Effect of Nitriding Potential K_N on the Formation and Growth of a “White Layer” on Iron Aluminide Alloy

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This paper investigates the effect of nitriding potential under well-defined gas nitriding conditions on the formation and growth of a compound layer called “white layer” on a FeAl40 (with the composition of 40 at. pct Al) iron aluminide alloy. The nitriding potential was systematically varied in the range of 0.1 to 1.75 bar^{-1/2} at 590 °C for 5 hour nitriding time with an ammonia-hydrogen-nitrogen atmosphere. Characterization of the microstructure and phases formed within the white layer was performed using optical and scanning electron microscopy, X-ray diffraction (XRD), electron backscatter diffraction (EBSD), and glow discharge optical emission spectroscopy (GDOES). Experimental results indicated that the nitriding potential strongly influences morphology and crystal structure of the white layer. The nitride compound layer consists of the phases γ' -Fe₄N, ϵ -Fe₂₋₃N, and AlN. A mechanism is proposed for the formation and growth of the white layer, depending on the effect of the nitriding potential.

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I. INTRODUCTION

ALUMINIDE intermetallic alloys, based on phases of TiAl, FeAl, and Fe₃Al, have been of great scientific as well as industrial interest due to their beneficial properties at elevated temperatures such as excellent oxidation and creep resistance, and low density compared to Ni-based superalloys. These intermetallic alloys have great potential for substituting superalloy materials for applications in the aerospace and automotive industries.^[1,2] However, they also have disadvantages such as low ductility at room temperature, and poor tribological properties due to their insufficient surface hardness. To overcome these limitations, there is a lot of research to improve the surface properties of aluminides.^[3–5]

Iron aluminides based on the B2-FeAl intermetallic phase exhibit an aluminum content of up to 53 at. pct and can be used for high-temperature applications in which the working temperature can reach up to 800 °C.^[6,7] However, for mechanical parts which work under abrasive conditions, the hardness of 300 HV up to 400 HV of FeAl-based alloys is too low.^[8–10] Therefore, surface modification methods such as thermochemical surface treatments are applied to enhance the surface hardness and to improve the friction properties and wear resistance.^[8,9,11] Iron aluminides show a good response to nitriding treatment, including fine nitride precipitations, increasing the surface hardness.

However, there is a limited number of studies applying the nitriding process, which is known as a common surface hardening method, on iron aluminide alloys based on B2-FeAl. These studies focused mainly on the influence of temperature and incubation time on the nitride layer formation during gas^[9] and plasma nitriding processes^[11] in the range between 450 °C and 850 °C. Abnormal behavior in nitride layer growth was observed at temperatures above 600 °C, as both the thickness and the hardness of the nitride layers were significantly reduced. Besides, there was rarely a systematic study about the effect of nitriding atmosphere or nitriding potential K_N on B2-FeAl alloys. The nitriding potential describes nitride phases formation ability of the nitriding atmosphere, which is defined by $K_N =$

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$p\text{NH}_3/p\text{H}_2^{1.5}$ [$\text{atm}^{-1/2}$ or $\text{bar}^{-1/2}$]; where $p\text{NH}_3$ and $p\text{H}_2$ are the partial pressures of the ammonia and hydrogen gases, respectively.

Spies *et al.*^[9] carried out gas nitriding on an iron aluminide FeAl40 alloy at the above-mentioned range of temperature in ammonia atmosphere controlled nitriding potential K_N . They reported two disadvantages regarding the diffusion of nitrogen atoms at nitriding temperatures above 650 °C: (i) the nitrogen potential K_N was strongly reduced related to the thermal decomposition of NH_3 since the growth of the nitride layer was reduced, and (ii) an “external nitriding” process took place more strongly. Thereby, the iron atoms diffused outwards to the surface and combined with the nitrogen atoms of the gas atmosphere to form a compound layer of iron nitride phases, which prevented the further absorption of nitrogen atoms into the substrate. The authors^[9] stated that the optimum nitriding temperature was in the range between 450 °C and 550 °C. For the influence of nitriding potential on the microstructure and the properties of the nitride layer, the authors also gave preliminary evaluation results at 550 °C with two nitriding potential values of below $0.5 \text{ bar}^{-1/2}$ and above $2 \text{ bar}^{-1/2}$. The results showed that the structure of the nitride case comprised two zones; the outer zone was a “white layer” with a thickness of 1 to 3 μm and the zone beneath was a hard layer in which hexagonal AlN was precipitated.

In a plasma nitriding process, Zhang *et al.*^[11] investigated the effects of different nitrogen-hydrogen and nitrogen-argon gas mixtures at temperatures in the range of 450 °C to 700 °C with various times of 1 to 20 hour on the resulting nitride layer structure of a FeAl alloy. By using two different mixtures of gas compositions, 25 pct N_2 + 75 pct Ar and 75 pct N_2 + 25 pct Ar, the effect of the nitrogen content in the plasma atmosphere was investigated; these values correspond to the low and high nitriding potentials in the conventional gas nitriding. Again, the results showed abnormal growth kinetics of the nitride layer similar to that reported for the gas nitriding process. According to Zhang, nitride layers generated in a temperature range of 450 °C to 600 °C showed both high hardness and thickness. However, the authors also not have made any specific assessment of the influence of nitrogen content on the microstructure of the nitride layers.

Martin *et al.*^[10] carried out plasma-assisted nitriding at 600 °C for 15 minutes on ODS FeAl40 and found that the hardness of the nitride layer was due to the presence of an outer sublayer made of γ' - Fe_4N exhibiting moderate hardness values between 550 and 850 HV, and a much harder inner sublayer of AlN with 1400 HV.

Çelikyurek^[8] studied the nitriding effect on the Fe_3Al alloy by a salt bath nitriding process at 580 °C. Their results revealed that the hardness of the nitride layer had a value of about 1200 HV, while the matrix Fe_3Al had only 300 HV. Moreover, an increase in the nitriding duration did not affect the layer hardness but influenced the wear resistance to decrease. Celikyurek found that the layers formed on nitrified Fe_3Al mainly composed of AlN and Fe_3N nitride.

The above-mentioned studies have shown that appropriate nitriding temperatures are lower than 600 °C and that the microstructure of the generated nitride layers showed a twofold-layer structure consisting of a “white layer” and a “diffusion layer” depending on the applied nitriding parameters. However, up to now, no systematic study investigating the influence of the composition of the nitriding atmosphere on the nitriding effect of iron aluminide alloys has been conducted. At modern gas nitriding processes with ammonia, the nitriding potential K_N is used to set the atmosphere’s potential to enable a controlled diffusion of nitrogen into a material. The structure and properties of the nitride layer can be achieved as desired through the precise control of the composition of the atmosphere expressed as the nitriding potential K_N .

In this study, the main objective is to evaluate the effect of the nitriding potential on the formation and growth of the compound layer, also called “white layer”, on B2-FeAl alloys during the gas nitriding process using ammonia. Based on the obtained results, the effect of nitriding potential on the formed phases is thoroughly discussed, and an optimal K_N value is given for this alloy.

II. EXPERIMENTAL DETAILS

The investigated material was a B2-FeAl compound based intermetallic alloy with the composition of 40 at. pct Al. The ordered FeAl phase forms on the body-centered cubic (bcc) lattice, with B2 structure over a wide range of compositions. The ideally ordered B2 structure has a composition of 50 at. pct Fe-50 at. pct Al.^[1,12,13]

The specimens were machined with a diameter of 12 mm and a thickness of 5 mm. Before nitriding, they were wet-ground with SiC sandpapers up to 1200 grit and cleaned in ethanol to remove contaminants on the surface.

The nitriding experiments were carried out at 590 °C for the nitriding time of 5 hours in an atmosphere that contains NH_3 , H_2 , and N_2 gases. During the nitriding process, the nitriding potential K_N was controlled by hydrogen sensors used to measure the partial pressure of H_2 in the outlet exhaust gas. In order to investigate the effect of the composition of the gas atmosphere on the nitride layer formation, the nitriding potential K_N was varied in the range between 0.1 and $1.75 \text{ bar}^{-1/2}$.

The surface topography of the treated samples was investigated using a MIRA3 TESCAN scanning electron microscope (SEM). SEM analysis was done in order to characterize the morphology of the compound layer on the substrate for different K_N values. Besides, a tactile surface roughness measuring device MarSurf PS10 was used to determine the roughness average R_a of the nitrified samples’ surfaces.

Cross-sectional characterization of the nitrified samples was performed to investigate the microstructure and to assess the thickness of the nitride layer. Therefore, the samples were sectioned and metallographically polished

up to surface quality of $1\text{ }\mu\text{m}$, and finished with oxide polishing suspension. Due to the clear contrast between the nitride layer and the substrate, the samples were investigated in a non-etched condition. The microstructure and the thickness of the nitride layers were characterized by light optical microscopy on a Neophot 32 (LOM) equipped with an OLYMPUS UC30-camera and the OLYMPUS Stream Motion analysis software, and by scanning electron microscopy (SEM) at a MIRA3 TESCAN.

Glow discharge optical emission spectroscopy (GDOES) was performed on a Leco SDP-750 to analyse the element-concentration depth profiles of the nitrided samples.

X-ray diffraction (XRD) analysis was performed with a Seifert FPM URD 6 diffractometer operating in Bragg-Brentano configuration. XRD patterns of nitrided samples were determined with Cu-K α radiation ($\lambda_1 = 1.54056\text{ }\text{\AA}$, $\lambda_2 = 1.54439\text{ }\text{\AA}$) in order to limit the total penetration depth (approx. $4\text{ }\mu\text{m}$ for Cu-radiation). Patterns were recorded from $2\theta = 20$ to 150 deg at a scan rate of approximate $0.01^\circ/\text{min}$ with a step size of 0.02 deg . The phases present in the surface compound layers were determined by a Search-Match routine (Panalytical HighScore+) involving the ICDD PDF-4+ database. The quantitative phase fractions were then determined by the Rietveld refinement method, as implemented in the Maud software.^[14]

Electron backscatter diffraction (EBSD) was conducted by using a scanning electron microscope (SEM) of JEOL JSM-7800f equipped with an EBSD analysis system of EDAX Hikari Super. An acceleration voltage of 20 kV and a step-width of 50 nm were employed for EBSD measurements. EBSD data were analyzed using the free Matlab toolbox MTEX.^[15] The data were cleaned by removing data points with a confidence index < 0.1 .^[16] The presented EBSD phase maps are overlaid with the image quality.

III. RESULTS AND DISCUSSION

A. Surface Roughness and Topography

Figure 1 shows the surface roughness R_a as a function of the nitriding potential K_N . Generally, with increasing nitriding potential, the topography of the white layer changes, which affects the roughness of the samples' surfaces.

As seen in Figure 1, the relationship between roughness R_a and nitriding potential K_N shows a non-linear dependence and three stages can be distinguished. In the first stage, the roughness R_a increased with increasing nitriding potential K_N and reached a maximum at $K_N = 0.5\text{ bar}^{-1/2}$. With increasing K_N , in the second stage, there was a reversed trend in which R_a decreased to a minimum value at $K_N = 1\text{ bar}^{-1/2}$. In the final stage, the surface roughness again increased with increasing nitriding potential of values above $1.0\text{ bar}^{-1/2}$. Thus, the nitriding potential of the treatment process affected the roughness R_a value significantly.

SEM observations of the resulting surface topography clearly show the formation of an outer layer. As seen in Figure 2, the topography feature of the layer is divided into two categories. The first group displays small particles formed on the samples treated at $K_N \leq 0.25\text{ bar}^{-1/2}$. However, these particles do not cover the whole surface as shown in Figure 2(a) for the example of $K_N = 0.1\text{ bar}^{-1/2}$. As a result, their presence increases the roughness of the samples' surface, which correlates with the results in the first stage shown in Figure 1. The second group corresponds to the samples treated with K_N values above $0.25\text{ bar}^{-1/2}$ (Figures 2(b) through (d) with K_N values of 0.5 , 1.0 , and $1.5\text{ bar}^{-1/2}$). For these nitriding conditions, a compound layer that contains column-like particles covered the sample surfaces. According to the published results of Spies *et al.*,^[9] this compound layer consisted mainly of iron nitride and partly of aluminum nitride. Therefore, the development of the layer can be considered to follow the external-nitriding mechanism, which explains the change in the roughness of the nitrided samples corresponding to the second and third stages of Figure 1. As the nitriding potential increases, the compound layer developed uniformly on the sample surfaces, which reduced the surface roughness, resulting in the smallest roughness value corresponding with $K_N = 1\text{ bar}^{-1/2}$ (Figure 1, second stage). With further increasing nitriding potential, however, the compound layer became more porous and led to an increase in surface roughness (Figure 1, third stage).

B. Structure and Thickness of the White Layer

SEM observations on all cross-sectionally prepared nitrided samples showed that a surface layer was formed during the gas-nitriding process. As can be seen in Figure 3, the typical structure of the resulting nitride layer comprises different depth-dependent zones, such as an outer white layer and an underlying dark diffusion layer embedded with wave-shaped lines, which Zhang

Fig. 1—The surface roughness R_a of the treated samples for different nitriding potentials K_N .

Fig. 2—SEM images captured from the surface of treated samples processed under different nitriding potential values: (a) $K_N = 0.1 \text{ bar}^{-1/2}$, (b) $K_N = 0.5 \text{ bar}^{-1/2}$, (c) $K_N = 1.0 \text{ bar}^{-1/2}$, and (d) $K_N = 1.5 \text{ bar}^{-1/2}$.

et al. also have referred to Reference 11, and finally the substrate. In Figure 4, the effect of the nitriding potential on the white layer's structure is displayed at higher magnification. Figure 5 shows the thickness of the white layer with values in the range of 0.5 to 2 μm as a function of the nitriding potential K_N . It reveals that the characteristics of the white layer are different from each other with the change of K_N value. The influence of the nitriding potential on the behavior of the diffusion layer will be addressed in another paper.

The images of the structure of the white layer shown in Figure 4 are entirely consistent with the results of the roughness and topography of the samples' surfaces, respectively, given in Figure 2. As seen in Figure 4(a), in the case of $K_N = 0.1 \text{ bar}^{-1/2}$, the white layer was thin and discontinuous. The SEM image for $K_N = 0.1 \text{ bar}^{-1/2}$ (Figure 2(a)) proves that the white layer consists only of scattered discrete particles that do not cover the entire sample surface. With increasing K_N , these particles were more precipitated and thicker (Figures 2(b) and 4(b)). When increasing the nitriding potential up to $1.0 \text{ bar}^{-1/2}$, these particles covered the whole surface to form the uniformly developed white layer, which reduced the roughness (Figures 2(c) and 4(c)). With increasing thickness of the white layer, more and more column-like particles were embedded with further increasing K_N values, corresponding to $K_N = 1.5 \text{ bar}^{-1/2}$ (Figures 2(d) and 4(d)), so the surface roughness R_a value again increased.

Fig. 3—Typical structure of the nitride layer after nitriding at 590°C for 5 h with $K_N = 1.5 \text{ bar}^{-1/2}$, SEM.

Figure 5 shows that the thickness of the white layer is steadily increasing with increasing values of K_N . However, with $K_N < 1.0 \text{ bar}^{-1/2}$, the white layer is not continuous in the range of 0.5 to $1.5 \mu\text{m}$ as easily visible by the LOM method. As shown in Figures 2 and 4; it can be seen that the white layer thickness increased slowly, while its clusters of nitride phases developed spreadly to cover the surface that increased the roughness. For higher K_N values, particularly K_N above 0.75 to $1.0 \text{ bar}^{-1/2}$, the white layer covered the entire sample and developed more evenly, compared to K_N below 0.75 to $1.0 \text{ bar}^{-1/2}$, so the surface roughness tends to decrease (Figure 1).

Fig. 4—SEM cross-section images of the samples nitrided at 590 °C for 5 h with different K_N values: (a) $K_N = 0.1 \text{ bar}^{-1/2}$, (b) $K_N = 0.75 \text{ bar}^{-1/2}$, (c) $K_N = 1.0 \text{ bar}^{-1/2}$, and (d) $K_N = 1.5 \text{ bar}^{-1/2}$.

Fig. 5—Effect of nitriding potential on the thickness of the white layer at 590 °C for 5 h.

As discussed in the previous section, in case the value of K_N exceeds $1 \text{ bar}^{-1/2}$, the external nitriding process takes place more intensely. As a result the thickness of the white layer increases, and it becomes more and more porous with the development of iron nitride phases and other compounds, which are the cause of increasing roughness with high K_N , cf. Figures 4 and 5 at $K_N = 1.5 \text{ bar}^{-1/2}$.

The formation and growth of the white layer reflected significantly the influence of the nitriding potential at constant nitriding temperature and time.

C. Elemental Depth Distribution

Figure 6 displays a GDOES analysis of a sample treated with $K_N = 1 \text{ bar}^{-1/2}$ that demonstrates a typical concentration—depth distribution of the elements nitrogen, iron, aluminum, and oxygen. The nitrogen concentration exhibits a peak at a depth of 0.5 to 1 μm beneath the surface, and afterward, the content decreased gradually. This area of maximum nitrogen concentration corresponds to the white layer thickness, which had an average thickness of about 1.5 μm in the example shown. At the position A near the surface, the ratios of N/Al and N/Fe were 1.7 and 1.19, respectively. Up to position B, the ratios changed continuously to N/Al ~ 1.4 and N/Fe ~ 1.35 , respectively. This change in concentration ratios gives evidence that the white layer contains nitride phases of iron and aluminum. The proportion of iron nitride phases in the white layer near the surface is higher than that of the aluminum nitride phase. At deeper positions in the white layer, the N/Fe ratio decreases *vice versa* of N/Al. Besides, a small oxygen content was detected in the near-surface regions indicating that the outer surface has a porous structure.

D. Phase Composition and Structure of the White Layer

XRD patterns of the nitrided samples and the untreated base material are shown in Figure 7. The typical peaks of the B2-FeAl phase (PDF # 00-033-0020) are identified as denoted by number “1” in the XRD patterns. As seen in Figure 7, the B2-FeAl phase is the only phase detected for the untreated sample condition.

Fig. 6—Typical GDOES depth profile of chemical composition of a white layer formed during nitriding with $K_N = 1.0 \text{ bar}^{-1/2}$ at 590°C for 5 h.

For nitrided samples with increasing nitriding potential, the characteristic peaks of the FeAl phase in the XRD patterns decreased and disappeared at $K_N \geq 1 \text{ bar}^{-1/2}$. These results indicate that when the white layer formed and covered the entire surface no information from the substrate can be received, as shown in Figure 7(b).

The characteristic peaks of B2-FeAl are similar to bcc α -Fe (PDF # 00-006-0696, denoted as “2”), except for the superstructure reflections and small differences in the lattice parameters. Peaks of both phases overlap in the XRD patterns, which makes it difficult to distinguish between them. However, the lattice parameter of FeAl ($a = 0.291 \text{ nm}$) is a little larger than that of bcc ferrite ($a = 0.286 \text{ nm}$) as Al possesses a larger atoms size (0.143 nm) than Fe (0.128 nm). Therefore, the main peaks of bcc ferrite are shifted to the right of the B2 phase of the untreated sample.

Besides, the iron nitride phase of γ' -Fe₄N (PDF # 00-064-0134, denoted as “3”) is detected in all XRD-patterns of the nitrided samples. Additionally, another iron nitride phase ϵ -Fe₂₋₃N (PDF # 00-049-1663, denoted as “4”) is identified at $K_N \geq 1 \text{ bar}^{-1/2}$. These results prove that a certain amount of iron on the surface combines with nitrogen to form iron nitride phases creating the porous white layer.

Finally, an aluminum nitride phase of AlN (PDF # 00-025-1133, hexagonal structure, denoted as “5”) is also marked in XRD patterns of the samples treated, as shown in Figure 7.

These data imply that the structure of the white layer includes mainly iron nitride phases. The aluminum nitride phase is observed only at $K_N < 1 \text{ bar}^{-1/2}$, as shown in Figure 7(b).

Table I presents the results of the identification of phases and their volume fractions within the white layer, indicating the effect of the nitriding potential on the structure and composition of the white layer. It must be mentioned, that the XRD quantitative measurements were conducted by means of Cu-K α radiation, which penetrated the surface up to $3 \mu\text{m}$, and thus surpassed

the white layer's thickness. Therefore, the results obtained include the composition of the white layer and its adjacent subsurface region.

In the case of the nitriding treatment applying $K_N = 0.1 \text{ bar}^{-1/2}$, the layer was composed mainly of the phases AlN, α -Fe, and FeAl. Surprisingly in view of the small value of K_N , a very small amount of γ' -Fe₄N was also detected with a value of 2 vol pct. However, the investigations carried out in this study could not conclusively clarify the formation of this phase at such a low nitriding potential.

With further increasing nitriding potential $K_N > 0.1 \text{ bar}^{-1/2}$, the phase composition of the white layer changed. The data in Table I show that the volume fraction of γ' -Fe₄N phase increased with K_N up to $0.5 \text{ bar}^{-1/2}$. Subsequently, with a further increase of the nitriding potential to values $K_N \geq 0.75 \text{ bar}^{-1/2}$, the ϵ -Fe₂₋₃N phase formed and reached a value of 75 vol pct at $K_N = 1.5 \text{ bar}^{-1/2}$. The fraction of the remaining phases (AlN, FeAl, and/or α -Fe) decreased with increasing nitriding potential. This implies that with increasing K_N , iron atoms are available at the surface, e.g., due to an outward diffusion, for forming nitrides, yielding the external nitriding mechanism.

In gas-nitriding technology, the presence of the white layer is always associated with porosity as γ' -Fe₄N and ϵ -Fe₂₋₃N develop at increasing K_N values. The porous structure is an undesired consequence of nitrided samples since the presence of this type of defect will increase the roughness and degrade the surface properties in most cases.

The results of qualitative (Figure 7) and quantitative (Table I) XRD analysis systematically described the development of the phase composition of the white layer or at least the surface area within $3 \mu\text{m}$, respectively, as a direct effect of the nitriding potential applied during controlled gas nitriding of the FeAl alloy. The results also demonstrated that the white layer formation was due to the development of iron nitride phases by an external nitriding mechanism. However, the presented XRD results were influenced by the white layer's adjacent region and thus do not present the specific phase distribution within the nitride layer. Therefore, complementary EBSD measurements were conducted to obtain additional information on the crystal structure and the phase distribution in the selected area of the sample. Based on the XRD results presented in Figure 7 and Table I, two samples nitrided with the conditions of $K_N = 0.5$ and $1 \text{ bar}^{-1/2}$ were analyzed by the EBSD method. They represented the low and high nitriding potential corresponding to two primary phases (γ' and ϵ) of the white layer.

Figure 8 presents the results of EBSD measurements that were conducted on samples nitrided at 590°C for 5 hour with values of $K_N = 0.5 \text{ bar}^{-1/2}$ and $K_N = 1 \text{ bar}^{-1/2}$, respectively. When analyzing the EBSD data, only the iron nitride phases were indexed to evaluate the effect of K_N on the structure of the white layer. Already published studies indicated that there was hardly Al in the white layer, meanwhile, the nano-sized AlN lamellae precipitated in the diffusion zone.^[10] Since these

Fig. 7—XRD patterns (plotted on a square root scale) for untreated and treated samples: (a) low $K_N \leq 0.5 \text{ bar}^{-1/2}$; (b) high $K_N > 0.5 \text{ bar}^{-1/2}$, Cu- K_α radiation.

Table I. The Phase Composition of the White Layers

K_N ($\text{bar}^{-1/2}$)	Phase Composition (Vol Pct) ^a			
	FeAl $\pm$ Fe $_{\alpha}$ (bcc) ^b	Fe $_4$ N	Fe $_{23}$ N	AlN
Untreated	100	—	—	—
0.10	39 $\pm$ 3	2 $\pm$ 1	—	59 $\pm$ 5
0.25	14 $\pm$ 2	45 $\pm$ 4	—	41 $\pm$ 4
0.50	14 $\pm$ 2	50 $\pm$ 4	—	36 $\pm$ 3
0.75	12 $\pm$ 2	45 $\pm$ 4	12 $\pm$ 2	31 $\pm$ 3
1.00	—	21 $\pm$ 2	63 $\pm$ 5	16 $\pm$ 2
1.50	—	8 $\pm$ 1	75 $\pm$ 6	17 $\pm$ 2

^aCu- K_α , information depth 0 to 3 μm .

^bXRD pattern of FeAl overlaps with that of α -Fe.

nano-sized particles are beyond the resolution limit of conventional EBSD only the signal of the surrounding regions such as a bcc matrix was detected.

At the low value of $K_N = 0.5 \text{ bar}^{-1/2}$ (Figure 8(a)), the white layer, which was very thin and not dense, was formed on the surface. EBSD analysis showed that its composition was mainly γ' -Fe $_4$ N phase formed above the α -Fe substrate (in which nano-sized AlN lamellae were embedded, based on the literature^[10]). The wave-like features, indexed with green color in the EBSD phase map in Figure 8(a), were γ' -Fe $_4$ N close to the surface and became α -Fe with increasing distance from the surface. The existence of these structures was also consistent with a formation mechanism proposed by

Zhang *et al.*^[11] This result not only proved that the white layer structure was γ' -Fe $_4$ N, but also clarified the reason for the presence of α -Fe and AlN phases in the XRD results of $K_N = 0.5 \text{ bar}^{-1/2}$.

Meanwhile, with the increasing value of $K_N = 1.0 \text{ bar}^{-1/2}$, the white layer became thicker and denser in comparison to the previous case, and largely composed of a compact ϵ -Fe $_{23}$ N layer (Figure 8(b)). Specifically, it seemed that there was a local double layer of ϵ/γ' , in which a compact layer of ϵ -Fe $_{23}$ N formed on a sublayer of γ' -Fe $_4$ N. Nevertheless, the EBSD results cannot clearly prove whether this “ γ' sublayer” should be considered as a “true” sublayer of the white-layer for several reasons: At positions, where the presumably “ γ' sublayer” appears thicker, the layer was blown up by pores (marked by grey arrows in Figure 8(b)). The origin of the pores was considered to relate to the ‘precipitation’ of molecular nitrogen (N_2) in the nitride layer, which had a high dissolved N content under the condition of high nitriding potential. Furthermore, it seems that wave-like features have occasionally formed adjacent to the surface (marked with white arrows in Figure 8(b)), and were subsequently overgrown by ϵ -Fe $_{23}$ N surface layers. These wave-like features of γ' -Fe $_4$ N adjacent to the surface were not detected in case of low nitriding potential $K_N = 0.5 \text{ bar}^{-1/2}$. Their occurrence can be explained by the fact that with increasing nitriding potential the amount of N that penetrates the nitride layer also increases. Especially in

Fig. 8—EBSD measurements of the samples nitrided at 590 °C for 5 h with: (a) $K_N = 0.5 \text{ bar}^{-1/2}$; and (b) $K_N = 1.0 \text{ bar}^{-1/2}$ (grey arrows in indicate porous zones beneath $\epsilon\text{-Fe}_{2.3}\text{N}$ layer, white arrows indicate locally wave-like shaped $\gamma'\text{-Fe}_4\text{N}$ sublayer regions).

the adjacent region to the surface and the white layer with a very high dissolved nitrogen content inside, precipitation of iron nitride phases occurred strongly and resulted in an increase in residual stress by phase transformations.^[17] This leads to an assumption that because of the effect of the very high residual stress, the iron atoms were displaced and rearranged in a wave-like form in the adjacent region to the surface and combine with dissolved N atoms to precipitate $\gamma'\text{-Fe}_4\text{N}$. Therefore, it is assumed that they belong to the diffusion layer and are not really related to the white layer. This finding requires further investigations and will be investigated in future research which deals in particular with the processes within the diffusion layer of nitrided B2-FeAl alloy.

Generally visible in Figure 8(b), the wave-like features were also observed in the diffusion layer near the surface similar to the ones already observed in case of $K_N = 0.5 \text{ bar}^{-1/2}$. The $\epsilon\text{-Fe}_{2.3}\text{N}$ was also found, while the $\alpha\text{-Fe}$ was not present in the region. Therefore, with the structure as described, the obtained XRD analysis results of the white layer showed mainly the iron nitride phases of $\gamma'\text{-Fe}_4\text{N}$ and $\epsilon\text{-Fe}_{2.3}\text{N}$ with an amount of 16 vol pct AlN ($K_N = 1 \text{ bar}^{-1/2}$) caused by the influence of its neighborhood layer.

The EBSD results have shown the effect of the nitriding potential on the phase composition of the white layer with and the formation of iron nitride phases corresponding to the nitriding conditions.

E. Mechanism of the Development of White Layers on B2-FeAl

The aim of the modern controlled nitriding process is to measure and control the nitriding potential in the nitriding atmosphere to obtain the desired nitrogen concentration and phase composition in the nitride layers on iron-based alloys. The experimental Lehrer diagram for pure iron^[18] is widely used by researchers and engineers to determine the reference nitriding potential for the formation of nitride layers, specifically

for the prediction of the phase composition of compound layers. In this study, the Fe-N Lehrer diagram is calculated by using Commercialized Thermo-Calc software and shown in Figure 9.

According to the phase analysis results presented in Table I, at $K_N = 0.1 \text{ bar}^{-1/2}$ the “white layer” consisted of about 2 vol pct of $\gamma'\text{-Fe}_4\text{N}$ phase. Comparing this value with the boundary nitriding potential of α/γ' for pure iron in the Lehrer diagram shows that the value of $K_N = 0.1 \text{ bar}^{-1/2}$ detected in the present study is less than calculated for pure iron (Figure 9). Likewise, the formation of the $\epsilon\text{-Fe}_{2.3}\text{N}$ phase at higher $K_N \geq 0.75 \text{ bar}^{-1/2}$ is also small than the corresponding boundary nitriding potential of γ'/ϵ indicated in the Lehrer diagram.

During the nitriding process, the absorbed nitrogen atoms interact with the constituents of the substrate to form nitride phases of aluminum and iron. The sequence of the formation of phases is usually determined by the relative thermodynamic stability of the relevant nitride phases. To illustrate the nitride phases relative stability, a metastable isothermal section of the Fe-Al-N system has been calculated using the ThermoCalc software based on the TCFE7 database (see Figure 10). Thereby, the B2-FeAl phase is contained as an extended solid solution of $\alpha\text{-(Fe, Al)}$ with disordered A2/bcc structure. A temperature of 585 °C was chosen in order to avoid complications by the eutectoid reaction in the Fe-N system, which was somewhat below 590 °C, according to the employed database.

The blue dashed line in Figure 10 illustrates the phase evolution upon adding N to a FeAl40 alloy. As soon as N is added to the alloy, the AlN phase is expected to precipitate, since the compositional point is located within the $\text{AlN} + \alpha$ two-phase field, thereby depleting the $\alpha\text{-(Fe, Al)}$ phase by Al. Upon having 28 at. pct N in the alloy, the α phase has lost virtually all Al at the cost of AlN formation, and only upon a further increase of the N content first the γ' and upon surpassing 36 at. pct ϵ is formed (Figure 10). The ThermoCalc results predict correctly that AlN precipitates first when adding N to

B2-FeAl alloy, which leads to the formation of AlN and pure iron (α -Fe). Furthermore, it needs a higher chemical potential of N (or high nitrogen content) to form iron nitride phases.

In the nitriding process for B2-FeAl iron aluminide alloy, different types of nitride layers develop depending on the nitriding potential. The nitride layers can form in one of the following cases:

1. A nitride layer with a diffusion zone consisting of the two phases AlN and α -Fe forms. From empirical results, as discussed in the previous sections, the authors predict that this layer can be achieved under nitriding conditions with $K_N < 0.1 \text{ bar}^{-1/2}$.
2. A nitride layer which consists of phases AlN, γ' -Fe₄N, ϵ -Fe_{2.3}N, and α -Fe forms at nitriding conditions with $K_N \geq 0.1 \text{ bar}^{-1/2}$. The nitride layer may include the development of an outer compound layer

Fig. 9—Lehrer diagram is calculated by the Thermo-Calc software with TCFE7 database.

of iron nitride phases, called a “white layer”, and an inner diffusive layer corresponding with the “external and internal” nitriding processes

Based on schematic illustrations of the wave-line forming mechanism of Zhang,^[11] the authors propose a model demonstrating the formation of the white layer on FeAl40, as shown in Figure 11, which includes the following steps:

Step 1: Nitrogen atoms diffuse from the nitriding atmosphere onto the surface of FeAl samples. They interact with the atoms below the surface and diffuse into the substrate along the grain boundaries (Figure 11(a)).

Step 2: Due to the chemical affinity of nitrogen with metal atoms, Al atoms will separate firstly from the FeAl matrix and form AlN. More Al diffuses to the grain boundaries and combines with nitrogen to form AlN. The formation of AlN needles consumes aluminum from the ordered lattice of B2-FeAl, and consequently, α -Fe results between the AlN needles. Hence a lamellar microstructure of AlN/ α -Fe is formed (Figures 11(b) and (c)).^[11]

Because the limit solubility of N in α -Fe is very small, nitrogen atoms will combine with iron atoms to form iron nitride phases depending on K_N . Based on the Lehrer diagram for pure iron,^[18] the authors suggest the existence of the phases γ' -Fe₄N and/or ϵ -Fe_{2.3}N, respectively, at each investigated K_N value (Figures 11(d) through (f)). The formation of pure iron nitride on top of the surface is an indication for an external nitriding process that occurs involving outward diffusion of Fe.

Furthermore, the diffusion of nitrogen atoms along the grain boundaries into deeper regions of the substrate corresponds to an internal nitriding process, which leads to the formation of AlN and iron nitride phases, thus contributing to the formation of the “diffusion zone” of the nitride layer.

Fig. 10—The isothermal section of Fe-Al-N ternary phase diagrams at 585 °C (A temperature of 585 °C was chosen in order to avoid complications by the eutectoid reaction in the Fe-N system, which was somewhat below 590 °C, according to the employed database) calculated based on the TCFE7 excluding the gas phase N₂ and hence featuring also the metastable iron nitride phases ϵ and γ' . Note that the indicated phase equilibria with N contents higher than corresponding to the ϵ + AlN two-phase region neither conform with experimental reality, neither are they relevant for the current work.

Fig. 11—Schematic illustrations of a mechanism of the effect of the nitriding potential K_N on the “white layer” formation: steps a, b, c are referred from the wave-line forming mechanism of Zhang^[11] (Reprinted from^[11] under the terms of the Creative Commons CC BY license (<http://creativecommons.org/licenses/by/3.0/>)); and steps d, e, f are expanded by authors to explain white layer formation.

The results of GDOES (Figure 6), XRD (Figure 7), and EBSD (Figure 8) analyses confirm the predicted mechanism of the formation of the white layer on FeAl40 material. At low nitriding potential K_N below $0.1 \text{ bar}^{-1/2}$, only the Al atoms interact with N atoms to precipitate AlN, and at the same time to form the α -Fe phase (Figure 11(c)). In this case, the obtained nitride layers on similar alloys have the previously reported lamellar structure.^[9–11] Due to the low nitriding potential, the white layer would not form on the FeAl40 surface. With further increase in K_N , the white layer includes compound phases of γ' -Fe₄N ($K_N \geq 0.1 \text{ bar}^{-1/2}$) and/or ϵ -Fe_{2.3}N ($K_N \geq 0.75 \text{ bar}^{-1/2}$) (Figures 11(d) through (f)) that would gradually cover the sample surface. The analysis results show that the proportion of iron nitride phases increases at the surface while the fractions of AlN and α -Fe decrease. After the white layer reaches a sufficient thickness, the main peaks of the AlN and α -Fe phases were not detectable in the XRD patterns anymore.

- The formation of active atoms of N from the decomposition reaction of ammonia in a nitriding atmosphere and the atoms absorb deep into the sample surface along grain boundaries,
- Diffusion of Al atoms from the inside of grains to the grain boundaries,
- Formation of AlN and release of α -Fe,
- Formation of γ' -Fe₄N precipitates,
- Formation of ϵ -Fe_{2.3}N phase on γ' -Fe₄N phase precipitates with increasing K_N value, (locally, there seems to be ϵ/γ' double layer)
- Formation of a “white” compound layer. Corresponding to the nitriding conditions, the layer’s composition is either the γ' phase at an appropriate low value of K_N ; or ϵ phase at high values of K_N . Occasionally a double layer of ϵ/γ' is formed locally.

IV. CONCLUSIONS

The formation and growth of the white layer on B2-FeAl alloy were studied for different nitriding potentials of the ammonia atmosphere affecting the composition and thickness of the case at fixed nitriding conditions of 590 °C for 5 hour.

Detailed studies using SEM, LOM, XRD, and EBSD indicate that on all nitrided specimens, a thin white layer of varying thickness is formed. If a low nitriding potential is used, the white layer is formed inhomogeneously and comprises of clusters of nitride phases, which are mainly Fe₄N phases. The appearance of nitride phase clusters increases the surface roughness.

When a high nitriding potential is applied, the nitride phase clusters will cover the whole sample surface to form the white layer. The white layer composes mainly of iron nitride phases of the type Fe₄N and Fe_{2.3}N. Its thickness increase with further increasing nitriding potential K_N , causing a change in surface roughness. The optimal characteristics in terms of surface roughness of the nitrided surface correspond to nitriding potentials K_N in the range of 0.75 to $1.0 \text{ bar}^{-1/2}$.

A mechanism for the formation of the white layer has been proposed, explaining the nitriding behavior of FeAl40 alloy occurring during the gas nitriding process as a function of different K_N values.

As known in the state-of-the-art nitriding process, the structure and composition of the nitride layer can be controlled by adjusting the nitriding potential of the atmosphere. Comparable basic knowledge is applied to FeAl materials, showing that the nitriding potential parameter has a significant effect on the structure and composition of the resulting white layer. In future work, the effect of a compound layer forming as a function of the nitriding potential K_N on the growth kinetics and the properties of the diffusion zone will be examined more closely.

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