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Insight into the microstructural stability and thermal fatigue behavior of nitrided layers on martensitic hot forging tools

Review Article

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Abstract: The aim of this study is to evaluate some aspects related to the thermal-induced decomposition of the nitrided layers in dies used for hot forging made of tempered martensitic tool steel. Nitriding is used to improve the functional properties and durability of forging dies. The degradation of the tool surface without nitrided layers can be considered as an example of quenched and tempered steel. Thermal decomposition of nitrided layers on steel is an issue that is little known in the literature, especially when it concerns the decomposition under tribomechanical loading conditions. Changes occurring on the tool surface caused by service-life conditions have become the basis for considerations regarding the thermal stability of the nitrided layers. Material issues influencing the functional properties of dies have also been discussed. The conducted state-of-the-art literature reviews and metallographic analysis have shown that it is advisable to conduct further research on phase transformations related to the decomposition of nitrided layers. The strategy for further studies is also suggested.

Keywords: *Nitrided layers • Microstructural stability • Thermal fatigue • Hot forging dies*

1. Introduction

Hot precision forging tools operate under complex stress conditions at high contact pressures. Their external surface damage is caused by the synergy of various wear mechanisms, which include thermomechanical and tribological stress components. It is indicated that their durability is determined by abrasive and adhesive wear, thermomechanical fatigue, as well as deformation of their operating surface [1,2]. It is assumed that the temperature on the tool surface may temporarily exceed the tempering temperature [1,3]. This may result in local changes in the tool microstructure and, therefore, lead to local softening of the tool surface layer, which is exposed to long-term contact between the tool and the workpiece. It is believed that the softening is related to the growth of carbide precipitates [3]. The formation of a softened layer reduces the tool's resistance to plastic deformation, which causes local deformation of the service-life surface (Figure 1). This is particularly true when the tool wear surface is exposed to frictional sliding due to the flow of the workpiece material. It was found that the presence of thermal loads coexisting with mechanical loads can significantly affect the phase transformation temperatures, including leading to a decrease in the A_{c1} temperature [4,5]. As a result, the temperature can reach a range close to austenitization. Therefore, if we also take into account the possibility of phase transformations, thermal fatigue is also superimposed on structural stresses, which are associated with volumetric changes.

Taking into account the above considerations, the magnitude of thermal and mechanical loads of forging tools between the tool and workpiece are the main factors that determine the durability of the tool. The extremely difficult working conditions discussed above require the use of high-quality tool steels, the further heat treatment of which is determined by the required hardness of the tool. Damage to the dies is generally limited to the near-surface layers. The destruction of the operational surface

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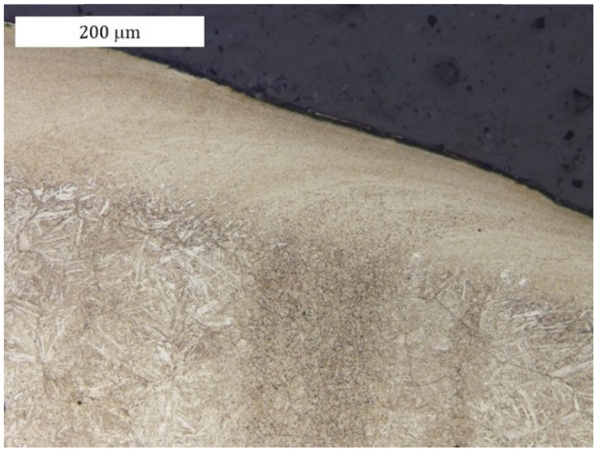


Figure 1. The surface of a punch used in the hot forging process after severe plastic deformation. Light microscopy, etched state. Author's unpublished materials.

layer of forging tools opens up wide possibilities for using surface engineering methods to improve its properties. An important contribution to the durability of tools is the use of surface layers that protect against wear, which include nitrided layers. Layers obtained in the classic high-pressure process, as well as low-pressure, ion, and plasma processes, are successfully used for this purpose [6–9]. The enrichment of the surface layer with nitrogen by internal diffusion is accompanied by an increase in the surface hardness to over 1,000 HV. The hardness of the nitrided layer exceeds the hardness of heat-treated steels by about 350–430 HV30 [10], which significantly affects the tribological behavior of tools and extends tool life. Surface hardening and residual compressive stresses occurring below the surface caused by nitriding provide very effective surface protection against fatigue crack initiation [11]. The fatigue properties of loaded surfaces are particularly effective if the compressive residual stresses are located at the same depth as the Hertzian stress concentrations [12]. The final performance properties of nitrided layers are determined by their effective thickness, as well as their chemical and phase composition, which depend on the nitriding parameters and the substrate material [6,7,11,13,14]. The improvement of the service-life surface properties, which affect the performance of forging tools, can be significantly improved by using a multi-gradient design strategy for coatings [15–17]. The use of transition layers results in better adhesion of coatings, which translates into a lower tendency to wear and delamination [15]. Nitriding is not only one of the most widely used surface engineering methods for forging tools but also for transition layers in multi-gradient coating systems [16,17].

The degradation of the tool surface without nitrided layers can be considered as an example of quenched and tempered steel and also described using hardness changes dependent on the achieved temperature. When nitrided steel is heated, the gradual degradation of the nitrided layer should also be taken into account when discussing the wear mechanisms of forging dies. Heating in the discussed situation will be associated with the occurrence of a series of microstructural features in the nitrided surface layer as a function of temperature caused by the forging process. While the transformations associated with the decomposition of martensite are widely known, the thermal decomposition of nitrided layers is an issue that has been little explored in the literature. Due to the short local time–temperature cycles, the phases formed are mostly non-equilibrium states. For this reason, it is important to gather knowledge in this area, as well as to determine further research. The conducted review aimed to fill the gaps in the existing knowledge in this area. This study does not constitute a comprehensive review of the literature but rather a personal consideration of the decomposition of nitrided layers in dies used for hot forging.

2. Improved mechanical properties of tool steel by nitriding

Nitriding has been known for many years as a basic surface treatment technology that improves the properties of many structural elements, including stamping and forging dies [6,10]. Spies and Dalke [10] indicated that nitriding increased the life of forging dies by a factor of 1.2–6, depending on the stress state and the production volume

of the hot working dies. Fatigue strength and crack initiation rate are significantly improved. Residual compressive stresses are of great importance in this respect, which causes cracks to move from the near-surface zone to the interior of the material [11,18]. It is also believed that the improvement in thermal fatigue strength is due to the opposing effect of these compressive stresses on the tensile stresses developed during thermal cycling [19,20].

Nitriding is carried out for previously heat-treated steels at temperatures lower than the eutectoid transformation occurring at 592°C. The solubility of nitrogen in ferrite is lower than in austenite, although higher than the solubility of carbon [21]. As a result of nitriding, ferrite becomes saturated with nitrogen and carbonitride precipitates are formed. Ultimately, the nitrided layer formed as a result of this thermochemical process consists of two sublayers: the external compound layer and the diffusion layer lying below.

The compound layer in unalloyed steels is composed of ε($Fe_{2-3}N$) nitrides, under which there is a γ′(Fe_4N) layer [22–24]. This outer layer is also referred to as the "white layer" because it does not undergo etching. It is indicated that the formation of this layer is accompanied by the formation of a high density of dislocations, which eliminate the distortions introduced by the nitrogen enrichment [25]. The γ′ phase (Fe_4N) roaldite is formed as a result of the low solubility of nitrogen in α-iron. As shown in Figure 2, the γ′(Fe_4N) phase is a stable phase at a nitrogen concentration of about 20 at%. It crystallizes in the FCC lattice, which is the same as austenite. At the same time, it is the least thermally stable phase in the Fe–N system [7]. It does not always occur but is formed during long-term nitriding. During annealing, it dissociates and forms nitrogen austenite and nitrogen gas. In the last stage of tempering, roaldite γ′(Fe_4N) is also formed together with ferrite as a result of the decomposition of retained austenite [26,27]. The magnetic anisotropy of the γ′(Fe_4N) phase is about three times lower than that of the solid solution of nitrogen in the iron α-Fe(N) [28]. Metastable precipitation of a transition nitride α″($Fe_{16}N_2$) has a lower nitride content than γ′(Fe_4N). They are formed in the initial stage of tempering of nitrogen martensite [27]. Iron nitride α″($Fe_{16}N_2$) precipitates as an intermediate phase during tempering of Fe–N martensite. It remains stable up to 300°C [26]. In the next stage, they transform into the γ′ (Fe_4N) phase [22,27]. Kardonina et al. [26] suggested that α″($Fe_{16}N_2$) can be considered as a distorted lattice of γ′(Fe_4N) nitrides. The ε nitride of variable composition $Fe_{2-3}N$ shows the widest range of occurrence from 15 to 33 at% [26,29]. As can be seen from Figure 2, the range of its occurrence is limited by the formation of the ξ(Fe_2N) phase. The morphologies and structures of iron nitrides have been studied by numerous authors [22,30–32]. It was found that α″-$Fe_{16}N_2$ nitrides occurring in the diffusion

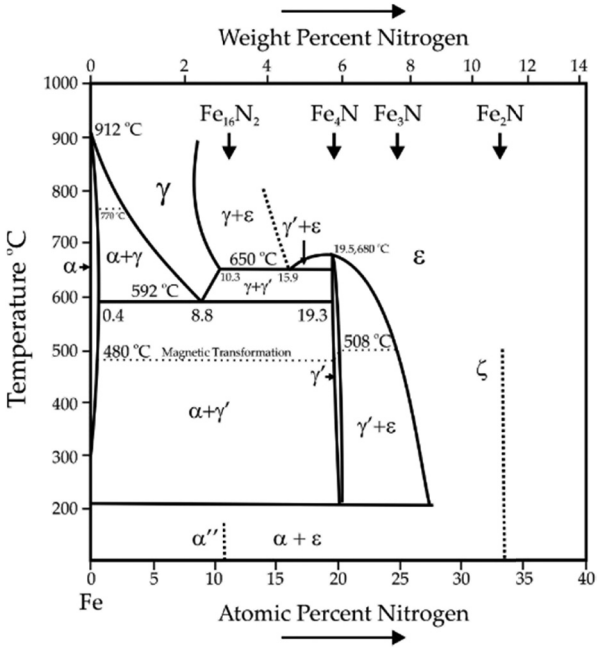


Figure 2. Fragment of the Fe–N diagram. Reprinted with permission from Gallego et al. [42]. Copyright 2004 by the American Physical Society.

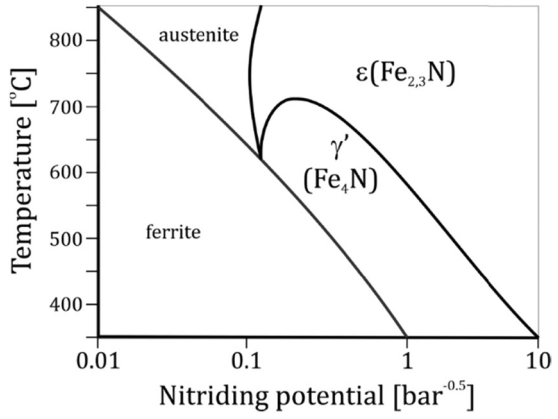


Figure 3. Lehrer's illustration of the most stable iron nitride phase as a function of temperature and nitriding potential. Redrawn based on Somers [34].

zone form fine platelet-like morphology, while γ′-Fe_4N nitrides form needle-like forms. The type of phases formed is strictly dependent on the nitriding potential. Figure 3, known as the Lehrer diagram, shows the formation of different phases of iron nitride as a function of temperature and nitriding potential [33,34]. It has been proven that proper control of nitrogen potential allows obtaining expanded martensite free of nitride precipitates [35,36]. Spies and Dalke [10] indicated that nitrided layers composed of ε-nitride and carbonitride with a hexagonal structure are characterized by high resistance to adhesive wear. This is confirmed by the research of Kochmański et al. [37], who noted that nitriding significantly increased resistance to tribological wear under dry friction conditions. The authors attribute this to increased hardness and reduced adhesive wear. However, it should be remembered that the crumbling of this brittle layer will favor the penetration of hard particles into the friction area. Moreover, its presence favors the initiation of fatigue cracks.

However, nitriding is mainly performed on alloy steels, which causes the formation of carbonitrides of alloying elements. This allows for obtaining higher hardness than in the case of non-alloy steels. Mainly, nitrides of alloying elements are formed – CrN and/or AlN. Chromium is one of the main alloying elements and has a greater affinity for nitrogen than iron, which leads to the formation of chromium nitride. Chromium forms mixed nitrides with aluminum and titanium, $Cr_xAl_{1-x}N$ or $Cr_xTi_{1-x}N$ [37–41]. Nitrides are formed as platelets parallel to the planes of the ferrite lattice due to the Baker–Nutting orientation relationship [21]. Titanium and vanadium are elements with a strong interaction with nitrogen, which means that from the beginning of nitriding, alloy nitrides based on these elements are also formed [39]. The presence of vanadium in the alloy promotes the nucleation of chromium nitrides, which results in their refinement [41].

The internal nitriding zone (diffusion zone) is formed by nitrogen ferrite and γ′(Fe_4N) nitrides, or possibly metastable α″($Fe_{16}N_2$) nitrides [23,27,43]. In the presence of alloying elements in this area, carbonitrides of these elements are also precipitated. The view of the internal nitriding layer in the light microscope image is shown in Figure 4. Manfridini et al. [23] observed the occurrence of two regions in the diffusion zone resulting from decreasing nitrogen content. The upper diffusion zone was formed by larger γ′(Fe_4N) nitrides, while the lower diffusion zone was formed by α″($Fe_{16}N_2$) nitrides.

3. Thermal degradation of nitriding layers

Issues related to the thermal degradation of non-nitrided forging tools are mainly related to tempering occurring in the surface layer, which is a known mechanism. Due to the fact that nitrided elements usually have a service life at low temperatures, issues related to their thermal degradation have not been widely discussed in the literature. In this respect, the influence of long-term annealing of the nitriding layer at temperatures lower than the nitriding temperature was analyzed. It is expected that the layers will be subject to decomposition with nitrogen release. In particular, the evolution of multiphase structures of nitrided layers in the annealing process is of great interest. At the same time, it is emphasized in the literature that nitrided layers show good thermal stability, which allows them to be used in applications on nitrided hot working tools [10]. However, it should be noted that, in this case, the effect of temperature is also accompanied by mechanical loads.

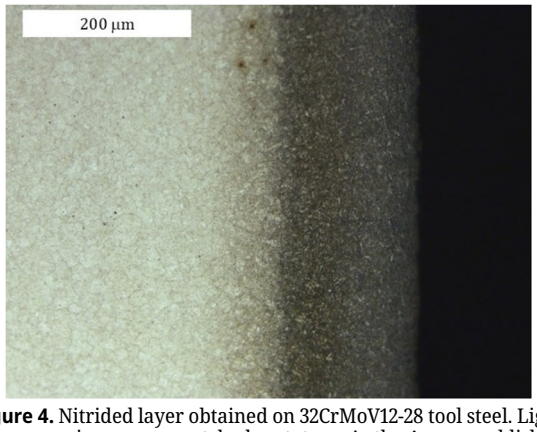


Figure 4. Nitrided layer obtained on 32CrMoV12-28 tool steel. Light microscopy, etched state. Author's unpublished materials.

Birol [44] observed that the surface hardening obtained by plasma nitriding is completely weakened by thermal fatigue. Wołowiec-Korecka et al. [7] found that the decomposition of the iron nitride layer (formed in the saturation phase) due to unfavorable structural changes leads to the reversal of stresses in the nitrided layer from compressive to tensile. The annealing of nitrided steel is accompanied by nitrogen emission to the atmosphere. Also, Schreiber et al. [45] observed a decrease in the concentration of the nitrided layer after annealing ferritic steel at 400°C. They also noted the transformation of the ε layer into a stable solid solution. Kardonina et al. [26] indicated that γ′ nitride (Fe_4N) remains stable up to a minimum of 400°C. Wołowiec-Korecka et al. [7] observed that annealing at 560°C led to a decrease in hardness as well as decomposition of the iron nitride layer. This resulted in the formation of a homogeneous γ′(Fe_4N) region instead of the ε + γ′ combination. The iron nitride layer did not become a source of nitrogen for the diffusion layer. Thus, no enrichment of the substrate material in nitrogen was observed, which would be manifested by an increase in the thickness of the diffusion layer [7]. This is confirmed by the research of Frączek et al. [46], who found that during the decomposition at high temperatures under reduced pressure, the diffusion of nitrogen is very limited. Similar observations were also presented by Liapina et al. [47]. The slight increase in the thickness of the diffusion layer is explained by the increase in the thickness of γ′ occurring at the expense of the decomposition of the ε phase, which was also observed earlier [48,49]. The reason is the establishment of phase equilibrium. Somers and Mittemeijer [50] investigated the differences in nitrogen diffusion in individual phase components formed as a result of the nitriding of pure iron. They found that the diffusion of nitrogen at temperatures around 360°C through the γ′ phase is slower compared to the diffusion through the ε phase. On this basis, Liapina et al. [47] pointed out that the growth of the γ′ sublayer into the substrate phase is less probable than its growth into the ε sublayer, which does not require nitrogen diffusion through the γ′ sublayer.

4. Degradation of nitrided 32CrMoV12-28 tool steel used for dies under high thermomechanical loads: A hot forging perspective

Research on the wear of nitrided dies made of 32CrMoV12-28 (1.2365) steel grade according to EN ISO 4957 standard, compatible with AISI H-10 steel, used in the hot forging process of automotive valves was conducted by a team from the Wrocław University of Science and Technology. The analyses presented in previous studies [13,51–54] indicated that differences in the destruction mechanisms dominating individual die zones may lead to differences in die wear. It is suggested that abrasive wear has a major contribution to the wear of forging tools [1,2,13,55]. Excessive abrasive wear of the die surface occurs in the area of the greatest material deformations [51]. The damages that form on the working surface of the die increase the friction between the preform material and the tool, which results in an increased tendency to stick a forged material to the tool. This results in the overheating of the die surface [51]. In particular, the long contact time of the forged material and the tool translates into a tendency to plastic deformation of the surface [55]. To reduce this friction and ensure the cooling of the dies, the appropriate selection of a cooling lubricant is required [52]. 3D scanning methods are helpful in assessing the durability of dies [53]. The chemical composition of the tool material also influences the wear of the dies [54]. A significant influence in this respect is exerted by the oxide layer formed on the die surface, which depends on its chemical composition [56].

The microstructure of the tested nitrided layers consisted of an internal nitriding layer, which was a nitrogen solution in alloy ferrite with fine-dispersed precipitations of alloy nitrides of nitriding components of steel, mainly chromium. An example of features resulting from abrasive wear of the 32CrMoV12-18 steel die is shown in Figure 5. Clear abrasion of the nitrided coating caused by tribological wear is visible (Figure 5a). In this zone, grooves were observed on the tool surface (Figure 5b).

During hot forging of steel, the die is exposed not only to significant mechanical loads but also to thermal effects caused by high working temperatures of the workpieces. The significant thermomechanical loads associated with the forging process cause the contact of the tool with the hot forged material to be accompanied by heat exchange between this material and the tool. The heat supplied to the tool during forging raises its surface temperature, resulting in degradation in the near-surface area. The tool material in the wear layer, due to heat transfer from the forged material, can temporarily reach a temperature close to the heated forged material in the near-surface area. As a consequence, hot forging tools experience intense and uneven temperature gradients due to cyclic heating and cooling of the die surface. Cyclic temperature changes occurring during forging in the surface layer of the die result in intensive dimensional changes of the tool, i.e., the material expands and contracts alternately. These stresses are reduced by preheating the die

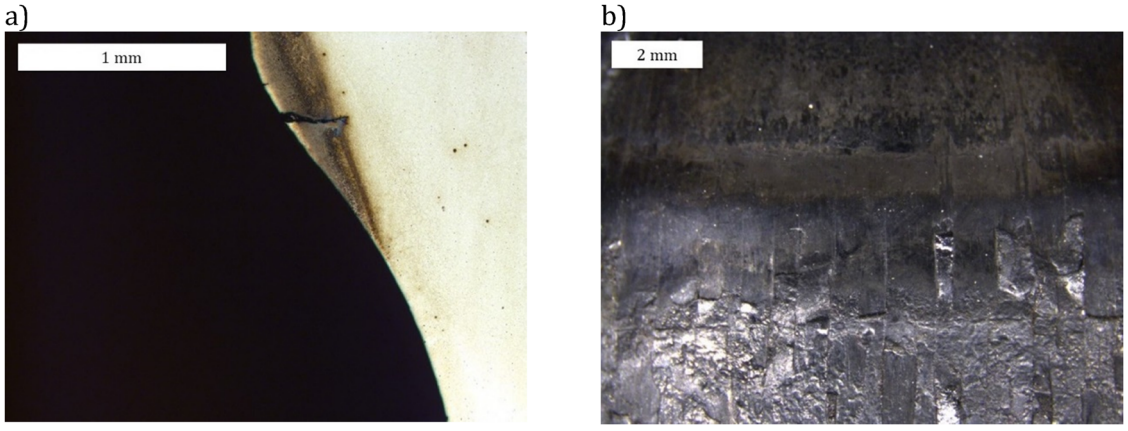


Figure 5. Visible surface abrasion in the central part of the die after forging 2,600 pieces, leading to local removal of the nitrided layer: (a) cross-sectional view and (b) visible groove on the die surface at the abrasion location. Light microscopy, etched state.

but it is not able to completely eliminate them. This results in the formation of thermal stresses in the material causing changes in thermal conductivity, which lead to cracking of their surface [1]. This type of change is characterized by the formation of a characteristic network of cracks on the surfaces of forging tools [13,51,57]. Nitriding does not completely protect the surface from cracking. It has been noted that cracks in the nitrided layer initially form as brittle cracks, and then the crack is intercepted by the ductile core material. Then, the crack develops as ductile cracks [10]. In cross-sections, they are observed as cracks perpendicular to the tool surface (Figure 6). They are located at similar distances from each other and are extinguished after reaching the substrate material (Figure 6a). In some cases, it was observed that the cracks remained closed in the diffusion layer (Figure 6b). Available literature data also indicate that the effect of heat causes a decrease in the hardness of the material near the surface [13,44,57–59]. Reducing the hardness in the near-surface region results in increased susceptibility to plastic deformation in the near-surface region (Figure 7). For comparison, the nitrided layer observed in the area with a low thermomechanical load of this die is also shown (Figure 7a). The near-surface hardness is a factor that determines the stability of residual stresses [10]. For this reason, it can be expected that a decrease in hardness is accompanied by a decrease in compressive stresses responsible for the fatigue strength of nitrided elements. At the same time, Spies and Dalke [10] indicated that up to a hardness value of 500 HV1, a linear relationship is observed with the fatigue strength of nitrided elements. The higher the hardness, the better the fatigue resistance.

The adhesion of the input material to the die surface at the forging stage is of great importance from the point of

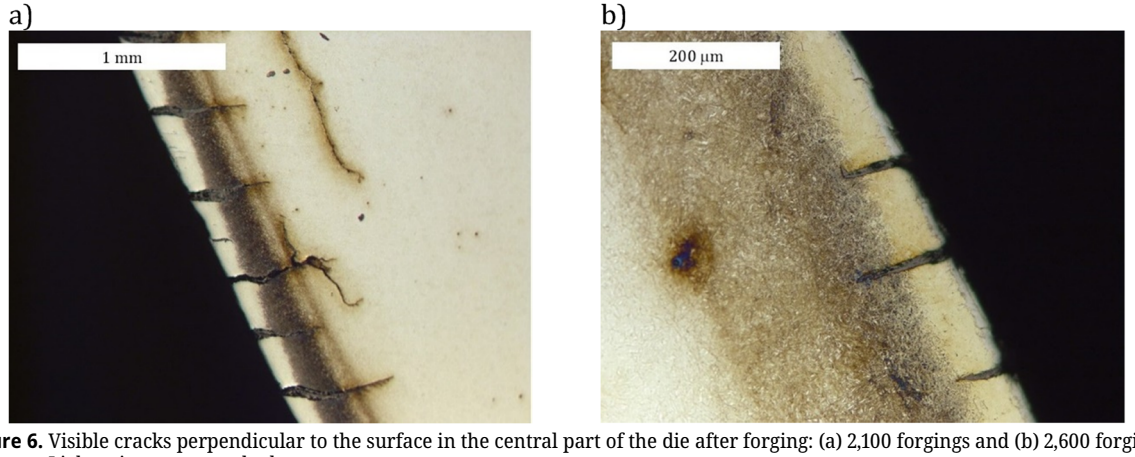


Figure 6. Visible cracks perpendicular to the surface in the central part of the die after forging: (a) 2,100 forgings and (b) 2,600 forgings. Light microscopy, etched state.

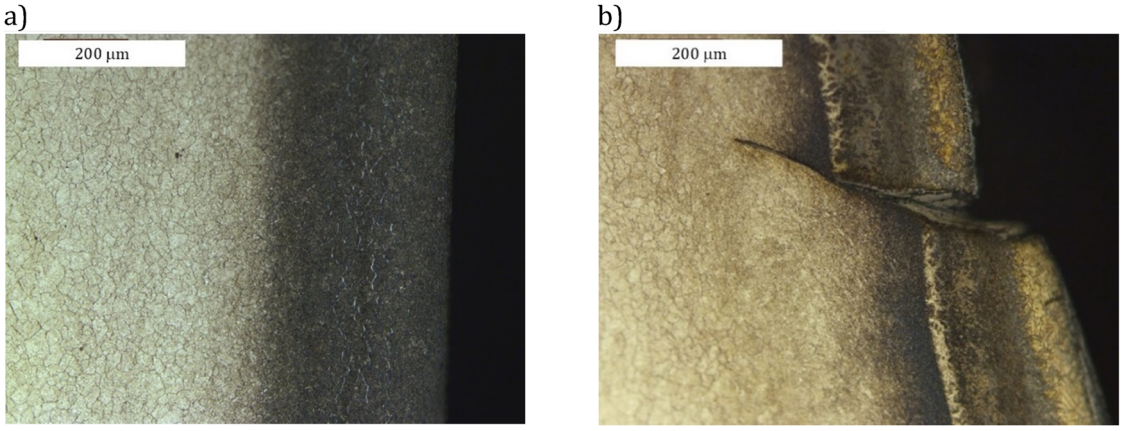


Figure 7. The die after forging 1,000 forgings: (a) area with low thermomechanical load; and (b) visible cracks perpendicular to the surface in the central, heavily thermomechanical loaded part of the die and plastic deformation occurring in this area. Light microscopy, etched state.

view of the durability of the dies. An example of such a deposit formed from the forged material on the die surface after the die has been seized is shown in Figure 8. In such a case, the adhesion of the preform material will result in the die surface heating up to very high temperatures. An example of very clear degradation changes in the nitrided coating area caused by the adhesion of the forged material is shown in Figure 9. They were characterized by the formation of a characteristic white layer in the surface zone. The accompanying high temperature is evidenced by oxidation occurring in fatigue cracks (Figure 9a). A similar nature of degradation features was exposed in the layers shown in Figure 10 after forging 1,100 pieces, 2,100 pieces (Figure 11), and 2,600 pieces (Figure 12). Observations conducted at higher magnifications indicate that this layer has a non-homogeneous character, which is characterized by the presence of needle-like precipitates in its area. The observed layer maintained continuity with the remaining area of the nitrided layer, which indicates its diffusion character (Figures 9–12). At the same time, a diversity of the evolved microstructures is visible. The micrographs reveal a thin zone that can most likely be attributed to a high nitrogen ferrite or austenite region. In this region, a darker etching phase with a fine-needle structure is observed in the microscopic image. The precipitates inside the grains grow significantly, taking on the shape of thick, irregular, or elongated needles.

In terms of microstructure, the observed layer is different from the white etching layer (WEL) that is observed on materials subjected to high tribomechanical loads [60–62]. Figure 13 shows a typical white featureless layer formed on the surface of a forging tool. Freisinger et al.

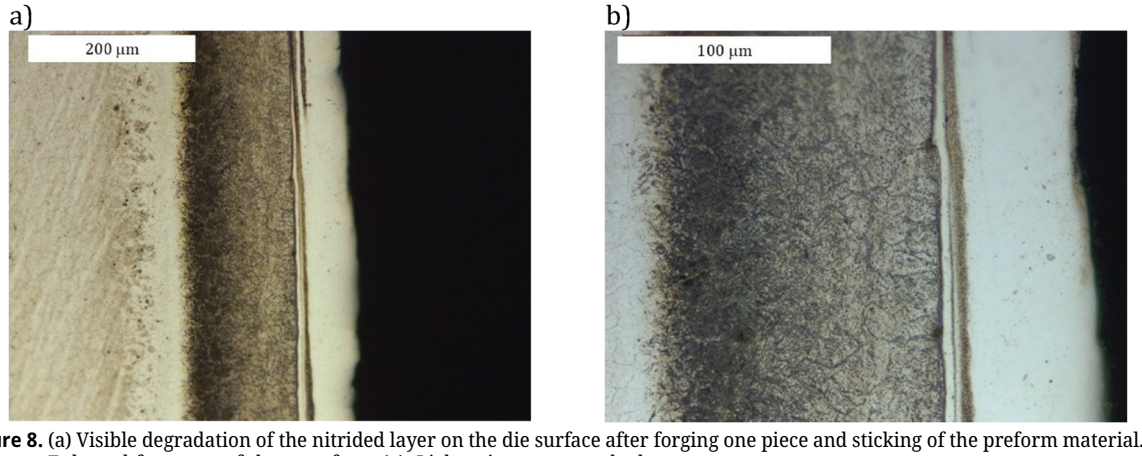


Figure 8. (a) Visible degradation of the nitrided layer on the die surface after forging one piece and sticking of the preform material. (b) Enlarged fragment of the area from (a). Light microscopy, etched state.

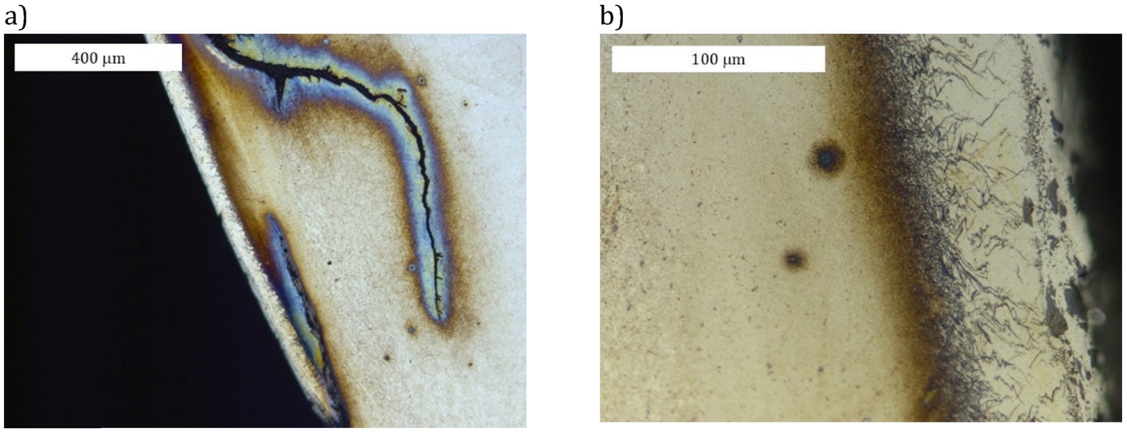


Figure 9. Visible degradation of the nitrided layer on the die surface after forging one piece and sticking the preform material. Visible oxidation of fatigue cracks was revealed by the etching in location I (a) and the formation of a white layer in the coating area in location II (b). Light microscopy, etched state.

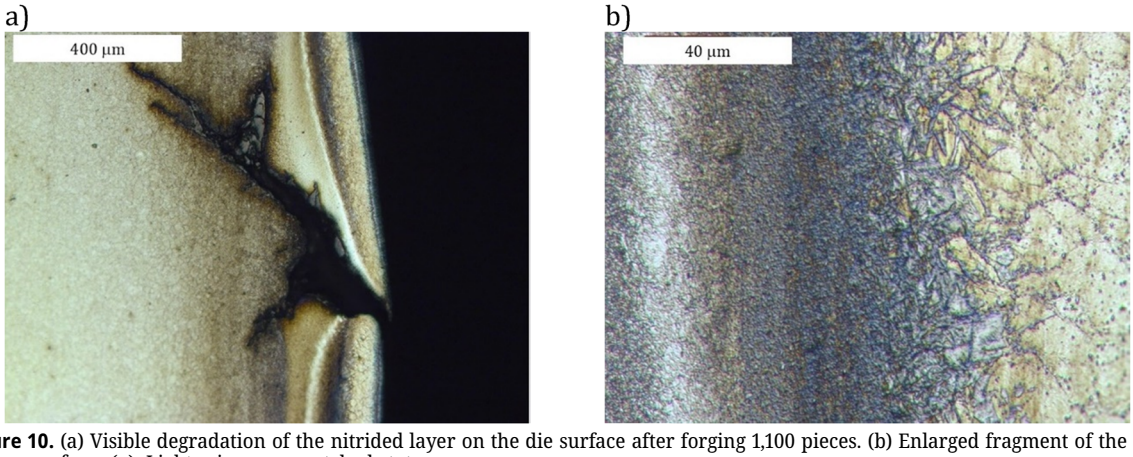


Figure 10. (a) Visible degradation of the nitrided layer on the die surface after forging 1,100 pieces. (b) Enlarged fragment of the area from (a). Light microscopy, etched state.

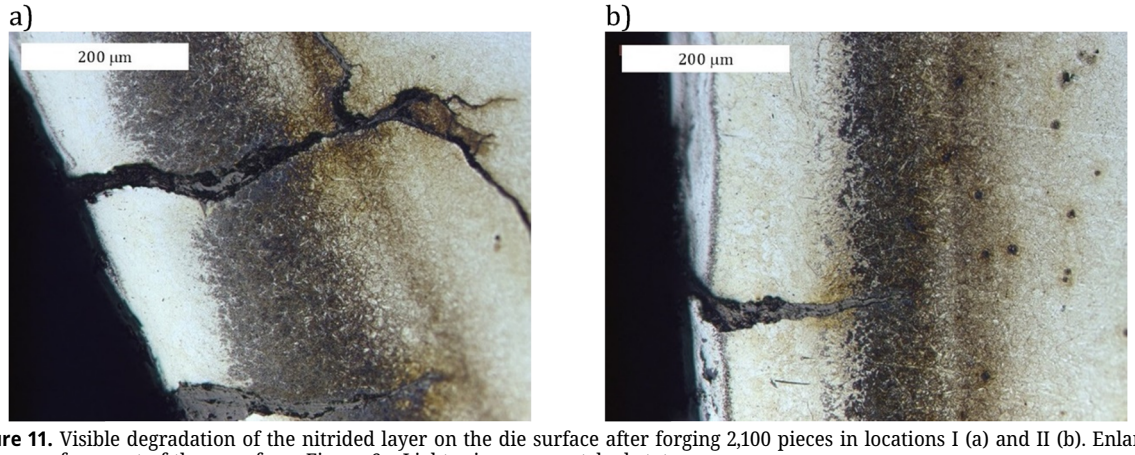


Figure 11. Visible degradation of the nitrided layer on the die surface after forging 2,100 pieces in locations I (a) and II (b). Enlarged fragment of the area from Figure 6a. Light microscopy, etched state.

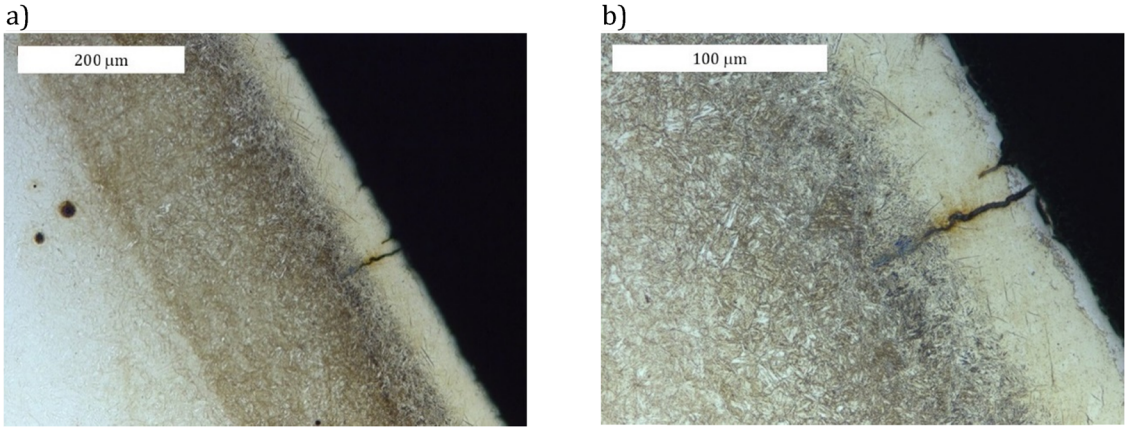


Figure 12. (a) Visible degradation of the nitrided layer on the die surface after forging 2,600 pieces. (b) Enlarged fragment of the area from Figure 6b. Light microscopy, etched state.

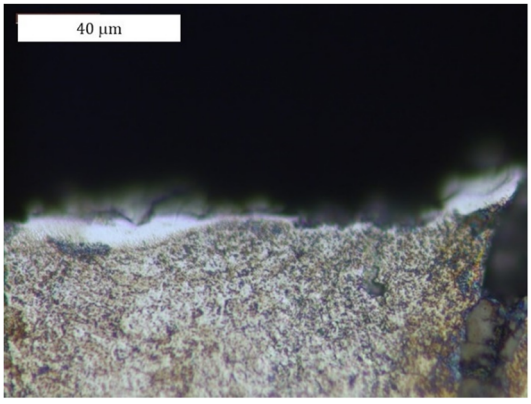


Figure 13. WEL formed on a forging tool. Light microscopy, etched state.

[63] found that the thermomechanical loading history has a significant influence on the subsurface changes. The formation of WEL, which occurred in the presence of high tangential forces, was accompanied by an increase in hardness. The decrease in hardness was associated with the decomposition and/or spheroidization of cementite.

In assessing the degradation mechanism of these areas, it should be considered whether the achieved tool surface temperature allowed the formation of a narrow zone in which the eutectoid transformation temperature of 592°C was exceeded. Then, nitrogen austenite would form in the diffusion zone. The high temperature of the forged material, which is heated to 1,050°C in the process, means that such a situation is likely to occur locally, directly at the tool surface [64]. In this case, a martensitic transformation can occur in the tool material during cooling, which occurs immediately after the removal of the preform. During cooling, the nitrogen-containing austenite can transform into microstructures convergent to the carbon-containing austenite, including bainite and martensite [65]. The martensitic transformation will be accompanied by a large change in the tool volume in the surface area, which may promote the formation of cracks. Thermal shocks can also induce cyclic austenitic and martensitic transformation processes in the near-surface region. The possibility of austenitization is also confirmed by other authors, who also point out that coexisting mechanical loads can lead to a decrease in the phase transformation temperature, including the A_{c1} temperature [4,5]. An important aspect is the fact that the solubility of nitrogen increases significantly in austenite, which can dissolve up to 2.8 wt% (10.3 at.) of nitrogen [26]. During the cooling of low nitrogen-containing austenite, eutectoid decomposition $\gamma \rightarrow \alpha + \gamma'$ or shear transformation $\gamma \rightarrow \alpha'$ may occur [26]. In such a situation, as a result of exceeding the optimum nitrogen concentration in the layer, which decreases the martensitic transformation temperature M_s, martensite may form, leaving a large amount of retained austenite. At the same time, nitrogen increases hardenability so that this area will have a higher hardenability than the base material. At the same time, nitrogen increases hardenability so that this area will show better hardenability compared to the base material. At low-temperature M_s, lamellar-structured martensite is formed, and the amount of martensite formed depends on the degree of undercooling below M_s and above M_f. Therefore, the lower the M_s, the less martensite and the greater the amount of retained austenite after cooling to ambient temperature. Nitrogen is a strongly stabilizing and austenite-forming element. Somers and Christiansen [21] indicated that strain-induced cubic martensite can form in metastable austenite, which promotes the precipitation of CrN. Kardonina et al. [26] showed that a nitrogen content of 8.2 at% lowers the M_s

temperature enough that the austenite remains stable after cooling to ambient temperature. Similar observations regarding the stability of high-nitrogen austenite were reported by Schneider [65]. Then, a single-phase structure can form at the surface, which is nitrogen-supersaturated austenite. Nitrogen supersaturation is used in the surface treatment of stainless steel. The metastable austenite formed in this way is called expanded austenite. In the microscopic image, the nitrogen-enriched layer is characterized by the formation of a light-colored layer [66–68]. Obtaining a fully austenitic structure in the surface region is, therefore, theoretically possible. It should be emphasized, however, that this seems unlikely because its formation is accompanied by the presence of very high compressive stresses, and high hardness is achieved, usually higher than 1,000 HV. Meanwhile, as indicated earlier, in the light-colored areas presented in this article, a decrease in hardness was noted. Moreover, Yurovskikh et al. [69] found that nitrogen ferrite remains stable up to temperatures of 760–780°C. There is no reason to assume that a non-etching layer of ε nitrides has formed in this region. This would require enriching this region with nitrogen, which is not possible in the technological process discussed here. Moreover, at atmospheric pressure, the stability of iron nitrides requires physical nitrogen [7].

It seems most likely that in the analyzed area, simultaneous partial denitrification and decarburization of the surface occurred. Decarburization in this area has already been observed in the studies presented by Hawryluk et al. [70]. Birol [44] studied the response of nitrided X32CrMoV33 steel (which corresponds to 32CrMoV12-28 steel according to EN ISO standard) to thermal cycles in the range from 450 to 750°C without additional mechanical loads. It was found that nitrided steel oxidizes more easily and also that the surface layer is partially denitrified. Kardonina et al. [26] found that the process of reducing the austenite lattice parameter, which occurs at temperatures of 840–850°C, may be a consequence of the decrease in nitrogen concentration due to the denitrification process. Various researchers have shown that during vacuum annealing of γ′(Fe_4N) nitride at temperatures above 650°C, this phenomenon can occur intensively up to a temperature of 850°C, where the denitrification of austenite lattice ends [26,69]. In such considerations, large needle-like structures can be attributed to the typical γ′-Fe_4N nitrides [30], which were deformed or enlarged during the decomposition stage. In the microscopic image, it can be seen that the number of these precipitates clearly decreased by approaching the surface until it disappeared completely. This is especially visible at high magnifications (Figure 10b). Schneider [65] observed large needle-like nitrides typical of Fe_4N in the coarse-grained ferritic base material in the diffusion zone formed during the slow cooling of supersaturated ferrite. γ′-Fe_4N nitrides precipitate at the grain boundaries and extend into the α solid solution [32]. Reducing the cooling rate favors the formation of larger precipitates in this phase. The α″-$Fe_{16}N_2$ phase also forms fine platelet-like nitrides [23]. A high surface heating temperature, but lower than the austenitization temperature, will promote partial (or complete) decomposition of carbonitrides. The least thermally stable phase in the Fe–N system is the γ′ phase, which dissociates during annealing and forms nitrogen austenite [7]. It has been reported in the literature that when the temperature increases significantly above the eutectoid transformation temperature, the γ′ phase present in the surface zone disappears (most likely due to the absorption of nitrogen by nitrogen austenite) [26]. According to Yurovskikh et al. [60,69], the absence of the ε phase layer on the surface during annealing will allow for a faster decomposition of the γ′ nitride. Also, carbon diffusion through the layer is greater when the nitrided layer does not contain a compound layer [10]. It is assumed that nitrogen removal occurs by volume diffusion of atoms to the interphase boundaries and the formation of nitrogen gas at them [26]. The γ′ nitride present in the surface region may partially disappear due to nitrogen absorption by ferrite. This allows a moderate amount of nitrogen to be dissolved in the ferrite, resulting in a metastable, supersaturated solid solution of nitrogen and carbon in α-iron. The solubility of nitrogen in ferrite is much lower, not exceeding 0.1% by mass (0.4 at.) of nitrogen [26].

5. Role of the nitrided layer microstructure

The gradient nature of nitrided layers provides the possibility of modeling their properties. At the same time, published research results on the behavior of nitrided elements used under cyclically variable loads are different from each other and often partially contradictory. This is understandable due to the differences in the microstructure of the produced nitrided layer. There is much evidence in the literature that the presence of a brittle compound layer is not desirable in hot work dies. This is due to its significantly lower impact strength than the diffusion layer, which results in lower resistance to thermal shock and impact loads. It is also a sensitive factor in the initiation of thermal fatigue [71]. This should be attributed to the facilitation of easy crack nucleation [72]. It has also been shown that dies with multi-layer nitrided layers show worse wear under high load conditions [35]. Pellizzari et al. [72] investigated the influence of different nitriding methods on thermal fatigue resistance. They

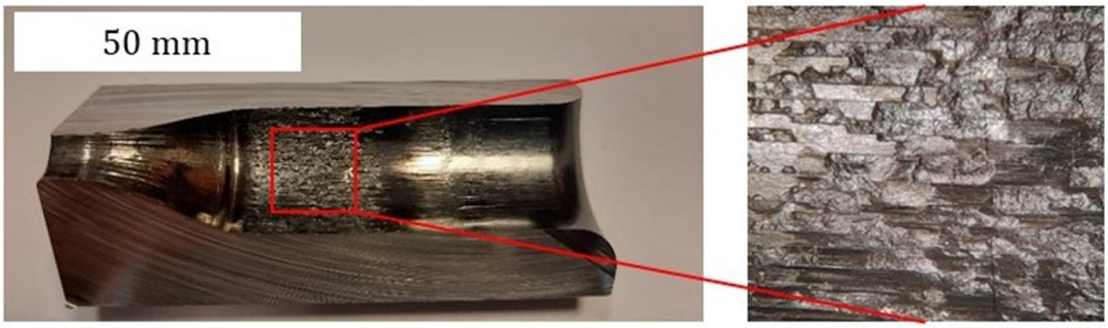


Figure 14. General view of die surface after forging 2,190 pieces of forgings. Stereoscopic microscopy.

analyzed the effectiveness of nitriding in relation to fatigue crack initiation. They found that the presence of a brittle compound layer in the material microstructure promotes crack nucleation. A similar approach was taken by Kundalkar et al. [20]. Somers and Mittemeijer [50] pointed out that porosity can also be observed in the nitrided layer, which is related to the formation of molecular nitrogen. Gronostajski et al. [73] analyzed the effect of phase composition on the susceptibility to cracking of forging tools. They showed clear differences in wear mechanisms depending on the microstructure of the nitrided layer.

The nitriding temperature is generally maintained below the eutectoid transformation temperature of 592°C [21]. This prevents the formation of austenite, which could then transform into martensite. This is accompanied by a large change in the volume. Nitriding carried out at a temperature higher than the eutectoid transformation leads, after slow cooling, to the formation of nitrogen-rich (2.35 wt%) braunite, a product of the eutectoid transformation ($\alpha(Fe) + \gamma'\text{-}Fe_4N$) (Figure 2), which is also confirmed by the results of experimental studies [10,74–77]. Braunite, also known as nitrogen perlite, is an undesirable microstructural component [78,79]. It has been proven to increase the brittleness and tendency to crack of the nitrided element [80,81]. Figure 14 shows a general view of the die surface, which underwent accelerated destruction resulting from the presence of braunite in the microstructure. The macroscopic image shows numerous surface cracks of a character not observed in the die, which did not show such microstructural features. Microscopic observations conducted on the cross-section showed that such a nature of changes was the result of the formation of subsurface circumferential cracks parallel to the surface (Figure 15). The cross-sectional image clearly shows massive cracks, which mainly originate from the surface. These cracks usually propagate downward, and some of them branch along the nitrided layer, leading to spalling. A dense network of radial cracks interconnecting as a result of the formation of circumferential cracks ultimately led to the crumbling of bands of material from the die surface.

In the tested matrix, apart from braunite, γ′ nitride precipitates were also observed, occurring in the form of

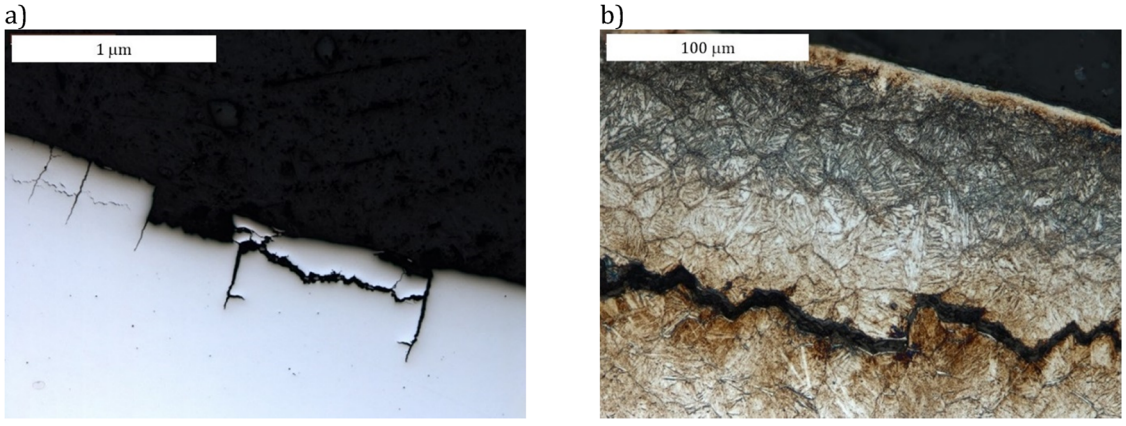


Figure 15. Cross-section obtained from a die in which the presence of brainite was detected: (a) undetched state and (b) etched state. Light microscopy.

a network of precipitates in the diffusion layer along the grain boundaries, which gradually disappeared with the depth of the diffusion layer. The presence of these hard precipitates at the grain boundaries, indicating high nitrogen saturation of the steel, was an additional factor contributing to the formation of cracks of this nature. The irregularly shaped γ′ phase nitride precipitates, invisible at lower magnifications, were concentrated on the grain boundaries of prior austenite (Figure 16). Such a microstructure showing the presence of a γ′ nitride network is more susceptible to chipping [73]. Its formation is facilitated by the high carbon content in steel. Carbon released during the transformation of carbides into nitrides can segregate to the grain boundaries and then form carbides there. Then, they are transformed into nitrides [21].

6. Influence of the diffusion layer thickness

Forging tools are subjected to strong abrasion and dynamic loads, which reduces their durability. Literature data confirm that the use of a nitrided layer allows for its increase. At the same time, it has been noted in the literature that the thickness of the diffusion layer is of significant importance for the durability of the die. There is a correlation between the maximum crack length and the thickness of the diffusion layer. Persson et al. [82] indicated that cracks are characterized by a direct propagation path at temperatures up to 700°C. At 850°C, cracks branch at a later stage, indicating rapid crack growth and propagation. Propagation is delayed when the cracks reach the high-strength material [82–84]. Hawryluk et al. [13] proved that the use of a thicker nitrided layer consisting of a diffusion layer on forging tools enables its longer service life in the presence of significant fatigue cracks. Figure 5 shows the macroscopic and microscopic images obtained on longitudinal sections of the die in the region of the constriction formed under operating conditions in the middle section of the die. Abrasive wear was observed, which led to the complete removal of the nitrided layer and local exposure of the parent material. Upon reaching the substrate material, rapid destruction of the matrix surface was observed, leading to the loss of its functional properties. This became the basis for the conclusion that the presence of the nitrided layer promotes increased die durability until the diffusion layer is mechanically removed [13]. Spies and Dalke [10] confirmed in this respect that after reaching the end of the nitrided layer, the initially brittle crack develops further as a ductile crack. Thermal cycles performed at high temperatures cause softening of the nitrided layer [82].

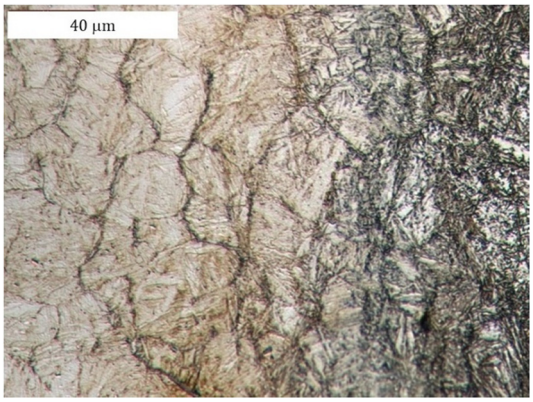


Figure 16. Enlarged fragment of the microstructure examined die. Visible braunite (right) and carbonitrides form a network at the grain boundaries (left). Light microscopy, etched state.

It is common knowledge that the thickness of the nitrided layer is influenced by the temperature and time of nitriding. Wang et al. [35] analyzed the nitrided layer thickness at the same nitriding temperature and process time. They found that the effective diffusion layer thickness grew with the increase of the nitriding potential. Therefore, the composition of the surface phase and the thickness of the nitrided layer can also be controlled by adjusting the nitriding parameters. The influence of the nitriding potential and nitriding temperature on the phase composition and nitrogen content of the ε phase can be represented using the extended Lehrer diagram (Figure 3).

7. Influence of the chemical composition of the substrate and the condition of its surface

The composition of nitrided coatings can be modified by appropriate selection of the material. Nitriding under industrial conditions takes place below the A_{c1} temperature of the iron–nitrogen system. Depending on the chemical composition of the nitrided material, this temperature can change significantly. The role of the chemical composition of the substrate material, including tool steels, has been well documented in previous studies [10,21].

One of the most important factors influenced by the chemical composition of the substrate is the thickness of the nitrided coating obtained. It was found that the thickness of the compound layer decreases with the content of alloying elements [10]. For example, the content of 3% molybdenum in 32CrMoV12-28 steel is able to reduce the

thickness of this layer by half, and the presence of chromium additionally enhances this effect. The diffusion layer is multiphase, the microstructure of which is characterized by not only a solid solution of nitrogen in ferrite but also by precipitations of iron nitrides and alloying elements. In steel grades that contain nitride-forming elements, e.g., chromium, molybdenum, vanadium, titanium, and aluminum, the solute nitrogen forms a small, fine dispersed nitride precipitate [10]. With the exception of aluminum, all nitride-forming elements are also carbide-forming elements, which results in the occurrence of carbonitrides as well. The alloy carbides in the steel matrix are transformed into nitrides because the nitrides of the metallic element are thermodynamically more stable than the carbides [21]. The content of nitride-forming elements has a major influence on the depth range of the diffusion zone. The thickness of this layer is also dependent on the concentration of alloying elements and decreases with their content [10]. This is due to the fact that the higher the content of the alloying element forming the nitride, the slower the rate of growth of the diffusion zone [21,39]. The microstructure of the obtained coating translates into its hardness. It was found in this respect that the increase in hardness is specific for each alloying element [10].

In alloy steels containing carbide-forming elements, a non-linear carbon content profile occurs, i.e., an enrichment of the carbon layer is observed before the diffusion zone [10]. This is due to the "pushing" of carbon toward the core against the advancing nitrogen concentration profile, as well as partial decarburization of the surface [10,21]. This is manifested by the often observed two-layer diffusion layer in the microscopic image. The level of carbon redistribution depends on the content of alloying elements and increases with the content of carbide-forming elements (and aluminum), which are also nitride-forming elements.

The final quality of the produced nitrided coating is also influenced by the surface condition of the substrate material [10,68,85,86]. Factors influencing surface passivation make it difficult to form an even layer or, in extreme cases, completely prevent nitriding [10,87]. Baranowska [68] pointed out that the higher the surface diffusivity, the greater the nitriding intensity. For this reason, proper surface activation is essential for nitriding [68,86].

8. Conclusions

Nitriding is used to refine the surface of forging tools in order to improve their tribological and fatigue resistance. The effect on the final properties of these layers depends on their phase composition and thickness, and these are determined by the chemical composition of the tool steel and the nitriding parameters. The basic mechanism of wear of hot work tool steels is thermal fatigue. However, there is little information in the literature on the long-term effect of temperature on the decomposition of nitrided layers, especially those that are severely plastic-deformed. For this reason, it is advisable to conduct further research on phase transformations related to the decomposition of nitrided layers.

Metallographic studies conducted on post-service-life dies indicate that the nitrided layer degrades under thermomechanical conditions. This leads to the formation of a thin layer of light color, sometimes with needle-like precipitates. The observed layer showed features typical of diffusion layers. The discussion conducted in this work and the existing state of the art allows us to suspect that partial decarburization and denitrification most probably occur in the near-surface layer of the dies. Consequently, the degradation of nitrided layers in this area is associated with partial decomposition of carbonitrides, leaving ferrite supersaturated with nitrogen. It is advisable to conduct further research in this area, in particular, to confirm the analyses performed by TEM methods. The various magnetic properties of the phases present in the microstructure of nitrided steel allow us to trust that FMR measurements may also be helpful in this respect. XRD patterns can also provide valuable information.

Author contributions

Conceptualization: ML, Data curation: ML, Formal analysis: ML, Investigation: ML, Methodology: ML, Visualization: ML, Writing – original draft: ML, Writing – review & editing: ML.

Conflict of interest statement

Authors state no conflict of interest.

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