

Article

Effect of Layer Thickness on the Practical Adhesion of Borided Monel 400 Alloy

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Abstract: This study presents new results on the practical adhesion behavior of a boride layer formed on Monel 400 alloy, developed using the powder-pack boriding (PPBP) at 1223 K for 2, 4, and 6 h of exposure times, obtaining layer thicknesses from approximately 7.9 to 23.8 μm . The nickel boride layers were characterized using optical microscopy, Berkovich nanoindentation, X-ray diffraction (XRD), and scanning electron microscopy (SEM) to determine microstructure, hardness distribution, and failure mechanisms over the worn tracks. Scratch tests were conducted on the borided Monel 400 alloy according to the ASTM C-1624 standard, applying a progressively increasing normal load from 1 to 85 N using a Rockwell-C diamond indenter, revealing that critical loads (L_{C1} , L_{C2} , and L_{C3}) increased with layer thickness. The tests monitored the coefficient of friction and residual stress in real time. Critical loads were determined based on the correlation between the normal force and visual inspection of the worn surface, identifying cracks (cohesive failure) or detachment (adhesive failure). The results exposed those cohesive failures that appeared as Hertzian cracks, while adhesive failures were chipping and delamination, with critical loads reaching up to 49.0 N for the 6 h borided samples. Also, the results indicated that critical loads increased with greater layer thickness. The boride layer hardness was approximately 12 ± 0.3 GPa, ~ 4.0 times greater than the substrate, and Young's modulus reached 268 ± 15 GPa. These findings underscore that PPBP significantly enhances surface mechanical properties, demonstrating the potential for applications demanding high wear resistance and strong layer adhesion.

Keywords: borided Monel 400; adhesion failure; layer thickness; scratch test; nickel borided



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1. Introduction

Nickel-based alloys are widely used in industrial applications due to their high resistance to corrosion and oxidation processes. In particular, Monel 400 is known for its excellent corrosion resistance in environments such as seawater, saline solutions, and aggressive acids, including hydrofluoric acid and phosphoric acid [1]. Based on these characteristics, its main applications include marine engineering, chemical processing, valves, pumps, tanks, electrical and electronic components, equipment for crude oil refining, food processing, gasoline manufacturing, power generation, and heat exchangers [2]. However, one of the main disadvantages of the Monel 400 alloy is its somewhat lower hardness compared to other nickel alloys. Since products made from this material are often exposed to high-flow conditions, they may be susceptible to failures caused by erosion, cavitation, or wear [3].

Different thermal, deposition, or thermochemical processes have been employed to improve the surface properties of nickel-based alloys. In this way, the powder-pack boriding process (PPBP) thermochemical treatment is widely used in the industry due to its

relative simplicity and low costs, as well as its contribution to enhancing mechanical and chemical properties due to the high hardness achieved at the surface, leading to excellent performance in industrial applications [4]. PPBP involves the diffusion of active boron atoms (from a boron-rich source) into the material's surface to form a hard, resistant boride layer [1]. On the other hand, practical adhesion is defined in [5] as the force or work required to remove or detach a film or coating from a substrate, regardless of where the failure occurs. As mentioned in [4], it is one of the most critical issues in the industry concerning hard coatings, as adhesion problems often lead to failures.

Krelling et al. (2019) examined the microstructure and properties of borided Monel 400 alloy, reporting a fivefold increase in surface hardness due to the formation of a silicide/boride layer, which led to significant improvements in wear resistance [6]. Similarly, Kukliński et al. (2020) investigated the effects of chemical composition and microstructure on wear resistance and microhardness in Monel 400 treated by laser boriding. Their findings showed that wear resistance improved by a factor of 4 to 10, depending on the parameters used in the laser boriding process [7].

In 2022, Günen et al. proposed a kinetic growth model for boride layers, establishing different experimental conditions. The authors observed that the Ni_2B layer thickness ranged from 35 to 290 μm , with hardness values between 1002 and 1476 $\text{HV}_{0.0025}$. Additionally, an activation energy of 33.7 kJ/mol for Ni_2B was calculated [1].

Campos-Silva et al. (2018) conducted a practical adhesion study on borided Inconel 718 alloy, examining the relationship between the adhesion of the coating-substrate system and indentation properties (residual stress, elastic modulus, and hardness), as well as the critical loads that generated tear channels. The results indicated that critical loads increased to 76 N with increasing layer thickness. Cohesive failure manifested as Hertzian cracks, preceded adhesive failure in chipping and delamination [8].

This study aims to evaluate the practical adhesion behavior of the borided Monel 400 alloy surface, taking into account that not enough research has been reported on this material in the open literature. Initially, Monel 400 alloy samples were treated using PPBP to achieve nickel boride layer thicknesses ranging from approximately 7.9 to 23.8 μm . This thermochemical treatment not only reduces energy consumption and costs compared to other treatment methods but also enhances the overall performance of the alloy for industrial applications. Subsequently, the adhesion properties of the borided Monel 400 samples were assessed by determining the critical normal loads (L_{CN}). Additionally, the study presents a detailed analysis of the failure modes observed in the scratch tracks, contributing to a deeper understanding of the material's durability and performance under operational conditions.

2. Experimental Details

2.1. PPBP Thermochemical Treatment

Rectangular specimens of Monel 400, with nominal dimensions of $20 \times 20 \times 5$ mm, were utilized for the study. The chemical composition of the alloy included 0.30 wt% C, 2.0 wt% Mn, 0.024 wt% S, 0.5 wt% Si, 63.0 wt% Ni, 28.0–34.0 wt% Cu, 2.5 wt% Fe, and 0.05 wt% Al. The specimens were metallographically prepared and packaged in a sealed cylindrical AISI 304 steel container, containing a powder mixture comprising 90 wt% B_4C and 10 wt% KBF_4 [4]. The samples were subjected to boriding at a temperature of 1223 K for durations of 2, 4, and 6 h, following the growth kinetics model proposed by Günen et al. (2022) [1]. Upon completing the powder-pack boriding (PPB) process, the container was removed from the furnace and allowed to cool slowly to room temperature. This process yielded nickel boride layer thicknesses in the range of approximately 7.9 to 23.8 μm , consisting of a mixture of nickel borides (Ni_2B , Ni_4B_3 , NiB) and copper precipitates.

2.2. Chemical and Mechanical Characterization

The borided samples were analyzed using X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation over a 2θ range of 30° to 100° , employing a PANalytical X'Pert/Pro diffractometer.

The resulting diffraction patterns were evaluated using the commercial software High Score Plus Version 4.5 to confirm the presence of nickel borides. Additionally, the samples obtained from the process were metallographically prepared in bakelite to observe the morphology of the cross-section and measure the layer thickness using optical microscopy (Olympus/GX-51, Olympus, Shinjuku City, Japan).

The nickel boride layers produced by PPBP were indented across the cross-section using a Berkovich nanoindentation technique with depth sensing, applying a constant load of 50 mN. Indentations were spaced approximately 5.0 μm apart to estimate the hardness (H) distribution and Young's modulus (E) using a TTX-NHT/CSM instrument and CETR software Version 1.8, following standard procedures of the ISO-14577-4, (2016) [9].

2.3. Scratch Test

The scratch test is widely employed to evaluate practical adhesion resistance in layer/substrate systems resulting from various thermal, thermochemical, or deposition processes, following the standard test method ASTM C1624-05 [5]. This test is commonly utilized to determine the mechanical strength of coatings with thicknesses up to 30 μm and subsequently calculate the critical loads required to induce layer failure. During the test, the coated sample is secured in the testing apparatus, where a diamond-tipped indenter moves at a constant speed. The normal load force (NF) is progressively increased, creating a wear track that exhibits various failure mechanisms on the layer's surface. These worn trajectories are analyzed in terms of the critical scratch load (L_{CN}) to estimate the characteristic failure mechanisms, which are correlated with visual inspections via microscopy, the friction coefficient (COF), and the residual depth (Rd) [10].

Scratch tests were performed on the polished surface of the boride layers obtained from the entire experimental set, as depicted in the schematic representation of the test in Figure 1. A commercial scratch testing machine (Revetest Xpress+, CSM Instruments, Graz, Austria) equipped with a Rockwell C diamond indenter with a 200 μm radius was utilized, according to the testing parameters outlined in Table 1. Multiple repetitions were conducted for each load, as stipulated by ASTM C1624-05, wherein NF, COF, and Rd were analyzed using a personal computer with Scratch-V6.2.12 software. After conducting the scratch tests, the channels on the surface of the borided Monel 400 were examined using optical microscopy and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), using a JEOL/JSM-7800F instrument (JEOL, Tokyo, Japan) at 20 kV.

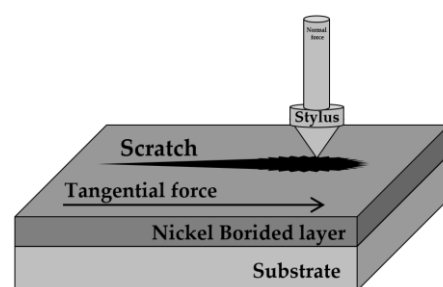


Figure 1. Schematic representation of the scratch test.

Table 1. Experimental parameters employed during scratch tests.

Parameter	Description
Range load	1 to 85 N
Speed rate	1.0 mm/min
Load rate	12 N/min
Scratch length	7.0 mm

Note: These parameters were selected to observe and identify cohesive failure mechanisms in detail, as described in the ASTM C1624-05 standard procedure.

The critical scratch loads (L_{CN}) on the worn tracks generated by the scratch tests were estimated by critical normal loads to the different damage levels of interest and the length using Equation (1).

$$L_{CN} = \left[L_{rate} \times \left(\frac{l_n}{X_{rate}} \right) \right] + L_{initial} \quad (1)$$

where L_{CN} is the specific critical scratch load, L_{rate} is the loading rate of force application in the specific scratch test, l_n is the scratch length, X_{rate} is the horizontal displacement rate, and $L_{initial}$ is the initial load established at the start of the scratch test [5].

3. Results and Discussion

3.1. Nickel Borides Microstructure

The morphology of the borided Monel 400 alloy layer exposed to 1223 K for 2, 4, and 6 h is presented in Figure 2. The cross-section reveals a thickness range of approximately 7.9 to 23.8 μm . X-ray diffraction (XRD) patterns were obtained under different conditions to verify the formation of nickel borides. According to the Ni-B phase diagram, various inter-metallic compounds (Ni_2B , Ni_4B_3 , Ni_3B) can form on the material's surface [11,12], as was observed in its characteristic degrees (see Figure 3). The formation of these compounds is linked to the composition of the powder mixture surrounding the sample, including factors such as the type of boron source and the proportions of the various ingredients. Additionally, the temperature and exposure time during the boriding process play a crucial role in this phenomenon.

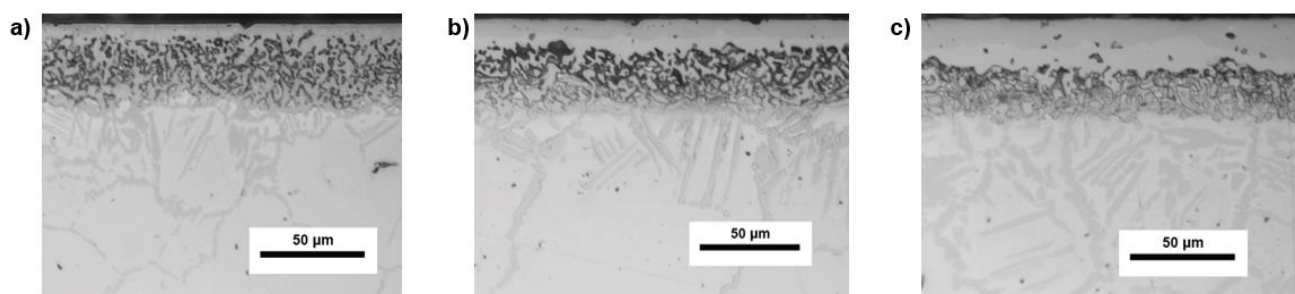


Figure 2. Cross-sectional views of the borided Monel 400 obtained at 1223 K with exposure times of (a) 2 h, (b) 4 h, and (c) 6 h.

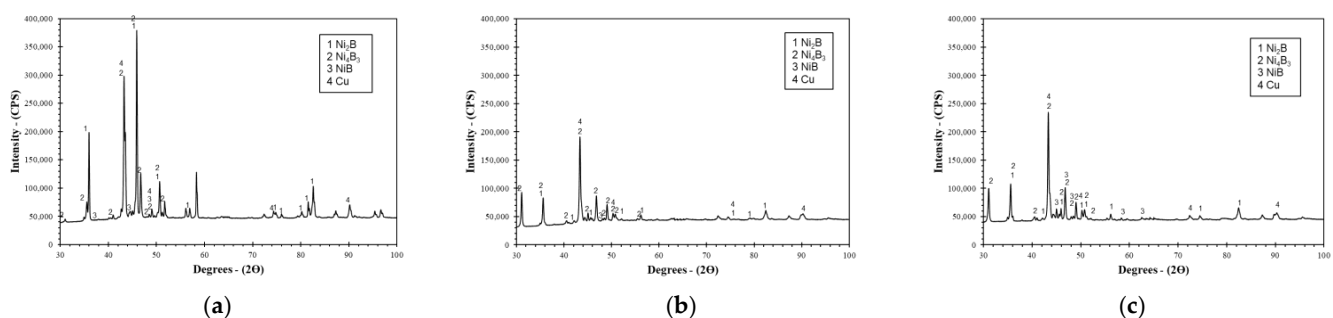


Figure 3. XRD patterns obtained at the surface of borided Monel 400 using scan normal procedure. The boriding condition was 1223 K: (a) 2 h, (b) 4 h, and (c) 6 h.

The X-ray diffraction (XRD) patterns of each sample, presented in Figure 3, are in good agreement with similar studies [1,2,6]. The XRD analysis predominantly reveals the presence of Ni_4B_3 , with a preferential crystallographic plane of $[0\ 2\ 2]$ at a 2θ angle of $\sim 44^\circ$. Peaks corresponding to Ni_2B with a crystallographic plane of $[2\ 1\ 1]$, Ni_3B with a plane of $[0\ 4\ 0]$, and Cu with a plane of $[1\ 1\ 1]$ are also observed, appearing at angles ranging from 35° to 90° , with varying intensities [1].

This observation suggests that the boriding process conditions directly influence the crystallographic orientation and the stability of the phases formed on the Monel 400 alloy. The dominance of the Ni_4B_3 phase, alongside other borides like Ni_2B and NiB , indicates a well-developed boride layer. The presence of the Cu peaks, derived from the base alloy, remains consistent across the samples, unaffected by the boriding treatment. The variations in peak intensity across the samples further suggest differences in phase concentration, which may be attributed to factors such as boriding time, temperature, and the specific composition of the boriding environment [13]. The identification of these crystallographic planes is critical, as it provides insight into the material's microstructure and potential mechanical properties. The preferential orientation of the boride phases could play a significant role in enhancing surface hardness, wear resistance, and other mechanical attributes, making these findings valuable for applications requiring durable surface layers [14].

3.2. Nickel Borided Mechanical Properties

Figure 4 shows the hardness (H) and elastic modulus (E) profiles, indicating that the hardness value for the nickel boride layer is approximately 12 ± 0.3 GPa, gradually decreasing across the layer until it reaches the substrate's hardness of ~ 3.3 GPa [2]. This implies that the hardness ratio between the nickel boride layer (PPBP) and the substrate is roughly four times greater (See Figure 5). Regarding the Young's modulus (E) of the borided Monel 400, the maximum value in the layer is about 268 ± 15 GPa [6]. It is important to note that the values below ~ 4.5 GPa do not significantly affect the scratch behavior, which aligns with the findings reported by Cimenoglu et al. [15]. Generally, the H/E ratio values suggest that the PPBP samples possess good resistance to plastic deformation within the layer. This characteristic is associated with improved behavior to prevent ceramic layer adhesion failures and ensure high wear resistance [16].

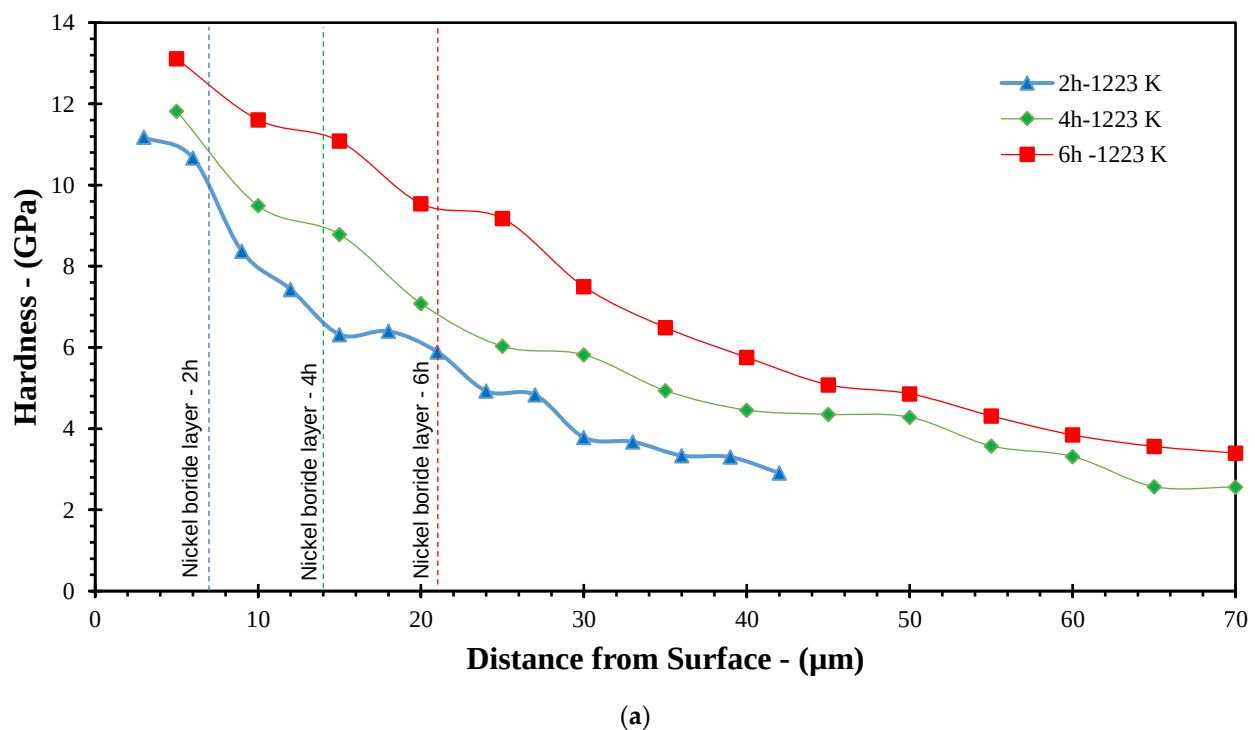


Figure 4. Cont.

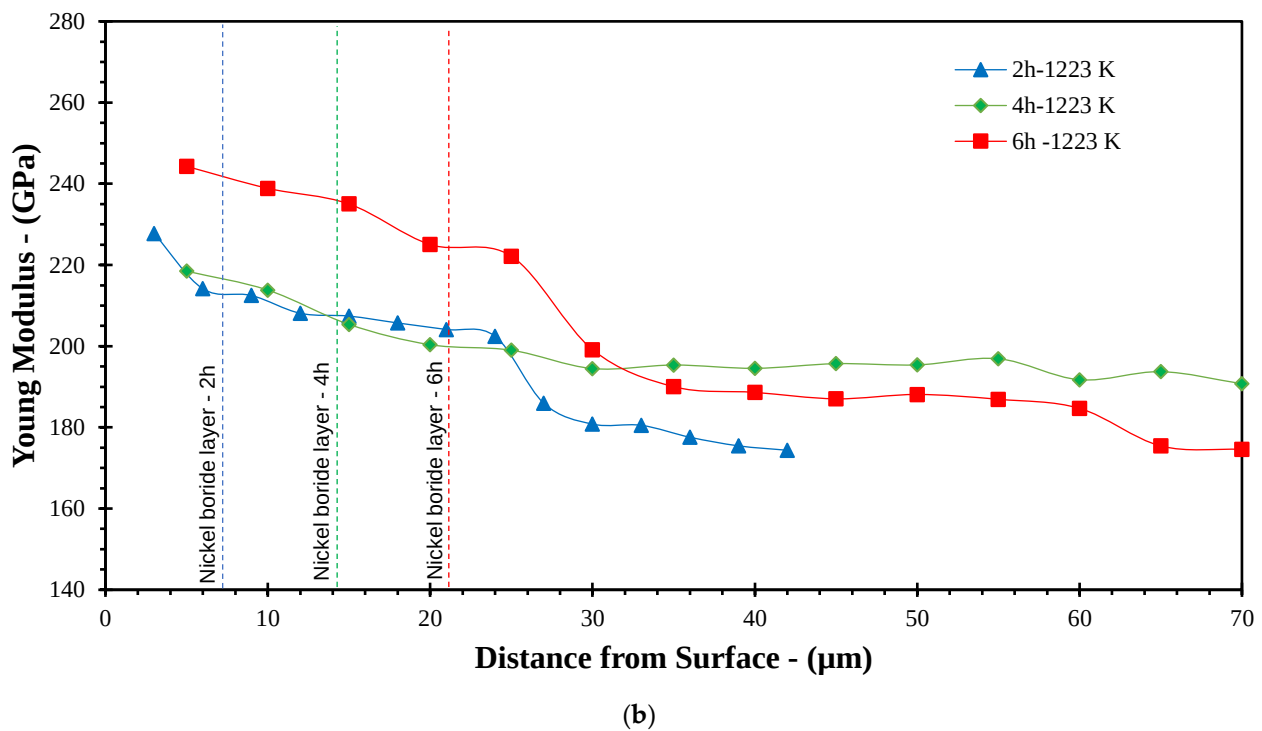


Figure 4. Profiles obtained on the cross-section of the nickel boride layer–substrate system: (a) Hardness (H) and (b) Young's modulus (E).

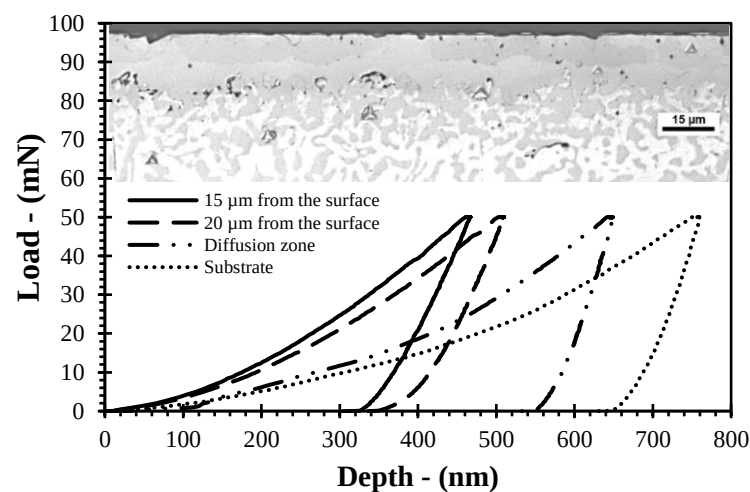


Figure 5. Load–unload curves obtained by nanoindentation at 6 h with 1223 K.

In Figure 5, the load–unload curves clearly illustrate the variation in mechanical properties as a function of depth from the material's surface to the substrate. According to Oliver and Pharr's theory, the region close to the surface (15 μm) exhibits the highest hardness and modulus of elasticity, with a slight decrease observed in the 20 μm region. The diffusion zone serves as a transitional area, displaying intermediate properties between the hardened surface and the substrate. This zone also shows increased ductility, reaching greater indentation depths under lower loads. Notice that the same behavior was observed in the layers exposed to 2 h and 4 h.

The residual stress distribution as a function of the distance from the surface for samples subjected to heat treatments at 1223 K for varying durations (2 h, 4 h, and 6 h) is shown in Figure 6, which was calculated using Chen et al. [17] expression. The results indicate a consistent pattern of compressive residual stress (σ_r) near the surface for all

treatment durations, which gradually decreases toward zero as the distance from the surface increases. This trend is in line with typical residual stress profiles observed in surface-hardened materials, where the compressive stress generated near the surface plays a significant role in improving the material mechanical performance; some observations are described below:

- **Treatment (2 h):** The shortest treatment time exhibited a relatively lower magnitude of compressive stress at the surface, with significant variations in stress levels as the depth increased. This suggests that the 2 h treatment might lead to insufficient boron diffusion into the material, resulting in a less uniform stress distribution;
- **Treatment (4 h):** The intermediate treatment duration generates a more stable and gradual reduction in compressive stress from the surface towards the material's interior. This indicates more effective stress relief compared to the shorter treatment, suggesting improved boron diffusion and nickel boride layer formation;
- **Treatment (6 h):** The longest treatment duration resulted in the highest compressive stress near the surface, with a smoother and more consistent transition to lower stress values deeper within the material. This outcome aligns with expectations that extended treatment times facilitate greater boron diffusion, leading to a thicker nickel boride layer and enhanced surface hardening.

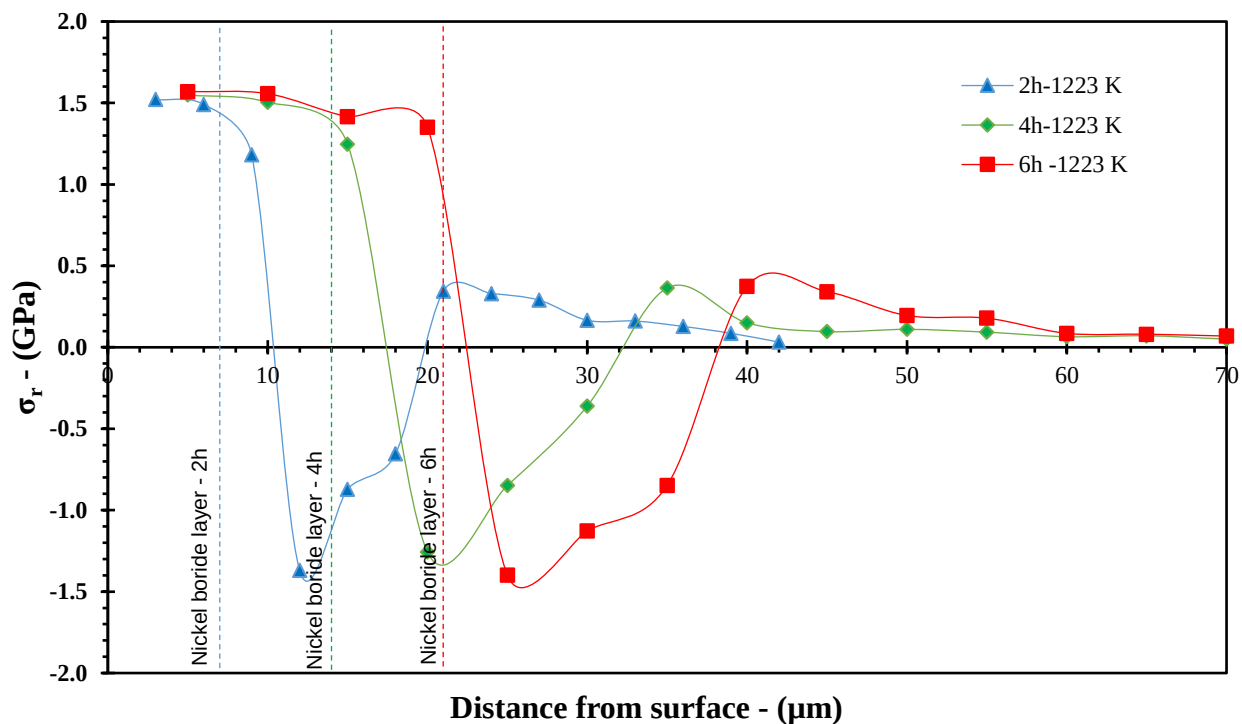


Figure 6. Residual stress distribution across the length of the nickel boride layer–substrate system.

On the other hand, the dashed vertical lines in Figure 6 represent the boundaries of the nickel boride layer for each treatment duration. As the treatment time increases, the nickel depth layer also increases, indicating that longer exposure to the boriding process enhances boron penetration into the substrate. This progression in layer thickness corroborates the trend of increasing surface compressive stress, which is known to improve surface durability and fatigue resistance significantly.

The observed decrease in compressive residual stress on the surface with longer treatment durations is consistent with the theoretical understanding of thermochemical treatment processes (less than ~2.0 GPa). Compressive residual stress is beneficial for mitigating crack propagation and enhancing the mechanical resilience of the material, which is critical for components subjected to cyclic loading conditions. Extended boriding times (notably the 6 h treatment) produce deeper boron diffusion, resulting in a thicker

hardened layer and a more substantial increase in compressive stress [18]. This characteristic is particularly advantageous for applications requiring high fatigue, strength and wear resistance.

3.3. Scratch Test Results

3.3.1. Estimation of Critical Loads in Nickel Boride Systems

Figures 7–9 present the behavior of the friction coefficient (COF) and the normal force (NF) measurements in relation to the scratch track. These graphs illustrate the increase in the COF signal as damage is observed along the scratch track. Specific levels and types of damage were evaluated for the scratch tracks, corresponding to the critical loads (L_{C1} , L_{C2} , and L_{C3} , respectively), revealing critical loads with cohesive and adhesive failure modes [19].

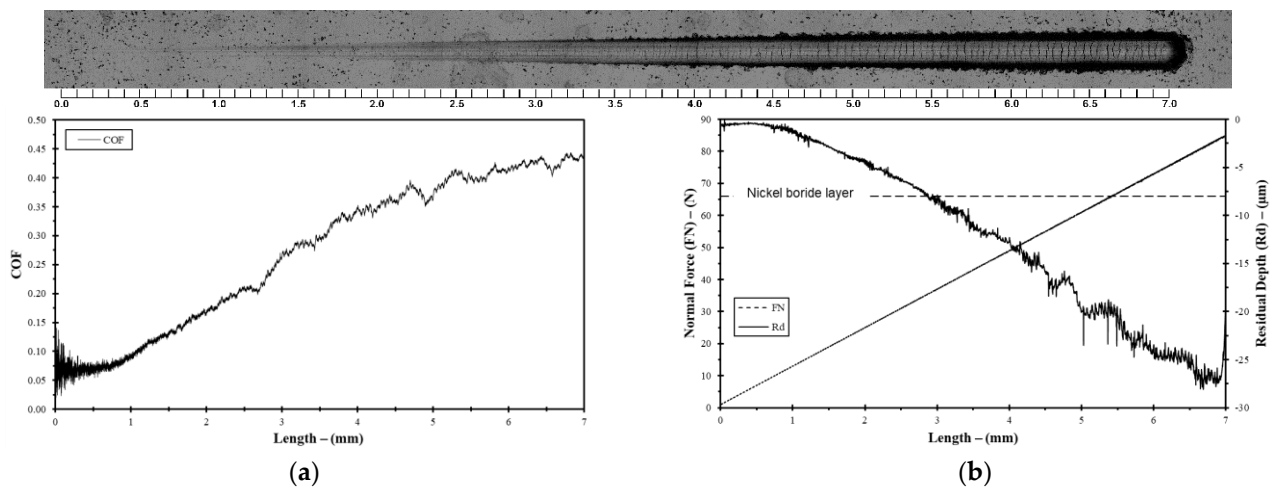


Figure 7. Scratch track length of the Monel 400 borided obtained at 2 h. (a) COF behavior, and (b) normal force (NF) and the residual depth (Rd).

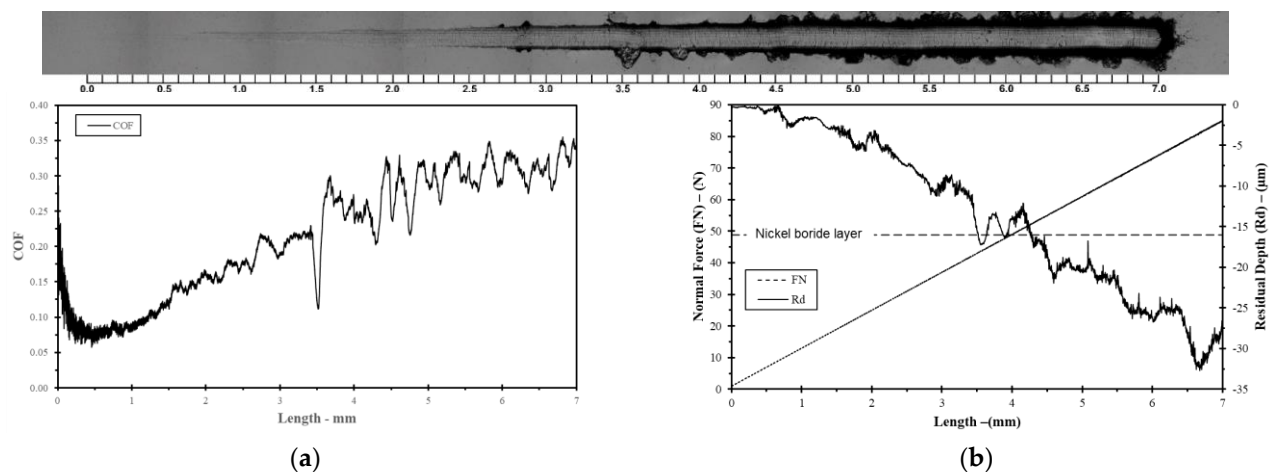


Figure 8. Scratch track length of the Monel 400 borided obtained at 4 h. (a) COF behavior, and (b) normal force (NF) and the residual depth (Rd).

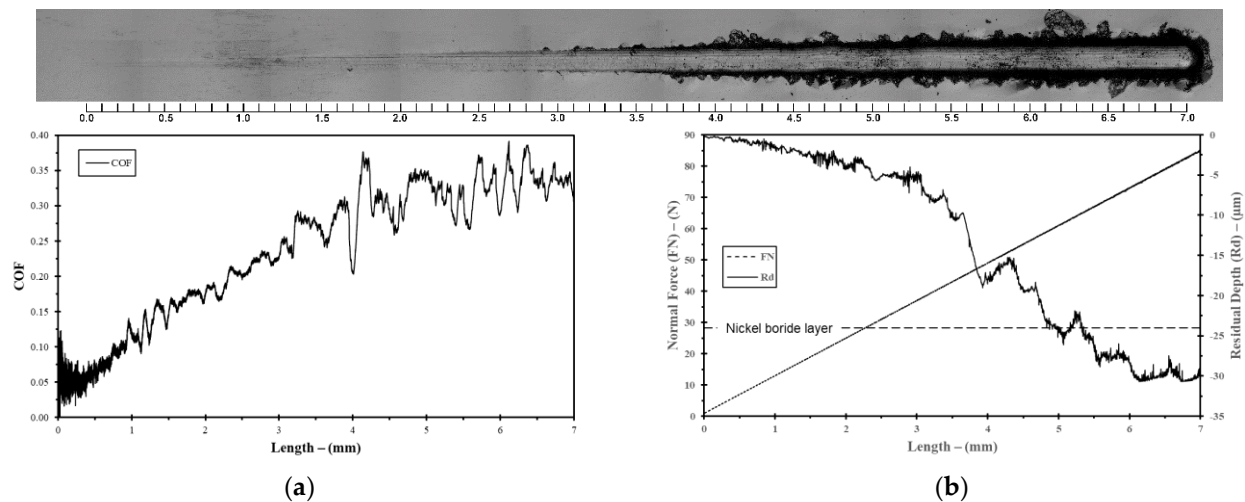


Figure 9. Scratch track length of the Monel 400 borided obtained at 6 h. (a) COF behavior, and (b) normal force (NF) and the residual depth (Rd).

Initially, the indenter moves across the surface of the boronized Monel, generating plastic deformation without detecting cracks or only identifying minor ones that increase with the rise in normal force. It is important to note that COF values reach their peak value, approximately 0.45.

Between COF behavior at 2 h, 4 h, and 6 h of treatment, it was possible to observe that the material's frictional properties evolve over time. For the case of the 2 h Sample (Figure 7a), the COF increases quickly, reaching a maximum value of 0.45 as cohesive damage mechanisms appear. This behavior is related to low residual stress (A compressive state of -0.8 GPa was observed), indicating limited boron diffusion, reduced mechanical resistance, and coating stability under scratch loads evaluated. For the 4 h Sample, the COF shows a more gradual rise, reaching a peak around 0.40 (as was observed in Figure 8a). The boride layer, with a higher and more uniform stress profile (A compressive state of -1.2 GPa was observed), allows better resistance to damage mechanisms like chipping, withstanding higher loads before a significant COF increase is observed. This increase in stress correlates with greater resistance to damage. Finally, for the 6 h Sample at critical loads, the COF in Figure 9a increases to maximum values of 0.42–0.45, where failure mechanisms such as spalling and delamination are observed. These high COF values and elevated residual stresses suggest that while the layer resists initial deformation well, the internal stresses induced by prolonged boriding times may lead to more severe failure under high loads. As was observed, the highest recorded compressive stress was around -1.5 GPa; this sample demonstrates the greatest initial resistance to scratching. However, these residual stress and COF values highlight how optimized boriding times enhance coating durability (failure mechanisms), though extended treatments may introduce internal stresses that increase susceptibility to severe failure modes at higher loads [8].

3.3.2. Adhesion Failure Mechanisms

The failure mechanisms observed in the scratch tests can be classified into two general categories, depending on whether the material layer behaves in a brittle or ductile manner. Different failure modes have been observed and documented in the context of scratch tests on different coated materials [8]. In the case of the nickel boride/substrate system, several types of cracks were identified, including arc tensile cracks, delamination/chipping, and spalling [20].

Critical loads, failure mechanisms, and residual depth estimated over the surface of the worn tracks developed on the nickel boride layer–substrate system are summarized in Table 2. Notice that critical loads were calculated using Equation (1). Also, based on the data the following considerations based on the observations were performed:

- The thickness of the nickel boride layer significantly increases with longer exposure times, reaching values of $7.9 \pm 0.7 \mu\text{m}$, $15.8 \pm 1.2 \mu\text{m}$, and $23.8 \pm 1.6 \mu\text{m}$ for exposure times of 2, 4 h, and 6 h, respectively. This increase in layer thickness indicates enhanced scratch resistance with longer exposure, which is crucial for improving the mechanical properties and durability of the treated system;
- **L_{C1} (Arc Tensile Cracks):** This failure mechanism appears consistently across all exposure times. However, the critical load for initiating arc tensile cracks decreases as the exposure time increases (19.0 N for 2 h, 16.6 N for 4 h, and 14.2 N for 6 h). This downward trend in critical loads suggests that although the layer becomes thicker, it may also accumulate internal stresses that make it more susceptible to this type of cracking under scratch forces;
- **L_{C2} (Chipping):** Chipping occurs at higher critical loads compared to arc tensile cracks, with values of 32.2 N for 4 h and 35.8 N for 6 h. This indicates that the mechanical integrity of the layer is improving with longer exposure times, as it can withstand greater forces before chipping occurs;
- **L_{C3} (Chipping):** Chipping is observed at the highest critical loads, reaching 43.0 N for 4 h and 49.0 N for 6 h. The increase in critical load with extended exposure time suggests that the cohesion between the nickel boride layer and the substrate strengthens over time, making it more resistant to severe damage under mechanical stress;
- The residual depth of the scratch tracks generally increases as the failure mechanisms progress from arc tensile cracks to spalling. For example, at 6 h of exposure, the residual depth increases from $2.3 \pm 0.01 \mu\text{m}$ (L_{C1}) to $18.5 \pm 0.55 \mu\text{m}$ (L_{C3}). This trend indicates that more severe failure mechanisms lead to deeper damage on the surface of the layer, highlighting the importance of optimizing the exposure time to balance mechanical properties and durability.

Table 2. Critical loads, failure mechanisms, and residual depth estimated over the surface of the worn tracks developed on the nickel borided layer-substrate system.

Exposure Time (h)	Nickel Boride Layer (μm)	Mechanism	Failure Mechanism	Critical Load—L _{CN} (N)	Track Length (mm)	Residual Depth (μm)
2	7.9 ± 0.7	L _{C1}	Arc tensile cracks	19.0 ± 0.10	1.5 ± 0.01	2.8 ± 0.02
		L _{C1}	Arc tensile cracks	16.6 ± 0.11	1.3 ± 0.01	2.5 ± 0.02
4	$15.8.0 \pm 1.2$	L _{C2}	Chipping	32.2 ± 0.27	2.6 ± 0.03	7.9 ± 0.11
		L _{C3}	Spalling	43.0 ± 0.33	3.5 ± 0.02	16.0 ± 0.94
6	$23.8.0 \pm 1.6$	L _{C1}	Arc tensile cracks	14.2 ± 0.09	1.1 ± 0.01	2.3 ± 0.01
		L _{C2}	Chipping	35.8 ± 0.22	2.9 ± 0.02	7.2 ± 0.34
		L _{C3}	Spalling	49.0 ± 0.35	4.0 ± 0.03	18.5 ± 0.55

In all repetitions of the experimental set conducted under the critical load (L_{C3}), the friction coefficient of the nickel boride/substrate system remained within the range of 0.15 to 0.45.

The classification of failure mechanisms can generally be approached in two ways, considering whether the layer behaves in a brittle or ductile manner during the scratch test (see Figure 10). The first category involves situations where the layer could be completely removed (brittle failure), while the second category implies that the layer experiences gradual wear [21]. Based on the experimental results obtained, Bull [19] proposed various failure modes as a consequence of scratch testing in coated materials. In the case of the nickel boride/substrate system, the presence of arc tensile cracks was observed at the initial critical loads (up to 35.8 N); these cracks develop as a result of unloading, similar to those reported by [22]. Subsequently, chipping and delamination appear due to the compressive

stresses generated by the movement of the indenter during the last two critical loads, as illustrated in Figures 11 and 12.

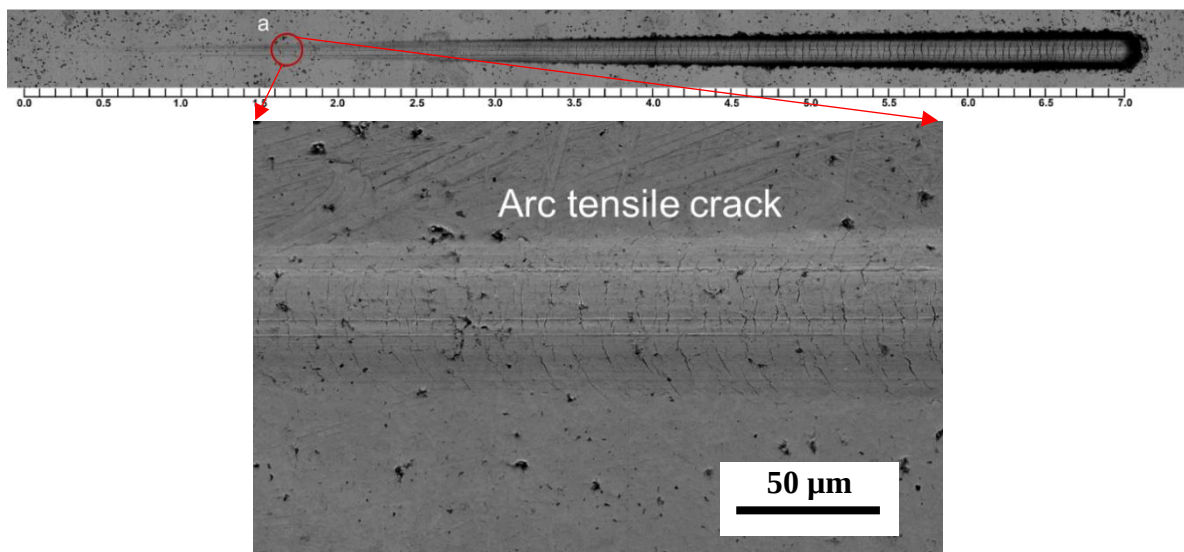


Figure 10. Failure mechanisms obtained over the worn surface for nickel boride layer–substrate system obtained at 1223 K with 2 h.

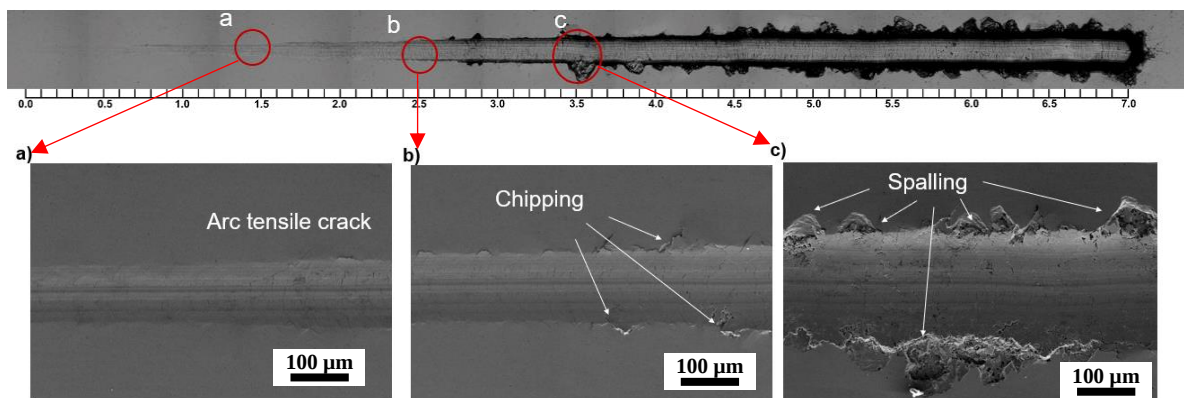


Figure 11. Failure mechanisms obtained over the worn surface for nickel boride layer–substrate system obtained at 1223 K with 4 h.

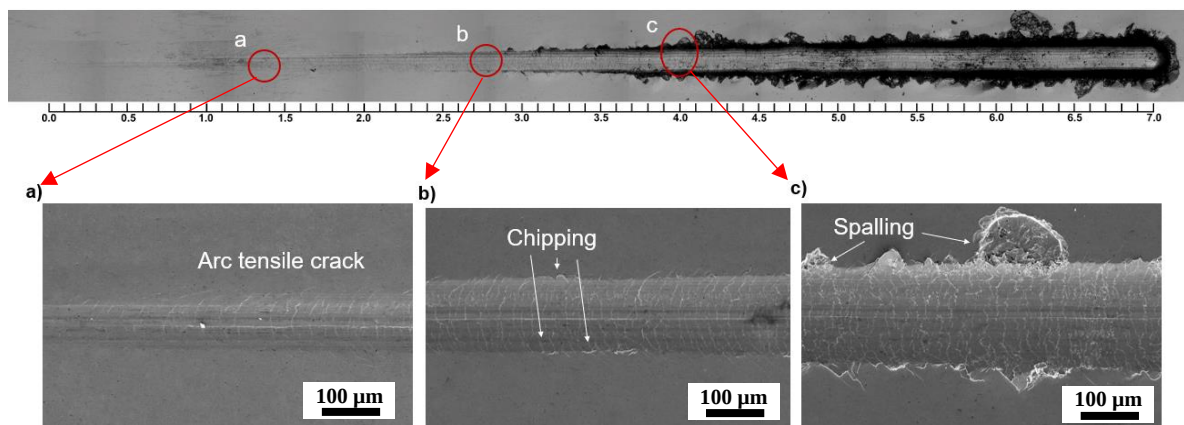


Figure 12. Failure mechanisms obtained over the worn surface for nickel boride layer–substrate system obtained at 1223 K with 6 h.

The critical loads (L_{CN}) were mainly classified into three categories, based on the results obtained from Figures 10–12, as well as Table 2:

- I. In all cases, at the beginning of the scratch tracks for low loads, a series of nested microcracks formed within the groove (see Figure 10a, Figure 11a, and Figure 12a). This type of failure, known as arc tensile cracks (cohesive failure), occurs as a result of the generation of tensile stresses behind the tip of the indenter, where several of these arcs form and propagate from the surface to the substrate. The variation in the COF signal is consistent with the presence of tensile cracks detected on the surface of the layer through SEM and recorded as L_{C1} ;
- II. With a further increase in load, reaching L_{C2} , the COF increases as layer spallation occurs (removal of chips from the layer outside the edge of the track without exposing the substrate). This type of failure (Figure 10, Figure 11b, and Figure 12b) is characterized by the separation of part of the nickel boride layer to minimize the amount of elastic energy stored by the compressive stress generated ahead of the indenter during testing [23];
- III. Delamination of the layer (removal of chips from the layer outside the edge of the track with substrate exposure—adhesive failure) was observed, defining the critical load L_{C3} . Based on Figure 10, Figure 11c, and Figure 12c, delamination developed due to compressive stresses in front of the indenter at the point where the depth of the indenter is almost equal to the thickness of the layer. The compressive stresses are followed by tensile stresses resulting from the deformation of the nickel boride layer, which is independent of the boride layer thickness. The size (or cracking area) of both chipping and delamination was much greater than that of arc tensile cracks, resulting in more pronounced COF values at the point of failure. Finally, the layer was completely removed from the scratch track.

4. Conclusions

The practical adhesion behavior of the boride layer on Monel 400 was thoroughly investigated in this study. The main conclusions are summarized as follows:

1. The powder-pack boriding (PPBP) treatments produced layer thicknesses ranging from approximately 7.9 to 23.8 μm , depending on the exposure time (2, 4, and 6 h) at 1223 K. XRD analysis confirmed the presence of nickel borides, primarily Ni_2B , Ni_4B_3 , and NiB , along with minor Cu inclusions. These phases indicate effective boron diffusion into the Monel 400 substrate, resulting in a well-structured and reinforced surface layer with enhanced mechanical properties;
2. Prolonged boriding times, particularly the treatment at 1223 K with 6 h, were most effective in generating a robust compressive residual stress profile, significantly improving the surface hardness ($\sim 12 \pm 0.3$ GPa) and structural integrity of the boride layer. The 2 h treatment induced a limited residual stress effect, while the 4 h treatment achieved a balanced stress profile and optimal layer thickness (~ 15.8 μm). These results underscore the need to adjust treatment durations based on specific application requirements to maximize compressive stress benefits while maintaining material stability;
3. The nickel boride layer's scratch resistance revealed that extended exposure times increased the layer's resilience against severe failure mechanisms, with critical loads for failure (L_{C1} for arc tensile cracks, L_{C2} for chipping, and L_{C3} for spalling) reaching up to 49 N in the 6 h sample. However, a decrease in critical load for arc tensile cracks suggests a trade-off between layer thickness and the accumulation of internal stresses. The coefficient of friction (COF) stability under critical load conditions indicates reliable mechanical performance, essential for high-stress applications;
4. During scratch tests, the COF and residual penetration depth were strongly correlated with the type and severity of damage in the boride layer. Consistent COF values (0.15 to 0.45) throughout the scratch test suggest that the enhanced surface properties contribute to the resistance against crack propagation and layer detachment under increasing load conditions;

5. Across the experimental conditions, adhesive failures (e.g., chipping and delamination) were observed as scratch loads increased, with the boride layer detaching from the substrate. This highlights the influence of compressive and tensile stresses on adhesion behavior. Balancing layer adhesion and toughness is critical to reducing these failure modes and extending the coated system's operational lifespan in demanding environments;
6. This study confirms the PPBP's effectiveness in enhancing surface hardness, adhesion, and wear resistance. Future research could further optimize layer properties by tailoring characteristics such as thickness, uniformity, and bonding strength. Additionally, finite element analysis (FEA) focusing on the stress distribution within the layer-substrate system would offer valuable insights for applications in diverse operational environments, enhancing the boride layer's functional performance.

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