2 +MQL technology [8] and LN_2 [6,9], it is possible to obtain similar mean surface roughness compared to conventional wet cooling. Furthermore, LN_2 ground surfaces also showed lower tensile residual stresses than wet grinding [10], promoted by the considerable reduction in the temperature of the process [9,10].

Although these researchers suggest that cryogenic grinding can improve surface integrity, only a few studies focus on fatigue behaviour. Balan et al. [24] found that the fatigue life of steel plates pre-manufactured by additive

manufacturing improved by 170% when using the cryogenic surface grinding with LN₂. This improvement was a consequence of the improvement in surface roughness and generation of compressive residual stresses. Fredj and Sidhom [25] used plates of AISI 304 to compare the effect of cryogenic grinding and wet grinding on fatigue behaviour using a threepoint bending test. The authors found that the cryogenic LN₂ increased the high cycle fatigue life compared to those specimens generated using wet grinding.

As already explained, the carburisation treatment is essential to produce automotive transmission components with excellent mechanical properties and then obtain the final surface by finishing operations. The literature review highlights that the studies that analyse the effect of cryogenic grinding on fatigue behaviour are limited to surface grinding for plates and materials without any surface carburisation treatment. Undoubtedly, it is fundamental to address the impact of cryogenic grinding on the surface integrity, and fatigue behaviour of carburised steels since its performance significantly differs from untreated steels. Furthermore, these results could be transferred into the automotive industry since carburisation treatment is usually applied in transmission components prior to finishing operations.

This study aims to analyse the effect of cryogenic grinding on surface integrity and fatigue behaviour of carburised 27MnCr5 steel. For this purpose, we produced fatigue samples using two cryogenic grinding conditions and conventional wet grinding as a reference. First, the surface integrity (texture, residual stresses, microhardness, and microstructure) of the fatigue specimens was analysed. Then fatigue tests were conducted, and residual stress relaxation was measured. Finally, a fractography analysis of broken samples was conducted. This methodology allowed us to establish a relationship between the surface integrity and fatigue performance of the specimens produced by the three different grinding conditions.

2. Material and methods

To compare the fatigue performance of mechanical pieces finished by the cryogenic grinding process and the

Table 1 – Weight percentage chemical composition for the 27MnCr5 in percentage.										
Steel	С	Mn	Si	Cr	В	Ti	Cu	S	Р	Al
27MnCr5	0.29	1.21	0.27	1.09	0.0002	0.002	0.19	0.028	0.015	0.023

conventional wet grinding, the steel 27MnCr5 provided by Sidenor Aceros Especiales S.L.U. was selected. This material is widely used for producing machined components (shafts, gears ...) of gearboxes in the automotive field. Table 1 shows the chemical composition of this ferrite-perlite steel. In the initial state, this material presented a ferrite-perlite structure with a surface hardness around 400–450 HV.

The geometry of the material is a cylindrical fatigue sample, following the specifications of the standard ASTM E466-96 (2002) [26]. Initially, the specimens were turned to obtain the geometrical shape and dimensions of Fig. 1. However, a diametral overstock of 0.5 mm was left in the central section. Then, the material was carburised to achieve a martensitic structure with a surface hardness of 720–770 HV (59–64 HRC) and a carburised layer between 0.7 and 0.9 mm.

Next, the specimens were divided into two batches: 1) specimens produced by cryogenic grinding and 2) by conventional flood grinding. The specimens of the first batch were ground using cryogenic grinding conditions studied in previous research [6]. In this research, we found a process working window for the cryogenic cylindrical grinding technology, in which the cryogenic ground surfaces achieved the surface quality required for automotive applications. Therefore, the two best grinding conditions that achieved the lowest surface roughness and good process stability were extracted. These two different cryogenic conditions (CGA and CGB) are shown in Table 2.

To grind the cryogenic specimens of batch number one, a Danobat LG-400S grinding machine, using a cubic boron nitride (CBN) grinding wheel from Mirka® Cafro with ref. 3D1V-400-15-5-25-27-B107-SA-100-V69 M was employed. The specimens were clamped to the machine using a selfadjusting chuck that dragged the sample from the left side and a counterpoint on the right side. To grind the samples a transverse feed strategy was selected. This strategy followed



Fig. 1 – Final geometry of torsional fatigue specimens.

the contour of the sample in two steps: i) roughing step using conventional wet grinding and ii) finishing step by cryogenic grinding. In a roughening step, a conventional wet grinding was carried out to obtain a diametral overstock of 0.3 mm in the central section of the sample. For this process, the transverse feed was set at 20 mm/min. To finish the specimens' preparation, samples were ground using LN2 as a cooling system to achieve the final dimensions shown in Fig. 1. The transverse feed was set at 10 mm/min in this second step. The LN_2 was supplied from a pressurised tank of 2 bar, using a phase separator followed by a conduit with a circular nozzle of 5 mm in diameter. The LN₂ jet was set over the wheel, inclined 45° from the horizontal plane but close to the wheel-piece assembly. Before the cryogrinding process, the grinding wheel was dressed to ensure the same surface quality for each specimen. The complete set-up for the cryogenic grinding is shown in Fig. 2.

Specimens of batch number two were used for the conventional wet grinding. In this case, the specimens were ground following a close condition and a similar strategy to the automaker industrial plant to produce shafts. A Lizzini IG FXS grinding machine, using a CBN wheel from Molemab® with the ref. B107-900804 was employed to produce the specimens. Table 3 shows the WG condition and feeds used for this wet condition. The grinding strategy consisted of a unique plunge grinding with high-speed oscillations in three steps: roughing, semi-roughing, and finishing. Before the wet grinding process, the wheel was dressed to ensure the equal quality of the results.

For cryogenic LN_2 , approach 24 specimens were prepared, 12 specimens per the grinding condition of Table 1, while for wet, 12 specimens were made following the machining conditions of Table 2. In total, 36 samples were ground to analyse the effects of LN_2 and wet grinding on the fatigue behaviour of the carburised 27MnCr5 steel.

As mentioned in the introduction section, prior to fatigue tests, the surface integrity of the LN_2 and wet specimens was characterised in terms of texture, residual stresses, microstructure defects, and microhardness profiles. The surface texture was analysed on one specimen per grinding condition using the Alicona IFG4 optical profilometer. The images' magnification objective was 50x, and the vertical and lateral resolutions were 100 nm and 2.135 μ m, respectively. Over the extracted images, surface roughness profiles were measured, obtaining the following surface texture parameters R_a , R_z , R_t , S_a , S_{sk} and S_{ku} . For the three first parameters, three repetitions were measured, and the mean and the standard deviation were reported.

Residual stresses were measured in the hoop, and the axial direction of the ground surfaces by X-ray diffraction (XRD)

Table 2 – Cryogenic grinding conditions to produce fatigue specimens.								
Surface name	V _s [m/ s]	V _o [m/ min]	Infeed [mm/min]	Traversal feed [mm/min]	Coolant			
CGA CGB	40 53	42 14	0.3 0.3	10 10	LN ₂ LN ₂			



Fig. 2 – Set-up of the cryogenic grinding tests of fatigue specimens.

technique, employing a portable diffractometer (PROTO iXRD). Residual stresses were measured at three points located in the gage length of each specimen. Five specimens of each batch were characterised, and the mean values were reported including the specific standard deviations. Complementarily, residual stresses were measured in run-out specimens to evaluate residual stress relaxation. To take the measurements, a CrK α (λ = 2.291 Å) radiation was used, with a voltage of 25 kV and a current of 5 mA, using around collimator (1 mm diameter). Measurements were performed in Ω mode with 7 inclinations (varying Psi angle from -37° to 37°) for axial and circumferential directions. The (2 1 1) diffraction plane of the martensitic structure was selected for the measurements. Diffracted peaks were fitted by a Gaussian model, and the diffraction elastic constants used to determine residual 10^{-6} stresses were: -S1 1.2 × MPa^{-1} , 1/2 $S2 = 6.04 \times 10-6 \text{ MPa}^{-1}$.

Regarding the microstructural analysis, one specimen per grinding condition was cut out by an electrical discharge machining (EDM) process to analyse the ground subsurface in the hoop (cutting direction) and the axial direction. These samples were mounted in resin capsules, where they were polished and then attacked by a Nital (5%) solution. Finally, the subsurfaces were observed through an optical microscope equipped with a digital camera Leica DMC 2900. The micrographs were taken using the Leica LAS software V4.9., with a magnification of x500. Additionally, to analyse the rehardening layer in the subsurface, certain samples were analysed through the scanning electron microscope (SEM). The FEI Nova NanoSEM 450 was used in this research. The samples were directly analysed in the SEM, using a constant electron high tension of 20 kV and a working distance of 5.6 mm.

To complete the surface integrity characterization, microhardness profiles HV0.05 were measured on the transversal section of three specimens per grinding condition, using a ZWICK hardness tester and a loading time of 10 s. Indentations were generated in four steps of 25 μ m near the surface, followed by four steps of 50 μ m, seven steps of 100 μ m,

Table 3 – Wet grinding conditions to produce fatigue specimens.								
Surface name	V _s [m/s]	V _o [m/min]	Roughing infeed [mm/min]	Semi-roughing infeed [mm/min]	Finishing infeed [mm/min]	Traversal feed [mm/min]	Coolant	
WG	70	30	0.66	0.44	0.22	700	Water miscible, semisynthetic emulsion 7.5%	

and a final increment of 500 $\mu m.$ Three repetitions per indentation were performed and the mean values were obtained to generate the plots.

Torsional fatigue tests were carried out in a MTS 809 teststar hydraulic machine, using a stress ratio of R = -1, a test frequency of 10 Hz and considering a run-out criteria of 2 million cycles. The fatigue strength of samples was determined using the commonly stair-case method [27–29]. After the fatigue tests, all the broken samples were carefully analysed by the optical microscope previously described to determine the failure initiation point. The initiations points were also analysed by the SEM to investigate the failure along the surface, using a constant electron high tension of 20 kV and a working distance in the range of (15–30 mm).

3. Results

3.1. Surface integrity characterization

3.1.1. Surface texture

Three-dimensional (3D) profiles of the material surface were generated with the optical profilometer. The extracted 3D profiles are shown in Fig. 3. The measurements were taken from the centre of the specimens (Fig. 3d). Due to contouring traverse feed grinding, the imprint left by the wheel passing is visible on the ground surfaces with variations in surface texture ranging in (\pm 0.5 µm). The imprint on the cryo-ground surface CGB (Fig. 3b) shows a minor slope with a more constant pattern than the cryo-ground surface CGA (Fig. 3a), which offers a similar imprint with a steeper slope.

In contrast, in the conventional WG (Fig. 3c), the imprint slope is clearly higher than in the cryogenic conditions. This effect might be a consequence of the pressure generated by the grinding wheel on the workpiece in the contouring (grinding aggressiveness), which depending on the grinding conditions, could induce slight vibrations in the process. On the WG sample, this effect is almost negligible, probably because of the high transversal feed (700 mm/min) that seems to reduce the vibration in the workpiece.

Table 4 summarises the results obtained in the surface texture measurements. In all tested surfaces, R_a was less than 0.3 μ m. Both cryogenic conditions produced rougher surfaces (CGA, $R_a \approx 0.24 \mu$ m; CGB $R_a \approx 0.25 \mu$ m) than the conventional wet grinding process (WG $R_a \approx 0.17 \mu$ m). This effect is also predominant for R_z and R_t parameters. Additionally, in Fig. 3, it is possible to see punctual valleys on the surface with depths close to 1.5 μ m on all tested surfaces. The WG condition shows a more homogeneous texture with a consistent patch between peaks and valleys (uniform green and blue areas in Fig. 3c) that might explain the reduction in surface roughness, especially in the case of S_a , which reached a smoother surface, $S_a \approx 0.21 \mu$ m.

Another clear difference between cryogenic conditions and the wet condition is the skewness (S_{sk}). Although the values of S_{sk} in the three conditions are similar, the sign is negative to the WG condition, showing presence of more abrupt valleys than peaks on the surface. The final difference between WG and cryogenic conditions is the kurtosis value (S_{ku}). For the WG condition, the S_{ku} reach 3.85, indicating a leptokurtic distribution with more peaks and valleys far from the mean. The CGA and CGB conditions are near the mesokurtic distribution.

3.1.2. Residual stresses

Fig. 4a shows the initial surface residual stresses induced in the fatigue specimens produced by wet grinding and the two cryogenic grinding conditions. It is essential to notice that all grinding conditions produced compressive residual stresses near the surface. These were more compressive in the axial direction than in the hoop direction. The reference wet grinding condition led to the most compressive residual stresses (-699 ± 66 MPa in the axial direction and -569 ± 74 MPa in the hoop direction). Surface residual stresses were 11% lower in the axial direction and 20% in the hoop direction when using LN₂ at a cutting speed of 40 m/s than under wet conditions. The magnitude of surface residual stresses decreased even more when using LN₂ at a cutting speed of 53 m/s.

Surface residual stresses were measured in run-out specimens to verify if they were relaxed during cyclic loading. As shown in Fig. 4b, the average surface residual stresses of WG samples presents a slight decrease during cyclic loading. Comparing the average values after the run-out with the initial values of Fig. 4a, the conventional WG samples show a reduction of -11% in the axial direction and -9% in the hoop direction. Curiosity, this effect is contrary in the cryogenic samples (CGA, CGB), where both conditions show average surface residual stresses in the hoop and the axial direction approximately 5–8% higher than the initial values. However, all run-out measurements present a discrepancy between ($\pm11\%$) that are in the uncertainty range (±74 MPa). Therefore, we can conclude that residual stress relaxation is not significant since it lays within the uncertainty of the measurements.

3.1.3. Microstructure

The subsurface of the fatigue specimens was analysed to reveal possible microstructure alteration in the material when grinding at finishing conditions with different cooling methods. Fig. 5 shows representative micrographs of the three tested conditions in both axial and hoop directions. As it can be seen, cryogenic conditions CGA and CGB did not induce modifications in the microstructure of the surface layer. Moreover, the hoop and axial direction present the same martensite microstructure with zero defects and without



Fig. 3 – Surface texture of fatigue specimens obtained from the optical profilometer. a) CGA, b) CGB, c) WG, and d) Description of surface analysed.

thermal damage. However, the result differs from the conventional WG process, in which slight alterations were produced in the material subsurface because of the aggressive grinding conditions.

In Fig. 5d, it is possible to observe that a tiny rehardening layer appears in the surface for both the axial and hoop direction with a mean thickness of 1.7 μ m. It is also possible to see that a thermally affected layer appeared behind the rehardening layer with depths around 7–8 μ m. Although the martensite is the predominant structure in the rehardening layer presents a more homogeneous structure with refined grains. The

martensite refinement might increase the compressive residual stresses in the WG specimens compared to the cryogenic specimen, explaining the differences in the residual stresses compared to the cryogenic samples, which did not present any defect in the subsurface.

3.1.4. Microhardness

Microhardness profiles of the three tested grinding conditions are illustrated in Fig. 6. Notice that no significant differences can be observed in the hardness profiles even when the microstructural analysis of the WG sample shows a tiny rehardening layer on the surface. The microhardness value is

Table 4 $-$ Surface texture indicators of LN ₂ and wet fatigue specimens.							
Specimen		R_{a} [μ m]	R _z [μm]	R _t [µm]	$S_a \left[\mu m \right]$	S_{sk}	S_{ku}
CGA	V _s = 40 m/s V _o = 42 m/min	0.24 ± 0.01	1.94 ± 0.12	2.20 ± 0.13	0.30	0.15	3.25
CGB	V _s = 53 m/s V _o = 14 m/min	0.25 ± 0.02	1.74 ± 0.20	2.10 ± 0.22	0.30	0.17	3.02
WG	V _s = 70 m/s V _o = 30 m/min	0.17 ± 0.01	1.29 ± 0.06	1.52 ± 0.13	0.21	-0.17	3.85



Fig. 4 – Surface residual stresses in the axial and hoop direction. a) Initial values of the fatigue specimens, and b) Final surface residual stresses of run-out fatigue specimens.

higher than 700 HV_{0.05} within the first 250 μ m and above 650 HV_{0.05} within the first 500 μ m. Therefore, the properties of the carburised layer were not affected by the tested conditions. It is widely accepted that hardness value shows a good relationship with yield and rupture stress in steels [30]. Therefore, the mechanical properties of the surface layer were not negatively affected by the cryogenic LN₂ cooling approach compared to the conventional wet grinding condition.

3.2. Fatigue characterization

Fig. 7 summarises the results obtained in the torsional fatigue tests following the staircase method. The specimens manufactured under conventional flood grinding conditions obtained the highest fatigue strength ($\tau_D = 618 \pm 29$ MPa). The fatigue strength of specimens produced by cryogenic grinding conditions barely decreased with respect to the reference condition: 4% when using a cutting speed of 40 m/s and wheel speed of 42 m/min, and 6% when using a cutting speed of 53 m/s and wheel speed of 14 m/min.

The fracture of the broken specimens was observed to verify if the cracks were initiated near the surface or below the carburised layer. Fig. 8 shows examples of fractures of the specimens manufactured by the three finishing conditions. It is possible to identify that for all tested conditions, the failure started along the surface and continued across the samples to the centre of the material. The crack was nucleated near the surface due to the highest shear stresses caused by the torque. Thus, the surface condition had predominately affected the crack initiation and early propagation stage.

4. Discussion

The fatigue strength was only slightly reduced when using both cryogenic grinding conditions, and therefore, the final surface integrity of the specimen influenced the fatigue performance. In order to analyse the effect of surface integrity (microstructural defects, mechanical propertiesmicrohardness, surface texture, and residual stresses) of machined components on fatigue performance, a local approach should be used [31]. As reported in the previous section, only the conventional grinding WG produced alterations in the near-surface microstructure. However, even with the reported defects, the microhardness profile of the three surface conditions was similar (differences lay in the uncertainty of measurements), and, consequently, the mechanical properties of the surface layer were similar too. Therefore, the slight differences reported in the fatigue tests are linked to variations in surface texture and surface residual stresses.

Novovic et al. [21] stated that when workpiece surface roughness values are between 2.5 and 5 μ m R_a, residual stresses have a higher impact on the fatigue life of machined components. To quantify the effect of surface texture/roughness on fatigue performance, the stress concentration factor should be determined [32]. In a recent paper, Madariaga et al. [31] calculated a stress concentration factor of 1.001 when $R_a \approx 0.3 \,\mu\text{m}$ on turned specimens. As reported in section 3.1.1, the roughness was $R_a < 0.3 \ \mu m$ on the tested surfaces. This behaviour suggests that the stress concentration factor was ≈1 and that roughness did not adversely affect fatigue performance. Additionally, the samples produced by conventional wet grinding showed a negative value of skewness (roughness), which is associated with more abrupt valleys that would lead to a decrease in fatigue strength. Nevertheless, specimens produced by wet grinding showed the highest fatigue strength. Thus, in the present paper, for the tested conditions, the differences in fatigue strength were caused by different initial surface residual stresses. This behaviour is consistent with previous works where carburised steels were treated by shot-peening. They also found that compressive residual stresses significantly impact the torsional fatigue behaviour [20,33].

With the objective of analysing the effect of surface residual stresses, three questions must be addressed: i) was there a relaxation in the residual stresses and thus influenced crack initiation-propagation? ii) why did residual stresses only slightly influence the fatigue strength despite having different values? and iii) can we establish a relationship between the magnitude of surface residual stresses and fatigue strength? We seek to answer these questions in the following paragraphs.





Fig. 5 – Microstructural and SEM analysis. a) Measurement scheme, b) CGA, c) CGB, d) WG conditions.

2.5 um



b)

Fatigue CGA V_s=40 m/s V_o=42 m/min

c)

Fig. 6 – Microhardness profiles for LN₂ and wet fatigue specimens.

Usually, the main residual stress relaxation occurs during the first loading, and the following cycles slightly increase the relaxation [34]. As depicted in Fig. 4, surface residual stresses of the WG condition present a slight reduction. However, to cause surface residual stress relaxation, plastic strains must be generated during loading. In this work, hardness was \approx 720HV_{0.05} at the surface and \approx 450HV_{0.05} in the bulk material. The yield stress (σ_y in MPa) of steels can be estimated using Eq. (1), where HV is the hardness in kg/mm². Then, the equivalent shear yield stress (τ_y) can be determined by Eq. (2) when applying Von Mises criteria [35]. Using these equations, a $au_{y}=$ 1143 MPa in the surface and $au_{y}=$ 694 MPa in the bulk material are obtained. The highest shear stress applied in the tests was 650 MPa on the surface (less in the bulk material). This value does not exceed the calculated yield stress and therefore confirms the absence of residual stress relaxation. For this reason, it is possible to conclude that the variations in residual stress measurements are effects of the uncertainty of the grinding process itself and XRD measurements.

7.2 µm

Im

2.5 um



Fig. 7 – Results of fatigue tests of fatigue specimens produced by wet and cryogenic grinding following the stair-case method. Open circles are run-out tests and crosses indicate broken specimens.



Fig. 8 – Examples of fractures when using a τ_{max} = 600 MPa, a) wet conditions, b) LN₂ at cutting speed of 53 m/s and wheel speed of 14 m/min, and c) LN₂ at cutting speed of 70 m/s and wheel speed of 30 m/min.

(1)

$$\sigma_{
m v} = -90.7 + 2.876 {
m HV}$$

$$\tau_{y} = \frac{\sigma_{y}}{\sqrt{3}} \tag{2}$$

Since it has been confirmed that surface compressive residual stresses did not vary during the cyclic loading tests, they prevent early crack initiation and propagation. Nevertheless, although the magnitude of surface residual stresses produced by cryogenic conditions was >10-20% lower than those generated by conventional wet grinding, the reduction in fatigue strength was minor, below 4–6%. To justify this effect, it is necessary to consider the mechanisms involved in the fatigue fracture: crack initiation and propagation.

In a recent work conducted by the authors [36], the wet and cryogenic grinding conditions employed in the present paper induced compressive residual stresses only within 20 μ m. Being so, surface residual stresses generated by the different grinding conditions only affected in the crack initiation, and the crack propagation was dominated by the properties of the carburised layer and bulk-material.

Although residual stresses induced by grinding processes only affected the crack initiation stage, it is possible to establish a reasonable empirical relationship between surface residual stresses and fatigue strength. Fig. 9 shows the fatigue strength regarding surface residual stresses in both axial and hoop directions. As expected, the fatigue strength increased when increasing the magnitude of compressive residual stresses, since the mean stress at the surface layer is reduced. Both axial and hoop residual stresses show a similar sensitivity (slope).

Since the only difference in the CGA and CGB conditions during the grinding operations was the grinding speeds. It seems that the aggressiveness of the grinding process directly affects the residual stresses produced on the surface, which also are linearly affecting the fatigue strength. The variations in the grinding wheel speed and the workpiece speed might change the friction coefficient and the contact time between the grinding wheel grains and the workpiece surface, which



Fig. 9 - Fatigue strength vs surface residual stresses.

may directly influence the temperature of the process and the residual stresses.

5. Practical implications for shaft manufacturing

The goal of this paper was to compare the surface integrity analysis and the fatigue performance of specimens of 27MnCr5 steel produced by cryogenic grinding and conventional wet grinding. Interestingly, the selected cryogenic grinding conditions almost did not reduce the torsional fatigue strength. Therefore, these conditions could be applied to manufacture shafts of automotive transmission components. This section aims to analyse the effect of determining fatigue strength on shaft dimensioning.

When a shaft of radius *r* is subjected to a torque M_t , the maximum shear stress τ_{max} is located in the outer diameter, which can be calculated using Eq. (3) [37]. To determine the minimum radius, the maximum shear stress must be lower than the shear fatigue strength ($\tau_{max} \leq \tau_D$). Using Eq. (3), it is possible to calculate the required r_w radius when using conventional wet grinding conditions that lead to a τ_{DW} fatigue strength in shafts subjected to a torque M_t (see Eq. (4)). Equally, it is possible to determine the needed r_i of a machining condition that obtains a τ_{Di} fatigue strength in shafts withstanding a torque M_t (see Eq. (5)). By dividing both expressions, the relationship between required r_w and r_i is given by Eq. (6).

$$\tau_{\max} = \frac{M_t}{\frac{1}{2}\pi r^4} \tag{3}$$

$$\tau_{\rm DW} = \frac{M_t}{\frac{1}{2}\pi r_w 4} \tag{4}$$

$$\tau_{\rm Di} = \frac{M_{\rm t}}{\frac{1}{2}\pi r_{\rm i} 4} \tag{5}$$

$$r_{\rm i} = r_w \sqrt[3]{\frac{\tau_{\rm DW}}{\tau_{\rm Di}}} \tag{6}$$

Table 5 shows the effect of tested cryogenic grinding conditions on the dimensions of a shaft subjected to torsion. Although the fatigue strength was reduced by 6% in the worst case, the shaft's radius must only be increased by 2.2%. For example, if a transmission component has a radius of 20 mm when applying wet conditions, a diameter of 20.5 mm is needed when using LN_2 at a cutting speed of 53 m/s and a wheel speed of 14 m/min. Undoubtedly, the impact on the final dimension is minimal, and the results obtained in the paper support the use of cryogenic conditions in manufacturing shafts.

Table 5 – Impact of fatigue strength on shaft dimensioning.							
Grinding condition	$ au_{ m D}$ [MPa]	$\mathbf{r}_i/\mathbf{r}_w$					
CGA $V_s = 40 \text{ m/s } V_o = 42 \text{ m/min}$	592	1.014					
CGB $V_s = 53 \text{ m/s} V_o = 14 \text{ m/min}$	579	1.022					
WG $V_s=70\mbox{ m/s}\ V_o=30\mbox{ m/min}$	618	1					

6. Summary and conclusions

This research studied the effect of the cryogenic grinding process on the surface integrity and torsional fatigue performance of the carburised 27MnCr5 steel. By comparing the surface integrity, the conventional wet grinding and the cryogenic grinding produced surfaces with zero defects in the microstructural analysis. Also, samples did not show any influence on the microhardness material characteristics that change the mechanical properties of the carburised layer. For this reason, the slight differences reported in the fatigue tests are directly linked to variations in surface texture and surface residual stresses. The following specific conclusions were obtained.

- The cryo-ground surfaces were rougher than the reference surface ground under the wet cooling, with maximum differences of around 0.1 μ m for R_a and S_a. The rougher surfaces of the cryogenic samples might be due to the imprint produced by the grinding wheel in the transverse contouring. Additionally, all tested samples produced surface roughness R_a less than 0.3 μ m. With this limit, it was also possible to demonstrate that the surface roughness did not adversely affect the fatigue performance since the stress concentration factor was estimated at ~1.
- Compressive surface residual stresses produced by the cryogenic conditions were lower, around (10–20%) than those generated by conventional wet grinding for both the axial and hoop direction. These residual stresses did not relax during fatigue tests because the local stresses did not exceed the yield stress. It should be noted that the yield stress of the carburised layer is higher than the bulk material.
- The reduction in fatigue strength was minor, below 4–6%. This reduction was mainly linked to the residual stresses state since all specimens were broken at the surface, and there was no stress relaxation during the fatigue tests. In fact, the higher the compressive residual stresses, the lower the mean stress at the surface and, consequently, higher fatigue strength.
- The slight differences observed in the fatigue strength are reasonable since the grinding affected layer is very shallow compared to the carburised layer. The surface condition affects the crack initiation (all cracks nucleated at the surface). However, most of the fatigue life is spent in the crack propagation through the carburised layer, which was comparable in all specimens.
- In order to compensate for the slight decrease in fatigue performance, shafts produced by cryogenic grinding should only increase the radius by 2.2% compared to those produced by conventional grinding.

This research demonstrates that the cryogenic grinding technology could be used for applications of cylindrical mechanical components that require to be finished by grinding, despite the slight changes in the surface integrity of the material and the minimal variation in torsion fatigue performance. Given the results of this research and the apparent possibility of eliminating liquid coolants that contaminate the environment in grinding processes, the authors propose to continue researching the application of LN_2 as cooling liquid to validate this technology in other grinding processes, grinding strategies, different materials, and additional fatigue conditions.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

- Alagumurthi N, Palaniradja K, Soundararajan V. Optimization of grinding process through Design of Experiment (DOE) - a comparative study. Mater Manuf Process 2006;21:19–21. https://doi.org/10.1080/AMP-200060605.
- [2] Sinha MK, Madarkar R, Ghosh S, Paruchuri VR. Some investigations in grindability improvement of Inconel 718 under ecological grinding. Proc Inst Mech Eng Part B J Eng Manuf 2019;233:727–44. https://doi.org/10.1177/ 0954405417752513.
- [3] Salonitis K. Grind hardening process. SpringerBriefs Appl. Sci. Technol. 2015 i-iv. https://doi.org/10.1007/978-3-319-19372-4.
- [4] Elanchezhian J, Pradeep Kumar M. Effect of nozzle angle and depth of cut on grinding titanium under cryogenic CO2. Mater Manuf Process 2018;33:1466–70. https://doi.org/ 10.1080/10426914.2018.1453151.
- [5] Schoop J, Sales WF, Jawahir IS. High speed cryogenic finish machining of Ti-6Al4V with polycrystalline diamond tools. J Mater Process Technol 2017;250:1–8. https://doi.org/10.1016/ j.jmatprotec.2017.07.002.
- [6] Abedrabbo F, Soriano D, Madariaga A, Fernández R, Abolghasem S, Arrazola PJ. Experimental evaluation and surface integrity analysis of cryogenic coolants approaches in the cylindrical plunge grinding. Sci Rep 2021;11:1–14. https://doi.org/10.1038/s41598-021-00225-6.
- [7] Pimenov DY, Mia M, Gupta MK, Machado AR, Tomaz ÍV, Sarikaya M, et al. Improvement of machinability of Ti and its alloys using cooling-lubrication techniques: a review and future prospect. J Mater Res Technol 2021;11:719–53. https:// doi.org/10.1016/j.jmrt.2021.01.031.
- [8] Sanchez JA, Pombo I, Alberdi R, Izquierdo B, Ortega N, Plaza S, et al. Machining evaluation of a hybrid MQL-CO2

grinding technology. J Clean Prod 2010;18:1840-9. https:// doi.org/10.1016/j.jclepro.2010.07.002.

- [9] Elanchezhian J, Pradeep Kumar M, Manimaran G. Grinding titanium Ti-6Al-4V alloy with electroplated cubic boron nitride wheel under cryogenic cooling. J Mech Sci Technol 2015;29:4885–90. https://doi.org/10.1007/s12206-015-1036-7.
- [10] Li CH, Lu BH, Ding YC, Cai GQ. Innovative technology investigation into cryogenic cooling green grinding using liquid nitrogen jet. Proc. - Int. Conf. Manag. Serv. Sci. MASS 2009 2009:1–4. https://doi.org/10.1109/ICMSS.2009.5302527.
- [11] Higgins Milton P, Norton RL. Machine design: an integrated approach. sixth ed. Pearson; 2020. https://linkinghub. elsevier.com/retrieve/pii/S0278612598800708.
- [12] M'Saoubi R, Outeiro JC, Chandrasekaran H, Dillon OW, Jawahir IS. A review of surface integrity in machining and its impact on functional performance and life of machined products. Int J Sustain Manuf 2008;1:203–36. https://doi.org/ 10.1504/IJSM.2008.019234.
- [13] Cherian Jose, Issac JM. Fatigue performance in grinding and turning: an overview. Int. J. Mod. Eng. Res. 2014;4:47–52. http://www.ijmer.com/papers/Vol4_Issue5/Version-6/IJMER-45064752.pdf.
- [14] Qin S, Zhang C, Zhang B, Ma H, Zhao M. Effect of carburizing process on high cycle fatigue behavior of 18CrNiMo7-6 steel. J Mater Res Technol 2021;16:1136–49. https://doi.org/10.1016/ j.jmrt.2021.12.074.
- [15] Grissa R, Zemzemi F, Manchoul S, Seddik R, Fathallah R. Predictive approach of high-cycle fatigue limit of finished turned AISI 316L steel. Int J Adv Manuf Technol 2019;105:845–57. https://doi.org/10.1007/s00170-019-04265-1.
- [16] Javidi A, Rieger U, Eichlseder W. The effect of machining on the surface integrity and fatigue life. Int J Fatig 2008;30:2050-5. https://doi.org/10.1016/ j.ijfatigue.2008.01.005.
- [17] Macek W, Rozumek D, Królczyk GM. Surface topography analysis based on fatigue fractures obtained with bending of the 2017A-T4 alloy. Meas. J. Int. Meas. Confed. 2020;152:107347. https://doi.org/10.1016/ j.measurement.2019.107347.
- [18] Macek W, Marciniak Z, Branco R, Rozumek D, Królczyk GM. A fractographic study exploring the fracture surface topography of S355J2 steel after pseudo-random bendingtorsion fatigue tests. Meas. J. Int. Meas. Confed. 2021;178. https://doi.org/10.1016/j.measurement.2021.109443.
- [19] Javadi H, Jomaa W, Texier D, Brochu M, Bocher P. Surface roughness effects on the fatigue behavior of as-machined inconel 718, Solid State Phenom, vol. 258; 2017. p. 306–9. https://doi.org/10.4028/www.scientific.net/SSP.258.306.
- [20] Ramesh S, Natarajan S, Sivakumar VJ. Effect of surface condition on the torsional fatigue behaviour of 20MnCr5 steel. Met Mater Int 2021;27:3132–42. https://doi.org/10.1007/ s12540-020-00658-0.
- [21] Novovic D, Dewes RC, Aspinwall DK, Voice W, Bowen P. The effect of machined topography and integrity on fatigue life. Int J Mach Tool Manufact 2004;44:125–34. https://doi.org/ 10.1016/j.ijmachtools.2003.10.018.
- [22] Yang D, Liu Z. Surface integrity generated with peripheral milling and the effect on low-cycle fatigue performance of aeronautic titanium alloy Ti-6Al-4V. Aeronaut J 2018;122:316–32. https://doi.org/10.1017/aer.2017.136.
- [23] Hashimoto F, Guo YB, Warren AW. Surface integrity difference between hard turned and ground surfaces and its impact on fatigue life. CIRP Ann - Manuf Technol 2006;55:81–4. https://doi.org/10.1016/S0007-8506(07)60371-0.
- [24] Balan ASS, Chidambaram K, Kumar AV, Krishnaswamy H, Pimenov DY, Giasin K, et al. Effect of cryogenic grinding on fatigue life of additively manufactured maraging steel. Materials 2021;14:1–16. https://doi.org/10.3390/ma14051245.

- [25] Ben Fredj N, Sidhom H. Effects of the cryogenic cooling on the fatigue strength of the AISI 304 stainless steel ground components. Cryogenics 2006;46:439–48. https://doi.org/ 10.1016/j.cryogenics.2006.01.015.
- [26] ASTM E 466 96 (Reapproved 2002). Standard practice for conducting force controlled constant amplitude axial fatigue tests of metallic materials. ASTM Int.; 2002.
- [27] Dixon WJ, Mood AM. A method for obtaining and analyzing sensitivity data. J Am Stat Assoc 1948;43:109–26. https:// doi.org/10.1080/01621459.1948.10483254.
- [28] Morrissey R, Nicholas T. Staircase testing of a titanium alloy in the gigacycle regime. Int J Fatig 2006;28:1577–82. https:// doi.org/10.1016/j.ijfatigue.2005.10.007.
- [29] Ekaputra IMW, Dewa RT, Haryadi GD, Kim SJ. Fatigue strength analysis of S34MnV steel by accelerated staircase test. Open Eng 2020;10:394–400. https://doi.org/10.1515/eng-2020-0048.
- [30] Pavlina EJ, Van Tyne CJ. Correlation of Yield strength and Tensile strength with hardness for steels. J Mater Eng Perform 2008;17:888–93. https://doi.org/10.1007/s11665-008-9225-5.
- [31] Madariaga A, Garay A, Esnaola JA, Arrazola PJ, Linaza A. Effect of surface integrity generated by machining on isothermal low cycle fatigue performance of Inconel 718. Eng Fail Anal 2022;137:106422. https://doi.org/10.1016/ j.engfailanal.2022.106422.
- [32] Perez I, Madariaga A, Arrazola PJ, Cuesta M, Soriano D. An analytical approach to calculate stress concentration factors of machined surfaces. Int J Mech Sci 2021;190:106040. https:// doi.org/10.1016/j.ijmecsci.2020.106040.
- [33] Benham PP. Case-carburization and other surface-hardening and residual stress treatments in relation to fatigue strength in torsion. Proc Inst Mech Eng 1963;177:87–94. https:// doi.org/10.1243/pime_proc_1963_177_013_02.
- [34] Schulze Volker. Modern mechanical surface treatment: states, stability, effects. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA; 2006.
- [35] Shigley JE, Mischke CR, Thomas Hunter Brown J. Standard handbook of machine design. third ed. McGraw-hill; 2004.
- [36] Madariaga A, Abedrabbo F, Soriano D, Fernandez R, Arrazola PJ, Cherguy O, et al. Effect of innovative finishing operations on the tribological performance of steel 27MnCr5. Procedia CIRP 2022;108:513–8. https://doi.org/10.1016/ j.procir.2022.03.080.
- [37] Craig RR, editor. Mechanics of materials. fourth ed. Wiley; 2020.



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