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THE INFLUENCE OF THE TIME OF TECHNOLOGICAL SOAKING OF NITRIDED EN-X37CrMoV5-1 TOOL STEEL AT A HIGHER TEMPERATURE ON THE STRUCTURE, MICROHARDNESS, AND TRIBOLOGICAL WEAR OF THE SURFACE LAYER

WPŁYW CZASU TECHNOLOGICZNEGO WYGRZEWANIA W PODWYŻSZONEJ TEMPERATURZE AZOTOWANEJ STALI NARZĘDZIOWEJ X37CrMoV5-1 NA STRUKTURĘ, MIKROTWARDOŚĆ ORAZ ZUŻYCIE TRIBOLOGICZNE WARSTWY WIERZCHNIEJ

Key words: tool steel; X37CrMoV5-1; nitriding; upper layer; microhardness; tribological wear.

Abstract The paper concerns the assessment of the influence of the duration of high-temperature soaking of steel intended for dies for extruding aluminium profiles on the structure, microhardness, and tribological wear of the top layer. Gas nitrided hot work tool steel X37CrMoV5-1 (WCL) was used in the tests. For technological reasons, before the extruding process, such dies are pre-heated for several hours to a temperature ranging from 400°C to 600°C. Due to the possibility of various unplanned situations (failures), the soaking time may be extended even up to more than ten hours. Therefore, soaking was used after the nitriding process due to the application nature of the research whose purpose was to identify changes occurring in the nitrided layer after soaking of dies at a higher temperature (520°C) and before starting the extruding process, and thus to determine for how long the dies may be held in a furnace without undesirable changes in the top layer. The examined samples were soaked in an industrial furnace at 520°C for 2 h, 4 h, 6 h, 8 h, 10 h, and 12 h. Samples heated to 520°C and then immediately cooled down and the reference material which was not heated after the nitriding process were also examined for comparison purposes. The obtained results of the tests of the microhardness of the nitrided layer indicate that it decreased as the soaking time increased to 6 hours. After this time, that parameter is stabilised and further heating up to 10 hours does not cause a significant decrease in the microhardness of the top layer. A further decrease in the microhardness of the layer was observed for samples soaked for 12 hours. The results of tribological tests showed an analogous course of changes in the tribological wear of the examined material as the soaking time increased. The performed tests indicate the possibility of holding dies at a higher temperature (520°C) for 10 hours. Further soaking at this temperature causes adverse changes in the top layer.

Słowa kluczowe: stal narzędziowa; X37CrMoV5-1; azotowanie; warstwa wierzchnia; mikrotwardość; zużycie tribologiczne.

Streszczenie Praca dotyczy oceny wpływu czasu wygrzewania w podwyższonej temperaturze stali przeznaczonej na matryce do wyciskania profili aluminiowych na strukturę, mikrotwardość oraz zużycie tribologiczne warstwy wierzchniej. W badaniach stosowano stal narzędziową do pracy na gorąco X37CrMoV5-1 (WCL) poddaną procesowi azotowania gazowego.

Matryce takie są przed procesem wyciskania poddawane wstępnemu nagrzewaniu do temperatury z przedziału 400°C do 600°C przez okres kilku godzin, co jest spowodowane względami technologicznymi. Z uwagi na możliwość wystąpienia różnych nieplanowanych sytuacji (awarii) czas wygrzewania może ulec wydłużeniu nawet do kilkunastu godzin. Zastosowany zabieg wygrzewania po procesie azotowania wynikał zatem z aplikacyjnego charakteru badań, które miały na celu określenie zmian zachodzących w warstwie azotowanej po wygrzewaniu matryc w podwyższonej temperaturze (520°C) przed rozpoczęciem procesu wyciskania, a tym samym określenie, przez jaki czas można przetrzymywać matryce w piecu bez pojawienia się niepożądanych zmian w warstwie wierzchniej. Badane próbki wygrzewano w piecu przemysłowym w temperaturze 520°C przez czas 2 h, 4 h, 6 h, 8 h, 10 h i 12 h. W celach porównawczych zbadano także próbki nagrzane do temperatury 520°C i od razu chłodzone oraz materiał wzorcowy, który nie był wygrzewany po procesie azotowania. Uzyskane wyniki badań mikrotwardości warstwy azotowanej wskazują na jej spadek wraz z rosnącym czasem wygrzewania do 6 godzin. Po tym czasie parametr ten ulega stabilizacji i dalsze wygrzewanie do 10 godzin nie powoduje istotnego spadku mikrotwardości warstwy wierzchniej. Dla próbek wygrzewanych przez okres 12 godzin odnotowano dalszy spadek mikrotwardości warstwy. Wyniki testów tribologicznych wykazały analogiczny przebieg zmian zużycia tribologicznego badanego materiału wraz z rosnącym czasem wygrzewania. Przeprowadzone testy wskazują na możliwość przetrzymywania matryc w podwyższonej temperaturze (520°C) przez okres 10 godzin. Dalsze wygrzewanie w tej temperaturze powoduje pojawienie się niekorzystnych zmian w warstwie wierzchniej.

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INTRODUCTION

Tools such as moulds and dies for extruding, forging, pressure casting, etc. are repeatedly subjected to cyclic thermal and mechanical loads. The repeating heating and cooling cycles cause thermal stresses that result in them becoming damaged. Unfavourable working conditions also cause damage on the surface of the tools in the form of, e.g., abrasive wear, thermal cracking and corrosion, etc. **[L. 1]**.

The life of such tools may be improved by properly selecting the chemical composition of steel used or by properly shaping the structure and properties of the top layer of the tool. The first method consists in the use of appropriate alloying elements (e.g., niobium, boron) **[L. 2, 3]**, and the second one in thermal and chemical treatment of the tool material, for example via nitriding **[L. 4, 5]**. The main advantage of this process is the improvement of surface properties of the material, and in particular, the obtaining of high hardness and resistance to abrasion, fatigue, and corrosion **[L. 6]**. An increase in surface hardness and the induction of residual compressive stresses **[L. 7]** increase the fatigue resistance of the material. Nevertheless, the periodic heating of the material to a temperature ranging from 500°C to 600°C causes decomposition of the nitrided layer coupled with the release of nitrogen, which results in the deterioration of thermal fatigue properties as the number of cycles increases **[L. 8]**.

Among various nitriding methods, gas nitriding is one of the most versatile surface treatment processes, and one of its main advantages is the precise control over the nitrogen absorption process by means of the thermodynamic chemical potential of nitrogen in the gas phase, which makes it possible to obtain layers that meet a variety of technological requirements **[L. 9]**. Its additional advantages are simplicity and cost-effectiveness **[L. 7, 10]**.

Two different structures are formed during the nitriding of steel, from the surface towards the core, known as the nitride precipitates zone and the diffusion zone. The precipitate zone consists of iron nitrides of phase ε (ε-Fe2-3N), phase γ (γ'-Fe4N), or a mixed phase (ε + γ') formed on the surface. The characteristics of the wear of the zone of the layer's nitride precipitates depend on numerous factors, such as the composition of the zone (ε/γ), its thickness and mechanical load method, etc. **[L. 11, 12, 13]**. On the other hand, the diffusion zone contributes to the improvement of fatigue strength. In such a structure, an excessive number of nitrogen atoms are arranged interstitially in the ferritic network and cause the formation of nitrogen precipitates **[L. 14, 15]**.

One of the commonly used materials for moulds and dies for extruding, forging, and casting is surface hardened chrome martensitic steel X37CrMoV5-1 intended for hot work tools, which contains 5% of Cr and 1% of Mo. It is a result of a combination of features such as strength at high temperatures, high ductility, and resistance to cracking **[L. 16]**, resistance to dynamic loads, as well as low thermal conductivity and thermal expansion coefficient **[L. 1]**. This steel also does not require a high hardening temperature; however, since it contains alloying components (Cr, Mo and Si), it is resistant to tempering and oxidation. A low content of expensive alloying components is also of no small importance from the economic point of view.

Because fatigue damage usually develops from the surface of the material, surface hardening of tools plays an important role in obtaining proper fatigue strength.

RESEARCH MATERIAL AND METHODOLOGY

Gas nitrided hot work steel X37CrMoV5-1 was the subject of the tests. The nitriding process was preceded by thermal improvement of the material to the required hardness of 48-50 HRC. Thus thermally treated, the material was subjected to regulated gas nitriding with automatic NITREG® control. This process was conducted in the following conditions:

- Two-stage nitriding;
- Nitriding temperature: 530°C;
- Nitriding duration: 18 h;
- Nitriding atmosphere: NH3 + N2; and,
- Nitric potential; 3.

Thus prepared, the samples were soaked in an industrial furnace at 520°C, applying a soaking duration of 2 h, 4 h, 6 h, 8 h, 10 h, and 12 h. Samples heated to 520°C and then immediately cooled down (0 h) and the reference material (W), which was not heated after the nitriding process, were also used for comparison purposes. The exampled samples were supplied by ALUFORM Sp. z o.o. This company also conducted nitriding and soaking processes.

Soaking used in the paper after the nitriding process resulted from the application nature of the research commissioned by the supplier of the material. Due to the fact that, before the extrusion process, the dies for aluminium extrusion are subjected for several hours to pre-heating to a temperature ranging from 400°C to 600°C, several dies are soaked in the furnace simultaneously (according to the approved production plan) in order to maintain continuity of the process. As there may be a variety of unforeseen situations during the production (production stoppage, failure etc.), it may happen that a die will be held in the furnace longer than planned. Therefore, the purpose of the performed tests was to identify changes occurring in the nitrided layer after the soaking of dies in a furnace at a 520°C and before starting the extruding process, and thus to determine for how long the dies may be held in a furnace without undesirable changes in the top layer.

The specimens for tests had a diameter of 20 mm and height of 25 mm. After thermal and thermal-chemical treatment, every sample was divided into two parts, and microsections were made to the roughness value of Ra = 0.1 µm on the cross sections that had been created. The surfaces of the microsections were then etched with 1.5% Nital in order to make the top layer visible. Samples prepared in this manner were observed on an OLYMPUS GX51 light microscope. The thickness of the nitrided layer was measured and photographs were taken. The microhardness of the top layer was determined using a Vickers microhardness tester made by Wolpert Wilson Instruments (model 401MVD). Vickers microhardness HV 0.5 was determined (load: 0.5 kG, time of withstanding the load: 10 s). Nine indents were made for each of the specimens in the precipitation zone. The tribological tests were carried out on Tribometer TRN (Anton-Paar) device in the ball-on-disc couple. The tests were carried out on the front surface of the cylinder, and a ball made of Al_2O_3, 6 mm in diameter (**Figure 1**) was used as a counter-specimen.

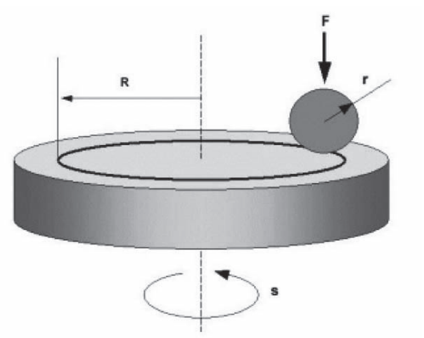

Fig. 1. The kinematic diagram of the friction couple used
Rys. 1. Schemat kinematyczny stosowanego węzła tarcia

Other conditions of the test were as follows:

- Friction couple load: 10 N;
- Sliding speed: 0.1 m/s,
- Friction distance: 2 km;
- Ambient temperature: 21 ±1°C;
- Relative humidity: 50 ±5%;
- The number of repetitions: 3.

Volumetric wear W_v and linear wear W_L were determined based on profilographometric measurements using a Mitutoyo Surftes SJ-500 profilograph. Volumetric wear Wv was determined from the following formula:

$$W_v = \frac{V}{F_n \cdot s}\left[\frac{mm^3}{N \cdot m}\right] \qquad (1)$$

where V – volume of the wear trace of the disc, F_n – the load applied, s – friction distance.

Linear wear W_L was read out directly from profilograms.

RESEARCH RESULTS AND ANALYSIS

The results of the observation of the structure of the top layer of the selected samples are shown in **Figure 2**. Two zones of the layer can be observed: the nitride precipitates zone γ′, which is closer to the surface, and a diffusion zone, which is closer to the core and is a solid solution of nitrogen in iron α.

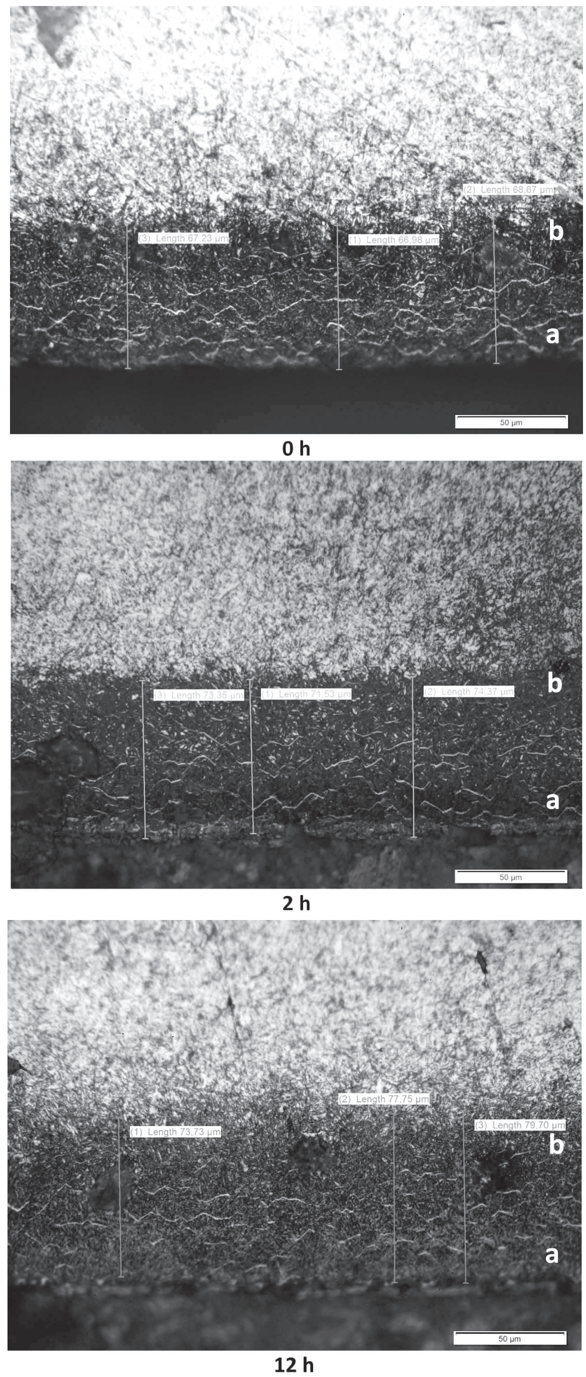

Fig. 2. The nitride precipitates zone (a) and the diffusion zone (b) in the top layer after nitriding and annealing of steel
Rys. 2. Strefa wydzieleń azotków (a) oraz strefa dyfuzyjna (b) w warstwie wierzchniej po azotowaniu i wyżarzaniu stali

Top layers with such a structure are usually formed as a result of a two-stage process of regulated gas nitriding in industrial conditions, i.e. in conditions described in this paper **[L. 17, 18]**. Another purpose of the analysis of microscope images was to detect potential microcracks in the top layer. The conducted observations have not revealed such defects. Changes in the thickness of the top layer that occurred along with the temperature are shown in **Figure 3**.

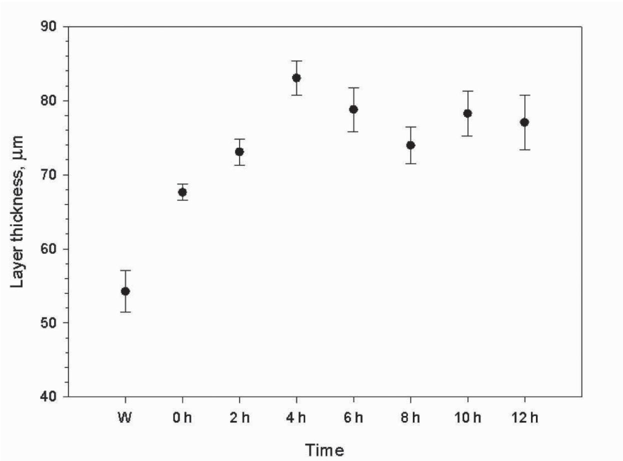

Fig. 3. Thickness of the top layer of the examined samples
Rys. 3. Grubość warstwy wierzchniej badanych próbek

According to the measurements, the thickness of the nitrided layer increased along with the soaking time to approximately 83 µm for a duration of 4 hours. Further soaking caused a small decrease in the layer's thickness with time to approximately 74 µm for 8 hours. After that time, there was a minor increase and the thickness of the layer stabilised at approximately 77 µm for the remaining soaking time. The obtained results indicate that the nitrided layer did not degrade as the time of soaking at 520°C increased. Moreover, its thickness increased for 4 hours. After that time, a small decrease in thickness and subsequent stabilisation were observed. However, these values are still higher than the layer thickness for the initial sample.

The influence of the soaking time on the hardness of the top layer is shown in **Figure 4**. The obtained results indicate the initial increase in microhardness by approximately 6%, compared to the reference material, for samples heated to 520°C and immediately cooled down. Then, a decrease in microhardness along with the soaking time was observed to the value of approximately 870 HV 0.5 for a duration of 6 hours. The extension of the soaking time to 10 hours did not cause any significant changes in the microhardness of the top layer. However, hardness was reduced to approximately 840 HV 0.5 after 12 hours of annealing.

Microhardness may be reduced as a result of a decrease in the number of nitride precipitates, which are responsible for high hardness of the top layer. It may also be caused by the partial decomposition of the layer

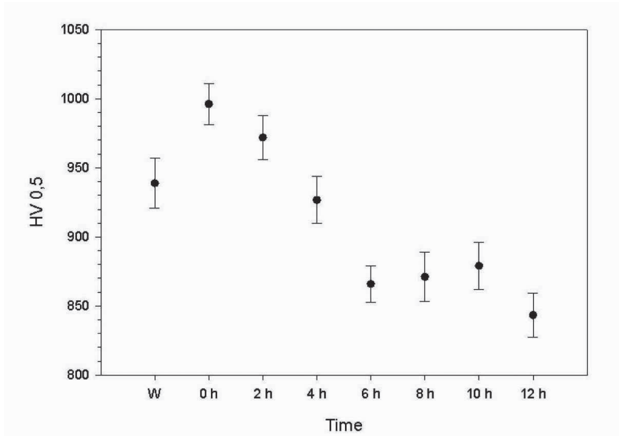

Fig. 4. HV 0.5 microhardness for the tested samples
Rys. 4. Mikrotwardość HV 0,5 badanych próbek

coupled with the release of nitrogen from its surface and the formation of oxides on it. This dependence is described in the paper **[L. 19]**, where the decrease in hardness of the nitrided layer was associated with its oxidation process, which in turn was caused by the decomposition of nitrides. The decrease in hardness can also result from a change in the degree of the dispersion of nitrides, because the size of these precipitates increases together with the increasing duration of annealing, and thus the hardness of the layer decreases.

The obtained results of tribological tests, in the form of volumetric wear, are shown in **Figure 5**. It can be seen in the diagram that soaking at 520°C initially causes an increase in tribological wear. This value increases to approximately $1.84*10^{-5}$ for soaking time of 4 hours, whereas values obtained for 2 h and 6 h variants are similar to it and are within the margin of error.

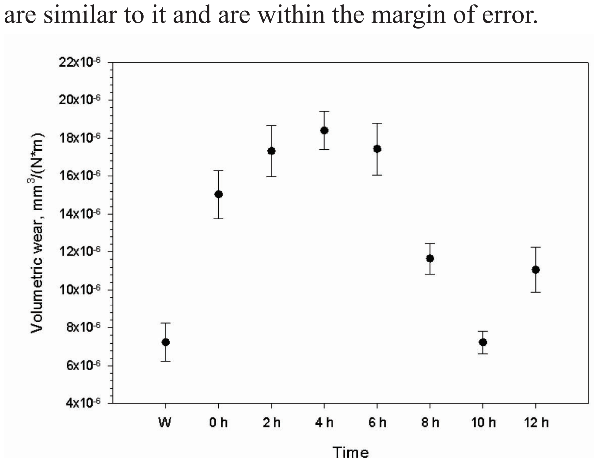

Fig. 5. Tribological wear of the top layer of the examined samples
Rys. 5. Zużycie tribologiczne warstwy wierzchniej badanych próbek

Further soaking leads to an increase in tribological wear resistance, and the greatest improvement was obtained for a material soaked for 10 hours, and its value is at a level obtained for the reference sample.

An analogous trend was obtained from linear wear measurements (**Fig. 6**). The diagram shows the initial increase in wear, which is reduced for the longest soaking times.

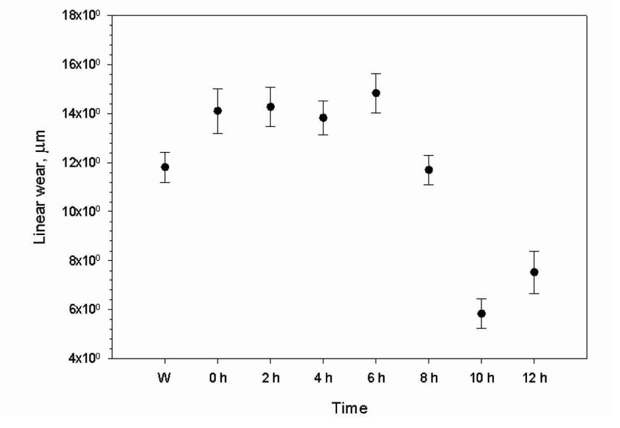

Fig. 6. Linear tribological wear of the top layer of the examined samples

Rys. 6. Liniowe zużycie tribologiczne warstwy wierzchniej badanych próbek

Tribological wear that increases together with time, coupled with the increasing thickness of the top layer, may be an indicator of the an increase in the diffusion zone at the cost of the hard nitride precipitates zone γ'. The obtained values of the friction coefficient are similar for all the obtained samples and amount to approximately 0.94.

CONCLUSIONS

- The thickness of the top layer increases along with the soaking time for approximately 4 hours and then is slightly decreased and stabilises. No degradation (formation of microcracks) of this layer was observed.
- The microhardness of the near-surface zone of the top layer is noticeably reduced when nitrided steel is soaked at 520°C for 6 hours. After this time, changes in this value are only minor.
- Initially, tribological wear increases along with the soaking time. Soaking for more than 6 hours causes a decrease in wear.
- The decrease in the hardness of the top layer and the corresponding increase in tribological wear may be caused by the decreasing number and/or increasing size (coagulation) of the nitride precipitates of alloying elements as well as the decreasing thickness of the precipitation zone in favour of the growing diffusion zone.

REFERENCES

1. ASM Handbook, Metalworking: Bulk Forming, 14A, Dies and Die Materials for Hot Forging, ASM International, Ohio USA, 2005, 47–61.
2. Kheirandish S., Noorian A.: Effect of Niobium on Microstructure of Cast AISI H13 Hot Work Tool Steel. Journal of Iron and Steel Research, International, 2008; 15(4): 61–66.
3. Noorian A., Kheirandish S., Saghafian H.: Evaluation of the mechanical properties of niobium modified cast AISI H13 hot work tool steel. Iranian Journal of Materials Science and Engineering, 2010; 7(2): 22–29.
4. Jiménez H., Devia D.M., Benavides V., Devia A., Arango Y.C., Arango P.J., Velez J.M.: Thermal protection of H13 steel by growth of (TiAl)N films by PAPVD pulsed arc technique. Materials Characterization, 2008; 59(8): 1070–1077.
5. Psyllaki P., Papadimitriou K., Pantazopoulos G.: Failure modes of liquid nitrocarburized and heat treated tool steel under monotonic loading conditions. Journal of Failure Analysis and Prevention, 2006; 6(6): 13–18.
6. Emami M., Ghasemi H.M., Rassizadehghani J.: High temperature tribological behaviour of 31CrMoV9 gas nitrided steel. Surface Engineering, 2010; 26(3): 168–172.
7. Akhtar S.S., Arif A.F.M., Yilbas B.S.: Evaluation of gas nitriding process with in-process variation of nitriding potential for AISI H13 tool steel. The International Journal of Advanced Manufacturing Technology, 2009; 47(5): 687–698.
8. Starling C.M.D., Branco J.R.T.: Thermal fatigue of hot work tool steel with hard coatings. Thin Solid Films, 1997; 308–309: 436–442.
9. Efe G.C.: Characterization of Gas-Nitrided 31CrMoV9 Steel. Materials and Technology, 2014; 48(6): 827–830.
10. Kugler G., Turk R., Večko-Pirtovšek T., Terčelj M.: Wear behaviour of nitrided microstructures of AISI H13 dies for hot extrusion of aluminium. Metalurgija, 2006; 45(1): 21–29.

11. Tercelj M., Smolej A., Fajfar P., Turk R.: Laboratory assessment of wear on nitrided surfaces of dies for hot extrusion of aluminium. Tribology International, 2007; 40: 374–384.
12. Karamis M.B., Gercekcioglu E.: Wear behavior of plasma nitrided steels at ambient and elevated temperatures. Wear, 2000; 243: 76–84.
13. Kang J.H., Park I.W., Jae J.S., Kang S.S.: A study on a die wear model considering thermal softening: (I) Construction of the wear model. Journal of Materials Processing Technology, 1999; 96: 53–58.
14. Sjostrom J., Bergstrom J.: Thermal fatigue testing of chromium martensitic hot-work tool steel after different austenitizing treatments. Journal of Materials Processing Technology, 2004; 153–154: 1089–1096.
15. Li S., Manory R.R.: Comparison of compound layer nucleation mechanisms in plasma nitriding and nitrocarburizing: the effect of CHn species. Journal of Materials Science, 1999; 34(5): 1045–1049.
16. Małkiewicz T.: Metaloznawstwo stopów żelaza (Iron Alloys Metallurgy), PWN, Warsaw – Cracow 1971.
17. Małdziński L.: Termodynamiczne, kinetyczne i technologiczne aspekty wytwarzania warstwy azotowanej na żelazie i stalach w procesach azotowania gazowego (Thermodynamic, kinetic and technological aspects of the formation of the nitrided layer on iron and steels in gas nitriding processes). Wydawnictwo Politechniki Poznańskiej (Publishing House of Poznań University of Technology); Rozprawy nr 374, Poznań 2002.
18. Hernandez M., Staia M.H., Puchi-Cabrera E.S.: Evaluation of microstructure and mechanical properties of nitrided steels. Surface and Coatings Technology, 2008; 202(10): 1935–1943.
19. Birol Y.: Effect of post-oxidation treatment on thermal fatigue behaviour of plasma nitrided hot work tool steel at elevated temperatures. Surface and Coatings Technology, 2011; 205(8–9): 2763–2769.