Varieties of gas and ionic nitrided microstructures in narrow gaps of 
AISI H10 dies for Al hot extrusion and their wear resistance

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Summary
Dies with narrow and deep gaps, made from AISI H10 die steel, were nitrided by various manufacturers of equipment for ionic and gas nitriding. The manufacturers themselves, based on their experience with extrusion dies, chose the optimal nitriding parameters. The microstructure obtained showed differences with regard to the presence or absence of a compound layer, its thickness and $\varepsilon/\gamma'$ phase ratio (XRD), nitriding depth and microhardness values. The nitriding depths obtained, the maximum microhardness of the nitrided surfaces and $\varepsilon/\gamma'$ phase ratio were usually similar on dies of the same manufacturer, while for different die manufacturers these values differ. Samples with the various nitrided microstructures mentioned were laboratory tested for wear resistance by a newly designed test rig that provided simulation of the tribological conditions of hot extrusion of aluminium. The results of the study indicate that dies with a greater nitriding depth (diffusion zone) in combination with a compound layer mainly composed of only one phase (in our case $\varepsilon$ phase) exhibited better wear resistance than those with a lower nitriding depth and with an equal share of the two phases.

Key words: Al hot extrusion, AISI H10 die steel, nitriding, microstructure, XRD, SEM, wear testing.

1. Introduction
Products made from Al alloys, due to their low weight and excellent mechanical characteristics, and the rapid development of new Al alloys, continue to improve and to gain in importance. This is valid especially for hot extruded (Figure 1a) products, which because of their very complex shapes, have found applications in the automotive, electrical and aircraft industries, household goods, etc. For extrusion dies AISI H13 die steel is mainly used but also AISI H11 and AISI H10. With regard to wear, the bearing surface of the die on which three different zones (sticking, transition and sliding regions, Figure 1b) occur, is the most important part of the die since it influences the surface quality of the extrudate and consequently the die life. Wear processes start in the transition zone due to chemical reaction of hot aluminium with the die surface (pitting), consequently leading to formation of craters and to their extension towards the outlet of the bearing surface during the extrusion process (Figure 1c). The temperatures on the bearing surface reach values up to 600 °C, and surface pressures usually amount up to 50MPa. Although for cutting tools and hot forming tools (dies) procedures of surface treatment such as PVD, duplex treatment, ionic nitriding, etc. are commonly used to achieve more wear resistant surfaces, for hot extrusion dies gas nitriding is by far the most (90-95 %) common surface treatment procedure today and will probably keep this position for many years. This is because this procedure is also effective on surfaces in very narrow and deep gaps, such as are present on the majority of dies used for extrusion of profiles. Improvement of wear resistance on die bearing surfaces in aluminium hot extrusion still today represents a great challenge to the die designer and manufacturing technologist since gas nitriding is technologically a very sensitive process with regard to achieving and maintaining the same quality of structure and microstructure. The formation of a compound layer on the nitrided surfaces is a very common phenomenon accompanying steel die nitriding and there is no consensus between researchers on whether the compound layer increases or decreases the wear resistance of the die surface in Al extrusion. Namely, the compound layer is usually composed of $\varepsilon$ and $\gamma'$ phases that are very hard and also brittle, especially the $\varepsilon$ phase. Creation of the compound layer is influenced by the following parameters: temperature and time of nitriding, die steel (chemical composition), gas mixture ratio and gas flow on the nitriding die surface (and furnace), partial pressure of nitrogen, time, etc. The success of ionic and gas nitriding on dies (AISI H10) with narrow and deep gaps is studied in this contribution. This study at the same time additionally contributes to elucidation of the question whether an iron nitride compound layer improves or reduces the wear resistance of dies used for aluminium hot extrusion. Furthermore, due to the variety of nitrided microstructures obtained, it also indicates which nitrided structures and microstructures are potentially more suitable for prolongation of die life.

2. Experimental: ionic and gas nitriding of dies with narrow gaps
This study is based on the analysis of microstructures on dies that were nitrided by eight different (acknowledged) manufacturers (Table 1) of equipment for ionic (manufacturers 1 and II) and gas (manufacturers III - VIII) nitriding. In order to compare the efficiency of nitriding in narrow gaps, sixteen
dies (Figure 2, Table 1) of AISI H10 (chemical composition: 0.30 C, 0.30 Si, 0.38 Mn, 3.0 Cr, 2.80 Mo, 0.45 V, Fe-to 100%) with 1 mm and 4 mm gaps (gap depth was 12 mm) were made. According to our instructions the time of the nitriding process including heating and the cooling had not to exceed 12 h, and the depth of nitriding had to be at least 120 μm. The manufacturers themselves, based on their experience with extrusion dies, chose the optimal gas mixture ratio and pressure, nitriding temperature, time, cooling, etc. where every manufacturer nitrided two dies. From the nitrided dies smaller blocks (30 mm x 30 mm x 20 mm) were sectioned, on which the microhardness profiles, the thickness of the compound layer and XRD were carried out. These blocks also served for testing the wear resistance of the nitrided microstructures. Dies with narrow and deep gaps were chosen for comparison of the efficiency of gas nitriding versus ionic nitriding since narrow and deep gaps are often present on dies for the extrusion of profiles of complex shape and they represent a restraint (inefficient in such narrow and deep gaps) on the use of ionic nitriding.

Figure 1: Principle of Al hot extrusion (a.), die bearing surface with sticking, transition and slipping regions (b.) and appearance of furrows after extrusion of 15,000 m of round profile (c.).

Table 1: List of manufacturers of ionic (ION) and gas (GSN) nitriding dies, compound layer thickness (CLT), nitriding depth (ND), and maximal microhardness (MMHRD) in 1 mm and 4 mm gap.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
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<tbody>
<tr>
<td>Type of nitriding</td>
<td>ION</td>
<td>ION</td>
<td>GSN</td>
<td>GSN</td>
<td>GSN</td>
<td>GSN</td>
<td>GSN</td>
<td>GSN</td>
</tr>
<tr>
<td>Die no.</td>
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<td>3.4</td>
<td>5.6</td>
<td>7.8</td>
<td>9.10</td>
<td>11.12</td>
<td>13.14</td>
<td>15.16</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Gap</th>
<th>CLT [μm]</th>
<th>ND [μm]</th>
<th>MMHRD [HV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1mm</td>
<td>/</td>
<td>170-30</td>
<td>1200-700</td>
</tr>
<tr>
<td>4mm</td>
<td>/</td>
<td>4mm</td>
<td>934-819</td>
</tr>
</tbody>
</table>

3. Microstructures, microhardness and XRD of nitrided surfaces

3.1 Ionic nitriding

Dies which were nitrided by manufacturers I and II showed differences both in the nitriding depth (diffusion depth) of the 1 mm and the 4 mm gap, as well as on the surface, with the formation of a compound layer (Table 1). It was characteristic that better effect of nitriding was achieved for 4 mm gap in comparison to the 1 mm gap for both manufacturers; manufacturer II was more successful in both cases, although nitriding in the 1 mm gap was still not satisfactory. Figure 3 shows a profile of microhardness versus nitriding depth at various positions (gap depth) in the 4 mm gap for manufacturer II. We can see that the nitriding depth was between 340 μm at the beginning and 100 μm at the end of the 12 mm gap (Table 1). For the 1 mm gap the corresponding values were of 150 μm at the beginning and 70 μm at the end of the gap, which were too low for the surface to be well nitrided. Microstructures for manufacturer I had no compound layers (Figure 4a) in 1 and 4 mm gaps. This was also true for manufacturer II, but only in the 1 mm gap, while in the 4 mm gap a compound layer of 0 - 5 μm was obtained. The fact that a compound layer in the 4 mm gap was obtained and none in the 1 mm gap can be attributed to the difference in flow (stream) of the gas mixture inside the 1 and 4 mm gaps, and consequently to differences in the gradients of the influential parameters (gas concentrations, temperature, etc.). Also with the second die both manufacturers obtained similar results for the nitriding depth and the highest microhardness on the surface. Manufacturer II could, therefore, satisfactorily nitride in 4 mm gaps only when these were shallower (cca 5 mm). In practice, the length of bearing surfaces is usually in the range of 3.5 mm to 12 mm.
3.2 Gas nitriding

It is characteristic of gas nitrided dies that in general they possessed a compound layer. Thickness of the compound layer and the nitriding depth usually differed a little with regard to 1 mm and 4 mm gaps (Table 1). On Figure 4a are shown typical microstructures with a compound layer whose thickness slightly changes from die to die, as well as from manufacturer to manufacturer. The maximal microhardness of nitrided layers, nitriding depth and compound layer thickness for different manufacturers (III - VIII) in 1 mm and 4 mm gap are given in Table 1. Phase analysis (XRD) of the nitrided surfaces from different manufacturers is shown on Figure 5.

In the gap of 1 mm manufacturer III reached a relatively small depth of nitriding, which amounted to cca 120 μm; the highest value of microhardness was cca 1146 Hv, while the thickness of the compound layer was 4-12 μm. The nitriding depth reached in the 4 mm gap was cca 110 μm, the thickness of the compound layer was cca 4-8 μm, and the highest value of microhardness was cca 1135 Hv. XRD phase analysis on the nitrided surface (Figure 5) revealed the presence of a considerably higher amount of ε phase than γ phase along with iron oxides. The estimated ε/γ phase ratio amounted to cca 6, which is relatively close to a monophasic ε structure of the compound layer.

Manufacturer IV in the 1 mm gap achieved a relatively high depth of nitriding, cca 160 μm; the highest value for microhardness was cca 1120 Hv, with a compound layer of cca 4-12 μm in thickness. The measured depth of nitriding in the 4 mm gap was cca 180 μm, while the thickness of the compound layer was slightly higher, that is of approximately 6-13 μm, with the highest value for microhardness of cca 1130 Hv. XRD (Figure 5) revealed the dominant presence of ε phase with a somewhat greater amount of γ phase compared to manufacturer III. The estimated ε/γ phase ratio was cca 3 (Figure 5), which is less than in the case of manufacturer III.

The dies of manufacturer V were characterized by a great depth of nitriding of cca 180 μm for both gaps; the thickness of the compound layer was of cca 8-14 μm, with the highest value of microhardness of cca 1130 Hv. The estimated ε/γ phase ratio amounted to cca 0.7 (Figure 5), which means that the compound layer had a high amount of γ phase.

The nitriding of manufacturer VI was characterized by a relatively small depth of cca 120-130 μm; the thickness of the compound layer was cca 8-12 μm, with the highest value of microhardness of cca 1030 Hv. XRD revealed a high amount of γ phase (estimated ε/γ phase ratio cca 0.8) and also an Fe₄C₃ peak, which probably means that the compound layer did not cover the whole nitrided surface. This fact consequently raises the question of the efficiency of gas nitriding in narrow and deep gaps by this manufacturer.
The nitriding of manufacturer VII was characterized by a relatively great depth; namely in the 1 mm gap the depth of the layer amounted to cca 160 μm, with a compound layer of cca 4-10 μm and in the 4 mm gap 170 μm in depth with a compound layer 6-12 μm thick. The highest values of microhardness amounted to cca 1100 Hv. XRD of the compound layer showed a high amount of ε phase and a small amount of γ' phase; the estimated ε/γ' phase ratio amounted to cca 4.

The nitriding of manufacturer VIII was characterized by a somewhat lower depth of cca 150 μm in both gaps; the thickness of the compound layer was cca 5-10 μm in the 1 mm gap and 6-12 μm in the 4 mm gap. The highest values of microhardness amounted to cca 1120-1150 Hv. XRD analysis revealed almost a monophasic structure of the compound layer, where the estimated ε/γ' phase ratio amounted to cca 10.

The reasons for the usually slightly different depth of nitriding and the thickness of the compound layer probably lie in the different flow of the gas mixture in 1 and 4 mm gaps.

4. Wear testing of nitrided samples
Wear testing was performed with a "block on cylinder" test rig (Figure 6) at the high temperatures and high contact pressure which are characteristic of the hot extrusion of aluminium. The testing parameters were: a normal force of 2200 N, a sliding velocity of 25 m/min and a temperature of the Al cylinder of 510 °C. Heated Al cylinders of AA 6063 alloy (0.5 Mg, 0.5 Si, 0.19 Fe, 0.05 Mn), representing the heated extrudate, had dimensions of ø146 mm x 35 mm, while the tested blocks had dimensions of 30 mm x 30 mm x 20 mm. Heating of the Al cylinders was carried out by means of an induction coil with half a turn of winding. On both sides of the Al cylinders copper discs were positioned through which the temperature on the Al was indirectly controlled (emission coef. of Cu is cca 0.8); namely, since the emission coefficient of Al is very low (cca 0.1-0.2) errors of direct measurement of the Al cylinder could otherwise consequently be very high. Further, the Cu-discs allowed testing to be carried out at high contact pressures and, as a consequence, the testing times required were shorter, and at the same time, plastic deformation of the Al cylinders was prevented. In the actual process of hot extrusion, slipping between the bearing surface of the die and the extrudate occurs in almost non-oxidizing conditions, which is why, during testing, we needed to supply argon to the test chamber (chem. comp. of argon: O₂ max 5 vppm, H₂O max 10 vppm, CO₂ max 0.5 vppm, N₂ max 20 vppm; vppm is volumetric parts per million).

The focus of our observation was the role of the compound layer in terms of wear resistance: its resistance to chemical reaction with hot aluminium in comparison to nitrided base material, the mode of compound layer removal from the bearing surface and the response of the newly revealed bearing surface to hot aluminium. The temporal progress of the wear process occurred as presented in Figures 7. The initial state of the tested surfaces is given on Figure 7a. It was noticed that the process of spalling of the compound layer began with cracking (Figure 7b) that lead to its gradually (partial) spalling (40-60%), as is presented in Figure 7c. This proves that ductility of the compound layer is essential for its retention on the bearing surface. Furthermore, on the spots where the compound layer was removed accelerated chemical attack by hot aluminium took place (Figure 7c). The main reason for this behaviour could be in the increased surface roughness on these spots (the layer has irregular thickness) with a consequent increase in surface (cca 100 %)10, potentially more appropriate for chemical reaction with hot aluminium.
The processes of compound layer spalling and accelerated chemical attack were observed on all tested blocks, the only difference being the time of partial compound layer removal. From Figure 7c it is also clearly visible that the compound layer was chemically more resistant to hot aluminium in comparison to the base die material, since the process of pitting on the compound layer hardly took place. The next phase in die surface deterioration is presented in Figure 7d as a consequence of intensive chemical reactions with Al, as well of the process of adhesion. In Table 2 are collected the approximate times of partial (cca 40 -60%) removal of the compound layer for different manufacturers or for some specific characteristics of the nitrided microstructures.

Mono-phased (ε or γ) structures of the compound layer are less brittle, of which the γ mono-phase structure is more favourable. From this point of view the compound layer of the third manufacturer is relatively good, but due to the low nitriding depth (low load-carrying capacity) partial removal (cca 40 -60%) of the compound layer occurred after one hour of testing. The same was also observed with the microstructure of the fifth manufacturer, thought it was of relatively high nitriding depth. The structure of this compound layer was mixed (ε/γ phase ratio cca 0.7).

Spalling of the compound layer after two hours of testing was observed for the nitrided microstructure of manufacturer VII. Namely, the γ phase in this compound layer was present in lower proportion and the nitriding depth was relatively high (cca 170 μm). The composition of the compound layer of manufacturer VIII was relatively close to an ε mono-phase with a relatively high nitriding depth (150 μm), that resulted in the beginning of spalling of the compound layer after two hour of testing. In the later phase of wear testing (eight hours) the formation of craters occurred (similar as presented in Fig 1c) that were the starting points for formation of furrows, especially at sites where the craters were more frequent.

The course of wear as presented in Figures 7a-d is typical of all the tested microstructures. The characteristics of the compound layer and of the diffusion zone influenced the dynamics of the wear processes, i.e. when the states presented in Figures 7a-d occurred. Nitrided microstructures with low nitriding depth and microhardness values, and a lower ε/γ phase ratio are more prone to earlier spalling of the compound layer. The compound layer thicknesses of all tested microstructures were the range of cca 2-14 μm and did not vary to such an extent to enable the study of the influence of thickness on spalling. Die life could also be prolonged by a higher nitriding depth, but in the case of repeated nitriding (dies are usually used several times), the danger of overnitriding exists.

Table 2: Approximate time of compound layer (CL) partial removal (40-60 %) for various manufacturers.

<table>
<thead>
<tr>
<th>Time</th>
<th>Manufacturer</th>
<th>1h</th>
<th>2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>III, V, VI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>IV, VII, VIII</td>
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</table>

Figure 6: Set-up of the “block on cylinder” test rig.

5. Conclusions
Specially made dies with deep (12 mm) and narrow (1 and 4 mm) gaps were nitrided by various manufacturers of equipment for gas and ionic nitriding. The efficiency of the two nitriding procedures in such gaps was compared. The gas nitrided microstructures obtained from the various manufacturers differed with regards to nitriding depth and maximum microhardness values, as well as to composition (structure, ε/γ phase ratio) of the compound layer. A mono-phasic compound layer was not obtained from any of the manufacturers. Small differences in nitriding depth and compound layer thickness in 4 mm gaps were noticed in comparison to 1 mm gaps. The different characteristics of the nitrided microstructures resulted in various times of compound layer spalling (removal) during testing for wear resistance. On the sites of compound layer removal accelerated chemical attack took place that increased wear on the die surface. The compound layer is chemically more resistant to hot aluminium in comparison to nitrided base material. Earlier removal of the compound layer consequently results in decreased die life and later removal leads to prolongation of die life. Nitrided microstructures with low nitriding depth and microhardness values, and lower ε/γ ratio are more prone to earlier spalling of the compound layer. Ionic nitrided dies exhibited greater difference in the efficiency of nitriding both with regard to 1 and 4 mm narrow gaps, as well as to manufacturer. For the 1 mm gap none of the manufacturers was effective but for the 4 mm gap the effectiveness of one the manufacturers would be satisfactory in the case of shorter (up to 5 mm) bearing surfaces.
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References