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(54) METHOD FOR DIFFUSION TREATMENT OF CORROSION-RESISTANT STEEL

(57) The invention is a method for the diffusion treatment of corrosion-resistant steel by nitriding or nitrocarburizing, which involves loading a workpiece into a treatment furnace, introducing a treatment atmosphere, heating the atmosphere to the process temperature, and introducing an activator, wherein the nitriding treatment atmosphere contains ammonia as a nitrogen donor, and the treatment nitrocarburizing atmosphere contains ammonia and carbon monoxide and/or carbon dioxide as a carbon donor. The method is characterised in that an activator - an alcohol or a mixture of alcohol and water in gaseous or liquid form - is first introduced into the treatment atmosphere when it reaches the target temperature, and is then supplied cyclically throughout the duration of the nitriding or nitrocarburizing process, with the alcohol concentration being at least 5% by volume and the amount of activator supplied being at least 10 ml per diffusion process.

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Description

[0001] The invention relates to a method for the diffusion treatment of corrosion-resistant steel. A passive chromium oxide layer naturally forms on the surface of objects made from corrosion-resistant chromium steel. While the passive layer protects against corrosion, it also inhibits the diffusion of elements like carbon or nitrogen into the steel during gas diffusion treatments (e.g., nitriding, carburizing, or nitrocarburizing) and this inhibition prevents the desired improvement of the mechanical properties of the workpiece surface. Consequently, the surface of the corrosion-resistant steel workpiece must be activated before the diffusion treatment can proceed effectively.

[0002] Many methods exist for activating the surface of corrosion-resistant steel prior to diffusion treatment. One common approach involves chemical processes where a chemical compound is introduced into the processing space and this compound directly or indirectly removes the passive oxide layer from the workpiece surface.

[0003] Patent TWI548778B discloses a method for activating the surface of corrosion-resistant steels by placing the steel in a heating furnace, where the temperature is maintained between 450 and 650°C, and heating it for 5 to 10 minutes in an atmosphere containing water vapour and hydrochloric acid vapour to remove the passivation layer. Subsequent to this treatment, the stainless steel is subjected to a low-temperature carburizing or nitriding process.

[0004] Patent EP4249625A1 discloses a method for the diffusion treatment of a high-alloy steel workpiece, which involves loading the workpiece into a treatment furnace, introducing an activation gas composed of gaseous ammonia and a liquid organic solvent (such as formamide, xylene, or toluene), and then heating it to a temperature of 400°C to 500°C; a nitriding or carbonitriding gas is then introduced, and the workpiece is heated to another temperature at which the nitriding or carbonitriding process is carried out. While the activation gas is being introduced into the furnace, the liquid organic solvent is added periodically. It is introduced in portions of 10 ml to 80 ml at a uniform rate for 1 second to 2 minutes, with intervals of at least 10 minutes between each portion.

[0005] Patent KR20120124941A discloses a method of diffusion nitriding wherein, in a first step after loading a steel workpiece into a heat treatment furnace, the chamber's atmosphere is purged at room temperature with gaseous ammonia (NH_3) to remove oxygen and establish an ammonia atmosphere; in a subsequent step, the furnace chamber's temperature is raised to 200-500°C, and then while this temperature is maintained, carbon tetrachloride (CCl_4) or tetrachloroethylene (C_2Cl_4) is injected into the chamber to remove the passive layer on the workpiece, after which diffusion nitriding is carried out on the workpiece surface in an ammonia gas (NH_3) atmosphere. The substances used in this method, carbon tetrachloride and tetrachloroethylene, are classified as hazardous to both the environment and human health.

[0006] Patent description WO2005068679A1 discloses a method for activating the surface of a high-alloy steel workpiece before a diffusion treatment like gas nitriding or gas carburizing, which comprises introducing into a furnace a carbon donor gas containing at least one compound selected from acetylene, ethylene, propane, butane, and carbon monoxide, and ammonia as a nitrogen-containing gas, and heating the component to at least 300°C. In the presence of a metal catalyst in the furnace, hydrogen cyanide (HCN) is formed, which acts on the passive surface of the workpiece. At a hydrogen cyanide concentration of 100 mg/m^3, the surface of the workpiece is activated. Following this activation, a diffusion treatment is performed at a temperature of 550°C, which causes the precipitation of nitrides or carbides.

[0007] The method disclosed in patent document WO2006136166 involves the use of unsaturated hydrocarbons or halogenated hydrocarbons during the nitriding and carburizing of corrosion-resistant steels.

[0008] Patent EP0588458B1 discloses a method for nitriding austenitic steel that comprises heating the steel in a gas atmosphere containing fluorine or fluorides to activate its surface, followed by subjecting the activated steel to a nitriding atmosphere at a temperature below 450°C to form a nitrided layer. In this two-step process, the passive layer of the stainless steel surface is converted into a fluorine-containing surface layer that is permeable to nitrogen atoms in the subsequent nitriding step. However, using halogen- or halide-containing gases for activation is a challenging method to apply. Such an atmosphere is known to be aggressive towards the interior of process equipment and can lead to severe pitting of the furnace, fittings, and other components.

[0009] Patent JPH10219418A describes a method for activating the surface of corrosion-resistant steel using acetone. First, a high-chromium alloy steel is placed in a nitriding furnace and heated in an ammonia gas atmosphere. Once the steel reaches the target nitriding temperature, acetone and hydrogen gas (as a carrier gas) are introduced into the furnace. The thermal decomposition of the acetone on the steel's surface forms highly active carbon monoxide and reducing radicals. This process degrades the passive layer on the high-chromium steel, which facilitates subsequent nitriding with the ammonia gas.

[0010] Patent EP0812929A1 discloses a method for the gas nitriding or carbonitriding of an alloy steel workpiece, specifically corrosion-resistant steel with a chromium content exceeding 13%, within an ammonia-containing atmosphere. Prior to nitriding or carbonitriding, the workpiece undergoes pre-carburization. This involves introducing a dissociable carbon source, typically an alcohol and preferably methanol, into a furnace heated to a temperature of 500°C to 600°C. The pre-carburizing atmosphere is maintained with a methanol-to-nitrogen-containing gas ratio of approximately 1:1, where the nitrogen-containing gas is preferably ammonia.

[0011] The aim of the invention was to develop a method for activating the surface of corrosion-resistant steel subjected to gas diffusion treatment, with the method being effective and simple to implement while not requiring additional operations, such as protecting cleaned surfaces against re-passivation, the use of extra devices, or being harmful to the environment. The solution according to the invention is designed to eliminate the need to neutralize toxic gases for steel surface activation, while also being free from the tendency to form deposits in the furnace and ensuring minimal wear of the heating chamber's surface and its equipment.

[0012] The method of diffusion treatment of corrosion-resistant steel by nitriding or nitrocarburizing comprises a step of loading the treated workpiece into a treatment furnace, a step of introducing a treatment atmosphere, a step of heating the treatment atmosphere to a temperature at which the nitriding or gas nitrocarburizing process is carried out, and a step of introducing an activator to the surface of the treated workpiece, wherein the treatment atmosphere for gas nitriding contains ammonia as a nitrogen donor, while the treatment atmosphere for gas nitrocarburizing contains ammonia as a nitrogen donor and carbon monoxide and/or carbon dioxide being a carbon donor, characterised in that the activator such as alcohol or a mixture of alcohol with water in gaseous or liquid form is introduced into the treatment atmosphere for the first time when the treatment atmosphere reaches the target temperature for the process being conducted, and then cyclically throughout the duration of the nitriding or gas nitrocarburizing process, wherein the alcohol concentration is not less than 5% by volume, and the amount of the activator supplied is not less than 10 ml per one diffusion treatment process.

[0013] Preferably, the diffusion treatment is carried out at a temperature of at least 450°C for a duration of at least 1 hour.

[0014] The activator is preferably dosed into the treatment atmosphere at a temperature of at least 300°C.

[0015] Furthermore, the nitrogen potential (Kn) of the treatment atmosphere during the diffusion treatment is preferably in the range of 0.1 to 15 $atm^{-1/2}$.

[0016] Preferably, the carbon potential Cp of the treatment atmosphere in the nitrocarburizing process is not greater than 2%.

[0017] The method of diffusion treatment of corrosion-resistant steel according to the invention is effective and does not require complicated setup. The substances used as activators in the diffusion treatment process are environmentally safe, eliminating the need for additional exhaust gas disposal. Furthermore, these substances prevent the formation of deposits and do not cause excessive wear on the heating chamber's surface or equipment.

[0018] The method of diffusion treatment of corrosion-resistant steel is explained in more detail through exemplary descriptions of the processes according to the invention, illustrated in the figures, which include photographs of the surface of samples subjected to nitriding treatment according to the invention, made with an optical microscope, in which Fig. 1 shows a photograph of the sample surface after the nitriding process at a temperature of 500°C and an ammonia flow rate of 5 l/min., Fig. 2 shows a photograph of the sample surface after the nitriding process at a temperature of 500°C and an ammonia flow rate of 15 l/min., Fig. 3 shows a photograph of the sample surface after the nitriding process at a temperature of 500°C and an ammonia flow rate of 45 l/min., Fig. 4 shows a photograph of the sample surface after the nitriding process at a temperature of 535°C and an ammonia flow rate of 5 l/min., Fig. 5 shows a photograph of the sample surface after the nitriding process at a temperature of 535°C and an ammonia flow rate of 15 l/min., Fig. 6 shows a photograph of the sample surface after the nitriding process at a temperature of 535°C and an ammonia flow rate of 45 l/min., Fig. 7 shows a photograph of the sample surface after the nitriding process at a temperature of 570°C and an ammonia flow rate of 5 l/min ., Fig. 8 shows a photograph of the sample surface after the nitriding process at a temperature of 570°C and an ammonia flow rate of 15 l/min., Fig. 9 shows a photograph of the sample surface after the nitriding process at a temperature of 570°C and an ammonia flow rate of 45 l/min., and Fig. 10 shows a photograph of the sample surface after the nitrocarburizing process at a temperature of 570°C and an ammonia flow rate of 15 l/min.

Embodiment 1

[0019] Two samples of X30Cr13 material, cut from a 30 mm diameter rod, were prepared with dimensions of 30 mm in diameter and 10 mm in height. The samples were loaded into a retort furnace with a chamber volume of approximately 450 litres and a working space of 400x400x600 mm. Each sample was placed in a basket on a mesh to ensure the free flow of the atmosphere. Following the loading of the samples, heating of the furnace to 360°C was initiated while the furnace retort was concurrently purged with a nitrogen flow rate of 5 m^3/h. At 360°C, the inert gas atmosphere was exchanged for a nitriding atmosphere through the introduction of ammonia at a constant flow rate of 50 l/min over a period of 1 hour. The nitriding atmosphere was then heated to the target nitriding temperature of 570°C. The nitriding process was carried out for a duration of 5 hours with a constant ammonia flow rate of 10 l/min and a nitrogen potential (Kn) in the range of 0.25 to 0.30 $atm^{1/2}$. During the nitriding process, an activator-a mixture of 20% ethyl alcohol and 80% water-was introduced into the atmosphere. The activator was supplied in 20 ml portions every 20 minutes, each over a period of 30 seconds. The first introduction occurred when the nitriding atmosphere's temperature reached 570°C. Five hours after the initial activator introduction, the furnace was purged with nitrogen and the samples were cooled. The samples were removed from the furnace once the temperature had fallen below 50°C.

[0020] The average thickness values of the diffusion layer formed on the samples and the corresponding deviations are

presented in Chart 1.

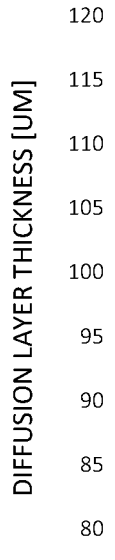


Chart 1. Thickness of the effective nitrided layer on X30Cr13 steel

Embodiment 2

[0021] This embodiment describes nine nitriding processes performed on samples made of 440B material. The samples, with dimensions of Ø30 x 10 mm, were cut from a 30 mm diameter rod. In each process, two samples were nitrided. The nitriding was carried out in the same furnace and with the same initial conditions as described in Embodiment 1. The initial steps of loading the samples and preparing the furnace for nitriding were identical to those described in Embodiment 1. The nitriding processes were conducted using a combination of three distinct temperatures (500°C, 535°C, and 570°C) and three corresponding ammonia flow rates (5, 15, and 45 l/min).

[0022] The following table lists the nitriding process parameters for each of the nine samples. Table 1: Nitriding Process Parameters for 440B Samples (Ø30 x 10 mm) from Embodiment 2

Sample No.	Process temperature [°C]	Ammonia flow rate [l/min]	Nitrogen potential Kn [atm 1/2]
1	500	5	2.7 - 2.8
2	500	15	6.5 - 6.8
3	500	45	10.0 - 11.0
4	535	5	0.6 - 0.7
5	535	15	2.4 - 2.5
6	535	45	4.5 - 4.8
7	570	5	0.2 - 0.25
8	570	15	2.4 - 2.5
9	570	45	4.5 - 4.8

[0023] Each nitriding process was carried out for 10 hours. During the nitriding process, a 20 ml activator-a mixture of 50% ethyl alcohol and 50% water-was introduced into the nitriding atmosphere according to the scheme described in Embodiment 1. Following the nitriding, the posttreatment procedure was continued as detailed in Embodiment 1.

[0024] The average thickness values of the diffusion layer formed on the samples and the corresponding deviations are presented in Chart 2.

[0025] Optical microscope photographs of the sample surfaces, obtained after each of the nine nitriding processes, are shown in Figs. 1-9.

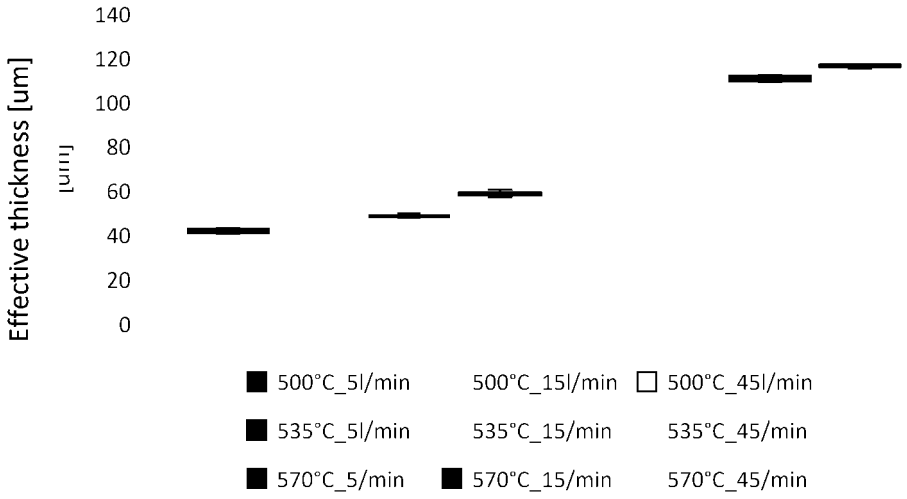


Chart 2. Effective thickness and thickness distribution in nitrided layers on 440B steel after activation with ethyl alcohol and water at different temperatures and ammonia flows.

Embodiment 3

[0026] This embodiment describes the nitro-carburizing process for samples of X30Cr13 material. The samples, with dimensions of Ø30 x 10 mm, were cut from a 30 mm diameter rod. The initial steps of loading the samples and preparing the furnace for nitriding were identical to those described in Embodiment 1. The nitro-carburization process was carried out in the furnace described in Embodiment 1. The process parameters included a constant ammonia flow rate of 15 l/min and a nitrogen potential (Kn) in the range of 0.37 to 0.42 atm $^{1/2}$. A carbon-bearing gas was also introduced to maintain a carbon potential (Cp) in the range of 0.6 to 0.7. Nitro-carbonation processes were carried out at 570°C and flow rate of 15 l/min or 45 l/min. Each nitro-carbonation process was carried out for 5 hours. During the nitriding process, a 20 ml activator a mixture of 50% ethyl alcohol and 50% water was introduced into the nitriding atmosphere according to the scheme described in Embodiment 1. After completion of the nitrocarburizing process , the procedure described in Example 1 was continued.

[0027] The average thickness values of the diffusion layer formed on the samples and the corresponding deviations are presented in Chart 3.

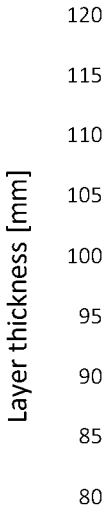


Chart 3. Effective thickness and distribution of the diffusion layer on X30Cr13 steel after the nitrocarburizing process described in Embidiment 3.

[0028] Figure 10 shows a photograph of the sample's surface, taken with an optical microscope after the nitrocarburization process.

Claims

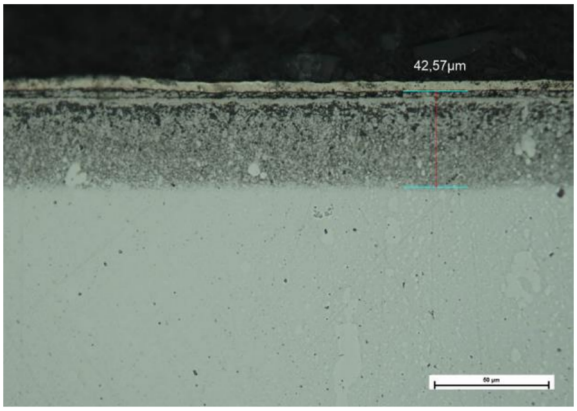
1. The method of diffusion treatment of corrosion-resistant steel by nitriding or nitrocarburizing comprises a step of loading the treated workpiece into a treatment furnace, a step of introducing a treatment atmosphere, a step of heating the treatment atmosphere to a temperature at which the nitriding or gas nitrocarburizing process is carried out, and a step of introducing an activator to the surface of the treated workpiece, wherein the treatment atmosphere for gas nitriding contains ammonia as a nitrogen donor, while the treatment atmosphere for gas nitrocarburizing contains ammonia as a nitrogen donor and carbon monoxide and/or carbon dioxide being a carbon donor, **characterised in that** the activator such as alcohol or a mixture of alcohol with water in gaseous or liquid form is introduced into the treatment atmosphere for the first time when the treatment atmosphere reaches the target temperature for the process being conducted, and then cyclically throughout the duration of the nitriding or gas nitrocarburizing process, wherein the alcohol concentration is not less than 5% by volume, and the amount of the activator supplied is not less than 10 ml per one diffusion treatment process.

2. The method according to claim 1, **characterised in that** the diffusion treatment is carried out at a temperature of at least 450°C for a duration of at least 1 hour.

3. The method according to claim 1, **characterised in that** the activator is dosed into the processing atmosphere at a temperature of at least 300°C.

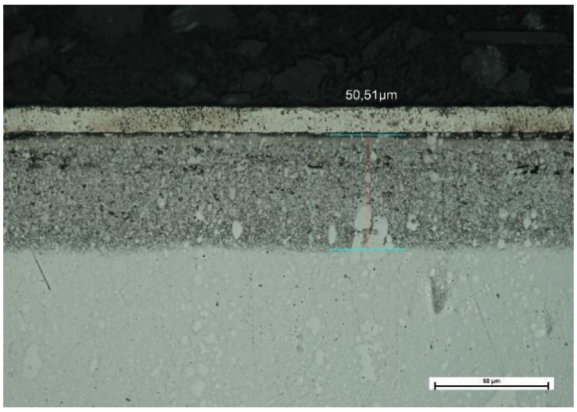
4. The method according to claim 1, **characterised in that** the nitrogen potential (Kn) of the treatment atmosphere during the diffusion treatment is in the range of 0.1 to 15 atm $^{-1/2}$.

5. The method according to claim 1, **characterised in that** the carbon potential Cp of the treatment atmosphere in the nitrocarburizing process is not greater than 2%.



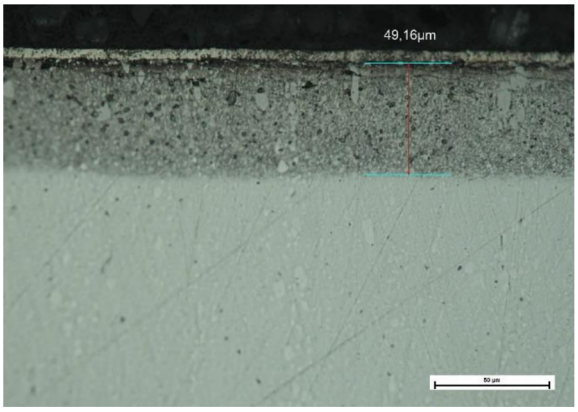
T – 500°C, NH_3 flow rate – 5 l/min

Fig. 1



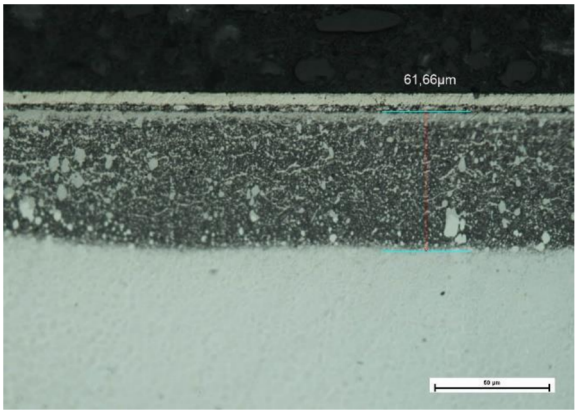
T – 500°C, NH_3 flow rate – 15 l/min

Fig. 2



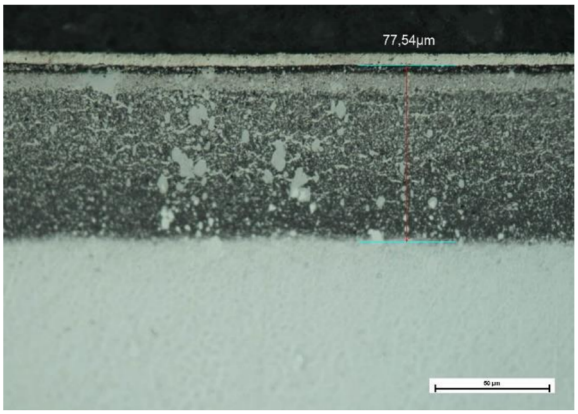
T – 500°C, NH_3 flow rate – 45 l/min

Fig. 3



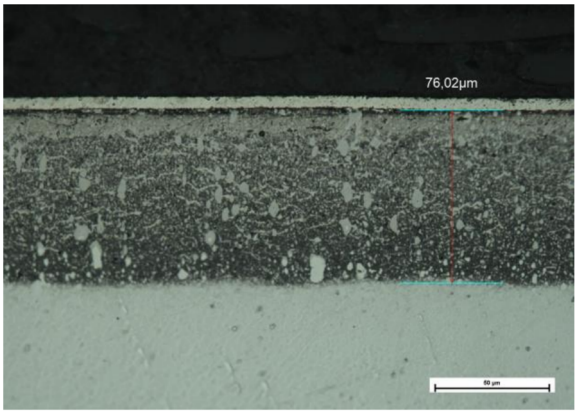
T – 535°C, NH_3 flow rate – 5 l/min

Fig. 4



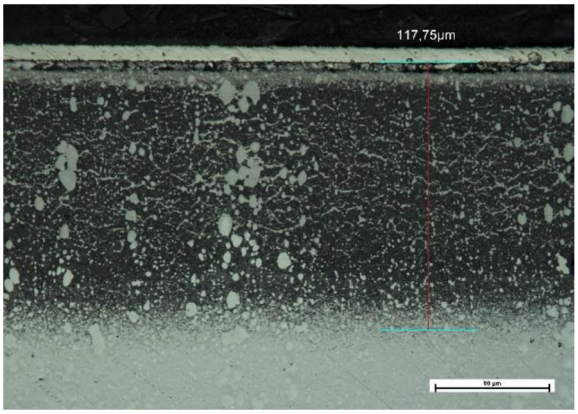
T – 535°C, NH_3 flow rate – 15 l/min

Fig. 5



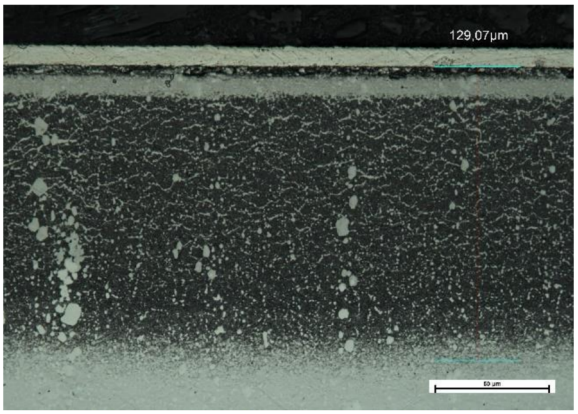
T – 535°C, NH_3 flow rate – 45 l/min

Fig. 6



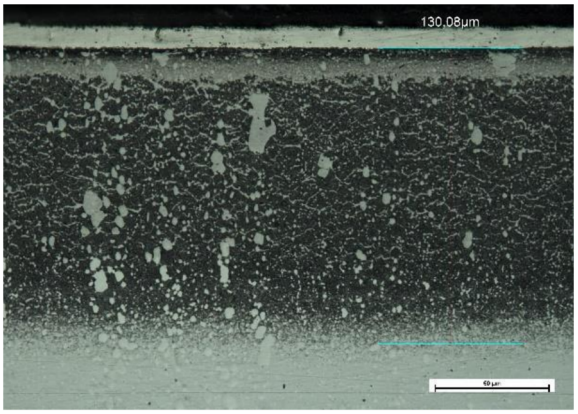
T – 570°C, NH_3 flow rate – 5 l/min

Fig. 7



T – 570° C, NH_3 flow rate – 15 l/min

Fig. 8



T – 570°C, NH_3 flow rate – 45 l/min

Fig. 9

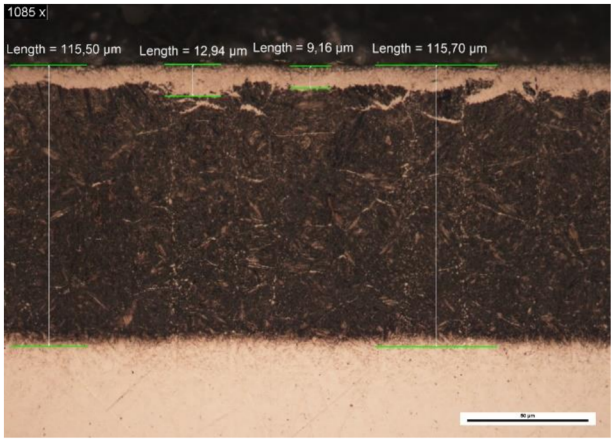

1085 x
Length = 115,50 µm
Length = 12,94 µm
Length = 9,16 µm
Length = 115,70 µm

Fig. 10

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EUROPEAN SEARCH REPORT

Application Number
EP 25 18 9457

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	EP 4 249 625 A1 (PARKER NETSUSHORI KOGYO CO LTD [JP]) 27 September 2023 (2023-09-27) * paragraphs [0026], [0143] - [0162]; claims 1-15 *	1-5	INV. C23C8/02 C23C8/26 C23C8/32 C23C8/80
A	CN 116 083 915 A (UNIV XIAN TECHNOLOGY) 9 May 2023 (2023-05-09) * paragraphs [0003] - [0017]; claims 1-5 *	1-5	
A	CN 112 359 314 A (SINOSTEEL LUONAI MATERIALS TECH CORPORATION) 12 February 2021 (2021-02-12) * paragraphs [0001] - [0004]; claims 1-4 *	1-5	

TECHNICAL FIELDS SEARCHED (IPC)

C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	4 November 2025	Chalaftris, Georgios

CATEGORY OF CITED DOCUMENTS

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04-11-2025

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 4249625 A1	27-09-2023	CN 116457493 A	18-07-2023
		EP 4249625 A1	27-09-2023
		JP WO2022107753 A1	27-05-2022
		KR 20230088445 A	19-06-2023
		TW 202235641 A	16-09-2022
		US 2024011142 A1	11-01-2024
		WO 2022107753 A1	27-05-2022
CN 116083915 A	09-05-2023	NONE	
CN 112359314 A	12-02-2021	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 4249625 A1 **[0004]**
- KR 20120124941 A **[0005]**
- WO 2005068679 A1 **[0006]**
- WO 2006136166 A **[0007]**
- EP 0588458 B1 **[0008]**
- JP H10219418 A **[0009]**
- EP 0812929 A1 **[0010]**