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(54) **Aluminum-containing ferritic stainless steel having excellent high temperature oxidation resistance and toughness.**

(57) There is disclosed a ferritic stainless steel essentially consisting of C: not more than 0.03 %, Si: less than 0.25 %, Mn: less than 0.25 %, P: not more than 0.03 %, S: less than 0.001 %, N: not more than 0.03 %, Cr: 15 - 25 %, Al: 3 - 6 %, at least one of REM, Y and alkaline earth metals: 0.01 - 0.2 %, optionally at least one of Nb, V and Ti: 0.05 - 1 % and the balance of Fe and unavoidable incidental impurities. This steel has excellent high temperature oxidation resistance, especially resistance to abnormal oxidation and high toughness and is suitable for manufacturing foil substrate for metallic catalytic converters for automobile exhaust gas treatment.

EP 0 480 461 A1

Field of the Invention

The present invention relates to an aluminum (Al)-containing ferritic stainless steel for use in automobile exhaust-gas-treating apparatuses, heating apparatuses and the like.

Background of Invention

Al-containing ferritic stainless steels have excellent high temperature oxidation resistance and thus are widely used for parts of heating apparatuses such as stove chimneys, electric heating means, etc.

Recently, such steels also have come to be used as the substrate of catalytic converters in place of ceramic materials conventionally used therefor. As is well known, ceramics are weak against thermal shock and have large heat capacity and thus they require a long time to e heat up to the temperature for the catalytic reaction. Therefore, metallic catalaytic converters, which are free from the defects of ceramic ctalytic converters, are now attracting the attention of those skilled in the art. The substrate of metallic catalytic converters is formed of metal foil having a thickness of around 50 microns.

This substrate is used in an exhaust gas atmosphere, in which catalytic reaction takes place and, therefore, has to have excellent high temperature oxidation resistance. In view of this fact, high-Al ferritic stainless steels essentially comprising 20Cr-5Al and containing rare earth metals (REM), yttrium (Y), etc. are used for this purpose. However, even these steels are not fully satisfactory in terms of high temperature oxidation resistance and abnormal oxidation occurs if they are subjected to high temperature oxidation for a prolonged period of time. Higher power engines, which emit higher temperature exhaust gas, are now coming into use and adoption of manifold converters, which are placed nearer to the engine, is contemplated and thus converters inevitably have to treat exhaust gas of higher temperature.

Conventional steel materials for metallic converters are not satisfactory under such conditions and Al-containing ferritic stainless steels having far better high temperature oxidation resistance are desired. Steels of this kind are disclosed in Japanese Laid-Open Patent Publications Nos. 63-76850, 63-45s351, etc. These steels withstand oxidation for less than 200 hours at 1150°C. However, the oxidation resistance of this level is now no longer a sufficient level of oxidation resistance.

It is well known that Al-containing ferritic stainless steels are inferior in the toughness of slabs and hot-rolled sheets and, especially, that steels for metallic cataalytic converters containing high levels of chromium (Cr) and Al are poor in toughness and thus cause difficult problems when they are manufactured in a mass production line.

It is known that increasing the contents of Cr, Al, REM, Y, etc. is effective for improving high temperature oxidation resistance of high-Al ferritic stainless steels. However, increasing contents of Cr, Al, REM and Y degrades the toughness of slabs and hot-rolled steel sheets produced therefrom and thus making the manufacture more difficult and inviting poor yield or making production impossible. Besides, REM and Y are very expensive materials and thus the increased incorporation threarof raises the cost of the products. Therefore, the contents of Cr, Al, REM and Y cannot be increased so much.

Under the circumstances, a need exists for a novel ferritic stainless steel that has an excellent high temperature oxidation resistance suitable for a metallic catalytic converter material, good toughness and excellent manufacturability and which contains Cr, Al, REM and Y of the same levels as the conventional stainless steels for metallic converters.

The present invention is intended to provide a Fe-Cr-Al-REM, Y ferritic stainless steel for metallic catalytic converters having sufficient high temperature oxidation resistance, excellent toughness and good manufacturability, wherein the Al_2O_3 formed on the surface thereof does not suffer abnormal oxidation. We discovered that manganese (Mn) oxide compounds penetrate into the Al_2O_3 formed on the surface of the steel immediately before the abnormal oxidation occurs. So we thought of inhibiting the formation of Mn oxide compounds and the penetration thereof into the Al_2O_3 layer and we found that a ferritic stainless steel having excellent high temperature oxidation resistance under ultra-thin condition and further excellent toughness as well as good manufacturability can be obtained by restricting both the Mn and Si contents to less than 0.25 % respectively and optionally adding V, Ti and Nb to the conventional Al-containing ferritic stainless steel.

Summary of the Invention

The present invention provides a ferritic stainless steel essentially consisting of:

C: not more than 0.03 %
Si: less than 0.25 %

Mn: less than 0.25 %
P: not more than 0.03 %
S: less than 0.001 %
N: not more than 0.03 %
Cr: 15 - 25 %
Al: 3 - 6 %
at least one of REM, Y and alkaline earth metals:
0.01 - 0.2 %
balance of Fe and inevitable incidental impurities and
a ferritic stainless steel essentially consisting of the above-described composition and further contains:
at least one of Nb, V and Ti: 0.05 - 1 %.

In the present invention, the Mn content is preferably 0.21 % or less and more preferably 0.13 % or less. The Si content is preferably 0.22 % or less and more preferably 0.17 % or less.

The reason for defining the composition of the steel of the present invention as above is generally as follows.

C: From the viewpoint of oxidation resistance, generally the higher the C content, the higher the liability to occurrence of abnormal oxidation. The toughness of slabs and hot coils of high-Al-containing ferritic stainless steels deteriorates as the C content increases. In consideration of these facts, the C content is limited to not more than 0.03 %.

Si: Si content is the most significant factor in the steel of the present invention. Generally, it is considered that Si is effective for high temperature oxidation resistance. In the case of high-Al-containing ferritic steels, however, the high temperature oxidation resistance thereof is markedly improved by reducing the Si content. We found that the high temperature oxidation resistance of high-Al-containing ferritic stainless steels is markedly improved by reducing both the Si content and the Mn content simultaneously. Also, the toughness of the high-Al-containing ferritic stainless steel can be markedly improved by reducing the Si content. We found that the above-described effects are brought about if the Si content is reduced to less than 0.25 %.

Mn: In the present invention, the Mn content is significant. Generally Mn is effective for improving hot-workability. In the case of the present invention, however, Mn has a deleterious effect on high temperature oxidation resistance. We found that the high temperature oxidation resistance of high-Al-containing ferritic stainless steels is markedly improved by reducing the Mn content and further by increased addition of Cr, Al, REM, Y, etc. The toughness of the steel of the present invention is also remarkably improved by reduction of the Mn content and the effect is achieved by reducing the Mn content to less than 0.25 %. That is, the lower the Mn content, the better the effect and thus the Mn content is defined as less than 0.25 %.

P: P is an element which is deleterious to high temperature oxidation resistance as well as toughness of steels and, therefore, the lower the P content, the better the steel properties in general. In the case of the present invention, the P content should be not more than 0.03 %.

S: S forms compounds with REM, Y, etc. which degrade the surface properties as non-metallic inclusions. Also S consumes metallic REM, Y etc., which are effective for high temperature oxidation resistance. These adverse effects are great when the content is 0.001% or more. That is, the high temperature oxidation resistance is improved by reducing the S content to less than 0.001 %. In the present invention, the S content is defined as less than 0.001 %.

N: N reduces toughness of steels of the kind contemplated by the present invention. Also, it forms AlN consuming Al, which is effective for providing the steel with high temperature oxidation resistance, and thus inducing abnormal oxidation. The lower the N content, the better the oxidation resistance. In the present invention, the N content is defined as not more than 0.03 %.

Cr: Cr is a fundamental element that provides the steel with high temperature oxidation resistance. At least 15 % of Cr is required in order to exhibit its effect. On the other hand, Cr in excess of 25 % deteriorates the toughness of slabs and hot coils, causing difficulty in manufacturing. Thus the Cr content is defined as 15 - 25 %.

Al: Al is an essential element as well as Cr for providing the steel with high temperature oxidation resistance. In the foil material contemplated by the present invention, abnormal oxidation readily occurs. In this sense, addition of not less than 3 % of Al is necessary. In the present invention, however, the Al content need not be excessively high. Rather, Al in excess of 6 % deteriorates the toughness of slabs and hot coils. Thus the Al content is defined as 3 - 6 %.

REM, Y and alkaline earth metals: These are important elements which improve the high temperature oxidation resistance of Fe-Cr-Al alloys. They greatly improve the protecting effect of the formed oxide film, well inhibit abnormal oxidation, which easily develops in very thin materials, and improve adherence of the produced oxide film to the substrate. With a content of less than 0.01 %, the effect is not exhibited. To the contrary, at a content in excess of 0.2 %, they adversely affect hot-workability, making manufacture difficult, and form non-metallic inclusions impairing the surface properties. Thus the content of these elements is defined as 0.01 - 0.2 %.

Nb, V and Ti: When contained in suitable amounts, these elements combine with C and N in the steel and greatly improve the toughness of the steel. The steel of the present invention is used in severe high temperature environments and thus is required to be provided with excellent high temperature strength. Addition of these elements is very effective for this purpose. Addition of 0.05 % or more is required. The maximum amount is limited to 1 % since addition of excessive amount hardens the steel.

Brief Description of the Attached Drawing

The invention will now be specifically described with reference to the attached drawing, which is a graph showing the influence of Mn and Si on the impact strength of 20Cr-5Al-0.1Ti-0.1La steels at room temperature.

Specific Disclosure of the Invention

The high temperature oxidation resistance of high-Al-containing ferritic steels is provided by the Al_2O_3 which forms on the surface of the steel. Therefore, it is considered that the high temperature oxidation resistance will be improved as the Al content is increased. Test specimens of the compositions indicated in Table 1 respectively having a thickness of 50 microns were subjected to an oxidation test at 1150 °C and the time until abnormal oxidation occurred was measured. The results are also indicated in Table 1. From these results, it is apparent that with increase in the contents of Cr and Al and addition of REM, high temperature oxidation resistance is improved and the steel becomes less susceptible to abnormal oxidation.

Then, steels of the compositions as indicated in Table 2, which further contained REM, were tested. 30 kg heat of each steel was melted in vacuum and casted and the ingot was forged. All the steel samples developed cracking during forging and further working was impossible. This fact proved that increase of Cr, Al and REM is impossible from the viewpoint of manufacture. So we conducted an extensive study in order to develop a steel having excellent high temperature oxidation without increasing contents of Cr, Al and REM. As a result, we found that some Mn oxide compounds had penetrated into the formed Al_2O_3 surface film immediately before abnormal oxidation occurred. Thus we thought that these Mn oxide compounds adversely affected high temperature oxidation resistance of the steel and further study was conducted on inhibition of formation of the Mn oxide compounds. Thus we found that the formation of said Mn oxide compound is inhibited by reducing the content of Mn and Si.

Steels of the compositions as indicated in Table 3 were prepared and respectively made into 50 micron thick test specimens, which were subjected to oxidation test at 1150 °C. The time up to the occurrence of abnormal oxidation was measured and the effect of the contents of Mn and Si was checked. The results are also indicated in Table 3. Table 3 shows that decrease in the Mn and Si contents prolongs the time until abnormal oxidation occurs and is very effective for improving the high temperature oxidation resistance. Specifically, pronnonced effect was obtained by reducing the contents of Mn and Si respectively to less than 0.25 %. That is to say, a ferritic stainless steel having highly improved high temperature oxidation resistance was obtained by merely reducing the contents of Mn and Si without increasing the contents of Cr, Al and REM over that of the conventional steel for metallic catalytic converters.

Further, the effect of Mn and Si on the improvement of toughness of hot-rolled steel sheets was examined. Respectively 100 kg heats of 20Cr-5AL-0.1Ti-0.1La steels containing various amounts of Mn and Si were melted in vacuum and casted, and the ingots were forged and hot-rolled. The hot-rolled specimens were subjected to Charpy impact test. The results are shown in the attached drawing. The drawing shows that the impact test value rises as the Mn content decreases and the reduction in the Si content also increases the impact test value.

As has been described above, various tests were carried out and it was found that reduction of the Mn and Si contents of a high-Al-containing ferritic stainless steel brings about excellent high temperature oxidation resistance without increasing the contents of Cr, Al and REM over those of the conventional composition. The thus obtained high-Al-containing ferritic steel exhibits excellent toughness and is amenable to the mass production by the conventional equipment, which has been difficult with a steel of this kind.

The invention will now be illustrated by way of working examples.

Respectively 30 kg heats of the steels of the compositions indicated in Table 4 were melted and casted and the ingots were forged, machined, hot-rolled and, thereafter, made into 30 micron thick sheets by repeating annealing and cold rolling. These samples were subjected to an oxidation test at 1150 °C and the time upto the occurrence of the abnormal oxidation was measured. The results are also shown in Table 4. The results show that for the steels of the present invention the time required for the occurrence of abnormal oxidation was remarkably prolonged in comparison with conventional steels, that is, the oxidation resistance of the steel of the present invention is greatly improved.

Also the results of the test on impact toughness of the hot-rolled specimens are shown in Table 4. The results show that the toughness is also remarkably improved in the steel of the present invention.

As has been described above, the present invention provides an inexpensive steel material having excellent high temperature oxidation resistance and excellent toughness without adding unnecessarily large amounts of Cr, Al, REM and Y.

Table 1

(Wt%)

Sample	C	Si	Mn	P	S	Cr	Al	N	REM	Time up to abnormal oxidation (h)
A	0.014	0.35	0.37	0.025	0.0008	18.07	3.21	0.015		50
B	0.017	0.31	0.35	0.024	0.0008	20.05	5.09	0.013		70
C	0.012	0.32	0.34	0.024	0.0007	20.06	5.11	0.017	0.10	190

Table 2

(Wt%)

Sample	C	Si	Mn	P	S	Cr	Al	N	REM
D	0.022	0.33	0.33	0.025	0.0008	20.01	5.08	0.015	0.20
E	0.021	0.30	0.32	0.025	0.0007	20.04	6.25	0.014	0.09

Table 3

(Wt%)

Sample	C	Si	Mn	P	S	Cr	Al	N	REM	Time up to abnormal oxidation (h)
F	0.014	0.07	0.09	0.025	0.0007	20.05	5.07	0.012	0.10	740
G	0.016	0.12	0.06	0.024	0.0008	20.04	5.09	0.013	0.09	670
H	0.013	0.21	0.11	0.024	0.0008	20.03	5.11	0.013	0.09	430
I	0.015	0.08	0.20	0.024	0.0007	20.10	5.13	0.017	0.09	510
J	0.013	0.37	0.10	0.025	0.0006	20.14	5.15	0.010	0.10	330
K	0.015	0.34	0.27	0.024	0.0004	20.10	5.13	0.015	0.09	290
L	0.021	0.30	0.30	0.025	0.0008	20.07	5.09	0.011	0.08	220
M	0.013	0.34	0.50	0.024	0.0008	20.10	5.13	0.012	0.09	140
N	0.019	0.30	0.78	0.025	0.0008	20.08	5.14	0.010	0.09	80

Table 4

	Sample	C (wt%)	Si	Mn	P	S	Cr	Al	N	REM	Y	Ca		Time up to abnormal oxidation (h)	Charpy impact strength (kgf·m/cm²)
Working Examples	1	0.014	0.07	0.04	0.025	0.0003	16.91	5.71	0.012		0.09		Nb:0.50	710	4.1
	2	0.017	0.14	0.13	0.024	0.0006	18.16	5.10	0.013	0.07				600	3.0
	3	0.018	0.10	0.13	0.024	0.0007	20.10	5.12	0.017	0.08				630	3.1
	4	0.012	0.22	0.19	0.025	0.0008	20.09	4.98	0.016	0.04			Ti:0.04 V:0.08	280	2.5
	5	0.011	0.17	0.02	0.025	0.0008	20.11	4.88	0.014		0.08			920	2.7
	6	0.014	0.21	0.21	0.025	0.0008	23.12	4.29	0.009	0.02	0.02	0.01	Nb:0.31 Ti:0.06	240	2.0
Com. Examples	7	0.013	0.33	0.53	0.025	0.0004	16.27	5.67	0.013		0.08		Nb:0.49	120	1.4
	8	0.015	0.33	0.47	0.025	0.0005	18.33	5.04	0.012	0.08				130	1.3
	9	0.011	0.31	0.46	0.025	0.0007	20.13	5.05	0.009	0.05				120	1.4
	10	0.015	0.35	0.42	0.025	0.0007	20.15	5.01	0.012	0.05			Ti:0.05 V:0.06	90	1.4
	11	0.012	0.32	0.46	0.025	0.0008	20.09	4.89	0.017		0.09			130	1.0
	12	0.017	0.35	0.29	0.025	0.0007	23.21	4.29	0.015	0.02	0.02	0.01	Nb:0.31 Ti:0.08	60	1.3
	13	0.015	0.46	0.08	0.024	0.0218	23.30	4.30	0.014	0.02	0.02	0.01	Nb:0.30 Ti:0.08	130	1.2

Claims

1. A ferritic stainless steel essentially consisting of:
C: not more than 0.03 %,

Si: less than 0.25 %,
Mn: less than 0.25 %,
P: not more than 0.03 %,
S: less than 0.001 %,
N: not more than 0.03 %,
Cr: 15 - 25 %,
Al: 3 - 6 %,
at least of one of REM, Y and alkaline earth metals:
0.01 - 0.2 % and balance of Fe and unavoidable incidental impurities.

2. The steel of Claim 1, wherein the Mn content is not more than 0.21 %.

3. The steel of Claim 2, wherein the Mn content is not more than 0.13 %.

4. The steel of Claim 1, wherein the Si content is not more than 0.21 %.

5. The steel of Claim 4, wherein the Si content is not more than 0.17 %.

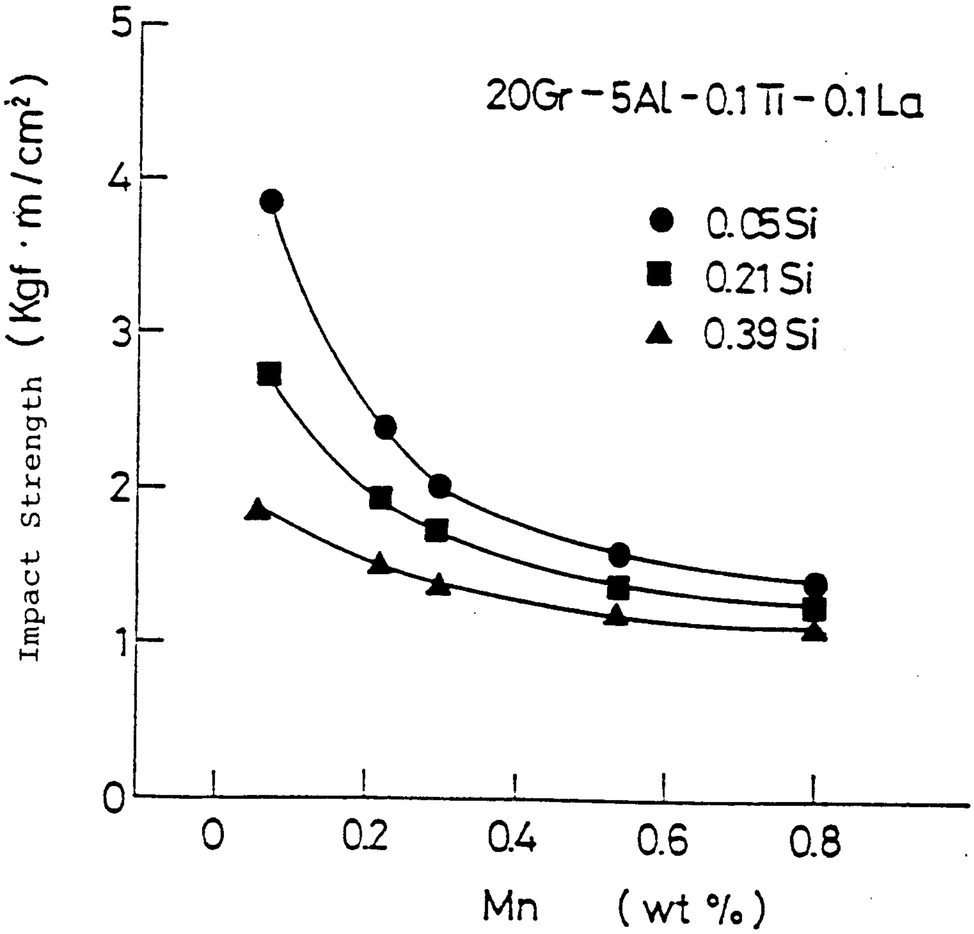
6. A ferritic stainless steel essentially consisting of:
C: not more than 0.03 %,
Si: less than 0.25 %,
Mn: less than 0.25 %,
P: not more than 0.03 %,
S: less than 0.001 %,
N: not more than 0.03 %,
Cr: 15 - 25 %,
Al: 3 - 6 %,
at least of one of REM, Y and alkaline earth metals:
0.01 - 0.2 %,
at least one of Nb, V and Ti:
0.05 - 1 %
and balance of Fe and unavoidable incidental impurities.

7. The steel of Claim 6, wherein the Mn content is not more than 0.21 %.

8. The steel of Claim 7, wherein the Mn content is not more than 0.13 %.

9. The steel of Claim 6, wherein the Si content is not more than 0.21 %.

10. The steel of Claim 9, wherein the Si content is not more than 0.17 %.


20Gr - 5Al - 0.1Ti - 0.1La
0.05Si
0.21Si
0.39Si
Impact Strength (Kgf · m/cm²)
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
Mn (wt %)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 7384

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 033 203 (ALLEGHENY LUDLUM STEEL CORPORATION) * claims 1-14 ; page 4, paragraph 5* *	1-5	C 22 C 38/18
X	EP-A-0 246 939 (KAWASAKI STEEL CORPORATION) * claims 1,4,7,10 ; page 18, Table 3, examples C-1 and C-2* *	1-10	
A	US-A-3 171 737 (SPOONER ET AL.) * claims 1-6 ; page 2, Table, example B * *	1-10	
A	SU-A-552 369 (KOLIADA ET AL.) * complete document* *	1-10	
A	GB-A-2 079 065 (SHARETREE LTD.) * page 1, l.54-72 ; claims 2-4* *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 22 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	06 January 92	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention

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