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## (54) Fe-Mn-Al-C alloy and method for manufacturing the same

(57) An Fe-Mn-Al-C alloy and a method for manufacturing the same are revealed. The Fe-Mn-Al-C alloy whose composition is 23~34wt.% Mn, 8~9.5wt.% Al, and 1.4~1.8wt.% or 1.45~1.8 wt.% C, with the balance being iron (Fe) is formed by melting of the above components. Then the alloy is solution heat-treated at 980°C~1200°C and then quenched so that microstructure of the alloy is a full austenite phase. And dense nanoscale (Fe, Mn)<sub>3</sub>AlC<sub>x</sub> carbides (κ'- carbides) are formed within austenite matrix by spinodal decomposition during the

quenching process. Thereby strength and ductility of the alloy are significantly improved. Moreover, after nitriding treatment, a nitride layer having predominantly aluminum nitride (AIN) with face-center-cubic (FCC) structure and a relatively small amount of iron nitride (Fe $_4$ N) with FCC structure is formed on surface of the alloy. Thereby surface hardness and corrosion resistance are improved. Thus use efficiency and application efficiency of the alloy are further increased.

#### Description

#### BACKGROUND OF THE INVENTION

[0001] The present invention relates to An Fe-Mn-Al-C alloy and a method for manufacturing the same, especially to An Fe-Mn-Al-C alloy containing 23~34wt.% Mn, 8~9.5wt.% Al, and 1.4~1.8wt.% or 1.45~1.8 wt.% C with the balance being Fe and a method for manufacturing the same by melting a mixture of the above components. The Fe-Mn-Al-C alloy has properties of high strength, high ductility, high surface hardness and high corrosion resistance.

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[0002] In technical filed of Fe-Mn-Al-C alloys and manufacturing methods of the same available now, a lot of prior arts including "Relationship between Microstructures and Tensile Properties of an Fe-30Mn-8.5Al--2.0C Alloy", Materials Transactions, 2010/04/28, Vol. 51, No. 6, pp1084-1088 (hereafter called reference 1), "Phase transitions in an Fe-9Al-30Mn-2.0C alloy", Scripta Materialia, 2007, Vo. 57, pp 809-812 (hereafter called reference 2), "Microstructure control and ductility improvement of the two-phase  $\gamma$ -Fe/ $\kappa$ -(Fe, Mn)3AIC alloys in the Fe-Mn-Al-C quaternary system", Intermetallics, 2004, Vo. 12, pp607-617 (hereafter called reference 3), and US2013/0081740A1 (TW201313923A1) "COMPOSI-TION DESIGN AND PROCESSING METHODS OF HIGH STRENGTH, HIGH DUCTILITY, AND HIGH COR-ROSION RESISTANCE FE-MN-AL-C ALLOYS" (hereafter called reference 4) are revealed. The reference 1 and reference 2 are research papers of the inventors and the reference 4 is inventor's application for a patent. Refer to p. 1084, reference 1, Introduction from line 28 of the left column to line 1 of the right column: "In these studies, it is seen that the as-quenched microstructure of Fe-(29-30) % Mn - (7.7-9) % Al-(1.5~2.5) % C alloys was  $\gamma$ phase containing fine  $\kappa'$  carbides. (19.20)", the reference 19 and 20 here are the same as the reference 2 and the reference 3 mentioned above. The techniques related to the reference 2 and the reference 3 are revealed in the p1084, reference 1. That means the reference 2 and the reference 3 are recited as prior arts. Thus the techniques revealed in the p1084, reference 1 are unable to approve that the result of the reference one (Conclusion, p1088) can be applied to an Fe-Mn-Al-C alloy containing 29~30wt.% Mn, 7.7-9 wt.% Al, 1.5~2.5wt.% C with the balance being Fe.

[0003] Refer to the reference 3, an Fe-Mn-Al-C alloy containing 29~30wt.% Mn, 7.7~9wt.%Al and 1.5~2.5wt.% C with the balance being Fe is revealed. The alloy is solution heat-treated at 1373K (1100 °C). Then dual-phase structure having austenite and  $\kappa$ -carbides is obtained after the furnance is cooled. The room temperature tensile test results indicate that the tensile strength is about 900 Mpa and the elongation rate is about zero, as indicated in Abstract line 3-5 and shown in Fig. 8, page 613. In order to improve ductility of the alloy at room temperature (refer to page614-615, citation

3), the alloy is solution heat-treated at 1373K (1100 °C) and then is processed by various aging treatment at 1073K (800 °C). Thus coarse, microscale (>10  $\mu$ m) $\kappa$ carbides and austenite, whose microstructure is γ/κlamellar, is obtained. The room temperature tensile test results indicate that the tensile strength is about 1050 Mpa and the elongation rate is about 11%. It is obvious that the strength and ductility of the alloy processed by techniques in the reference 3 are far more smaller than those of the alloy processed by techniques in then reference 4. Moreover, the reference 3 only mentioned that the alloy whose microstructure is γ/κlamellar is generated by aging at 800°C, not revealed that high density of nanosized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides (κ'- carbides) are formed within austenite matrix by spinodal decomposition during the quenching process of the solution heat-treatment mentioned in the reference 4.

[0004] Furthermore, as the title "Relationship between Microstructures and Tensile Properties of an Fe-30Mn-8.5Al-2.0C Alloy" and Conclusions at the last page of the reference 1 revealed, the research subject of the reference 1 is limited to a single Fe-Mn-Al-C alloy with a specific ratio of each component including 30wt.% Mn, 8.5wt.% Al, 2.0wt.% C, with the balance being Fe. So is the reference 2 "Phase transitions in an Fe-9Al-30Mn-2.0C alloy", the research object is a single Fe-Mn-Al-C alloy with a specific ratio of each component including 30wt.% Mn, 9wt.% Al, 2.0wt.% C, with the balance being Fe. The reference 1 and the reference 2 are research papers of the inventor of the present invention in which nanoscale ordered κ'-carbides are first found to precipitate coherently within the austenite matrix under quenched state after solution heat-treatment. The microstructure obtained improves mechanical properties of the alloy. However, the research subjects of the reference 1 and reference 2 are the Fe-Mn-Al-C alloys each of which with a specific ratio of each component (such as 2.0wt.% carbon and 8.5 or 9 wt.% aluminum). The research result can only be applied to that kind of Fe-Mn-Al-C alloy (as mentioned in Conclusions, page 1088, reference 1). Thus it is uncertain that whether the conclusion of the reference 1 and the reference 2 can be applied to other alloys or not.

[0005] The techniques for processing Fe-Mn-Al-C alloys with specific ratio of each component (such as 2.0wt.% carbon) revealed in the reference 1 and the reference 2 are not susceptible of industrial application. Even experts familiar with metals know that different positions at the same metal block are not homogeneous, impossible to have the same composition completely. Refer to "STRUCTURE AND PROPERTIES OF ENGINEERING ALLOYS" William F. Smith, page 94, second edition, and take the most common carbon steel AISI-SAE1040 as an example. The composition analysis result of the carbon steel shows that carbon(C) is ranging from 0.37 to 0.44 weight percent and Mn is ranging from 0.60 to 0.90 weight percent. Refer to "The Making, Shaping and Treating of Steel" Edited by Harold E. McGannon,

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page 1130, the analysis result of the AISI 4340 alloy steel shows that its composition is  $0.38 \sim 0.43$  wt.% C,  $0.60 \sim 0.80$ wt.% Mn,  $0.20 \sim 0.35$  wt.% Si,  $1.65 \sim 2.00$  wt.% Ni,  $0.70 \sim 0.90$ wt.% Cr,  $0.20 \sim 0.30$ wt.% Mo, <0.035 wt.% P and <0.040 wt.% S. Thus it is obvious that the techniques revealed in the reference 1 and the reference 2 and used to process alloys with a specific ratio of each component such as 2.0 weight percent of carbon are not susceptible of industrial application.

[0006] Spinodal decomposition (a kind of phase transformation) is observed only in very few materials, such as metal alloys, oxide glasses (refer to Wiley international Editions, Fundamentals of Physical Metallurgy, pp 390-391 and pp396-397). Spinodal decomposition is quite/entirely different from phase transformations in general alloys such as second-phase precipitates generated by nucleation & growth. For example, in the reference 3, coarse  $\kappa$ '-carbides having  $\gamma/\kappa$  lamellar microstructure are formed in the alloy by aging at 800°C and this results from nucleation & growth. The conditions for spinodal decomposition are demanding and as followings: (1) A phase diagram of a binary alloy system has a stable miscibility gap. (2) The phase change is spontaneous, with no energy carrier ( $\Delta G^*<0$ ) for nucleation. (3) During phase separation, interfacial energy existing between two phases and coherency strain energy should be very low. Thus composition range and temperature zone for spinodal decomposition are narrower than the miscibility gap. Take a Fe-Mo alloy system in which spinodal decomposition occurs as an example. Its composition range for spinodal decomposition is ranging from 17~20at% of Molybdenum (Mo) (refer to "Spinodal Decomposition in Fe-Mo-Co and Fe-Mo-V Ternary System" by Takao KOZAKAI et al., pp. 159-164). For range expansion of spinodal decomposition to a lower amount of Mo, different ratio of cobalt (Co) or vanadium (Va) is added to form a ternary alloy system. However, the composition range and temperature zone for spinodal decomposition are still limited to a smaller range (as shown in Fig. 2, page 163). Thus the occurrence of spinodal decomposition in the alloy is difficult, requiring a lot of demanding conditions (such as specific composition range and temperature zone) being matched.

[0007] In addition, the inventor has reviewed articles related to metal materials (including textbook, journal papers, conference papers and website information) and has found that once metals already known to have spinodal decomposition being treated by a quenching process after solution heat-treatment, spinodal decomposition will not occur during the quenching process. In asquenched, the alloy is in a single phase (refer to "STRUCTURE AND PROPERTIES OF SPINODALLY DECOMPOSED Cu-Ni-Fe ALLOYS", pp347-349, Royal Society Publishing"An X-Ray study of the Dissociation of an Alloy of Copper, Iron and Nickel", pp368-378, or AMERICAN SOCIETY FOR METALS, Phase Transformations, Chapter 12, p497 Spinodal Decomposition). The alloy needs to be heated up to the temperature inside spinodal

decomposition region so as to make spinodal decomposition occur.

[0008] Take A-B binary alloy as an example, there is a small composition fluctuation at the early stage of heating. The wave amplitude of the component is quite small, not sufficient to form precipitate of the second-phase. Thus at the moment, the two phases are called A-rich and B-rich. Along with the increasing heating time, the wave amplitude is increased so that the precipitate is generated (refer to "Phase Transformations in Metals and Alloys", pp 308-311). This precipitate has the same composition as the precipitate generated out of the spinodal decomposition region but the difference is in that the precipitate continues to grow with the increasing heating time and has different precipitate coarsening. Generally, the alloy with spinodal decomposition needs to be heated up to the temperature within spinodal decomposition region for quite a long time so as to separate the precipitate from the matrix completely. Take "Cu-Fe-Ni alloy" as an example. The phase transformation time of the alloy is as long as 11 weeks to be heated at 650°C (as shown in"An X-Ray study of the Dissociation of an Alloy of Copper, Iron and Nickel", pp368-378). Thus the alloys with spinodal decomposition available now have phase transformation at constant temperature.

[0009] It is learned that spinodal decomposition is seldom occurred in the binary and ternary systems due to demanding conditions difficult to be matched. As to the quaternary alloy Fe-Mn-Al-C alloy revealed in the present invention, a complete phase diagram has not been established yet. The inventor dedicated to find out the composition of the quaternary alloy that has spinodal decomposition and production of dense nanoscale  $\kappa$ '-carbides during the quenching process so as to make the quaternary alloy of the present invention become susceptible of industrial application.

[0010] Thus the inventor's research (reference 4, US2013/0081740A1) overcomes the problem of demanding conditions of spinodal decomposition. However, each element/component contained in the Fe-Mn-Al-C alloy revealed in the reference 4 has a larger range. This has negative effect on the occurrence of spinodal decomposition and the industrial application. Moreover, the inventor of the present invention thinks that spinodal decomposition during a quenching process, derivative κ'-carbides, size and distribution of (Fe,Mn)<sub>3</sub>AIC) and their effects on mechanical properties of the alloy require further analysis and repetitive research to clarify the key techniques, especially the ratio of carbon and aluminum and their relation, so as to be susceptible of industrial application. Thus there is room for improvement and a need to provide an alloy more susceptible of industrial application.

#### SUMMARY OF THE INVENTION

[0011] Therefore it is a primary object of the present invention to provide an Fe-Mn-Al-C alloy and a method

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for manufacturing the same. The Fe-Mn-Al-C alloy that contains 23~34wt.% Mn, 8~9.5wt.% Al, and 1.4~1.8wt.% C with the balance being Fe is produced by melting of a mixture of the components mentioned above. The alloy is solution heat-treated at 980°C~1200°C and then quenched to obtain fully austenitic Fe-Mn-Al-C alloy whose microstructure is a full austenite ( $\gamma$ ) phase. And high density of nano-sized (Fe,Mn)\_3AlC\_x carbides ( $\kappa$ '-carbides) are formed within austenite matrix by spinodal decomposition during the quenching process. Thereby strength and ductility of the alloys are significantly improved. The use efficiency and application efficiency of the alloys are further increased.

[0012] It is another object of the present invention to provide an Fe-Mn-Al-C alloy and a method for manufacturing the same in which materials for the Fe-Mn-Al-C alloy includes 23~34wt.% Mn, 8~9.5wt.% Al, and 1.45~1.8wt.% C with the balance being Fe. Thus the nanoscale (Fe,Mn) $_3$ AlC $_x$  carbides (κ'- carbides) formed are with higher density. And strength and ductility of the alloy are significantly improved.

[0013] It is a further object of the present invention to provide an Fe-Mn-Al-C alloy and a method for manufacturing the same in which Fe-Mn-Al-C alloy is treated by nitriding so that a nitride layer consisting predominantly of aluminum nitride (AlN) with face-center-cubic (FCC) structure and a relatively small amount of iron nitride (Fe<sub>4</sub>N) with FCC structure is formed on surface of the alloy. Thereby surface hardness and corrosion resistance of the alloy are improved. The use efficiency and application efficiency of the alloy are further increased.

# DETAILED DESCRIPTION OF THE PREFFERED EMBODIMENT

**[0014]** An Fe-Mn-Al-C alloy of the present invention is produced by melting a mixture containing  $23\sim34$ wt.% Mn,  $8\sim9.5$ wt.% Al, and  $1.4\sim1.8$ wt.% C with the balance being Fe.

**[0015]** The Fe-Mn-Al-C alloy of the present invention is solution heat-treated at  $980^{\circ}\text{C} \sim 1200^{\circ}\text{C}$  and then quenched to obtain the alloy whose microstructure is a full austenite ( $\gamma$ ) phase. Moreover, high density of nanosized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '- carbides) are formed within austenite matrix by spinodal decomposition during the quenching process.

[0016] The Fe-Mn-Al-C alloy of the present invention is an alloy having high hardness and high corrosion resistance. The high corrosion resistant Fe-Mn-Al-C alloy with high hardness includes an Fe-Mn-Al-C alloy and a nitride layer. The Fe-Mn-Al-C alloy is produced by melting of a mixture of 23~34wt.% Mn, 8~9.5wt.% Al, and 1.4~1.8wt.% C with the balance being Fe. Then the alloy is treated by solution heat-treatment at 980 °C~1200 °C and then a quenching process so that the microstructure of the alloy is a full austenite ( $\gamma$ ) phase. During the quenching process, nano-sized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '- carbides) with high density are formed within austen-

ite matrix by spinodal decomposition. The nitride layer is formed on surface of the Fe-Mn-Al-C alloy by nitriding the quenched alloy at 450 °C ~550 °C. The nitride layer on surface of the alloy includes predominantly aluminum nitride (AlN) with face-center-cubic (FCC) structure and a relatively small amount of iron nitride (Fe $_4$ N) having FCC structure.

**[0017]** A method for manufacturing a high-strength and high-ductility Fe-Mn-Al-C alloy includes following steps:

Step 1: Melting a mixture containing by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.4~1.8 percent carbon (C), and the balance being iron (Fe) to form an alloy:

Step 2: Processing the alloy with a solution heat-treatment at 980 °C~1200 °C and then quenching the alloy so that microstructure of the alloy is a full austenite ( $\gamma$ ) phase. And high density of nano-sized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '- carbides) are formed within austenite matrix by spinodal decomposition during the quenching process after the solution heat-treatment.

Step 3: Processing the quenched alloy with an aging treatment at 450 °C~550 °C.

**[0018]** A method for manufacturing Fe-Mn-Al-C alloy with high strength, high ductility, high hardness and high corrosion resistance according to the present invention comprising the steps of:

Step 1: Melting a mixture that contains by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.4~1.8 percent carbon (C), with the balance being iron (Fe) to form an alloy;

Step 2: Processing the alloy with a solution heat-treatment at 980 °C~1200 °C and then quenching the alloy so that microstructure of the alloy is a full austenite ( $\gamma$ ) phase. And high density of nano-sized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '- carbides) are formed within austenite matrix by spinodal decomposition during the quenching process after solution heat-treatment.

Step 3: Placing the quenched alloy into a plasma nitriding chamber/or gas nitriding chamber and performing a nitriding treatment at 450 °C $\sim$ 550 °C to form a nitride layer on surface of the alloy. The nitride layer includes predominantly AIN with face-center-cubic structure and a relatively small amount of Fe $_4$ N with FCC structure on surface of the alloy.

**[0019]** When the nitriding treatment is carried out by a plasma nitriding chamber, the gas used for the nitriding treatment includes 20 percent to 80 percent nitrogen gas and the balance hydrogen gas. A pressure in the plasma nitriding chamber is 1 to 6 torr.

**[0020]** When the nitriding treatment is carried out by a gas nitriding chamber, the gas used for the nitriding treatment includes 20 percent to 80 percent ammonia gas

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and the balance nitrogen gas, or a mixture of ammonia gas, nitrogen gas and hydrogen gas.

[0021] In addition, materials for the Fe-Mn-Al-C alloy further includes 23~34wt.% Mn, 8~9.5wt.% Al, and 1.45~1.8wt.% C with the balance being Fe. The ratio of carbon is further modified to 1.45~1.8wt.%. Thus the nanoscale (Fe,Mn) $_3$ AlC $_x$  carbides ( $\kappa$ '- carbides) formed are more dense. Therefore strength and ductility of the alloy are significantly improved.

[0022] Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details, and representative devices shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

#### Claims

- 1. An Fe-Mn-Al-C alloy comprising by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.4~1.8 percent carbon (C), with the balance being iron (Fe) and being formed by melting of a mixture containing the by weight 23~34 percent manganese (Mn), the 8~9.5 percent aluminum (Al), the 1.4~1.8 percent carbon (C), with the balance being iron (Fe);
  - wherein the Fe-Mn-Al-C alloy is processed by a quenching process after solution heat-treatment so as to make microstructure of the Fe-Mn-Al-C alloy become a full austenite ( $\gamma$ ) phase; high density of nano-sized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '- carbides) are formed within austenite matrix by spinodal decomposition during the quenching process.
- A high-hardness and high-corrosion resistance Fe-Mn-Al-C alloy comprising:

an Fe-Mn-Al-C alloy formed by melting of a mixture containing by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.4~1.8 percent carbon (C), with the balance being iron (Fe); wherein the Fe-Mn-Al-C alloy is processed by a quenching process after solution heat-treatment so that microstructure of the Fe-Mn-Al-C alloy become a full austenite ( $\gamma$ ) phase; high density of nano-sized (Fe,Mn)3AlCx carbides ( $\kappa$ '- carbides) are formed within austenite matrix by spinodal decomposition during the quenching process;

a nitride layer formed on surface of the Fe-Mn-Al-C alloy by nitriding the quenched alloy at 450 °C  $\sim$ 550 °C and the nitride layer having predominantly aluminum nitride (AlN) with face-centercubic (FCC) structure and a relatively small amount of iron nitride (Fe<sub>4</sub>) with FCC structure.

- 3. The alloy as claimed in claim 1 or claim 2, wherein the Fe-Mn-Al-C alloy further contains by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.45~1.8 percent carbon (C), with the balance being iron (Fe).
- A method for manufacturing a high-strength and high-ductility Fe-Mn-Al-C alloy comprising the steps of:

Step 1: Melting a mixture that contains by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.4~1.8 percent carbon (C), with the balance being iron (Fe) to form an Fe-Mn-Al-C alloy;

Step 2: Processing the Fe-Mn-Al-C alloy with a solution heat-treatment at 980 °C~1200 °C and then quenching the Fe-Mn-Al-C alloy so that microstructure of the Fe-Mn-Al-C alloy is a full austenite ( $\gamma$ ) phase; nano-sized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '- carbides) with high density are formed within austenite matrix by spinodal decomposition during the quenching process after the solution heat-treatment; and

Step 3: Processing the quenched Fe-Mn-Al-C alloy with an aging treatment at 450 °C ~550 °C.

**5.** A method for manufacturing a high strength, high ductility, high hardness and high corrosion resistance Fe-Mn-Al-C alloy comprising the steps of:

Step 1: Melting a mixture that contains by weight 23~34 percent manganese (Mn), 8~9.5 percent aluminum (Al), 1.4~1.8 percent carbon (C), with the balance being iron (Fe) to form an Fe-Mn-Al-C alloy;

Step 2: Processing the Fe-Mn-Al-C alloy with a solution heat-treatment at 980 °C~1200 °C and then quenching the Fe-Mn-Al-C alloy so that microstructure of the Fe-Mn-Al-C alloy is a full austenite ( $\gamma$ ) phase; high-density nano-sized (Fe,Mn)<sub>3</sub>AlC<sub>x</sub> carbides ( $\kappa$ '-carbides) are formed within austenite matrix by spinodal decomposition during the quenching process after the solution heat-treatment; and

Step 3: Placing the quenched Fe-Mn-Al-C alloy into a plasma nitriding chamber or a gas nitriding chamber and performing a nitriding treatment at 450 °C -550 °C to form a nitride layer on surface of the Fe-Mn-Al-C alloy while the nitride layer having predominantly of aluminum nitride (AlN) with face-center-cubic (FCC) structure and a relatively small amount of iron nitride (Fe $_4$ N) with FCC structure on surface of the alloy.

6. The method as claimed in claim 5, wherein gas used for the nitriding treatment includes 20 percent to 80 percent nitrogen gas with the balance being hydrogen gas when the nitriding treatment is carried out by the plasma nitriding chamber; a pressure in the plasma nitriding chamber is 1 to 6 torr.

7. The method as claimed in claim 5, wherein gas used for the nitriding treatment includes 20 percent to 80 percent ammonia gas with the balance being nitrogen gas, or a mixture of ammonia gas, nitrogen gas and hydrogen gas when the nitriding treatment is carried out by the gas nitriding chamber.

8. The method as claimed in claim 4 or claim 5, wherein the Fe-Mn-Al-C alloy further contains by weight 23-34 percent manganese (Mn), 8-9.5 percent aluminum (Al), 1.45~1.8 percent carbon (C), with the balance being iron (Fe).



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Application Number EP 14 17 0843

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### ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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#### REFERENCES CITED IN THE DESCRIPTION

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