



US 20070292300A1

(19) **United States**(12) **Patent Application Publication**
Rosberg et al.(10) **Pub. No.: US 2007/0292300 A1**(43) **Pub. Date: Dec. 20, 2007**(54) **FERRITIC STAINLESS STEEL****Publication Classification**(76) Inventors: **Andreas Rosberg**, Sandviken (SE);
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Witt, Sandviken (SE)(51) **Int. Cl.****C22C 38/18** (2006.01)**C22C 38/06** (2006.01)(52) **U.S. Cl.** **420/63; 420/62**

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(57)

ABSTRACT(21) Appl. No.: **11/578,252**(22) PCT Filed: **Apr. 13, 2005**(86) PCT No.: **PCT/SE05/00523**

§ 371(c)(1),

(2), (4) Date: **Jun. 14, 2007**(30) **Foreign Application Priority Data**

Apr. 16, 2004 (SE) 0401046-8

Ferritic steel alloyed with a balanced quantity of chromium, aluminium and reactive elements and that has the following composition (in % by weight): Ni up to 1 Cr 15-25 Al 0.75-3.7 Si max 0.6 Mo and/or W 0-3 Ti and/or Nb 0-1 Cu up to 0.2 N up to 0.2 one or more of the reactive elements Zr, Hf and REM>0 balance iron and normally occurring impurities, wherein the equation $Cr+3Al \geq 26$ is satisfied. The ferritic stainless steel is suitable for use as substrate material in catalytic converters for diesel engines in heavy vehicles at temperatures in the interval of 600-900° C. and a specific relation between the content of chromium and aluminium being satisfied.

FERRITIC STAINLESS STEEL

[0001] The present invention relates to a ferritic steel alloy for the use as substrate material in catalytic converters for diesel engines in heavy vehicles at temperatures in the interval of 600-900° C. and a specific relation between the content of chromium and aluminium being satisfied.

BACKGROUND

[0002] In connection with an increasing transportation need, the number of heavy vehicles having diesel-driven motors has increased continuously the latest years, but thereby also the environmental problems with the exhaust fumes from these motors. In addition to ultra-fine particles that are regarded to have a negative impact on the health, diesel engines also produce a number of different undesired exhaust fumes, such as above all CO and NO_x. When the needs for exhaust emission control of diesel-driven vehicles, particularly heavy diesel-driven vehicles, such as trucks, buses, industrial trucks or the like, increase because of new legislation requirements in above all Europe and USA, such technique will need to be introduced in the major part of newly produced diesel vehicles. On the basis of the technique used today in diesel vehicles, it has turned out that marked differences between internal combustion engines intended for diesel and petrol engines makes it necessary to develop and adapt catalytic converters especially for diesel combustion.

[0003] For the manufacture of monoliths for catalytic converters, usually two methods are used: extrusion of a ceramic material or corrugation of thin strips or foil of a Fe—Cr—Al-alloy. The advantage of the ceramic monolith has traditionally been that the manufacturing costs have been low in comparison with metal monoliths. When the monolith size increases, which is the case for diesel engines in heavy vehicles, such as trucks, busses, industrial trucks etc., the manufacturing costs for the ceramic monoliths increase faster than for metal monoliths, which implies that over a certain size, metallic converters give a better economy. With growing size and for the use in big diesel vehicles, ceramic monoliths have also other disadvantages, such as, e.g., insufficient mechanical properties, longer time for heating, shorter service life, large manufacturing costs. For instance, a metal monolith can be manufactured with thinner wall thicknesses, normally between 1/2 and 1/3 in comparison with corresponding ceramic monolith, which gives lower pressure drop, so-called “back pressure”, larger efficient area and larger catalytic capacity. Thereby, the monolith can be made smaller in volume and with a design that is more flexible. The thermal conductivity is better in metal, which entails smaller risk of overheating than in ceramic monoliths. Diesel engines are frequently used in vehicles having long operating periods and where the cost for shutdown and change of catalytic converter is high. The requirements on service life and reliability of the catalytic converter, and hence the supporting material, are, therefore, also high. The most commonly occurring metal foil used for catalytic converters for diesel engines is today the same as is used for petrol engines and consists mainly of a Fe—Cr—Al of 19-21% Cr, 5-7% Al, one or more reactive elements, e.g., Zr, Y, Hf, La and Ce and the balance iron including naturally occurring impurities. This material has acceptable, but not optimal, oxidation properties for the temperature intervals used in diesel engines and has poor mechanical

properties because of the high content of aluminium, which involves inferior machining properties and a high manufacturing cost. Thus, there is a need for a material having good properties in cyclic oxidation at maximum temperatures in the interval of 600-900° C. and good production economy.

DESCRIPTION OF THE PRIOR ART

[0004] Today's exhaust emission-control materials are optimized for the purification of exhaust fumes from petrol engines, which operates at temperatures above 900° C. and particularly between 1000-1200° C. It is generally known that Fe—Cr—Al-alloys form an α -aluminium oxide at temperatures above 900-950° C., which gives lower oxide growth and better oxidation properties than γ -aluminium oxide. Experience has shown that Fe—Cr—Al-alloys require an aluminium content of over 4.5% in order to form single-phase α -aluminium oxide applied in catalytic converters. Catalytic converters for diesel engines are assumed to have an operating temperature below 600° C. that presents occasional or regular peaks of up to maximum 900° C., which entails that the most critical temperature range for the oxidation properties is 600-900° C. and thereby these conditions impose new demands on the oxidation resistance of the material. At these temperatures, a Fe—Cr—Al-alloy forms a mixed oxide substantially consisting of chromic oxide and γ -aluminium oxide where the chromic oxide is less stable and risks being evaporated or peeled off from the surface, while the aluminium oxide is considerably more stable. An oxide to the greatest part composed of aluminium oxide is, from experience, also advantageous for the adhesion of the coating, a so-called wash-coat that is applied to the metal surface of the completed monolith. However, it is relatively unknown how this mixed oxide performs in temperatures below 900° C. and how the composition of the steel affects the growth and composition of the oxide. The Japanese patent application no JP2000297355 discloses a steel for the use in exhaust systems at temperatures $\geq 800^\circ$ C., which in principle is a Fe—Cr-alloy including additives, where, e.g., copper is added for improved workability. The low aluminium content of maximum 0.15%, gives, however, a relatively high oxidation rate at temperatures $\geq 800^\circ$ C., and therefore the material is not suitable for the manufacture of thin foil where the demands on oxidation rate are higher. The Japanese patent application no JP2002004011 aims at the use in exhaust systems at temperatures between 650-800° C., but as in the previous example, the material is not alloyed with aluminium and hence has a similar oxidation resistance and is accordingly not suitable for the use as foil material in a catalytic converter in diesel vehicles.

[0005] The manufacturing costs of Fe—Cr—Al-alloys are generally high due to low hot ductility and crack sensitivity in hot working as well as low impact strength and workability at room temperature. Therefore, an improvement in these mechanical properties in order to lower the manufacturing cost is to prefer and above all for catalytic converters for heavy diesel engines, since these require a large quantity of material and thus are more price-sensitive than materials used today according to the above.

SUMMARY

[0006] Therefore, it is an object of the invention to provide a ferritic stainless steel for use as substrate material in catalytic converters for diesel engines in heavy vehicles at

temperatures in the interval of 600-900° C. and a specific relation between the content of chromium and aluminium being satisfied. Moreover, the steel should be cost effective.

DESCRIPTION OF THE INVENTION

[0007] These objects are attained by a ferritic steel alloyed with a balanced quantity of chromium, aluminium and reactive elements and that has the following composition (in % by weight):

Ni	up to 1
Cr	15-25
Al	0.75-3.7
Si	max 0.6
Mo and/or W	0-3
Ti and/or Nb	0-1
C	up to 0.2
N	up to 0.2

one or more of the reactive elements Zr, Hf and REM

[0008] >0

balance iron and normally occurring impurities, wherein the equation $Cr+3Al \geq 26$ is satisfied.

[0009] In those cases where the reactive element is Zr and/or Hf, the content of Zr and/or Hf is >0-0.5% by weight, preferably >0-0.2% by weight. In those cases where the reactive element is REM, such as Ce, Sc, La and Y, the content is maximally 0.2% by weight. Irrespective of which reactive element has been chosen, the total content of reactive elements is preferably maximally 0.5% by weight.

[0010] On the surface of the alloy according to the present invention, chromic oxide is formed during operation at temperatures up to 900° C., which promotes the formation of a pure aluminium oxide where a relation between high contents of chromium and the aluminium content in the substrate according to the composition above can be observed.

[0011] The chromium content of the alloy should be within the interval of 15.0-25.0% by weight, preferably 17.0-23.0% by weight, most preferably 20-23% by weight.

[0012] With the purpose of optimising the properties of the alloy in the application substrate material for catalytic converters in diesel engines for heavy vehicles, it has turned out that the best results for the decisive properties for the service life, such as strength and oxidation resistance, are presented when the equation $Cr+3Al \geq 26$ is satisfied, preferably is $Cr+3Al \geq 29$.

[0013] Additives of reactive elements, such as Zr, Hf and/or rare earth metals (REM) such as, for instance, Sc, Y, La and Ce, improves the oxidation resistance additionally by decreasing the tendency of peeling and flaking, i.e., the tendency of the oxide getting loose from the metal upon cooling or mechanical deformation for both aluminium oxides and chromium oxides.

[0014] The total content of rare earth metals (REM) should be limited to maximum 0.2% by weight, wherein one or more of the elements Ce, La, Sc and/or Y may be added. The preferred content of REM should be within the interval of 0.01-0.2% by weight.

[0015] Addition of one or more of the elements Ti, Nb, Zr and Hf gives, together with carbon and nitrogen, precipitations of carbides and/or nitrides, which provide the material with increased mechanical stability and resistance to grain growth, thereby improving the mechanical properties of the material.

[0016] Since hafnium is regarded to have similar effect on the properties of the alloy, this element may replace zirconium entirely or partly. Zr and/or Hf may be present up to contents of 0.5% by weight in total. The preferred content of zirconium and/or hafnium should however be maximum 0.2% by weight, mostly for economical reasons. Preferably, this content should be within the interval of >0-0.2% by weight.

[0017] In aluminium-alloyed ferritic steels, nickel has an embrittling effect, and therefore the content of Ni should be limited to max. 1.0% by weight, preferably max. 0.7% by weight.

[0018] Molybdenum may be added in the alloy in order to achieve improved strength at temperatures above 600° C. In the alloy according to the present invention, molybdenum may entirely or partly be replaced by tungsten in order to obtain a similar effect. The content of Mo and/or W should be 0 up to 3% by weight, preferably >0 up to 2.5% by weight and most preferably >0 up to 1.0% by weight.

[0019] In addition to what has been described above, the alloy may also contain impurities, depending on the raw material and the manufacturing process. One such example is Mg, which may for this type of alloys cause pores during casting, and should therefore not be present in contents above 0.05% by weight. Another example is V, which may have a positive effect on the grain size in the steel but implies a higher cost and should therefore not be present in contents above 0.1% by weight. A third example of such an impurity is Co, which increases the cost for the material, whereby the Co content should be limited to maximally 0.05% by weight. Co may also imply contamination of other steel grades. A further example of an impurity is Cu. Cu deteriorates among other things the hot ductility for this type of alloys and may therefore render the material difficult to hot work, whereby the Cu content should be limited to maximally 0.05% by weight.

[0020] By an adjusted balance of chromium and aluminium, the material according to the invention has obtained a considerable decrease of the oxidation rate in the temperature range of 600-900° C., which is the critical temperature range for the use as supporting material in catalytic converters for diesel engines. These properties are obtained when the alloy satisfies the formula $Cr+3Al \geq 26$, preferably $Cr+3Al \geq 29$, within the stated limits of chromium and aluminium, which gives a favourable oxide formation and oxide composition. Moreover, additives of reactive elements, such as rare earth metals, for example Sc, Y, La and/or Ce, contribute to a good adhesion of the oxide and thus decreases the risk of peeling and flaking at these temperatures. The alloy has also good mechanical properties in both warm as well as cool state, which entails low manufacturing costs and a good economy in the completed product.

[0021] The final product of the material may be manufactured in the form of strip or foil having a thickness of less

than 200 μm or in the form of wire having a diameter of less than 200 μm , and is intended for use as supporting material in catalytic converters for diesel engines at temperatures that maximally amounts to 600-900° C.

[0022] Table 1 shows some examples of compositions of an alloy according to the present invention, as well as a comparative example.

TABLE 1

Element	Example 1 (% by weight)	Example 2 (% by weight)	Example 3 (% by weight)	Comparative Example 4 (% by weight)
Ni	0.18	0.24	0.28	0.08
Cr	20.95	20.94	22.42	22.11
Al	3.2	3.09	2.94	0.83
Mo	<0.01	0.01	2	2.02
W	<0.01	0.01	<0.01	<0.01
Ti	0.01	0.004	0.1	0.12
Nb	<0.01	0.01	0.81	0.77
Zr (Hf)	<0.01	0.01	<0.01	0.002
C	0.1	0.01	0.105	0.097
Si	0.39	0.28	0.45	0.11
P	0.011	0.013	0.016	<0.003
S	0.01	0.0001	0.01	0.001
N	0.013	0.018	0.022	0.032
Mn	0.1	0.11	0.18	0.11
Ce	0.036	0.044	0.016	0.009
La	0.018	0.022	0.008	0.0045
Co	0.02	0.03	0.03	<0.01
V	0.05	0.05	0.09	0.028
Cu	<0.01	0.01	0.03	<0.01
Mg	0.05	0.0065	<0.05	<0.05

[0023] The alloy according to the present invention may be manufactured by conventional pyrometallurgy and casting with ingot casting or continuous casting followed by hot working and then cold working into final dimension. The product may be further machined to foil, thin strip or wire. The alloy may also be directly cast into strip, sheet-metal plate or foil having width/thickness relation of >50 with thickness after casting of below 5 mm, followed by cold working or a combination of hot and cold working. Feasible alternative ways of manufacture are that a substrate material having lower aluminium content is coated with pure aluminium or an aluminium alloy so that the proper composition is attained. Coating of the substrate alloy with aluminium alloy may be effected by previously known processes, such as, for instance, dipping in melt, electrolytic coating, roll bonding of strips of the substrate alloy and the aluminium alloy, deposition of solid alloy of Al from a gas phase by so-called CVD- or PVD-techniques. The coating with alloy of Al may be effected after the substrate alloy has been rolled down to the desired final thickness of the product, or in larger thickness. In the later case, a diffusion annealing may be carried out in order to provide a homogenization of the material after which rolling in one or more steps is carried out in order to provide the completed product. Rolling may also take place directly on a coated product having larger thickness than the desired completed thickness. In this case, the rolling may be followed by annealing. An example of manufacture of foil of a Fe—Cr—Al-alloy by PVD-deposition is disclosed in patent U.S. Pat. No. 6,197,132 B1.

1: Ferritic stainless steel alloy comprising (in % by weight):

Ni	up to 1
Cr	15-25
Al	0.75-3.7
Si	max 0.6
Mo and/or W	0-3
Ti and/or Nb	0-1
C	up to 0.2
N	up to 0.2

one or more of the reactive elements Zr, Hf and REM >0

balance iron and normally occurring impurities,

wherein the equation $\text{Cr}+3\text{Al}\geq 26$ is satisfied.

2: Ferritic stainless steel alloy according to claim 1, comprising Cr 17.0-23.0% by weight.

3: Ferritic stainless steel alloy according to claim 1, comprising Al 1.5-3.5% by weight.

4: Ferritic stainless steel alloy according to claim 1, comprising Zr and/or Hf $>0.5\%$ by weight.

5: Ferritic stainless steel alloy according to claim 1, comprising REM maximally 0.2% by weight.

6: Substrate material in catalytic converters for diesel engines comprising the ferritic stainless steel alloy according to claim 1.

7: A catalytic converter for a diesel engine operating at 600-900° C., comprising a substrate formed from a ferritic stainless steel alloy comprising (in % by weight):

Ni	up to 1
Cr	15-25
Al	0.75-3.7
Si	max 0.6
Mo and/or W	0-3
Ti and/or Nb	0-1
C	up to 0.2
N	up to 0.2

one or more of the reactive elements Zr, Hf and REM >0

balance iron and normally occurring impurities,

wherein the equation $\text{Cr}+3\text{Al}\geq 26$ is satisfied.

8. (canceled)

9: Ferritic stainless steel alloy according to claim 2, comprising Cr 20.0-23.0% by weight.

10: Ferritic stainless steel alloy according to claim 3, comprising Al 2.5-3.5% by weight.

11: Ferritic stainless steel alloy according to claim 4, comprising Zr and/or Hf $>0.2\%$ by weight.

12: Ferritic stainless steel alloy according to claim 5, comprising REM 0.01-0.2% by weight.

13: Ferritic stainless steel alloy according to claim 1, wherein $\text{Cr}+3\text{Al}\geq 29$.

14: Ferritic stainless steel alloy according to claim 7, comprising Cr 17.0-23.0% by weight.

15: Ferritic stainless steel alloy according to claim 14, comprising Cr 20.0-23.0% by weight.

16: Ferritic stainless steel alloy according to claim 7, comprising Al 1.5-3.5% by weight.

17: Ferritic stainless steel alloy according to claim 16, comprising Al 2.5-3.5% by weight.

18: Ferritic stainless steel alloy according to claim 7, comprising Zr and/or Hf > 0-0.5% by weight.

19: Ferritic stainless steel alloy according to claim 18, comprising Zr and/or Hf > 0-0.2% by weight.

20: Ferritic stainless steel alloy according to claim 7, comprising REM maximally 0.2% by weight.

21: Ferritic stainless steel alloy according to claim 20, comprising REM 0.01-0.2% by weight.

22: Ferritic stainless steel alloy according to claim 7, wherein $Cr+3Al \geq 29$.

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