

Article

An Industrial-Scale Study of the Hardness and Microstructural Effects of Isothermal Heat Treatment Parameters on EN 100CrMo7 Bearing Steel

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Abstract: The 100CrMo7, commonly employed for bearings in rotating machinery, relies on precise heat treatment parameters to ensure an optimal microstructure and, in turn, mechanical properties. Typically, an austenitizing treatment, followed by rapid cooling in a salt bath for martempering or austempering, is crucial in achieving the desired microstructure and hardness. The present industrial-scale study involved a comparative analysis between martempering and austempering routes regarding the hardness and microstructure evolution of EN 100CrMo7 large-size rings. The investigation delves into the effects of austempering temperatures, holding times, and austenitizing temperature. Furthermore, the role of tempering in reducing the amount of retained austenite was also considered. The results indicate that martempering yielded the highest hardness values while austempering exhibited a decrease in hardness at the center of the rings, though a lower amount of retained austenite (in the range of 3.0–4.9 vol.%) was detected in comparison with martempering. In addition, a 850 °C austenitizing temperature reduced the hardness by 16% in the center of the rings and promoted a high content of upper bainite, thus suggesting its inefficacy for the involved large-size rings. In contrast, a 880 °C austenitizing temperature maintained consistently high HRC values across the ring's height. Lastly, the analysis highlighted that the cooling rate played a more crucial role than the austempering holding time. Such industrial-scale investigations performed on real components improve the knowledge and control of heat treatment parameters in comparison with the nominal guidelines provided by steel suppliers. These outcomes offer insights for optimizing industrial heat treatment parameters, with practical implications for enhancing steel bearings' microstructural and mechanical performance and lifespan.

Keywords: 100CrMo7 bearing steel; martempering; austempering; microstructure; bainite; hardness



Citation: Fortini, A.; Bertarelli, E.; Cassola, M.; Merlin, M. An Industrial-Scale Study of the Hardness and Microstructural Effects of Isothermal Heat Treatment Parameters on EN 100CrMo7 Bearing Steel. *Appl. Sci.* **2024**, *14*, 737. <https://doi.org/10.3390/app14020737>

Academic Editor: José António Correia

Received: 16 December 2023

Revised: 10 January 2024

Accepted: 12 January 2024

Published: 15 January 2024



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1. Introduction

Rolling bearings play a crucial role in machinery design, demanding high durability and reliability to ensure continuous operation, minimizing the need for maintenance shutdowns [1,2]. They must exhibit a high service life irrespective of the environmental conditions they are exposed to [1,3–5].

Among the several alloys explored within bearing steels, only two categories of steels find widespread application: steels that are hardened throughout their sections into a martensitic or bainitic condition and steels with soft cores but hard surface layers achieved by case or induction hardening [3,6]. Bearing steels are usually subjected to heat treatment to develop martensitic microstructures, delivering the required high hardness crucial for effective resistance to rolling contact fatigue [7]. Hypereutectoid through-hardening steels exhibit fatigue and wear resistance, along with dimensional stability. Hence, they are suitable for crafting bearing components. The EN 100Cr6 type is the typically adopted bearing steel (e.g., ball and roller bearings, spinning tools, punches, and dies), employed in

both hardened and tempered states, renowned for its high hardness, compressive strength, and abrasion resistance.

Among the thermal treatment operations developed to promote specific microstructure and, in turn, enhance the mechanical properties of steel components, martempering and austempering are two interrupted quenching procedures widely adopted for bearing steels [8–11]. Martempering in industrial practice is performed by quenching the steel to slightly above the martensite start temperature M_s , then holding it to promote a uniform temperature throughout the piece, and finally air-cooling it to room temperature [12]. This slow cooling rate prevents the generation of residual stress and distortion akin to those induced by quench hardening [13]. Furthermore, austempering involves quenching from the austenitizing temperature into a molten salt bath, typically held between 200 °C and 400 °C, until the austenite transforms into bainite. The austempering makes it possible to successfully harden challenging geometries that are impossible to harden with conventional quenching [12]. The obtained lower bainite microstructure exhibits a balance of ductility, strength, and toughness, though the austempering route requires more careful control than hardening by conventional quenching [8,9,12,14]. To date, most applications rely on martensitic hardening procedures. However, a bainitic microstructure is more suitable for large components where the precise control of the transformation strain is crucial for minimizing machining costs. Furthermore, bainitic microstructures exhibit superior performance compared to martensitic ones under conditions of hydrogen embrittlement or in impact scenarios where increased toughness is needed [9]. As a result, austempering is preferred when machining costs increase due to distortion issues [15].

Thus far, several studies have attempted to evaluate the impact of temperature/time heat treatment parameters on the microstructural characteristics and associated mechanical behavior of bearing steels [9,10,16–19]. Vamsi Krishna et al. [10] explored the impact of austempering and martempering treatments on AISI 52100 bearing steel and argued that austempered steel demonstrated the highest impact strength, which increased with soaking time. On the contrary, the martempered samples exhibited the lowest wear rate in both abrasion and dry sliding wear tests. Notably, the annealed steel exhibited the lowest hardness and was more susceptible to wear, but the average friction coefficient in dry sliding wear was the lowest and increased in martempered and austempered samples. Chakraborty et al. [9] sought to ascertain the optimum austempering process window (temperature, time, and heating/cooling rate) for SAE 52100 steel to develop a duplex bainitic + martensitic microstructure. The austempering conducted at 270 °C for 30 min and followed by water quenching, improved hardness, tensile and impact strength: these findings were associated with the optimal microstructure where a weak phase constrained by a hard phase matrix improved the mechanical properties as compared to a full hard single-phase.

In addition to the above-mentioned issues regarding the heat-treatment route of bearing steels, a key factor is the amount of retained austenite (RA) within the matrix [20–22]. Based on the specific needs of each application, RA may be required to enhance rolling contact fatigue performance, particularly in contaminated lubricating conditions [3,7,23,24]. Conversely, it may be avoided if dimensional stability is crucial, i.e., where bearings operate for extended durations at elevated temperatures [21]. Indeed, high RA contents decrease the ultimate strength of the material [23,25,26] and lead to a smaller dimensional stability due to phase transformation [22].

Within this context, the present study addresses the effects of heat treatment parameters, typically adopted in industrial-scale heat treatment routes, on the microstructure and hardness of EN 100CrMo7 steel high-thickness rings. The paper opens with an overview of the literature concerning bearing steels, emphasizing the impact of temperature/time heat treatment parameters on the microstructural characteristics and mechanical behavior. Section 2 outlines the experimental methodologies employed in this study to assess the microstructural and hardness properties in response to the investigated isothermal heat treatment routes. Section 3 provides insights into the experimental findings, encompass-

ing microstructural characterization and hardness evolution for the high-thickness rings. Furthermore, the amount of retained austenite and the role of austenitizing temperature were considered. Finally, Section 4 delves into the obtained results from an industrial perspective, highlighting the strengths and weaknesses of the different austenitizing and isothermal heat treatment parameters.

The novelty of the present study consists of an industrial-scale investigation of real components to improve the knowledge and control of heat treatment parameters with respect to the nominal guidelines provided by the supplier. Indeed, the geometry of the investigated EN 100CrMo7 rings represents an attempt to use the material above the nominal range of application in terms of hardenability, since the ring wall thickness was 60% higher than the one suitable for the safe hardenability limit for the material. As a result, the heat treatment facility empowers customers to cut down on final expenses, steering away from more expensive materials with increased hardenability.

2. Materials and Methods

This study analyzes large rings (132 mm in outer diameter, 32 mm in thickness, and 64 mm in height, see Figure 1a) manufactured with the EN 100CrMo7 bearings steel provided by Ovako (Ovako AB, Stockholm, Sweden). The simplified geometry of the rings fully represents real components with high-wall thickness, even if they exceed the upper limit for hardenability, as indicated in the supplier's technical information datasheet [27]. The chemical composition of the steel measured by a G.N.R. S7 Metal Lab Plus (G.N.R., Agrate Conturbia, Italy) quantimeter is reported in Table 1. The chemical composition was measured at the ring's core, at half thickness, and near the surface; n. 3 samples for each location, on a longitudinal cross-section, were analyzed. As can be seen, the composition meets the standard for EN 100CrMo7 steel according to UNI EN ISO 683-17:2023 [28].

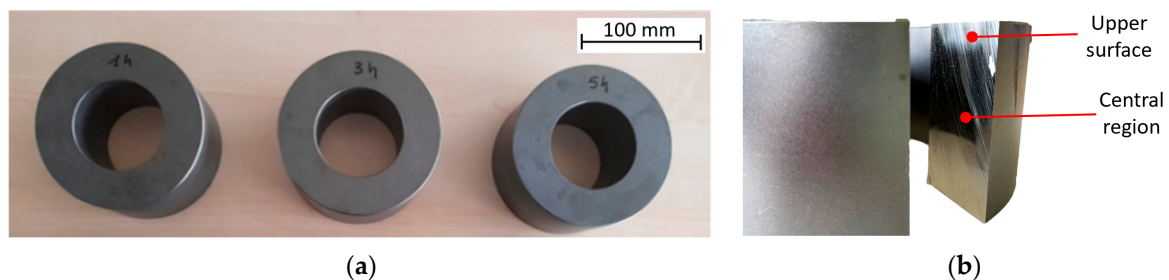


Figure 1. Digital images of the EN 100CrMo7 rings: (a) top view; (b) radial section.

Table 1. Chemical composition (wt.%) of the analyzed EN 100CrMo7 steel.

	Chemical Composition (wt.%)—Fe Balance									
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
Average	0.959	0.300	0.295	0.011	0.010	1.679	0.181	0.192	0.024	0.178
St. Dev.	0.018	0.017	0.010	0.002	0.003	0.023	0.008	0.006	0.006	0.008

For the microstructural analysis, standard metallographic procedures were followed, and the final chemical etching was performed using a 4% Nital solution (4% HNO₃ in ethanol). The analyses were conducted on a radial section of each ring (see Figure 1b). The investigated sections were the upper surface of the ring (i.e., the last that faced the quenching medium and, in turn, the worst condition considering its cooling rate) and the central region (i.e., half the height of the ring, at the center). Micrographs were captured either by a Leica DMI8 A (Leica, Wetzlar, Germany) light optical microscope (LOM) or by a Zeiss EVO MA15 (Carl Zeiss, Jena, Germany) scanning electron microscope (SEM) in secondary (SEI-SEM) and backscattered electron imaging (BSE-SEM) modes.

Brinell hardness measurements were carried out under a 187.5 kgf load and using a 2.5 mm diameter spherical indenter (referred to as HBW 2.5/187.5) with the AT130D Ernst (Cisam-Ernst, Induno Olona, Italy) hardness tester. Hardness tests were carried out according to the UNI EN ISO 6506-1:2014 standard [29]. The mean Brinell hardness value was calculated as an average of five random indentations obtained from various locations along the thickness of the ring. The Rockwell C hardness (HRC) was measured by the AT130D Ernst hardness tester in agreement with the UNI EN ISO 6508-1:2016 standard [30]. HRC tests were carried out on a radial section and in the center of the ring's thickness, analyzing the hardness evolution from the upper to the lower surface of the ring (i.e., along the ring's height), with 19 indentations at 3 mm intervals.

Different heat treatment routes were settled to study the effect of heat treatment parameters on the microstructural characteristics of the steel and hardness according to the dimension of the component and comprising both austempering and martempering. In all cases, austenitizing was performed in an Alaplant FP 120.200 C-A (Alaplant Srl, Pessano con Bornago, Italy) pit furnace. Based on the supplier datasheet, the austenitization temperatures were chosen according to the indicated temperature range. The dwelling time and the cooling parameters were defined to obtain the thermal equilibrium of the large-size investigated rings and follow practical experience from the industrial perspective. According to the supplier datasheet, the reported critical temperatures were M_s 186 °C, A_{c1} 730 °C, and A_{c3} 750 °C.

Trial n.1 comprised a comparison between the martempering and austempering process routes. Hence, the EN 100CrMo7 rings were pre-heated and austenitized at 880 °C for 150 min. In martempering, the ring was quenched into a salt bath settled at 180 °C for 30 min and then cooled to room temperature in calm air. No tempering treatment followed. In austempering, the rings were quenched into a salt bath settled at 240 °C and 220 °C for 300 min, respectively, and then cooled to room temperature in calm air. The salt bath temperatures were set according to the information provided by the datasheet [27]. The heat treatment routes investigated in Trial n.1 are reported in Figure 2.

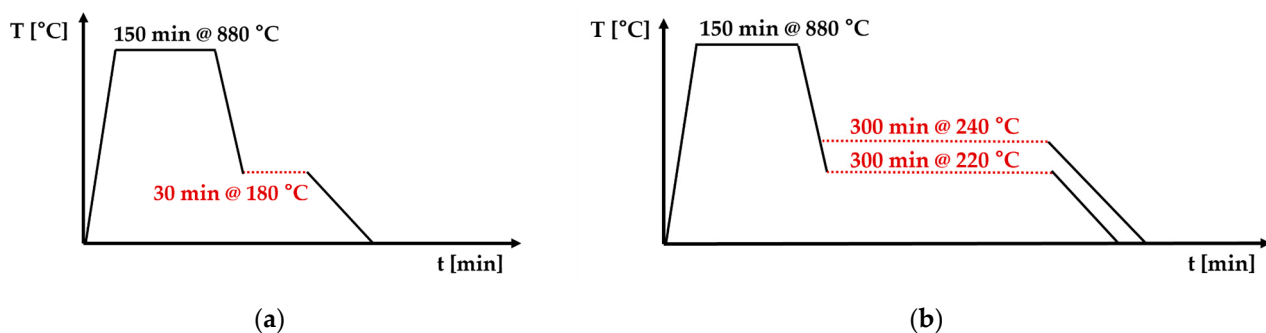


Figure 2. Heat treatment routes on the EN 100CrMo7 rings—Trial n.1: (a) martempering; (b) austempering.

Concerning the heat treatment conditions investigated in Trial n.2, the effect of a final tempering was assessed, as depicted in Figure 3. Trial n.2 involved the same routes as Trial n.1 with the addition of a final tempering consisting of heating at 230 °C for 120 min and cooling to room temperature in calm air, according to the datasheet [27].

Finally, to evaluate the role of austenitizing conditions and of the holding time of quenching in the salt bath, Trial n.3 was developed (Figure 4). Two austenitizing temperatures/times conditions, i.e., 880 °C for 150 min and 850 °C for 60 min, and three different holding times in the molten bath were investigated. The n. 6 rings were quenched in a salt bath at 220 °C for 60 min, 180 min, and 300 min, respectively. All the rings were finally tempered by heating them at 230 °C for 120 min and cooling them to room temperature in calm air, as previously applied in Trial n.2.

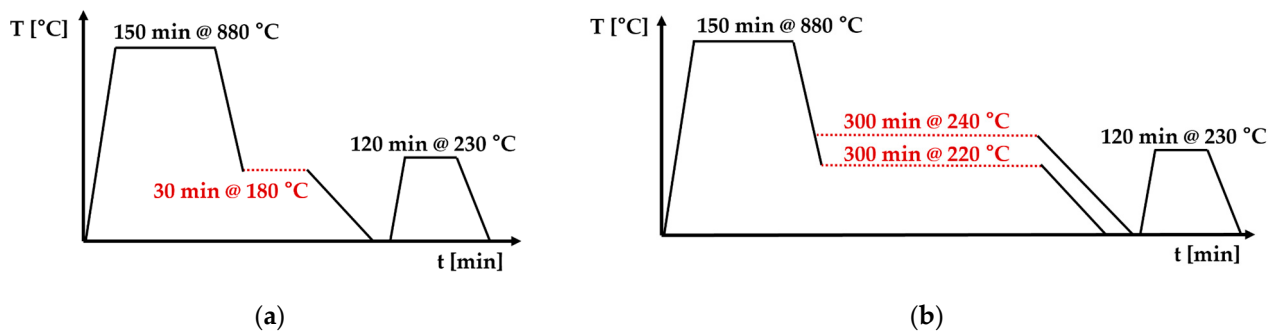


Figure 3. Heat treatment routes on the EN 100CrMo7 rings—Trial n.2: (a) martempering and tempering; (b) austempering and tempering.

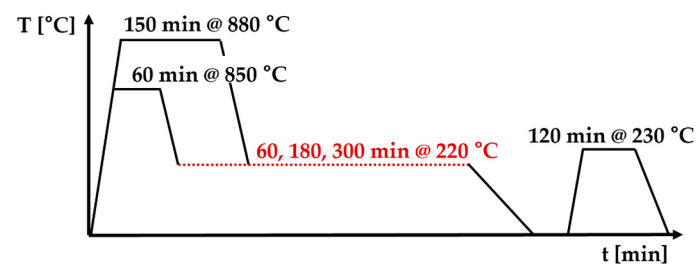


Figure 4. Heat treatment routes on the EN 100CrMo7 rings—Trial n.3: effects of two different temperatures/times conditions and different holding times in the salt bath.

The content of retained austenite was determined by the G.N.R. AreX XRD analyzer, equipped with a Mo X-Ray tube with a 1 mm monocapillary collimator, as per the ASTM E975-03 standard [31]. XRD measurements were conducted on the above-described samples for metallographic analyses, i.e., the upper surface and the central region of the ring.

Lastly, to deepen the role of austenitizing temperature on the hardenability of the material, the average grain size of the prior austenitic microstructure was evaluated. The grain boundaries were highlighted through a modified Khon method [32]; the austenitizing of a pre-polished sample under an air atmosphere promoted the oxidation of the grain boundaries because of their high reactivity. The sample was thus water-quenched to avoid the nucleation and the growth of a ferrite–pearlite pattern that could hide the austenite boundaries. On the polished surface of these heat-treated samples, the boundaries of the austenite grains became visible and distinctly observable at room temperature. Hence, the prior average austenitic grains size, G , was measured according to the “Mean Line Intercept Method” as per the ASTM E112 standard [33].

3. Results

3.1. As-Received Material

The initial phase of the study involved microstructural investigations and Brinell hardness tests on the as-received material. Figure 4 shows the representative LOM (Figure 5a) and BSE-SEM (Figure 5b) micrographs of the microstructural features of the EN 100CrMo7 steel in the as-received condition. The steel was supplied in a spheroidizing heat-treated condition, as highlighted by the presence of globular carbides uniformly distributed within the ferritic matrix. No remarkable differences along the ring height or thickness were detected. In the as-received condition, the EN 100CrMo7 steel with a mean hardness of 209 ± 1 HBW was measured in accordance with the expected one, as indicated in the material data sheet [27].

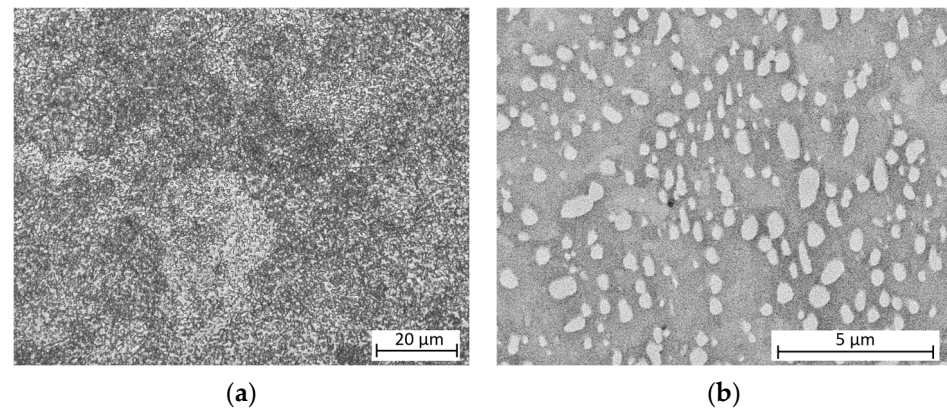


Figure 5. Micrographs of the EN 100CrMo7 steel in the as-received condition: (a) OM micrograph and (b) BSE-SEM micrograph.

3.2. Trial n.1—Martempering vs. Austempering

The effects of martempering and austempering routes were analyzed by comparing the HRC hardness evolution along the ring's height (d) and in the center of the ring's thickness for the heat-treated EN 100CrMo7 rings, as summarized in Figure 6. As expected, the highest HRC values are observed for the martempered ring, that exhibits around 66 HRC along the ring's height. The austempered rings, regardless of the temperature of the salt bath, attain HRC values around 60 with slight differences (about 2 HRC points) between the surfaces and the center of the ring's thickness.

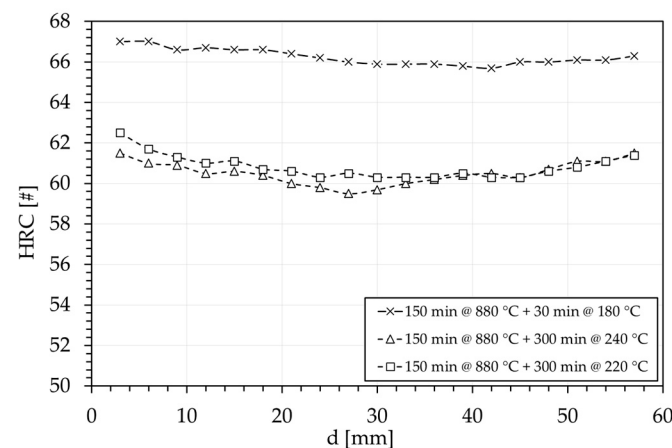


Figure 6. Hardness evolution (HRC) along the ring's height (d) for the heat-treated EN 100CrMo7 rings—Trial n.1.

Such results were substantiated by the SEM analyses, as can be observed by the micrographs reported in Figure 7. For the martempered ring (Figure 7a,b), the microstructure consisted of tetragonal martensite (matrix) and spheroidized carbides (orthorhombic crystal structure and $(\text{Fe,Cr})_3\text{C}$ stoichiometry, as reported elsewhere [12]). The microstructure at the surface of the ring (Figure 7a) showed a completely martensitic matrix with undissolved globulized cementite. Conversely, in the central region of the ring (Figure 7b), where the cooling rate during quenching was lower, some dark regions, ascribed as the incipient formation of upper bainite [34], were detected (see red arrows in Figure 7b). By contrast, the microstructure of the austempered rings mainly consisted of bainite, retained austenite, and undissolved carbides, homogeneously distributed within the matrix and with a fine and uniform size. The representative micrographs of the upper surface and the center region for austempering performed at 240 °C and 220 °C, respectively, are depicted in Figure 7c–f. As stated above, also for the austempered rings, the center of the rings revealed some regions ascribed as the incipient formation of upper bainite (see red arrows in Figure 7d,f).

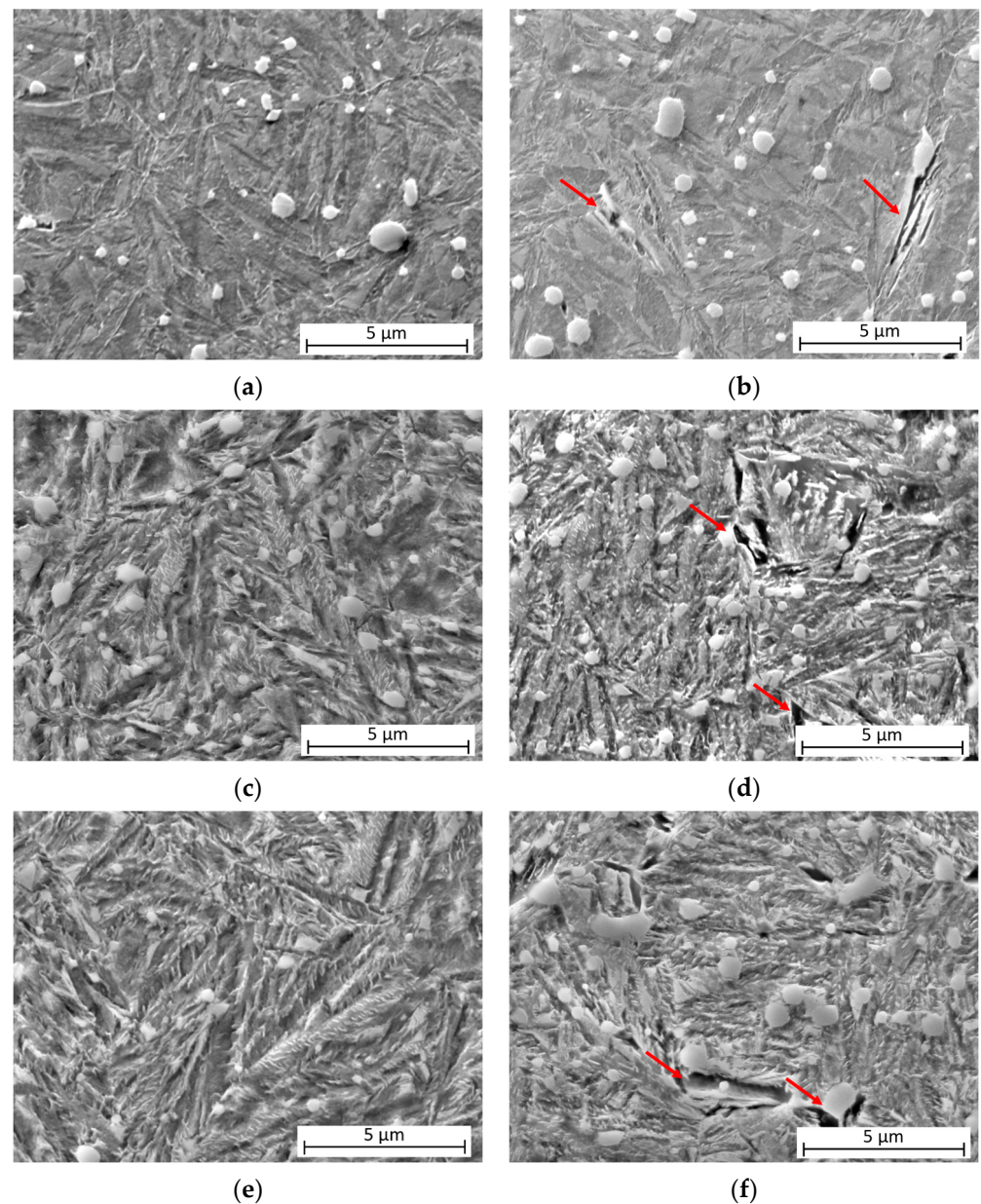


Figure 7. SEI-SEM micrographs of the heat-treated EN 100CrMo7 rings—Trial n.1: (a,b) austenitizing at 880 °C for 150 min, martempering at 180 °C for 30 min, and cooling to room temperature in calm air for the upper surface and central region, respectively; (c,d) austenitizing at 880 °C for 150 min, austempering at 240 °C for 300 min, and cooling to room temperature in calm air for the upper surface and central region, respectively; (e,f) austenitizing at 880 °C for 150 min, austempering at 220 °C for 300 min, and cooling to room temperature in calm air for the upper surface and central region, respectively.

3.3. Trial n.2—Effect of Tempering

From the above-reported results on martempering and austempering routes, the contribution of a final tempering treatment was investigated. Figure 8 displays a comparison of the HRC evolutions along the ring's height after tempering performed at 230 °C for 120 min. Considering the martempering route, no remarkable changes in HRC values were detected from the surface to the center after tempering. The final tempering led to quite a uniform reduction of about 4 HRC in hardness values along the ring's height points with respect to the untempered conditions. By contrast, the final tempering performed on the austempered rings enhanced the contribution of the salt bath temperature, as indicated by the HRC

evolution along the ring's height. As seen, the austempering and tempering treatments pointed out a slight hardness reduction in the center of the ring that, for the highest salt bath temperature, reached up to about 3 HRC points. The higher the temperature of the salt bath, the lower the obtained HRC values.

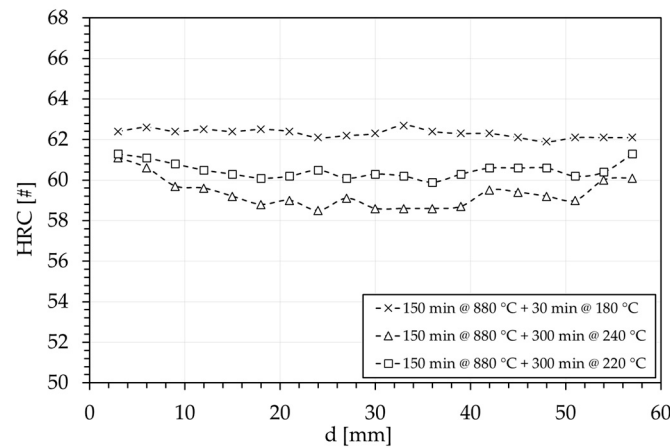


Figure 8. Hardness evolution (HRC) along the ring's height (d) for the heat-treated EN 100CrMo7 rings after tempering—Trial n.2.

Figure 9 displays the BSE-SEM micrographs of the tempered rings. Concerning the martempering and tempering condition (Figure 9a,b), a complete microstructural transformation of the matrix can be observed; due to tempering, the martensitic matrix is less tetragonal, even if it maintains a lathy morphology and if a higher density of spheroidized small carbides can be detected. Conversely, for the same investigated region, and regardless of the austempering temperature, no remarkable microstructural effects were observed in the tempered microstructure of the rings for the upper surfaces (Figure 9c,e). This experimental finding agrees with [12]; it is well-known that the tempering of bainitic microstructures mainly reduces internal stresses. By contrast, in the central region, the microstructure was mainly composed of lower bainite; nevertheless, some regions of upper bainite (see red arrows in Figure 9d,f) were detected.

3.4. Trial n.3—Effect of Austenitizing Temperature and Austempering Holding Times

Lastly, to assess the possibility of reducing the austenitizing temperature up to the minimum expected within the range of the datasheet for the EN 100CrMo7 steel [27], 850 °C and 880 °C austenitizing temperatures were compared. Furthermore, the contribution of three different holding times, i.e., 60 min, 180 min, and 300 min, was investigated. The experimental outcomes are reported in Figure 10. For the lower austenitizing temperature, it was observed that, regardless of the holding times, the center of the rings exhibited a drop in HRC values; the results reported in Figure 10a show that the drop is up to 16% with respect to the surface for the shorter holding times. Note that, for the 300 min holding time, this decrease is less than 10%. After austenitizing at 880 °C, no remarkable changes in HRC values were detected along the ring's height, regardless of the investigated holding times. In comparing the austenitizing temperatures (Figure 10a,b), it is worth noting that the hardness values at the surfaces are similar, about 61 HRC for the same austempering temperatures and irrespective of the holding times.

In addition to the HRC evolution, the average grain size G was estimated, as depicted in the representative LOM micrographs of Figure 11. Specifically, for the ring quenched from 850 °C, the grain size was equal to 10, while for the ring quenched from 880 °C, the grain size was equal to 8.

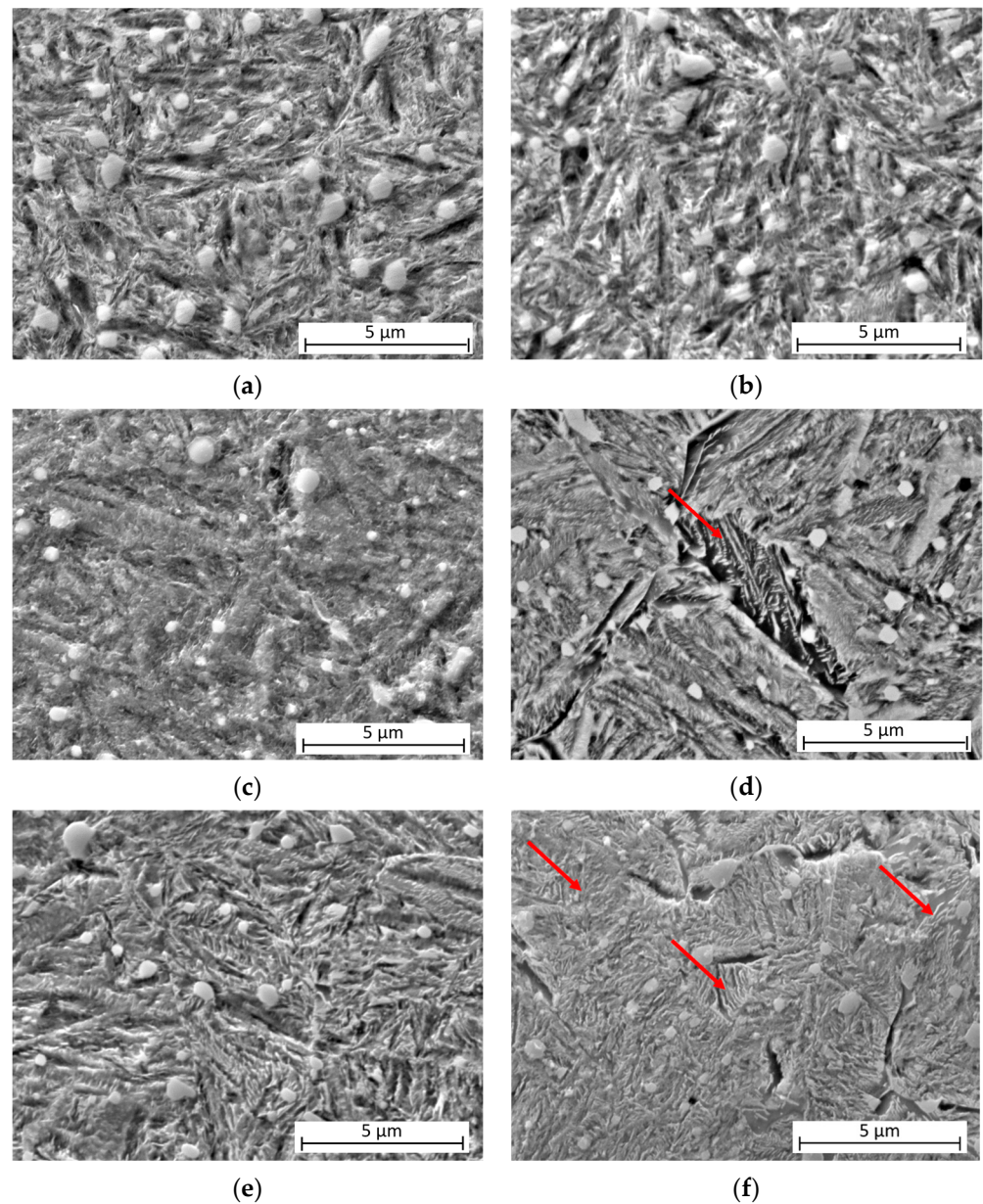


Figure 9. SEI-SEM micrographs of the heat-treated EN 100CrMo7 ring—Trial n.2: (a,b) austenitizing at 880 °C for 150 min, martempering at 180 °C for 30 min, cooling to room temperature in calm air and tempering at 230 °C for 120 min, and cooling to room temperature in calm air for the upper surface and central region, respectively; (c,d) austenitizing at 880 °C for 150 min, austempering at 240 °C for 300 min and cooling to room temperature in calm air, and tempering at 230 °C for 120 min and cooling to room temperature in calm air for the upper surface and central region, respectively; (e,f) austenitizing at 880 °C for 150 min, austempering at 220 °C for 300 min and cooling to room temperature in calm air, and tempering at 230 °C for 120 min and cooling to room temperature in calm air for the upper surface and central region, respectively.

The representative SEM micrographs of the EN 100CrMo7 rings austenitized at 850 °C and 880 °C are displayed in Figure 12. Concerning the austempering routes that followed the austenitizing performed at 850 °C, a comparison between the microstructure at the surface (Figure 12a,c) and at the center (Figure 12b,d) for 60 min and 300 min of holding time, respectively, can be carried out. The lower bainite matrix is predominant at the surface, whereas, at the center, an increased amount of upper bainite is detectable (see red arrows in Figure 12b,d). Such an amount is appreciable for the 60 min holding time (Figure 12b).

By contrast, on increasing the austenitizing temperature to 880 °C, the 60 min holding time (Figure 12e) still revealed regions of upper bainite (see red arrows in Figure 12f) but these were finer than the ones observed for the 850 °C austenitizing temperature.

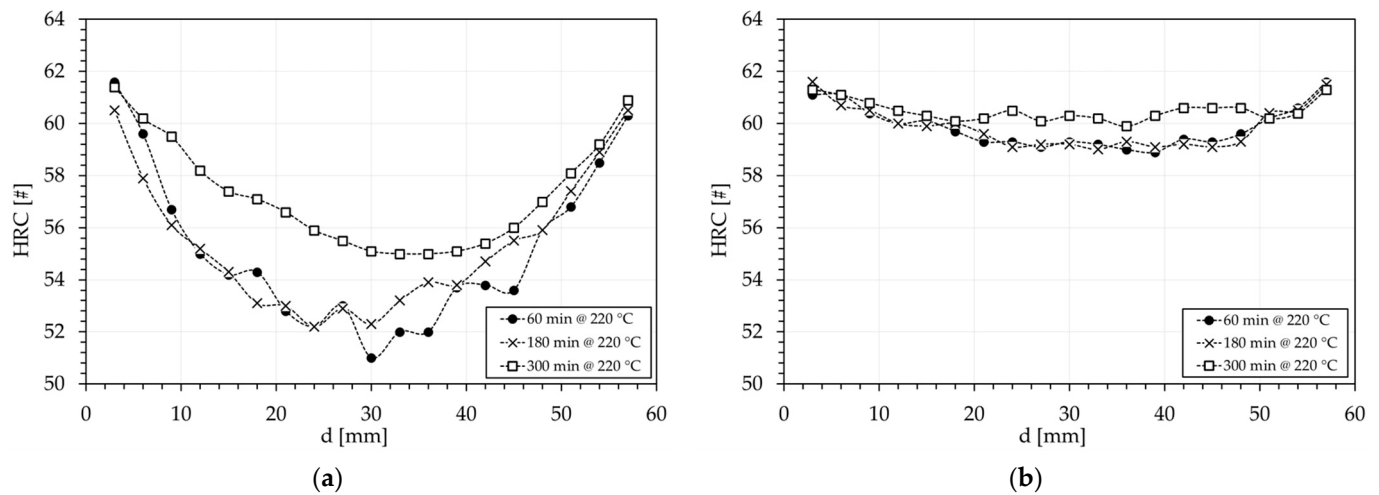


Figure 10. Hardness evolution (HRC) along the ring's height (d) for the heat-treated EN 100CrMo7 ring—Trial n.3 with (a) austenitizing at 850 °C for 60 min and (b) austenitizing at 880 °C for 150 min.

Finally, the amount of residual austenite (RA) was measured using the diffractometric method. This aims to provide insight into RA presence after quenching and after quenching and tempering for the different process routes, having practical effects related to the dimensional stability of the investigated large-size rings. Table 2 summarizes the RA contents (vol.%) for all the investigated heat-treatment routes. For the martempering treatment, the RA contents were the highest. Furthermore, by comparing the 850 °C and 880 °C austenitizing, it was observed that the RA contents increased as the austenitizing temperature/time increased. In all cases, the final tempering led to a significant reduction in the RA content; only for the martempering and tempering ring in the central region was the RA content higher than 1 vol%.

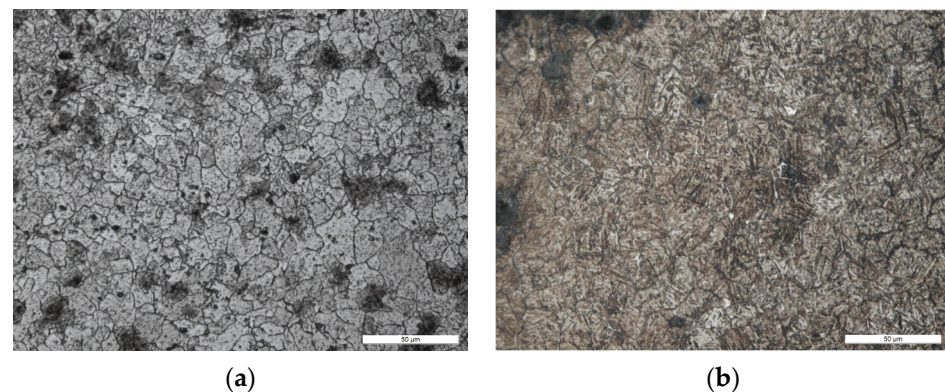


Figure 11. LOM micrographs of the EN 100CrMo7 steel after the modified Kohn method to reveal the prior austenitic grain size: (a) quenched from 850 °C and (b) quenched from 880 °C.

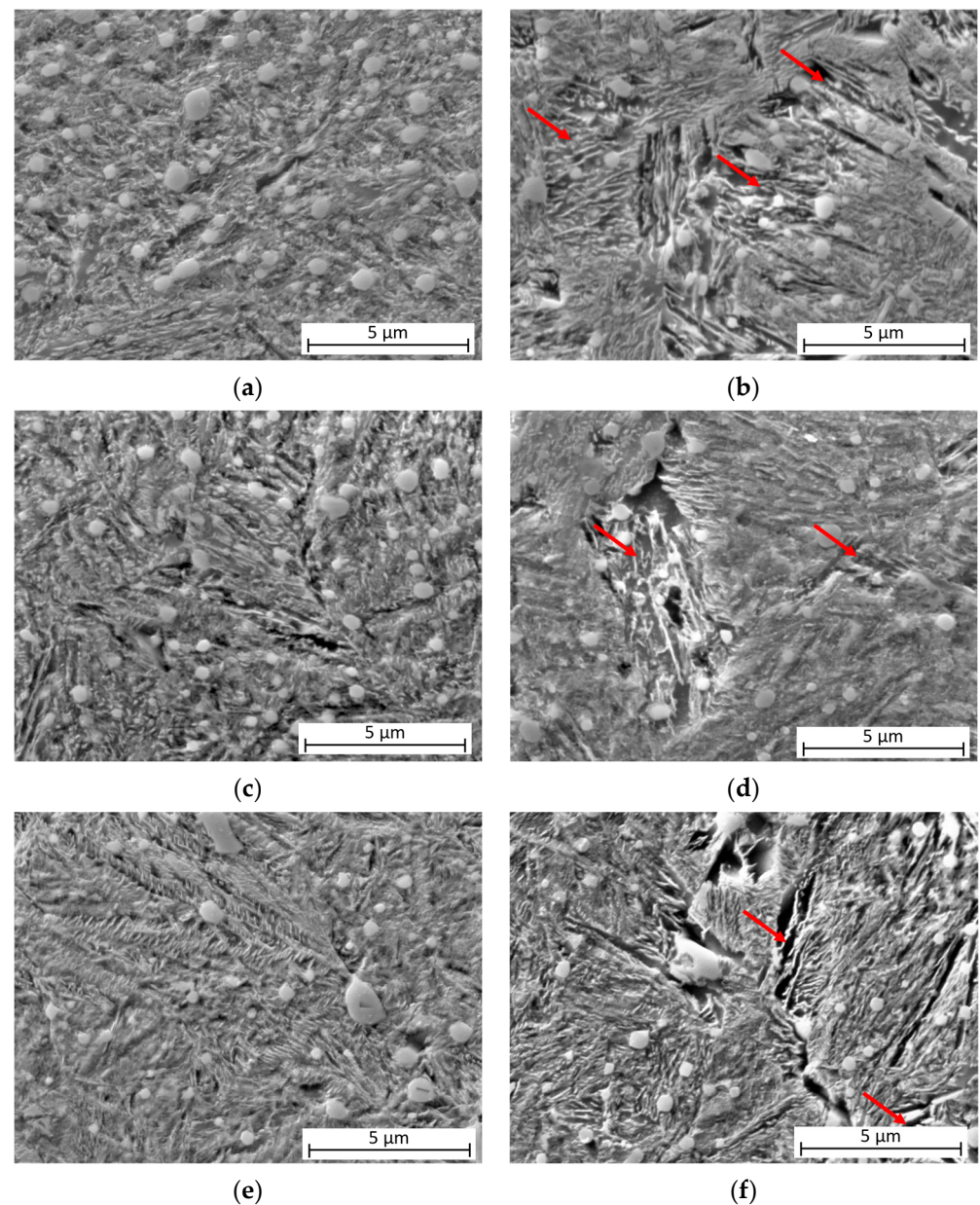


Figure 12. SEI-SEM micrographs of the heat-treated EN 100CrMo7 ring—Trial n.2: (a,b) austenitizing at 850 °C for 60 min, austempering at 220 °C for 60 min and cooling to room temperature in calm air, and tempering at 230 °C for 120 min and cooling to room temperature in calm air for the upper surface and central region, respectively; (c,d) austenitizing at 850 °C for 60 min, austempering at 220 °C for 300 min and cooling to room temperature in calm air, and tempering at 230 °C for 120 min and cooling to room temperature in calm air for the upper surface and central region, respectively; (e,f) austenitizing at 880 °C for 150 min, austempering at 220 °C for 60 min and cooling to room temperature in calm air, and tempering at 230 °C for 120 min and cooling to room temperature in calm air for the upper surface and central region, respectively.

Table 2. Measured RA contents (vol.%) for all the investigated heat-treatment routes.

	Retained Austenite (vol.%)			
	Austenitizing 850 °C		Austenitizing 880 °C	
	Austempering 220 °C for 300 min	Austempering 220 °C for 300 min + tempering	Austempering 220 °C for 300 min	Austempering 220 °C for 300 min + tempering
Upper surface	1.9–2.3	<1.0	3.0–4.8	<1.0
Central region	2.5–2.8	<1.0	3.1–4.8	<1.0
			Austempering 240 °C for 300 min	Austempering 240 °C for 300 min + tempering
		Upper surface	<1.0	<1.0
		Central region	<1.0	<1.0
			Martempering 180 °C for 30 min	Martempering 180 °C for 30 min + tempering
		Upper surface	5.1–6.4	<1
		Central region	11.2–13.1	1.9–2.1

4. Discussion

The effects of the different heat-treatment procedures on the hardness and microstructural characteristics of the EN 100CrMo7 bearing steel high-thickness rings were analyzed through a dedicated industrial-scale investigation.

At first, the effects of martempering and austempering were compared (Trial n.1). As expected, the microstructure of the steel after martempering carried out at 180 °C is composed of a mixture of untempered tetragonal martensite, carbides, and retained austenite (see Figure 7a). These microstructural features led to the highest HRC values (Figure 6). The HRC evolution along the ring's height is almost constant and the role of the detected incipient formation of upper bainite (see arrows in Figure 7b), as suggested in [34], appeared to be negligible in the measured bulk hardness evolution. By contrast, austempering at 240 °C and 220 °C led to a reduced HRC along the ring's height (Figure 6) and the corresponding microstructures (Figure 7c–f) revealed appreciable microstructural variations between the surface and the center of the rings where the incipient formation of upper bainite was detected too.

By the comparison between the untempered (Trial n.1) and tempered (Trial n.2) conditions in the martempered rings, the tempering treatment promoted the microstructural transformation and the consequent softening of the martensite (see Figures 7a,b and 9a,b), as confirmed by the decrease in hardness (see Figures 6 and 8), from about 67 HRC down to about 62 HRC. According to [21], after quenching, the microstructure of high-carbon bearing steels is mainly martensitic and composed of carbon oversaturated martensite with a significant amount of retained austenite—because the martensite start (M_S) and martensite finish (M_F) temperatures are low enough (M_F is below room temperature) to retain austenite—and alloyed carbides that were not fully dissolved during austenitizing (named undissolved carbides). For the 100Cr6 bearing steel, it was reported that quenching results in a predominantly martensite microstructure with approximately 6 vol.% of retained austenite and 3–4 vol.% of cementite particles that remain undissolved after the austenitizing process [3]. In the present case, the martempering produced up to 13.1 vol.% of RA (see Table 2), which is considerably higher than the one obtained with a direct quenching. Upon tempering, the RA amount was notably reduced to about 2 vol.% in the center and less than 1.0 vol.% in the surface. Concerning the austempering, the amount of RA was less than that of the martempering both at the center and at the surface (about 3.0–4.9 vol.%), which was considerably reduced—less than 1.0 vol.%—after tempering

within all the volume (see Table 2). In addition, for austempered and tempered rings, the different slight hardness reduction in the center of the ring for both temperatures was put in relation to the observed bainite microstructures (see Figure 9d,f).

Regarding the role of austenitizing temperature and austempering holding times (Trial n.3) on HRC evolution (Figure 10) and microstructural outcomes (Figure 12), several issues should be considered. The detected HRC evolutions can be ascribed either to the austenitic grain size (see Figure 11) or the hardenability of the investigated steel. The comprehensive review of bearing steels by Bhadeshia [3] explained that, while small bearings are usually through-hardened, since the hardenability is sufficient to attain the martensitic microstructure throughout the section, large bearings can be through-hardened by increasing the hardenability of the steel using higher concentrations of alloying elements. In this respect, the Mo-modified EN 100CrMo7 bearing steel, with its greater hardenability than the typical EN 100Cr6 steel, is a widely adopted material for large-size components, e.g., with wall thicknesses above 30 mm [34]. Nevertheless, regardless of the austempering holding time, the 850 °C austenitizing routes did not yield uniform hardness between the surface and center of the rings (Figure 10a). Even though, according to the supplier datasheet [27], the austenitizing temperature can be lowered down to 850 °C, such a temperature has been proven to be detrimental for the hardness in the center of the ring. The detected HRC values at the surface are above 60 HRC for all the investigated holding times (Figure 10a), as was the case for the 880 °C austenitizing routes (Figure 10b). Such an outcome should be analyzed from a twofold point of view: the increased grain size for the 880 °C austenitizing routes (Figure 11) promoted the martensitic transformation at the surface (Figure 12a,c) but, at the center, the microstructures were inhomogeneous, with large amounts of lath-like ferrite with cementite on the lath boundaries, likely to be referred to as lower bainite [35]. Thus, in agreement with [3], the properties of the core are adversely affected by the abnormal growth of austenite grains during heat treatment. As the austenitizing temperature is lowered, the pearlitic nose of the cooling curves is shifted to the left [12], i.e., the hardenability is lowered, thus affecting the microstructural transformation. Indeed, dealing with large components of uniform shape that must be rapidly cooled, this could result in a heterogeneous temperature distribution [3], as in the present case. In the center, it is highly likely that, before reaching the austempering temperature, the cooling curve had come across the upper pearlitic/bainitic transformation regions. Conversely, at the surface, an entirely upper bainitic microstructure has been observed (Figure 12a,c). In addition, the most important contribution to the bainite volume fraction and hardness is related to austempering temperature rather than austempering time, as reported in the literature for bearing steels [15,36]. This issue has been stressed in a previous study by the authors [37] and, in the present investigation, it has been further assessed. SEM observations highlighted the more significant differences between the surface and center of the ring (Figure 11a vs. Figure 11b and Figure 11c vs. Figure 11d) rather than between 60 min (Figure 11a) and 300 min (Figure 11c) holding times. This evidence is supported by the HRC values that are about 62 HRC for the surface and about 55 HRC for the center for the 300 min holding time, and about 62 HRC for the surface and about 51 HRC for the center for the 60 min holding time. Lastly, even if it is beyond the scope of the present investigation, the contribution of primary and secondary carbides against the holding times, and their effect on the bainitic transformation, cannot be neglected [38].

Furthermore, when comparing austempering routes at austenitizing temperatures of 850 °C and 880 °C, it was observed that an increase in the austenitizing temperature led to a corresponding increase in the RA. It is established that the amount of RA in hypereutectoid steels increases with austenitizing temperature [39] and is affected by the dissolution rate of the spheroidized carbides, which depends, in turn, on their size and distribution prior to the heating phase [4,34]. With the increase in the austenitizing temperature, more carbides are dissolved, and thus more carbon and alloying elements enter the solid solution of the austenite; hence, M_s lowers and more austenite is retained after quenching [21]. Consistent with these findings, the amount of RA achieved through austempering with an

austenitizing temperature of 850 °C was lower than that attained through austenitizing at 880 °C (1.9–2.8 vol.% compared to 3.0–4.9 vol.%). Sidoroff et al. [21] also suggested adopting a tempering temperature above 200 °C for a significant reduction in RA and at least 230 °C for the efficient removal of RA [40]. Note that such minimal RA content (see Table 2) ensured the dimensional stability of components [3]. Lastly, bainitic heat treatment can be considered the best one for bearing steels; it comprises the austempering close to M_s to keep a hardness compatible with bearing applications but for a suitable holding time to guarantee a complete austenite transformation. Indeed, the complete removal of retained austenite enables the avoidance of in-service dimensional variations, which are detrimental to bearing performance [21].

5. Conclusions

This research seeks a deeper insight into the knowledge and control of heat treatment parameters from an industrial perspective. Based on the experimental evidence, the study draws the following conclusions:

- Martempering led to the highest hardness values, about 66 HRC, and the evolution of hardness along the ring's height was quite uniform without detectable differences between the center and the surface regions. The obtained microstructure was composed of a mixture of untempered tetragonal martensite, carbides, and RA, whose content was up to 13.1 vol.% in the center before tempering;
- Regardless of the austempering temperature (220 °C vs. 240 °C), a slight decrease in hardness was measured at the center of the rings with respect to the martempering heat-treated condition. Nevertheless, a lower amount of RA (in the range 3.0–4.9 vol.%) was detected in comparison with the martempering;
- After tempering, the rings revealed overall HRC values lower than those of the untempered ones; for the martempering, the evolution along the ring's height was almost constant, whereas, for the austempering routes, a hardness reduction up to about 3 HRC points in the center of the ring was detected;
- For the martempering ring, after tempering, the amount of RA was notably reduced to about 2.0 vol.% in the center and less than 1.0 vol.% at the surface. The austempering routes showed a deeper reduction in RA, to less than 1.0 vol.%, both in the center and at the surface;
- Regarding the effect of the austenitizing temperature, the HRC evolutions along the ring's height detected for the 850 °C austenitizing temperature revealed that such a temperature was detrimental to the hardness in the center of the ring, regardless of the holding times. The measured hardness values were lowered down to 16% with respect to the surface for the shorter holding times (60 min). Hence, for the considered large-size rings, the choice of such a low austenitizing temperature seemed ineffective, as also confirmed by the high amount of upper bainite detected in the center of the ring. Conversely, the 880 °C austenitizing temperature was proven to be effective as the high and quite constant values of HRC along the ring's height;
- Overall, the experimental findings revealed that the role of the cooling rate (surface vs. center of the ring) was more detrimental to the resulting hardness and microstructure rather than the adopted austempering holding time.

Author Contributions: Conceptualization, E.B. and M.M.; methodology, M.C.; investigation, A.F. and M.C.; data curation, A.F.; writing—original draft preparation, A.F. and M.M.; writing—review and editing, E.B.; visualization, A.F.; supervision, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in the article.

Acknowledgments: The authors wish to gratefully acknowledge Lorenzo Bocchi for his valuable support during the experimental activities. Thanks are also due to Michele Gragnanini for his assistance.

Conflicts of Interest: Author Emanuele Bertarelli and Manuel Cassola were employed by the company Timaf Snc. They declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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