

CHEMISTRY

Metallurgy and high temperature chemistry

STUDY OF THE INFLUENCE OF LOW-TEMPERATURE
NITROCARBURIZING ON THE WEAR RATE OF
SINTERED LOW-ALLOY POWDER STEELS

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Received on March 24, 2025

Presented by V. Bankova, Member of BAS, on June 24, 2025

Abstract

The article studies the influence of low-temperature nitrocarburization on the microhardness and wear resistance of sintered alloys obtained from high-performance steel powders “ECOsintC” and “ECOsintHighCrA”. Nitrocarburization is carried out in laboratory conditions using the “Carbonit” method at 560 °C for 30 and 60 min. XRD analysis was performed to identify phases in the surface layer, while tribological tests following the “block-on-ring” method with an abrasive corundum disc assessed wear resistance. The results indicate that low-temperature nitrocarburization significantly enhances the microhardness and wear resistance of sintered alloys, highlighting a synergistic effect between alloy composition and surface thermochemical treatment.

Key words: ECOsint, sintering, nitrocarburizing, wear, microhardness

Introduction. Sintered steel parts, such as automotive valve seats, gears, and cams, are widely used in various industrial sectors due to their advantages over forged or cast components. These parts are subject to sliding, rolling, or abrasive wear during operation. These products are characterized by lower production costs, mainly due to cost savings associated with their manufacturing process, including production with a near-net shape, which minimizes the need for additional machining [1]. However, their mechanical properties are often lower compared to

forged products. This difference is due to the presence of residual porosity after the sintering process, which can affect the strength, wear resistance, and overall reliability of the components. Contemporary technologies offer solutions to improve the quality of sintered products. The use of advanced densification techniques and the addition of alloying elements such as manganese, chromium, and molybdenum can significantly improve mechanical properties by improving hardness, strength, and wear resistance [2–4]. Steels produced by powder metallurgy (PM) demonstrate superior wear resistance compared to those produced by traditional methods. The wear behaviour of PM steels is influenced by various factors, including the wear conditions, their metallurgical structure, chemical composition, and porosity level, with multiple mechanisms playing a role in this process. The dry sliding wear behaviour of sintered iron alloys has been investigated in several previous studies. These studies showed that the wear mechanisms are similar to those of forged materials under the same conditions. However, sintered materials contain varying amounts of pores and inhomogeneous structures, which create specific wear characteristics for PM-products [4,5]. Most studies have investigated the wear behaviour of various powder steels, noting the role of alloying elements in elucidating the wear mechanisms. Others have focused on investigating the influence of residual porosity resulting from the applied densification and sintering process. In fact, pores represent initiation sites for microplastic deformation and potential sites for the formation of initial microcracks. While the porosity inherent in sintered materials usually leads to reduced mechanical properties, it has been observed to increase wear resistance [6,7]. Secondary operations are effectively used in PM processing to improve wear and fatigue resistance, as well as to improve material properties such as strength and hardness. Chemical heat treatment methods such as carbonitriding, nitriding, and nitrocarburizing in a gas atmosphere are recognized for hardening sintered components. The application of the gas nitrocarburizing process to sintered structural parts as well as to iron-based powders has already been demonstrated in previous scientific papers. The surface properties of carbonitrided sintered compacts depend on both the quality of the substrate and the type and amount of nitride phases formed [8]. It is known that quenching improves the wear resistance of sintered components [9–12]. The influence of additional heat treatment on the wear rate has been less studied. In their publication, SUDHAKAR et al. [14] subjected sintered and heat-treated Fe-2Ni samples with different carbon contents to wear testing. It was found that hardness affects the wear rate, with heat-treated samples with a hardness of 40 HRC showing the maximum wear resistance.

This study sets a new goal related to the research of the wear characteristics of alloys, both after sintering and after applying low-temperature gas nitrocarburizing under different regimes.

Experimental. Iron-based powders marketed as ECOsintC (1.4% Cr, 0.8% Mo, 0.2% Mn, 1.0% Ni, 1.0% Cu, 0.6% C) and ECOsintHighCrA (2% Cr, 0.8% Mo,

0.2% Mn, 0.4% Ni, 0.7% C) were used to produce compacts ($10 \times 10 \times 50$ mm) at a compaction pressure of 500 MPa. Sintering was performed in an industrial furnace under a flowing nitrogen/hydrogen atmosphere at an isothermal temperature of 1140°C for 40 min. The sintered samples then underwent low-temperature gas nitrocarburization (LTGNC) at 560°C for 30 and 60 min, followed by furnace cooling. To assess the influence of process duration, the samples were treated in two separate nitrocarburization cycles.

Metallographic examination of the layers was performed. Phase identification of the alloy structures was conducted via X-ray diffraction (XRD) using a TDM-10 Tongda diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at room temperature. XRD patterns were recorded in 2θ coupled scanning mode over a range of 20° – 90° for comprehensive phase analysis. Diffraction peaks were matched with standard reference patterns using X'Pert High Score Plus software. The microhardness was measured on the surface before and after nitrocarburization, as well as in the depth of the layer, using the Vickers method. Wear resistance was evaluated using the “block-on-ring” method, where an abrasive corundum disc rotating at 250 rpm served as the counter body. Each sample underwent four test cycles, totalling 20 min and a wear distance of 1962 meters. After every 5-minute interval, samples were cleaned, and their weight was recorded using an electronic scale. Wear dynamics were determined based on the cumulative weight loss after each test cycle.

Results and discussion. Structure and phase analysis. The microstructural analysis of all samples subjected to nitrocarburization revealed the presence of a thin white layer with a thickness of about 5–6 μm . According to the phase analysis, this is a zone saturated with Fe_4N (γ') and Fe_3C , which are decisive in the wear process. After it there is a diffusion zone with a depth of about 130 μm . In depth a network of carbides and nitrides is also observed, characteristic of diffusion saturation of porous alloys (Fig. 1).

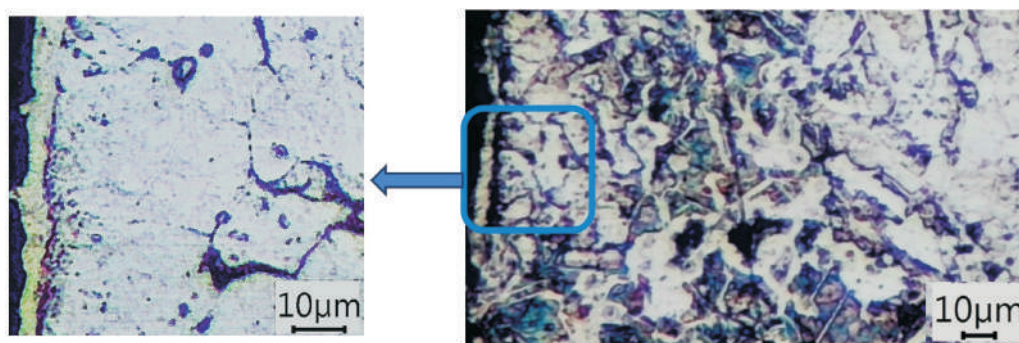


Fig. 1. Microstructural analysis of ECOSintHighCrA after sintering and LTGNC processes for 60 min

Figure 2 presents XRD patterns of the studied alloys ECOSintC (43) and ECOSintHighCr (44). The phase analysis of both alloys after the sintering process identifies the presence of α -Fe with crystallographic planes (110; 200; 211), which is expected since α -Fe is the primary phase in iron-based alloys.

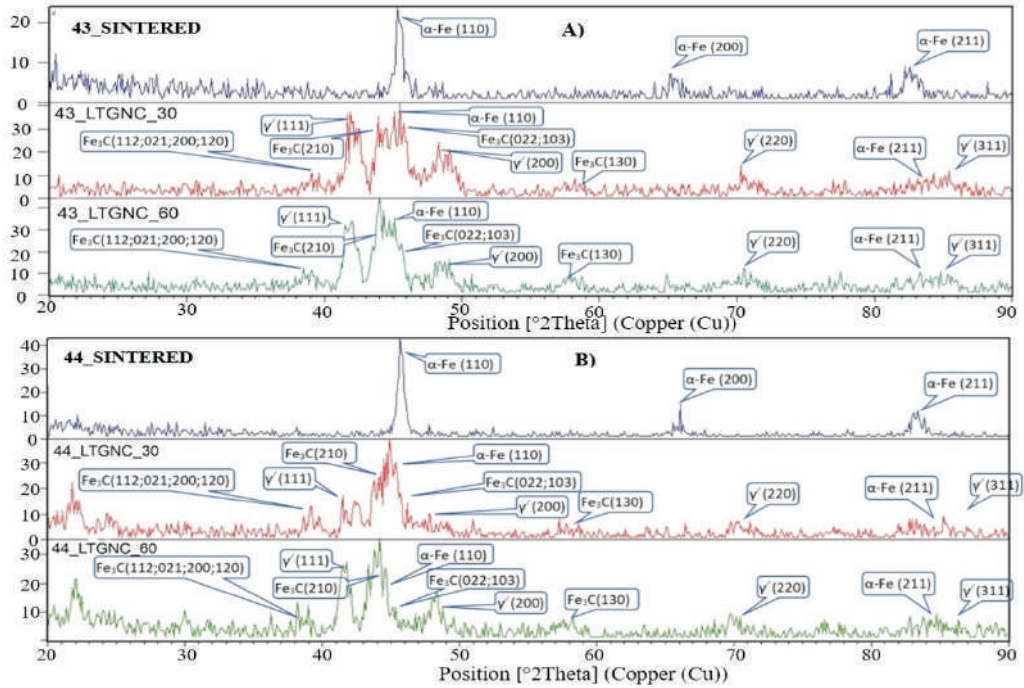


Fig. 2. XRD analysis of the PM alloys after sintering and LTGNC processes for A) ECOSintC (43); B) ECOSintHighCrA (44)

After low-temperature gas nitrocarburization process for 30 min, a nitride phase Fe_4N (γ') was identified in both types of alloys, which confirms the diffusion of nitrogen into the surface layer. The presence of the carbide phase Fe_3C confirms the enrichment of the material surface with carbon. During the low-temperature nitrocarburization process, a stable diffusion layer is formed in a short time and at a relatively low temperature. After a saturation time of 60 min, the X-ray diffraction patterns are identical to those after a processing time of 30 min, with clearly pronounced peaks of the formed nitride and carbide phases. The width of the diffraction peaks in both processing modes does not change significantly, which suggests that during the low-temperature gas nitrocarburization process, the risk of deformations in the structure is reduced and the formation of internal stresses is minimized. The formed nitride and carbide phases play a key role in improving the mechanical properties, wear resistance, and corrosion resistance of the material.

Microhardness. The microhardness of the surface of the sintered alloys obtained from the steel powders, as well as of the same test specimens after nitro carburization with saturation times of 30 and 60 min, was recorded. The measured microhardness (Fig. 3) of the metal matrix is 305HV0.2 for the ECOsintC alloy (43) and 370HV0.2 for the ECOsintHighCr alloy (44). The higher hardness of ECOsintHighCr is due to the higher content of alloying elements, which improves the mechanical properties of the alloy after sintering. The alloys are complexly alloyed, and during the sintering process, depending on the cooling rate, bainite and martensitic structures with high hardness can form [11,15].

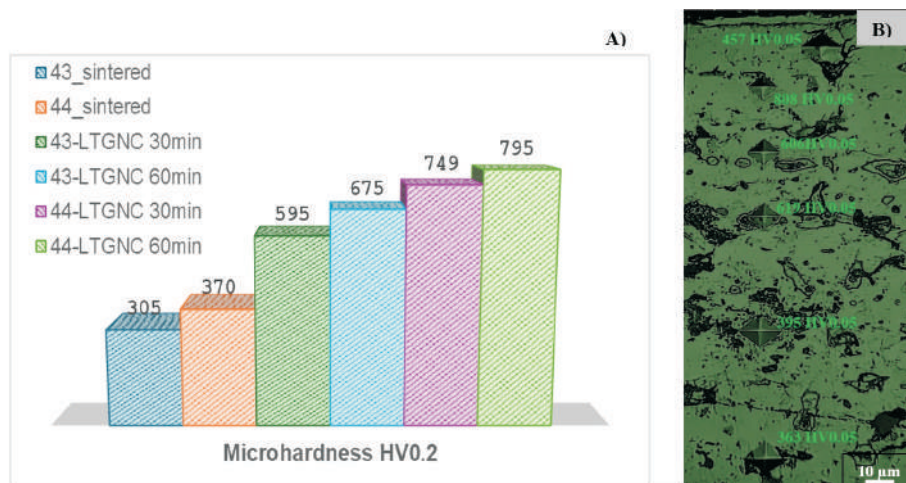


Fig. 3. A) Surface microhardness HV0.2 of alloys after sintering and after LTGNC processes for ECOSintC (43) and ECOSintHighCrA (44); B) Microhardness in depth for ECOSintHighCrA (44)

During the low-temperature gas nitrocarburizing process at 560 °C, the surfaces of the alloys become enriched with carbon and nitrogen. This process leads to the formation of various hard phases on the surface, including nitrides, carbides, and carbonitrides. These phases significantly enhance the material's hardness and contribute to improved wear resistance. In sintered alloys, the saturation process during nitrocarburizing is more intensive due to the presence of pores in the structure. These pores facilitate the diffusion of carbon and nitrogen, leading to the formation of a complex carbonitride surface layer. Additionally, carbon and nitrogen diffuse into the bulk material, forming solid solutions within the base alloy, which further enhances hardness and wear resistance. After nitrocarburizing, the measured microhardness of the metal matrix of the investigated alloys was significantly higher compared to that after sintering. For the ECOsintHighCr alloy, the microhardness reached 748 HV0.2 after 30 min of nitrocarburizing and 790 HV0.2 after 60 min. This indicates that a longer nitrocarburizing time improves hardness due to the increased formation of hard phases in the surface layer.

When examining the microhardness in depth, it was found that in the diffusion zone the values vary in a wider range, due to the porosity of the studied materials (Fig. 3). The higher hardness of the order of 600 HV0.05 is preserved to a depth of about 130 microns, after which values characteristic of sintered alloys without chemical-thermal treatment are recorded – 363 HV0.05.

Wear resistance. The data from the conducted study on the abrasive wear behaviour of the studied alloys under dry friction conditions are presented graphically in Fig. 4. The test specimens after the sintering process of both types of alloys show a significantly higher degree of wear than the specimens with a chemical-thermal treatment. The greater mass loss of 0.21 g for the entire test period is observed in the sintered alloy ECOsintC, which also shows a relatively lower hardness after sintering 305HV0.2.

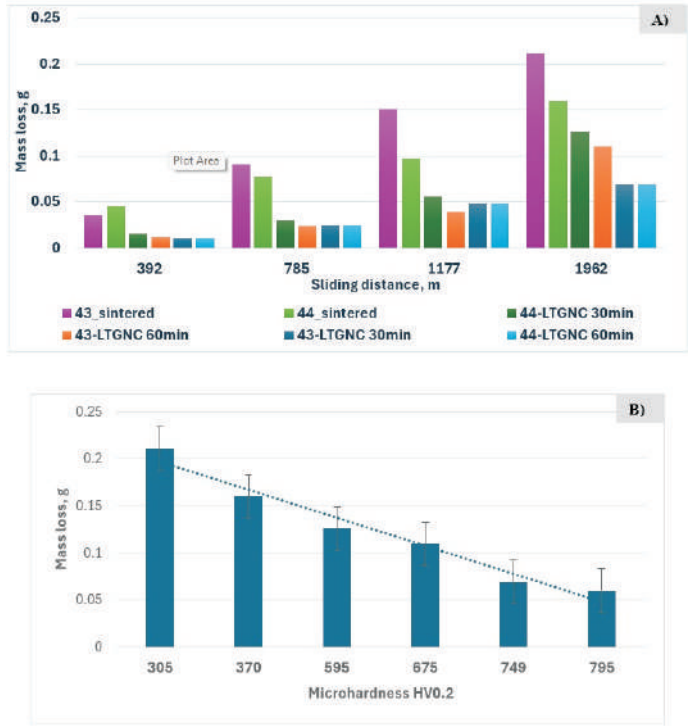


Fig. 4. A) Mass loss of alloy ECOsintC (43) and alloy ECOsintHigh CrA (44); B) Degree of mass wear depending on the microhardness of the layer

The nitrocarburizing process significantly enhanced the hardness of both alloys, which in turn positively influenced their behaviour under dry friction conditions. The formation of carbonitride phases on the surface and within the depth of the material had a beneficial effect, not only increasing hardness but also improving the wear resistance of the alloys. These phases contribute to the formation of

a harder and more durable surface layer, which is crucial for reducing wear under abrasive conditions.

The graphs show that samples subjected to thermochemical treatment with a longer saturation duration of 60 min exhibited a comparatively lower rate of mass loss. For the nitrocarburized samples of the ECOsintC alloy, the mass loss was nearly twice as low as that of the sintered samples. This improvement can be attributed to the deeper and more uniform diffusion of carbon and nitrogen into the material, resulting in a more robust surface layer with enhanced wear resistance. A lower degree of wear mass is observed for ECOsintHighCrA in all test cycles. This is due to both the formed γ' layer and the dense dispersion of alloying elements in the diffusion zone. The load is smoothly transferred, the possibility of cracks is limited and wear is reduced.

The results highlight the importance of the duration of the nitrocarburizing process in achieving optimal wear resistance. Longer treatment times allow for the formation of a more extensive and stable carbonitride layer, which significantly reduces wear rates.

When studying the influence of microhardness on the degree of wear (Fig. 4), a trend of significantly increasing the wear resistance of the studied alloys with increasing surface hardness was established.

Conclusion. In conclusion, the study demonstrates that nitrocarburizing is an effective method for enhancing the wear resistance of sintered alloys. The process not only increases surface hardness but also leads to the formation of a protective layer that significantly reduces mass loss under dry friction conditions. High hardness correlates with a lower wear rate of the investigated alloys, highlighting the importance of surface modifications in improving material performance. Specifically, for the ECOsintHighCr alloy, the initial microhardness after sintering was 350 HV0.2, but following nitrocarburizing, it increased significantly, reaching 748HV0.2 after 30 min and 790 HV0.2 after 60 min of treatment. This substantial improvement in hardness can be attributed to the diffusion of nitrogen and carbon, which promotes the formation of hard phases such as Fe_3C (γ'), Fe_4C , and alloy carbides.

The findings suggest that optimizing the duration of the nitrocarburizing treatment can lead to even greater improvements in the performance of these alloys, making them suitable for demanding applications where high wear resistance is required.

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