Elsevier Editorial System(tm) for International Conference on Metallurgical Coatings and Thin Films
Manuscript Draft

Manuscript Number:

Title: Evaluation of Electrochemical Boriding of Inconel 600

Article Type: Full Length Article

Section/Category: Symposia F and G

Keywords: Inconel alloys; electrochemical boriding; tribology

Corresponding Author: Dr. Vivekanand Sista, PhD

Corresponding Author's Institution:

First Author: Vivekanand Sista, PhD

Order of Authors: Vivekanand Sista, PhD; Ozgenur Kahvecioglu, PhD; Guldem Kartal, PhD; Qunfeng Zeng, PhD; Jong H Kim, PhD; Osman L Eryilmaz, PhD; Ali Erdemir, PhD; Servet Timur, PhD

Abstract: Inconel 600 and other nickel-based superalloys are used extensively for a variety of industrial applications involving high temperatures and aggressive environments. They are particularly resistant to high-temperature corrosion and oxidation, and boriding them can further enhance their corrosion resistance and impart much improved tribological properties. In this study, we investigated electrochemical boriding of Inconel 600 in a borax-based molten electrolyte bath at 950°C for a short period (just 15 minutes). This process yielded a very dense, uniform, and hard boride layer of more than 80 μm in thickness. In the boride layer, a variety of boride phases were identified by X-ray diffraction, and the morphology of the borided surfaces was further characterized by optical microscopy. Microhardness measurements across the boride layer indicated very high hardness values (between 1600 and 2100 HV0.1). In pin-on-disk wear tests under dry sliding conditions, the borided surfaces exhibited much superior wear performance compared to the base Inconel alloys (wear depth of 2-2.5 μm vs. 15-16 μm). This study showed that ultra-fast electrochemical boriding of Inconel alloys is feasible, and this method can be considered as a viable alternative to producing hard and protective layers on Inconel 600 by other techniques.

Suggested Reviewers: Prasadd Ayyagari PhD
Fellow, Brunel Centre for Advanced Solidification Technology Department, Brunel University
Prasadd.Ayyagari@brunel.ac.uk

Philip Nash
Materials Mechanical and Aerospace Engineering, Illinois Institute of Technology
nashp@iit.edu

MANUSCRIPT REPORT FORM

PAPER NUMBER (if known): 484

TITLE OF PAPER: Evaluation of Electrochemical Boriding of Inconel 600

CORRESPONDING AUTHOR: Vivekanand Sista

FULL MAILING ADDRESS: Argonne National Laboratory, Energy Systems Division, 9700 S.Cass Ave, Lemont, IL-60527, U.S.A

TELEPHONE: 630-252-1741

FAX: 630-252-5568

E-MAIL: vsista@anl.gov
vivek.sista@gmail.com

AUTHOR'S CERTIFICATION

This is to certify that I have obtained the necessary authorization for publication of the enclosed paper #484 (Evaluation of Electrochemical Boriding of Inconel 600) in the Proceedings of the ICMCTF 2012 Conference and in *Surface and Coatings Technology/Thin Solid Films* and that the paper is original and unpublished and is not being considered for publication elsewhere.

Corresponding Author

Vivekanand Sista

Argonne National Laboratory

Highlights

- Electrochemical boriding has been performed to form very hard, dense and homogeneous boride layers on Inconel 600.
- In 15min process duration resulted in very thick boride layers.
- Triboloigcal properties of borided Inconel 600 were superior to the unborided Inconel 600.
- Ni_2B and Ni_3B phases were obtained as the predominant phases on top of the borided surfaces.

*Manuscript

Evaluation of Electrochemical Boriding of Inconel 600

V. Sista[a], O. Kahvecioglu[b], G. Kartal[b], Q.Z. Zeng[c], J.H. Kim[a], O.L. Eryilmaz[a], A. Erdemir[a] and S. Timur[b]

[a] **Argonne National Laboratory, Energy Systems Division, Argonne, IL, USA**

[b] **Istanbul Technical University, Department of Metallurgy and Materials Engineering, Istanbul, Turkey**

[c] **Xian Jiaotong University, School of Materials Science and Engineering, Xi'an, Shaanxi, China**

Abstract

Inconel 600 and other nickel-based superalloys are used extensively for a variety of industrial applications involving high temperatures and aggressive environments. They are particularly resistant to high-temperature corrosion and oxidation, and boriding them can further enhance their corrosion resistance and impart much improved tribological properties. In this study, we investigated electrochemical boriding of Inconel 600 in a borax-based molten electrolyte bath at 950°C for a short period (just 15 minutes). This process yielded a very dense, uniform, and hard boride layer of more than 80 μm in thickness. In the boride layer, a variety of boride phases were identified by X-ray diffraction, and the morphology of the borided surfaces was further characterized by optical microscopy. Microhardness measurements across the boride layer indicated very high hardness values (between 1600 and 2100 $HV_{0.1}$). In pin-on-disk wear tests under dry sliding conditions, the borided surfaces exhibited much superior wear performance compared to the base Inconel alloys (wear depth of 2-2.5 μm vs. 15-16 μm). This study showed that ultra-fast electrochemical boriding of Inconel alloys is feasible, and this method can be considered as a viable alternative to producing hard and protective layers on Inconel 600 by other techniques.

Keywords: Inconel alloys, electrochemical boriding, tribology

1. Introduction

Nickel-based superalloys are used for a wide variety of demanding industrial applications like pumps, ball valves, pneumatic transport systems, high temperature fasteners, boilers, nuclear reactors, plungers for the glass industry, and turbine blades of aircraft engines [1]. They provide excellent resistance against harsh environments involving high temperatures, acidic and saline media, hot corrosion, and oxidation [1]. However, due to their high nickel content, these alloys are relatively soft and hence susceptible to abrasive, erosive, and adhesive wear damage [2]. In particular, galling, abrasion, and adhesive wear of the nickel-based superalloys may readily occur under unlubricated and severe loading conditions and limit their applications in tribology. The problems associated with nickel-based superalloy components arise due to their exposure to high temperatures and aggressive environments, in which the protective oxidation-resistant layer becomes damaged, and even under moderate contact pressures, the components tend to seize, gall, or experience fretting wear [1,3-5].

The wear resistance of nickel-based superalloys can be enhanced further by applying hard coatings (e.g., TiN-, ZrN-, and CrN-based coatings), which are already used on gears, bearings, and ball valves made from Inconel 718 [6]. Coating techniques include chemical vapor deposition (CVD) [7], physical vapor deposition (PVD) [8,9], and plasma assisted chemical vapor deposition (PACVD). However, long processing times (typically 12 h) and the unfavorable costs of the above-mentioned techniques make them less than ideal, especially when a relatively thick (i.e., 10 to 15 μm) and hard coating is needed to combat abrasive or erosive wear and achieve durability for the intended applications.

Besides the PVD and CVD coating processes, a wide variety of thermochemical surface treatments or thermal diffusion processes (like carburizing, nitro-carburizing, nitriding, and boriding treatments) are available for the enhancement of the surface metallurgical and tribological properties of most industrial components [10]. Among these processes, boriding offers excellent potential to achieve much higher hardness with a thick, dense, and homogeneous layer [11] that is resistance to wear, corrosion, and oxidation [12]. Since the boride layer is produced by a diffusion-based conversion process and is not an add-on coating like that produced by PVD or CVD, adhesion to the substrate is expected to be very strong, and hence, delamination will not be a major concern. Boriding (or boronizing) can be done in numerous ways, including powder pack, molten salt, laser, fluidized bed, plasma, electrochemical processes [10, 13, 14]. Among these, pack boriding has been found to be attractive and is prevalent in today's industry for the boriding of certain nickel-based superalloys for aerospace applications. Boriding is a thermal diffusion process in which the boron atoms are extracted from boron-containing media and deposited onto the specimen surface. Thereafter, the boron atoms diffuse into the substrate, resulting in the formation of mixed boride phases that are typically much harder and more wear resistant than the base metals or alloys [15]. In the case of nickel-based superalloys, electrochemical boriding has been shown to produce a very thick and dense layer of nickel and iron borides in a very short duration in intermetallics and steel [16–18].

In the present study we investigate the ultra-fast electrochemical boriding of Inconel 600 alloy and its tribological properties, especially in terms of wear under dry sliding conditions. To our knowledge, the electrochemical boriding of Inconel 600 has not been reported in the open literature. Due to the very long processing times, energy intensiveness, high cost, and large amounts of greenhouse and toxic gas emissions (especially fluorine), conventional boriding

processes are not well-suited for the Inconel alloys used in aerospace and defense applications [19–22]. Additionally, with conventional boriding, there are issues related to the spallation and extensive crack formation of the boride layers after the boriding operation due to the difference in the coefficients of thermal expansion and very high residual stresses [23]. In this study, we concentrated on the electrochemical boriding of Inconel 600 and its mechanical and tribological properties so as to demonstrate the ultrafast nature of this process compared to conventional boriding practices. In our boriding experiments, we were able to produce up to 80-µm-thick boride layers in about 15 min at a current density of 200 mA/cm^2. The boride layers show excellent adhesion to the substrate compared to the 50-µm-thick boride layer achieved in 10 h with conventional pack boriding [1]. Additionally, the wear resistance increased dramatically compared to the original substrate, ensuring long-term durability under harsh operating conditions. Due to its electrolytic nature, this process also does not result in any gaseous emissions, and the boride layers formed are very dense and hard. Accordingly, it holds high prospects for large-scale application with nickel-based superalloy materials.

2. Experimental

Commercially available Inconel 600 plates (nominal composition of Ni 72 wt.%, Cr 14-16 wt.%, and balance Fe) were obtained from a commercial source, and they were cut into 1.5”x1.5”x0.5”rectangular test coupons to fit into our electrochemical boriding unit. The Inconel samples were ground and polished to 1200 grit size SiC emery papers to remove the surface oxide layers and other contaminants from the surface. The samples were then ultrasonically cleaned in acetone for 5 min. The electrochemical boriding experiments were carried out in molten borax based (90% $Na_2B_4O_7$ + 10% Na_2CO_3) electrolyte in a SiC crucible at 950°C and a

current density of 200 mA/cm^2. The Inconel specimens acted as the cathode while two graphite plates served as the anodes. The details of the experimental procedure and equipment used can be found in our previous papers [16, 17]. To evaluate the tribological properties of unborided and borided surfaces, both 9.5-mm dia ball and 1.5”x1.5”x0.5”flat samples were cleaned with acetone in order to remove contaminants on the surface. Tribological tests were performed with a ball-on-disk friction and wear test machine at room temperature and a relative humidity of 45%. All tests were conducted for a total sliding distance of 230 m with a sliding speed of 63 mm/s under a normal load of 10 N (corresponding to a maximum Hertzian contact pressure of 1 GPa).

After the friction test, the wear scar diameter and 3D morphology were measured using a Olympus STM6 optical microscope and MICROXAM surface mapping microscope, respectively. The wear volumes of the flat samples were determined from the width of the wear scars and cross-sectional images of the wear track. The cross-sectional morphology of the boride layers was determined with the Olympus STM6 optical microscope. The phases of the boride layers were investigated by a Philips Xpert2 diffractometer with Cu-Kα radiation of 1.54 Å wavelength. Regular 2θ-ω and glancing angle scans were performed to determine the phases on the top and in the depth of the boride layers. Microhardness measurements were carried out using Wilson/Tukon equipment (Model 300) with a 100 g load. Daimler-Benz adhesion tests were performed to attain qualitative information on the adhesive strength of the boride layers to the base alloy. For this purpose we used a Rockwell C indenter and a 150 kg load, as prescribed in Ref. [24].

3. Results and Discussion

3.1. Morphology and thickness of the boride layers

The cross-sectional morphologies of boride layers formed on Inconel 600 alloys were examined by optical microscopy. Figure 1 shows the optical images of the boride layers formed for different process durations. The structure of the boride layers looks very dense and homogeneous. Unlike boride layers produced by conventional methods, it does not have a dendritic or tooth-like structure [22, 25]. Note that even after 5 min of boriding, a 30-µm-thick boride layer is produced by the current process. The boride layer thickness reaches 81 µm after 15 min of boriding, demonstrating the ultra-fast nature of the electrochemical boriding method used in our study.

Figure 2 is a plot of the thickness of the boride layer with respect to the boriding time. It reveals a nearly linear trend up to the boriding time period covered. These samples were borided at 950°C and a current density of 200 mA/cm^2. Boriding of Inconel alloys by pack boriding yields a 50-µm layer in 10 h at 950°C [1], which is a growth rate of 0.083 µm/min. By comparison, a 81-µm layer was produced by electrochemically boriding in 15 min at 950°C, yielding a growth rate of 5.4 µm/min. The industrial requirement for the thickness of the boride layer on Inconel alloys for many applications is around 50 µm, which can be achieved in 10 min by the method used in our study as opposed to 10 h in the case of conventional pack boriding.

For most industrial applications, a huge concern is spallation of the boride layers from the surface due to cyclic thermal and/or mechanical loading. In the case of electrochemical boriding, spallation occurs after boriding of the sample for more than 15 min at 950°C and 200 mA/cm^2 and then soaking it in the melt (applied current having been terminated) for an additional 1 h. This practice results in the remaining boron on the surface diffusing into the substrate and forming much thicker boride layers, especially in the case of steels [22]. However, as shown in Figure 3, such a post-processing or soaking treatment results in partial spallation or delamination

of the boride layer from the Inconel surface. This problem occurs because all boride forms of nickel are primarily brittle due to the difference in the coefficients of thermal expansions in the respective nickel borides. Another potential reason could be the high residual stresses within the mixed boride phases. This is one more reason why electrochemical boriding is superior to pack boriding: with the former we can control the synthesis parameters effectively to obtain a desired boride layer thickness needed for certain industrial applications, while with the latter, the sample must be borided for substantially longer processing times. Thus, for an optimum boriding operation, the post-processing or soaking period should be avoided in electrochemical boriding; otherwise, undesirable spallation or delamination may occur, as shown in Fig. 3.

3.2. X-ray diffraction studies

X-ray diffraction (XRD) studies of the untreated and borided Inconel 600 samples (at 950°C for different durations) were carried out using CuKα (λ = 1.54 Å) radiation by applying the regular 2θ-ω and glancing angle (1°) scan procedure; the resulting XRD profiles are shown in Figs. 4 and 5, respectively. In Table 1, the crystallographic characteristics of nickel and some of its borides are given to interpret the results obtained from the XRD studies.

Based on the XRD data, we concluded that the top boride layer is composed of multiple boride phases of Ni. Within the outermost or top layer, Ni_2B and Ni_3B phases exist as the most prevalent phases. These phases have tetragonal and orthorhombic crystal structures, respectively. The weight ratio of Ni_2B to Ni_3B is higher for the sample borided for 15 min and then held for 1 h in the electrolyte. The spallation of the boride layer from the surface might have been associated with the increased formation or presence of Ni_2B and perhaps with its crystal structure and the coefficient of thermal expansion difference between the Inconel 600 substrate (11.4 x 10^{-6}/°C) and the two borides: Ni_2B (7.64 x 10^{-6}/°C), Ni_3B (7.9 x 10^{-6}/°C) [26, 27]. The major

element (Ni) in the base alloy has a cubic crystal structure (Table 1). During boriding, this structure transforms to various nickel borides with different crystallographic orientation, structure, and proportion. It is known that a coating is durable when the atoms are oriented in the same direction and build up in the same crystal network. Deviation from the textural frame decreases the mechanical strength of the multiple boride phases due to the lattice strains when formed together [28]. Therefore, spallation can easily be detected, as there are internal stresses between the boride phases. Spallation was also detected in the adhesion tests, which will be discussed later.

3.3. Rockwell C adhesion and Vickers hardness tests

To evaluate the adhesion characteristics of the thick boride layers formed on Inconel alloy, we conducted Rockwell C indentation tests on borided surfaces according to the protocol prescribed by the Daimler-Benz methods. The results are shown in Fig. 6. As evident from Figs. 6a and 6b, there was no evidence of delamination or crack network formation, and excellent adhesion with a thick and homogeneous layer forming after very short durations of boriding. When the time of boriding was increased with the soaking time of 1h, the adhesion tests resulted in a gross delamination. Spallation occurs for longer duration of electrolysis and diffusion times due to the thermal expansion difference between Ni_2B and Ni_3B, as well as the brittleness of the nickel boride phases.

Based on the indentation results, 5 and 15 min of boriding results in almost no delamination, which fits the HF1 category, whereas the 15 min boriding with one-hour soaking indicated cracks and gross delamination, which fits the HF5 category with respect to the Daimler–Benz adhesion chart due to the presence of brittle nickel borides.

The hardness of the boride layers was measured by using a Vickers micro-hardness machine with a load of 100 g. The cross-sectional indentation marks and the hardness profiles are shown in Figs. 7 and 8, respectively. The hardness of base Inconel 600 substrate was around 200 HV. However, different regions in the thick boride layers exhibited different hardness values depending on the phases where the measurement was taken. The outer layer, which was determined by XRD to consist primarily of nickel borides, had hardness values ranging from 1600 HV to 2100 HV when a 100 g load was used.

3.4. Tribological characterization

Fig.9 shows the variations in the friction coefficients of the unborided and borided surfaces under dry sliding conditions against an alumina ball. The unborided Inconel surface against Al_2O_3 exhibited the highest friction coefficient (≈0.8) at the beginning of the test. Toward the middle, the friction coefficient decreased slightly to 0.7 but increased again to ≈0.8 toward the end of the test. The friction coefficients were 0.65 for 15-min boriding and 0.7 for 15-min boriding plus 1-hour soaking; these friction coefficients are lower compared to those of the unborided samples. These high values in friction result from a combination of adhesive and abrasive wear interactions during the sliding contacts. Specifically, adhesive interactions may be more dominant for un-borided Inconel slid against Al_2O_3, while hard and abrasive wear particles trapped at the sliding interface dominate for borided Inconel slid against Al_2O_3. In fact, some metallic-looking Inconel material had transferred to the ball side, as shown in Fig. 10a, confirming that adhesive interaction between original and transferred Inconel was perhaps occurring and creating higher friction. For the borided Inconel tests, we could not see any evidence of adhesive material transfer; instead, we observed some debris particles in and around

the contact spots on the ball side as well as deep scratches on the flat side, suggesting that severe plowing or scratching due to abrasive wear particles had occurred (see Figs. 10b and 10c).

Although these unborided and borided Inconel samples have similar friction coefficients, wear on the flat samples differed after the tribological tests. The optical micrographs of the worn surfaces for both the ball and the flat side reveal that the borided surfaces had much lower wear damage compared to the unborided surfaces. Visual examination of Figs. 10b and 10c revealed that boriding for 15 min resulted in lesser wear compared to boriding of 15 min with the additional 1-hour soaking treatment. We attributed this difference to the sporadic spallation of the nickel borides in the soaking treatment compared to boriding by itself. All three surfaces in Fig. 10 showed grooved features, demonstrating the two-body wear mechanism. Figure 10a indicates that the unborided Inconel 600 surface was completely worn out compared to the borided surfaces (Figs. 10b and 10c), with the load being 10 N. The borided surfaces (Figs. 11b and 11c) had the least wear depth compared to the unborided surface (Fig. 11a). Interestingly, the borided surface with 1-hour of soaking (Fig. 11c) had more wear compared to the borided surface without that treatment (Fig. 11b). Furthermore, the measured wear volumes for the unborided and borided surfaces on Inconel alloys show a remarkable difference, as apparent in Fig. 12. The measured wear volume is 7.2×10^7 μm^3 for the unborided Inconel, but much less for the borided surfaces, approximately 1.7×10^6 μm^3. Furthermore, the wear loss after the 15-min boriding (1.7×10^6 μm) is lower than that of the sample with the soaking treatment, which is 6.2×10^5 μm^3. This difference is due to the latter surface spalling off due to the brittleness of nickel borides and the difference in coefficients of thermal expansion.

4. Conclusions

Electrochemical boriding of Inconel 600 can be performed in 5 to15 min and results in a nominal boride layer thickness of 30 to 80 μm, as opposed to a 10-h long process that produces a 50-μm boride layer in the conventional pack boriding technique currently used by industry. The boride layers formed by electrochemical boriding were denser, more homogeneous, and more adherent to the base alloy compared to the pack-borided Inconel surfaces, which often suffer from premature delamination or spallation failures. The boride layers consisted of different types of nickel borides, and they were much harder than the unborided Inconel substrate, 1600-2100 HV vs. 200 HV.

The spallation of the layers in the soaking process may be attributable to some micro cracking in the boride layers due to differences in thermal expansion between the Inconel 600 substrate (11.4×10^{-6}/°C) and the two boride layers: Ni_2B (7.64×10^{-6}/°C) and Ni_3B (7.9×10^{-6}/°C) [26, 27] . We also believe that the spallation may be due to the high residual stresses produced while cooling down the sample from 950°C.

In sum, the tribological properties of the nickel boride layers compared to the unborided surfaces were far superior. As much as two orders of magnitude reduction in wear volume was attained after electrochemical boriding of Inconel 600 compared to the unborided Inconel in dry conditions.

Acknowledgments

The authors would like to thank the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, ITP, under Contract Number DE-AC02-06CH11357 with the U.S. Department of Energy for supporting this work. They would also like to thank Frederick Seitz, Materials Research Laboratory Central Facilities, University of Illinois, for performing the

X-ray diffraction study. Finally, the authors would like to thank Gerald Jeka for doing the microscopy imaging and helping in sample preparation

References

[1] W. Muhammad, K. Hussain, A. Tauqir, A. Ul Haq, and A.Q. Khan, Metall. Trans. A. 30A (1999) 670.

[2] D. Curtis, Mater. Design 14 (1993) 349.

[3] P. Goeuriot, F. Thevenot, and J.H. Driver, Thin Solid Films 78 (1981) 67.

[4] K. Stewart, Adv. Mater. Proc. 151 (1997) 23.

[5] A.K. Sinha, ASM Handbook, Heat Treating, American Society for Metals, Metals Park, OH, 1991, p. 437.

[6] J.A. Sue and T.P. Chang, Surf. Coat. Technol. 76-77 (1995) 61

[7] P.A. Steinmann and H.E. Hintermann, J. Vac. Sci. Technol. A 3 (6) (1985) 2394.

[8] E.J. Bienk, H. Reitz, and N.J. Mikkelsen, Surf. Coat. Technol. 76–77 (1995) 475.

[9] M. Stoiber, M. Panzenbock, C. Mitterer, and C. Lugmair, Surf. Coat. Technol. 142–144 (2001) 117.

[10] P. Gopalakrishnan, P. Shankar, M. Palaniappa, and S.S. Ramakrishna, Metall. Trans. A 33A (2002) 1475.

[11] S. Sen, U. Sen, and C. Bindal, Surf. Coat. Technol. 191 (2005) 274.

[12] K. Genel, Vacuum 80 (2006) 451.

[13] J. Lubas, Surf. Rev. Lett. 16 (5) (2009) 767.

[14] V. Sista, P. Nash, and S. Sahay, J. Mat. Sci. 42 (2007) 9112.

[15] A.G. Matuschka, Boronizing, Hanser and Heyden, Germany, 1980, p. 11.

[16] O. Kahvecioglu, V. Sista, O.L. Eryilmaz, A. Erdemir, and S. Timur, Thin Solid Films 520 (2011) 1575.

[17] V. Sista, O. Kahvecioglu, O.L. Eryilmaz, A. Erdemir, and S. Timur, Thin Solid Films 520 (2011) 1582.

[18] A. Greco, K. Mistry, V. Sista, O. Eryilmaz, and A. Erdemir, Wear 271 (2011) 1754.

[19] N. Ueda, T. Mizukoshi, K. Demizu, T. Sone, A. Ikenaga, and M. Kawamoto, Surf. Coat. Technol. 126 (2000) 25.

[20] Dong Mu, Bao-luo Shena, Chao Yanga, and Xin Zhaoc, Vacuum 83 (2009) 1481.

[21] K.G. Anthymidis, P. Zinoviadis, D. Roussos, and D.N. Tsipas, Mater. Res. Bull. 37 (2002) 515.

[22] G. Kartal, S. Timur, V. Sista, O.L. Eryilmaz, and A. Erdemir, Surf. Coat. Technol. 206 (2011) 2005.

[23] M. D. Smolin, V. G. Grebenkina, Yu. M. Goryachev, E. I. Shvartsman, and L. I. Panov, Powd. Metall. Met. Ceram. 23 (1984) 405.

[24] Metals -- Mechanical Testing; Elevated and Low-Temperature Tests; Metallography, American Society for Testing and Materials, Vol. 0301.

[25] G. Kartal, O.L. Eryilmaz, G. Krumdick, A. Erdemir, and S. Timur, App. Surf. Sci. 257 (2011) 6928.

[26] V. Hauk and H. Behnken, Structural and Residual Stress Analysis by Nondestructive Methods, Elsevier Science, 1997, p.187.

[27] S. Raju, K. Sivasubramanian, R. Divakar, G. Panneerselvam, A. Banerjee, E. Mohandas, and M.P. Antony, J. Nucl. Mat. 325 (2004) 18.

[28] A. Kelly and K.M. Knowles, Crystallography and Crystal Defects, 2nd edition, John Wiley and Sons, 2012, p.222.

List of Figures

Figure 1. Cross-section morphology of boride layers after (a) 5 min, (b) 10 min, (c) 15 min at 200 mA/cm^2.

Figure 2. Variation of total boride layer thickness with process duration at 950 °C.

Figure 3. Cross-sectional optical micrograph of the spalled boride layer borided at 950°C for 15 min with 1 h of soaking time.

Figure. 4. XRD profiles (regular 2θ–ω scans) of Inconel 600 alloys after (a) 15 min boriding and 1-h hold and (b) 15 min boriding and (c) base material.

Figure. 5. XRD profile (with glancing angle of 1°) of Inconel 600 alloys after (a) 15 min boriding and (b) 15 min boriding and 1-h hold at 950°C in borax-based electrolyte.

Figure. 6. Differential interference optical microscopy images of Rockwell C indentation marks on substrates borided at 950°C for (a) 5 min, (b) 15 min, and (c) 15 min plus 1-h hold in borax-based electrolyte.

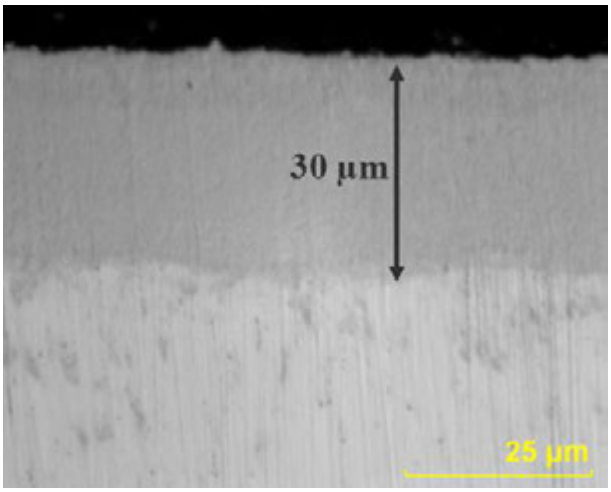
Figure 7. Cross-sectional micro-indentation marks (100 g load) of Inconel 600 alloy after (a) 15 min of boriding and (b) 15 min of boriding plus 1-h hold at 950°C.

Figure. 8. Cross-sectional hardness profiles from surface to matrix: (a) 15 min of boriding and (b) 15 min of boriding plus 1-h hold at 950°C.

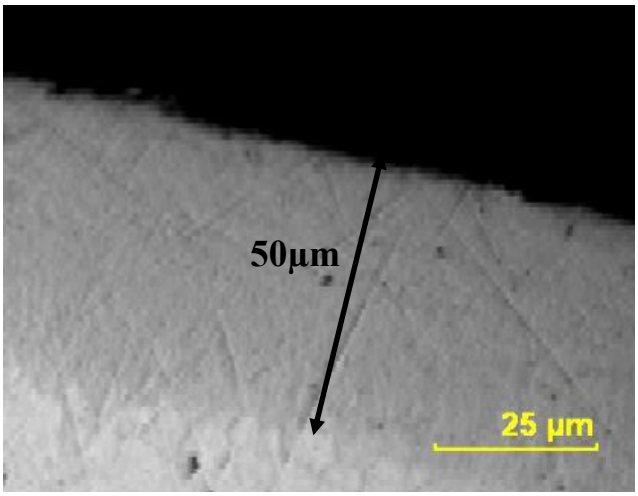
Figure 9. Variation of friction coefficients of Al_2O_3 balls during sliding against unborided and borided Inconel as a function of sliding distance.

Figure 10. Wear images of surfaces on ball and Inconel in dry air: (a) unborided Inconel alloy, (b) 15 min boriding, and (c) 15 min boriding plus 1-h hold.

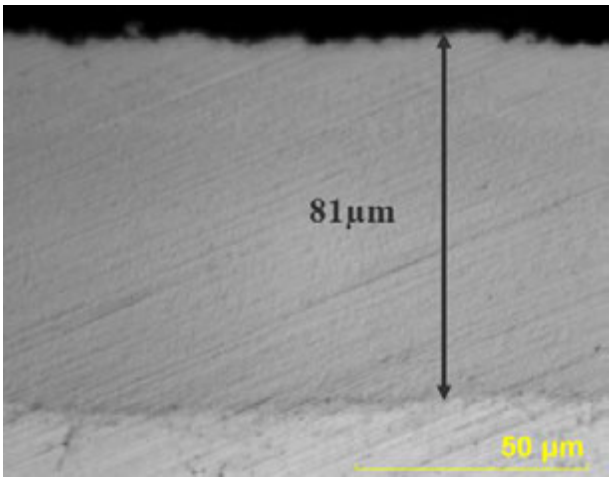
Figure1



(a)



(b)



(c)

Figure2

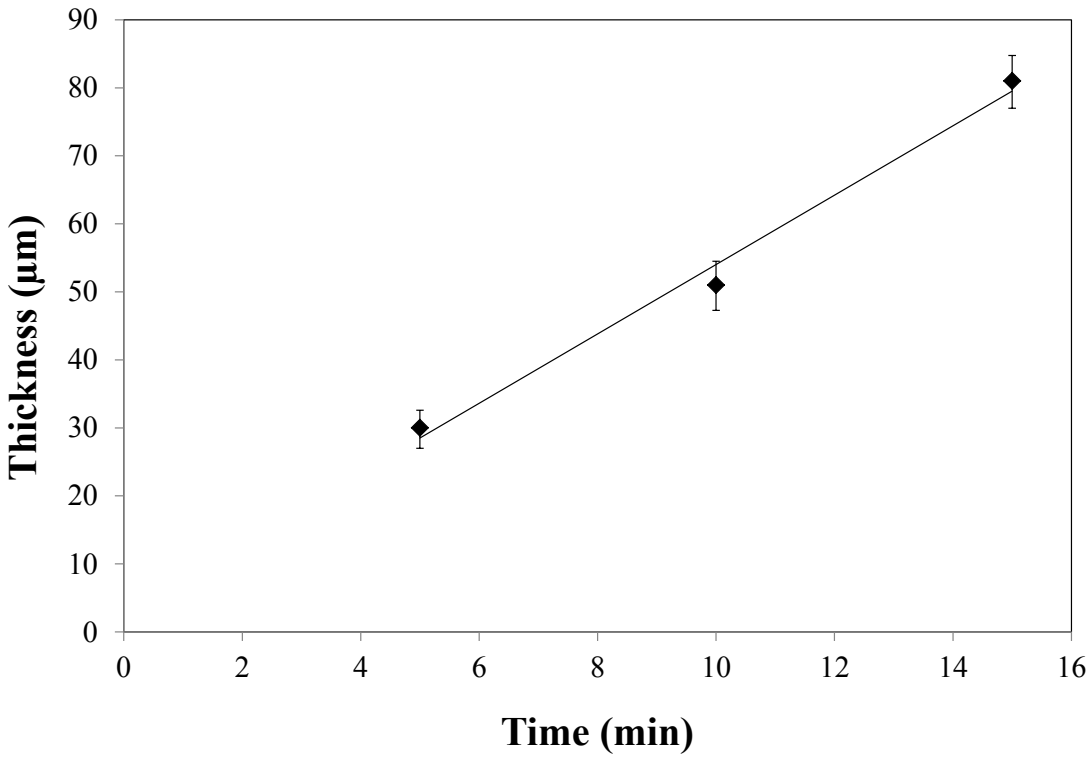

Thickness (µm)
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
Time (min)

Figure3

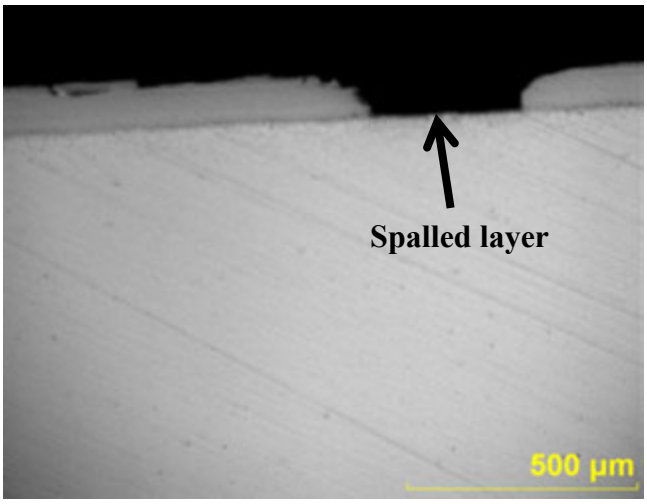


Figure4

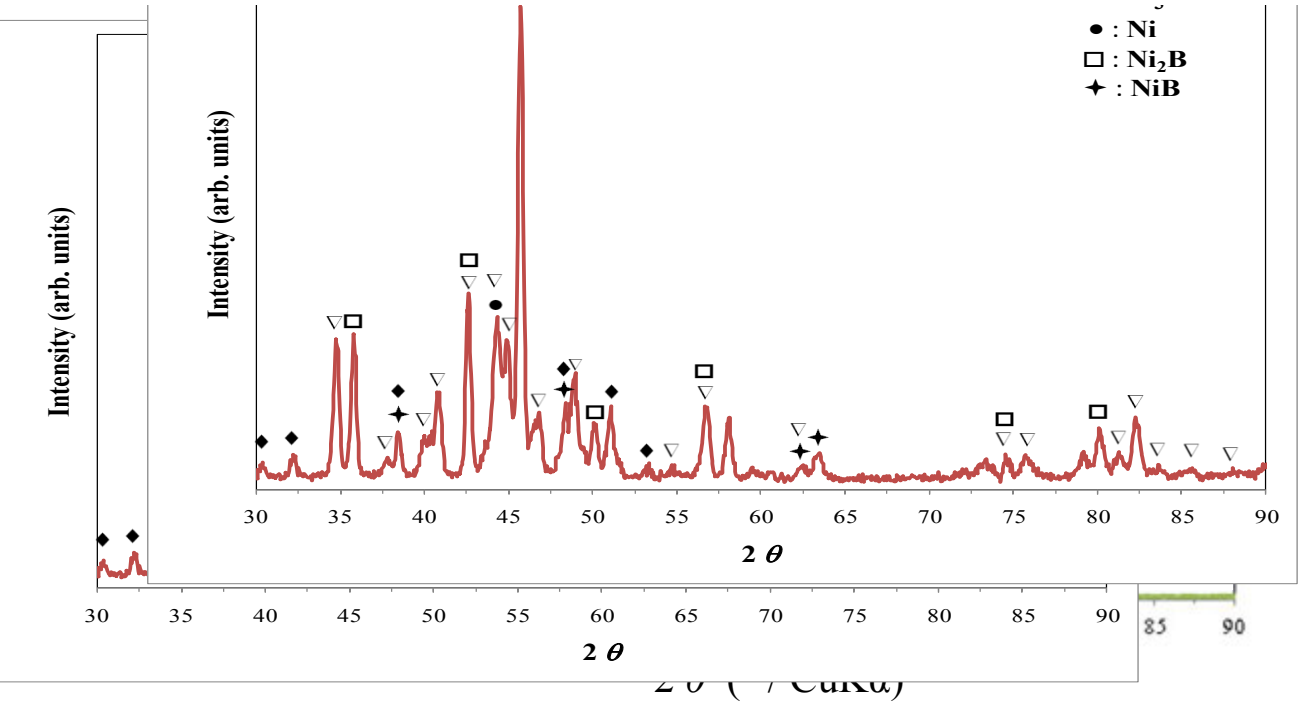
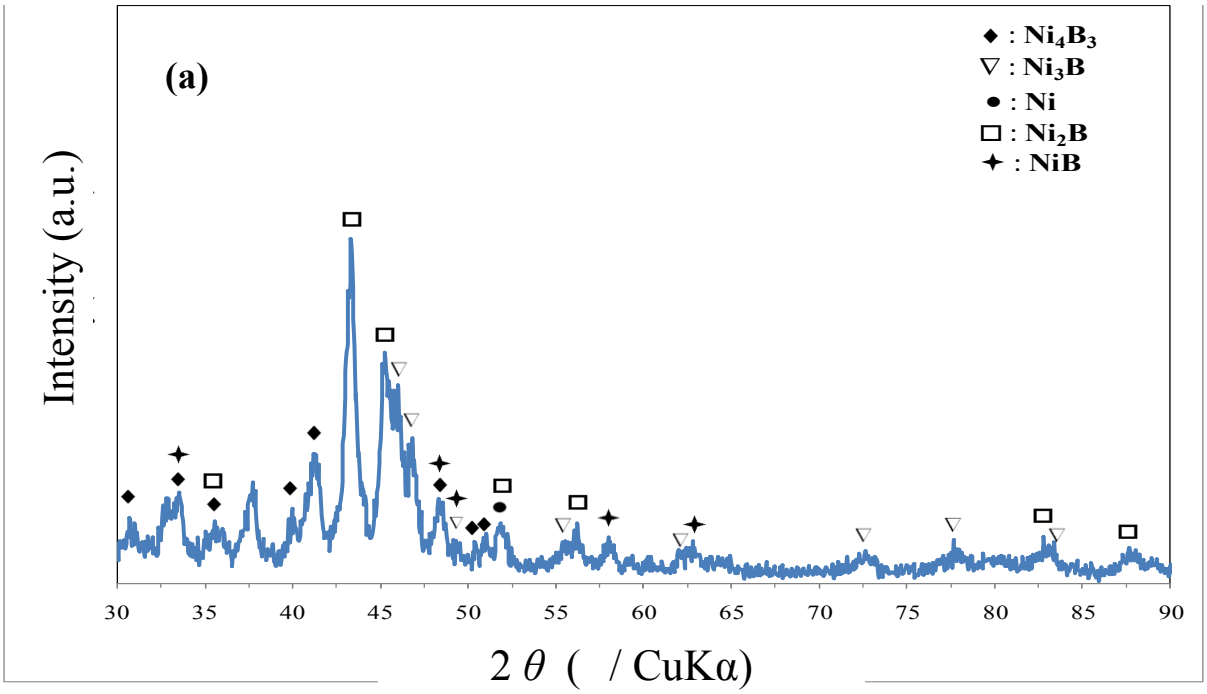

Intensity (arb. units)
2 θ
30 35 40 45 50 55 60 65 70 75 80 85 90
Intensity (arb. units)
2 θ
30 35 40 45 50 55 60 65 70 75 80 85 90
● : Ni
□ : Ni2B
✦ : NiB

Figure5


(a)
◆ : Ni_4B_3
▽ : Ni_3B
● : Ni
□ : Ni_2B
✦ : NiB
Intensity (a.u.)
30 35 40 45 50 55 60 65 70 75 80 85 90
2 θ (/ CuKα)

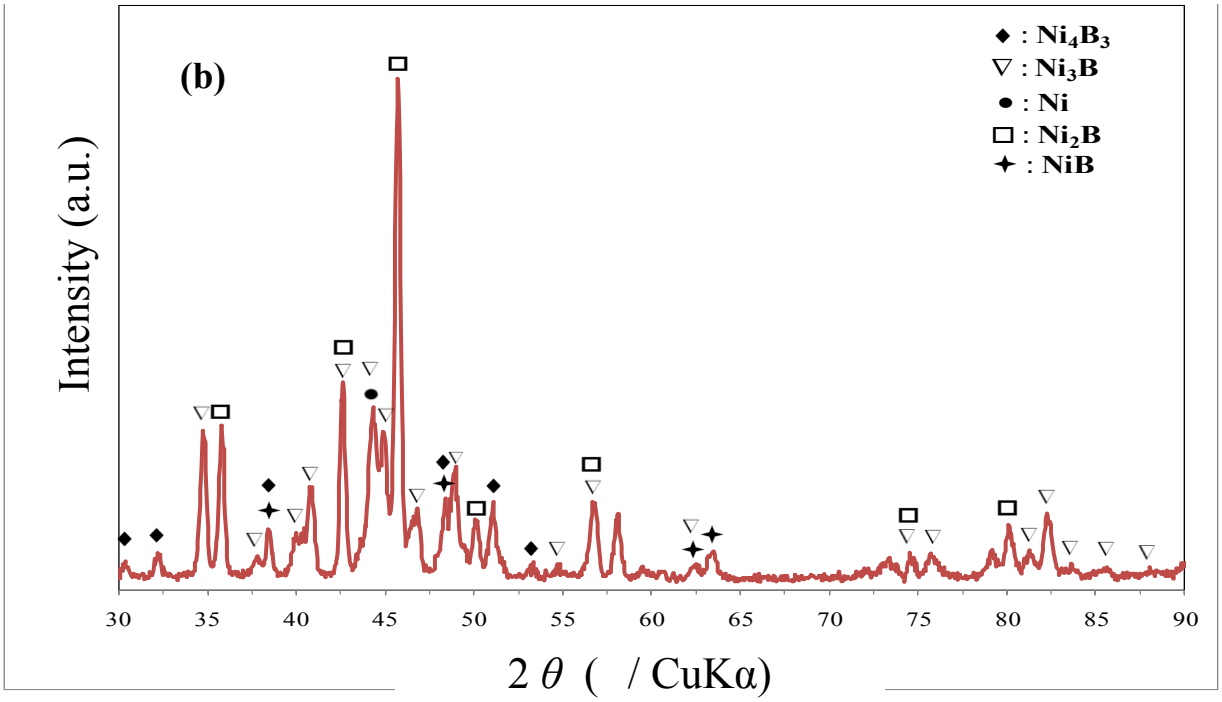
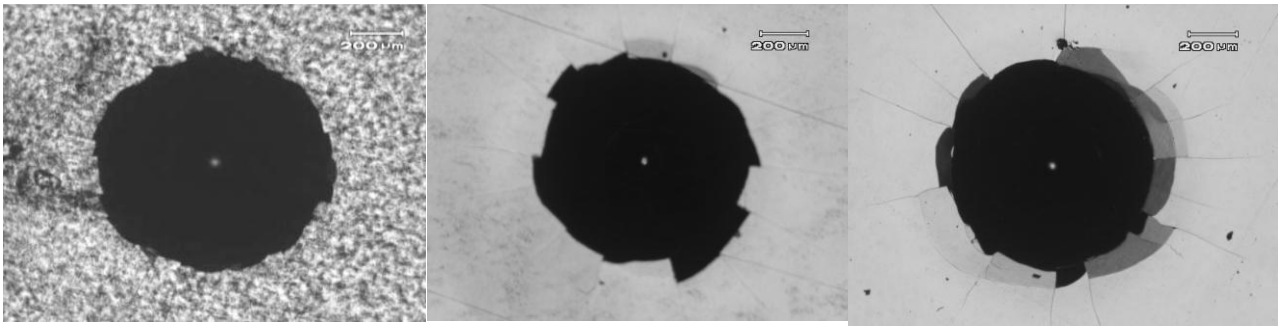
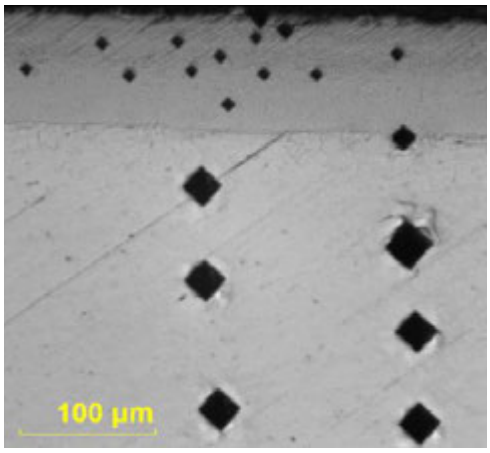

(b)
◆ : Ni_4B_3
▽ : Ni_3B
● : Ni
□ : Ni_2B
✦ : NiB
Intensity (a.u.)
30 35 40 45 50 55 60 65 70 75 80 85 90
2 θ (/ CuKα)

Figure6

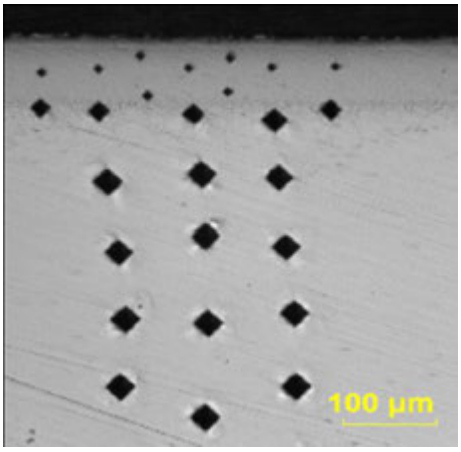


(a) (b) (c)

Figure7

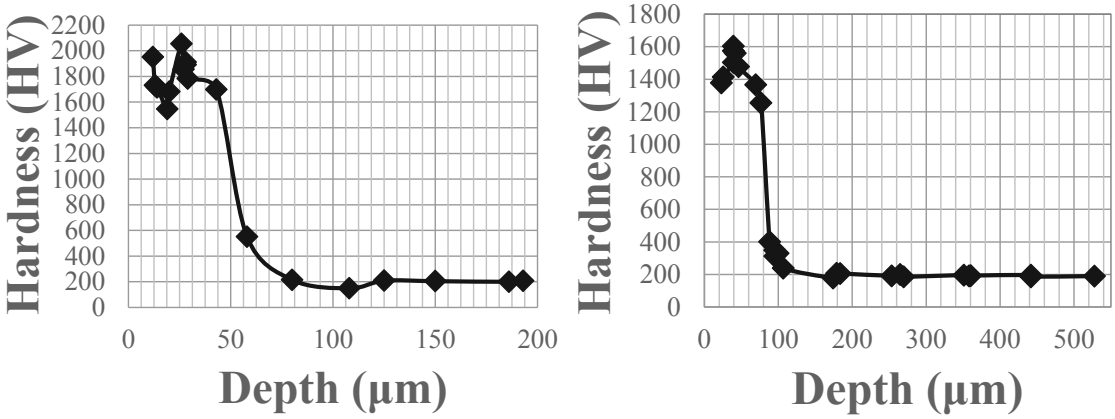


(a)



(b)

Figure8


Hardness (HV)
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Depth (μm)
Hardness (HV)
1800
1600
1400
1200
1000
800
600
400
200
0
0
100
200
300
400
500
Depth (μm)

(a) (b)

Figure9

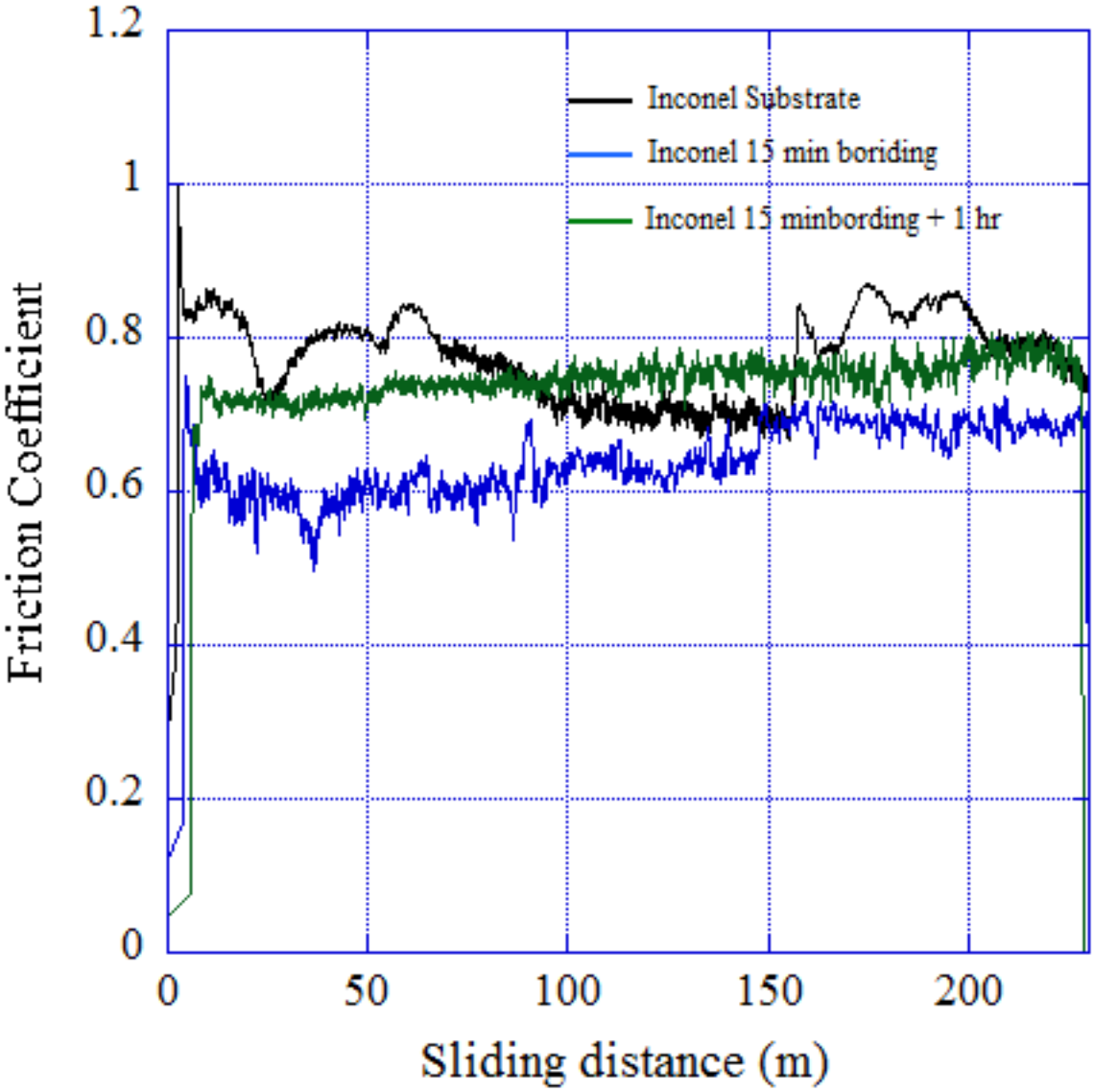
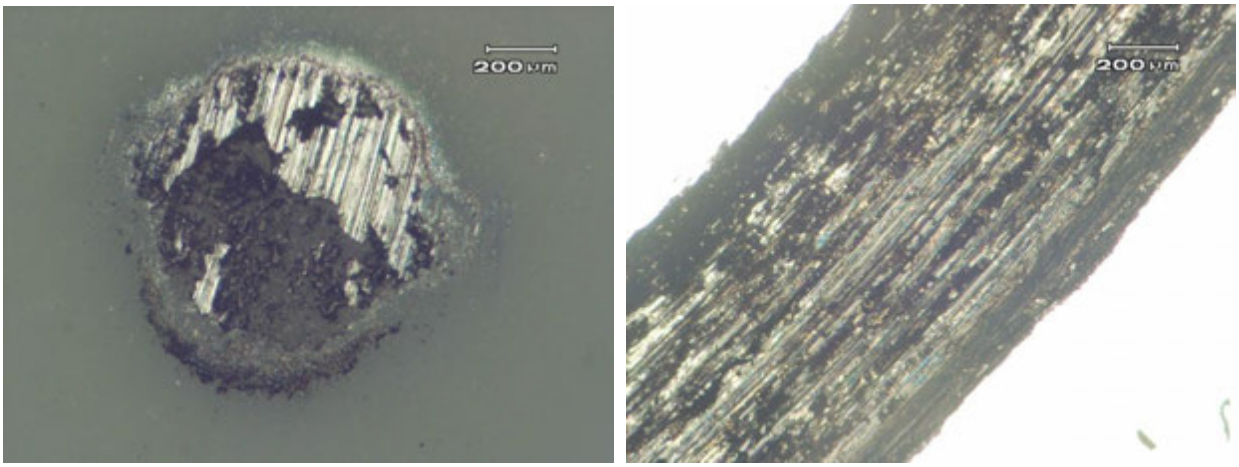
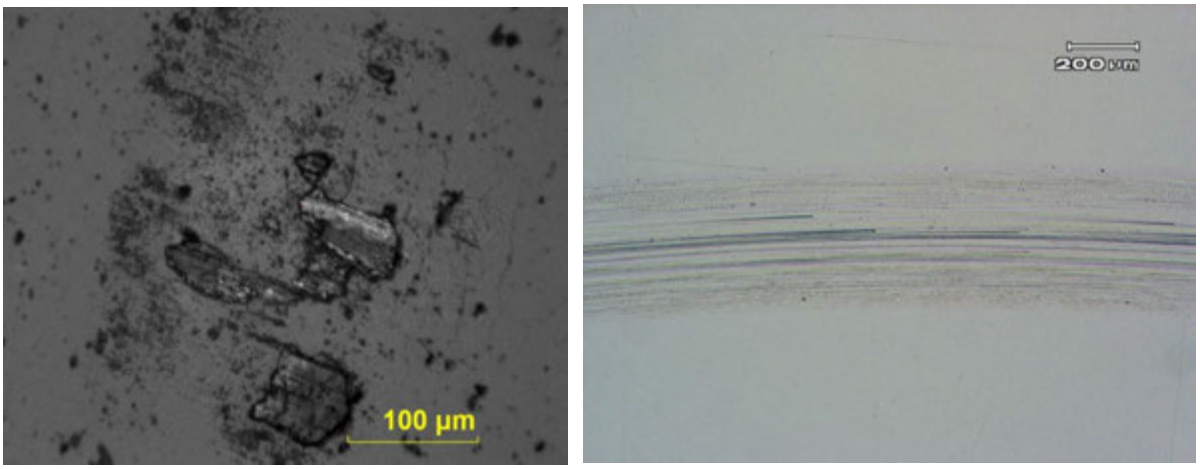

Inconel Substrate
Inconel 15 min boriding
Inconel 15 minbording + 1 hr
Friction Coefficient
Sliding distance (m)
0
0.2
0.4
0.6
0.8
1
1.2
0
50
100
150
200

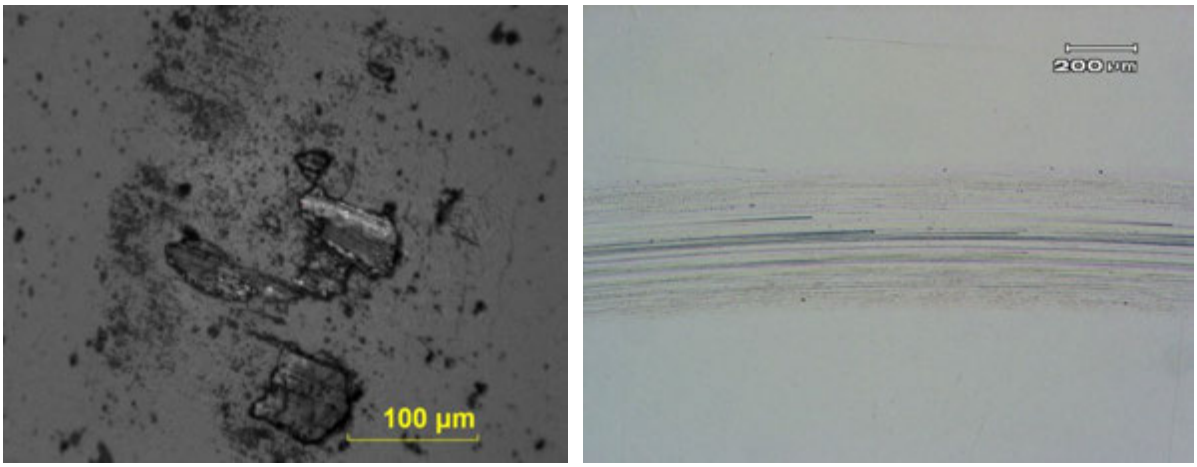
Figure10



(a)

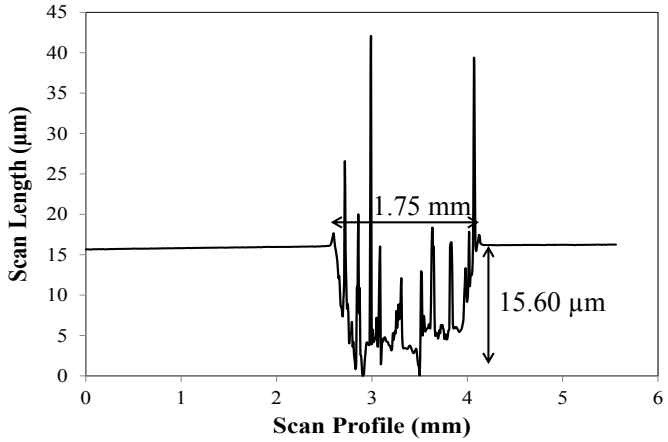


(b)

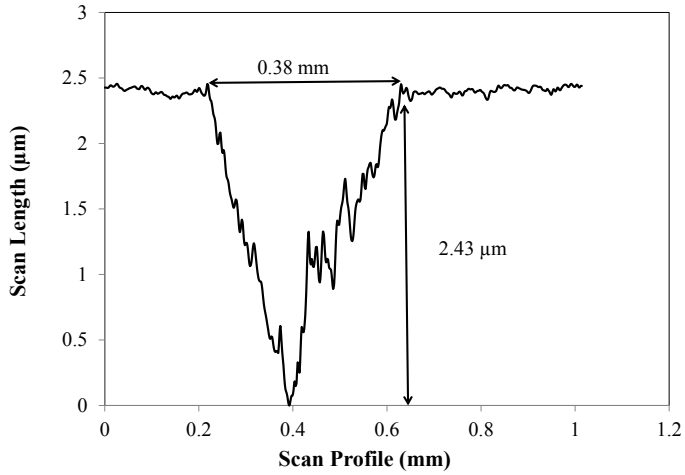


(c)

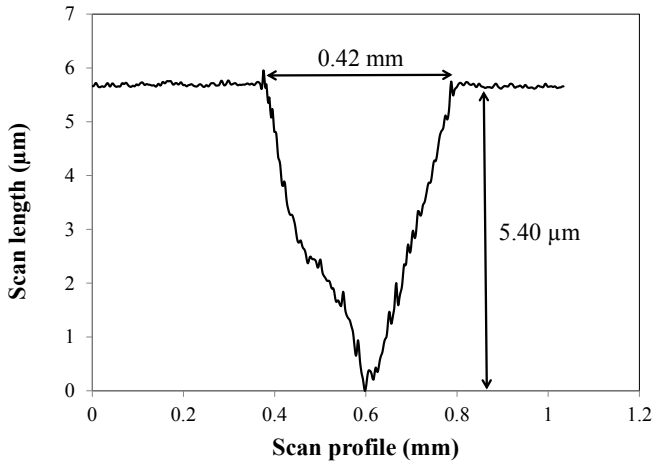
Figure11


Scan Length (µm)
Scan Profile (mm)
1.75 mm
15.60 µm

(a)


Scan Length (µm)
Scan Profile (mm)
0.38 mm
2.43 µm

(b)


Scan length (µm)
Scan profile (mm)
0.42 mm
5.40 µm

(c)

Figure12

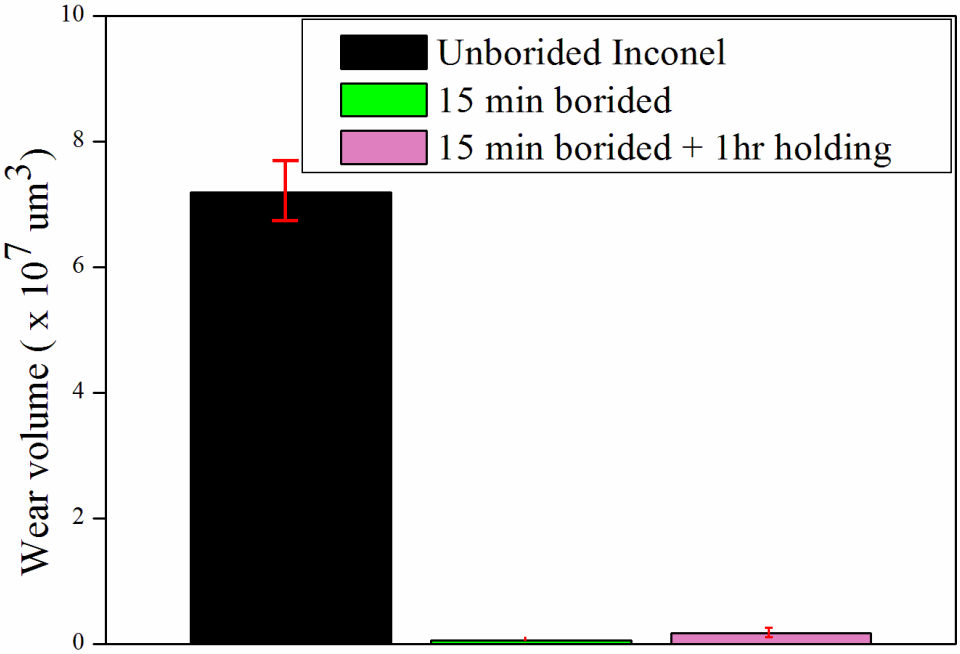

Unborided Inconel
15 min borided
15 min borided + 1hr holding
Wear volume (x 10^7 um^3)
0
2
4
6
8
10

Table1

Table 1. Crystallographic parameters of nickel and nickel borides

Phase	Ni #70-1849	Ni_2B #82-1697	Ni_3B #89-3822	Ni_4B_3 #73-1793	NiB #74-1207
Crystal structure	Cubic	Tetragonal	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	Fm m	I4/mcm	Pbnm	Pnma	Cmcm
Volume, $Å^3$	43.80	105.82	151.38	234.10	64.16
Lattice Parameters, Å	a = 3.525	a = 4.992	a = 4.389	a = 11.954	a = 2.925
	b = 3.525	b = 4.992	b = 5.211	b = 2.9815	b = 7.396
	c = 3.525	c = 4.2465	c = 6.619	c = 6.5684	c = 2.966
Density, g/cm^3	8.90	8.05	8.20	7.58	7.20
2θ ($I_{100,\%}$), °	44.481	45.886	46.004	43.676	45.195
d ($I_{100,\%}$), Å	2.0352	1.9761	1.9713	2.0708	2.0047

JCPDS Card Number.