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Datasheet for the decision of 5 July 2011

Case Number: T 0029/10 - 3.2.08

Application Number: 07003164.6

Publication Number: 1803832

IPC: C22C 38/44

Language of the proceedings: EN

Title of invention:
High-grade duplex stainless steel with much suppressed formation of intermetallic phases and having an excellent corrosion resistance, embrittlement resistance, castability and hot workability

Applicant:
Park, Yong Soo

Headword:
-

Relevant legal provisions:
EPC Art. 56

Relevant legal provisions (EPC 1973):
-

Keyword:
"Inventive step (no)"

Decisions cited:
-

Catchword:
-

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Case Number: T 0029/10 **-** 3.2.08

D E C I S I O N
of the Technical Board of Appeal 3.2.08
of 5 July 2011

Appellant: (**Applicant**):
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Decision under appeal: **Decision of the Examining Division of the European Patent Office posted 14 July 2009 refusing European patent application No. 07003164.6 pursuant to Article 97(2) EPC.**

Composition of the Board:

Chairman: T. Kriner
Members: R. Ries
E. Dufrasne

Summary of Facts and Submissions

I. By its decision posted 14 July 2009, the examining division refused European patent application 07003164.6 on the ground of lack of inventive step of the subject matter of claim 1 then on file.

II. On 2 September 2009, the applicant lodged an appeal against the decision of the examining division and paid the appeal fee on the same date. The statement setting out the grounds of appeal was received on 13 November 2009.

III. In the communication annexed to the summons to oral proceedings, the Board gave its provisional assessment of the case. In particular, it was indicated that document

D1: EP-A-0 545 753

would be considered for the assessment of novelty and inventive step of the claimed subject-matter.

IV. Oral proceedings took place before the Board on 5 July 2011. The appellant requested that the decision under appeal be set aside and a patent be granted on the basis of the request filed during the oral proceedings.

Independent claim 1 of this request reads as follows:

"1. High-grade duplex stainless steel with high corrosion resistance, embrittlement resistance, castability and hot workability which suppresses formation of intermetallic phases, consisting of

21.0 to 38.0% of Cr, 3.0 to 12.0% of Ni, 1.5 to 6.5% of Mo, 0 to 6.5% of W, 3.0% or less of Si, 8.0% or less of Mn, 0.32 to 0.45% of N, 0.1% or less of C, 0.0001 to 1.0% of MM, optionally containing at least one element selected from the group consisting of 0.5% or less of Ca, 0.5% or less of Mg, 1.0% or less of Al, 0.5% or less of Ta, 0.5% or less of Nb, 1.5% or less of Ti, 1.0% or less of Zr, 1.0% or less of Sn and 1.0% or less of In,
optionally containing 0.1% or less of B,
optionally containing one or more among 3.0% or less Cu and 3.0% or less of Co,
and a balance of Fe and incidental impurities on a weight basis,
wherein MM is rare-earth metallic mixtures consisting of atoms with atomic numbers from 57 to 71, containing at least 50% or more of Ce, a certain amount of La, Nd, Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm Yb, Lu and Sc, and 1% or less Fe,
a pitting resistance equivalent (PREW) defined by following formula (1) satisfying $40 \leq PREW \leq 67$:
$PREW = wt\%Cr + 3.3(wt\%Mo + 0.5wt\%W) + 30wt\%N$ --- (1);
wherein a value of [MM+Al][O+S] which is an equation of solubility products of MM and Al, O and S of steel;
wherein, in the case of a cast product, the value of the equation of the solubility products ranges from $1x10^{-5}$ to $5000x10^{-5}[\%]^2$, or
wherein, in the case of a hot working product, the value of the equation of the solubility products ranges from $0.1x10^{-5}$ to $2000x10^{-5}[\%]^2$."

V. The appellant's arguments can be summarized as follows:

The composition of the high-grade duplex stainless steels of the present invention aimed at improving the steel's resistance to embrittlement and corrosion, its castability and hot workability either by reducing the precipitation speed or even suppressing the formation of brittle phases such as sigma (σ) phase and khi(χ)-phase; (A1 publication paragraphs [0001], [0014], [0015]). The diffusion and precipitation of brittle intermetallic phases were delayed by adding appropriate amounts of rare earth metallic mixtures MM comprising elements (more than 50% Ce, La, Nd and Pr) having a large atomic number (A1 publication paragraph [0011]). At least by the composition of MM defined in claim 1, the claimed stainless duplex steel was novel over the disclosure of document D1 which in a very general way mentioned the addition of rare earth metals (REM) which were mainly composed of La and/or Ce (D1, page 6, lines 43, 44).

The major elements of sigma- and khi-phases were Cr, Mo and W which improved the steel's resistance to corrosion, but by minimizing the presence and the formation of σ- and χ-phases, the corrosion resistance was further improved. The mechanism on the retardation of the secondary phases resulting from the addition of Ce, La, Nd and Pr due to the difference of the atomic radii referred to in paragraphs [0011] and [0021] of the A1 publication was further explained in more detail in Figure 16, which was submitted during the oral proceedings.

The mechanisms how MM lowered the formation or precipitation of undesirable intermetallic phases described in the present application was not disclosed in document D1 which only referred in a very general manner to the optional addition of rare earth metals (REM) without giving any specific composition thereof.

The claimed duplex steel further differed from D1 by comprising increased amounts of nitrogen in the range of 0.32 to 0.45% which resulted in a significant improvement of the steel's resistance to pitting corrosion.

In document D1 nitrogen was confined to 0.24 to 0.32%, since nitrogen in excess of 0.32% was found to degrade the steel's toughness and corrosion resistance due to the formation of defects caused by the formation of nitrides in the heat affected zone during welding. D1 therefore dissuaded from adding more than 0.32% N. The adverse effect of low nitrogen contents on pitting corrosion was confirmed by the exemplifying steels given in Table 1 of D1: the steel compositions comprising low amounts of nitrogen in the range of 0.24 to 0.32% exhibited a high pitting potential (D1, Table 2). Contrary thereto, the claimed steel did not suffer from pitting corrosion.

The subject-matter of claim 1 was therefore novel and involved an inventive step.

Reasons for the Decision

1. The appeal is admissible.

2. Amendments; Article 84 and 123(2) EPC

Amended claim 1 results from a combination of the features described in claims 1 to 4, 7 to 9 and page 7, line 12 of the A1 publication (originally filed description page 14, lines 6 and 7). The composition of the claimed steel is clearly defined. Hence there are no formal objections to the present claims under Article 84 and Article 123(2) EPC.

3. Novelty and inventive step

3.1 Document D1 discloses a high-grade super duplex stainless steel composition having an excellent resistance to corrosion, a high strength and which is less susceptible to the precipitation of intermetallic compounds of σ- and similar phases and to embrittlement during normal welding and stress-relief heat treatment (D1, page 2, line 44 to page 3, line 19). The following table compares the composition (in wt %) of the claimed duplex stainless steel with that given in document D1.

Element:	present application	document D1:
Cr	21.0-38.0	23.0-27.0
Ni	3.0-12.0	5.0-9.0
Mo	1.5-6.5	2.0-4.0
W	0-6.5	>1.5-5.0
Si	≤3.0	≤1.0
Mn	≤8.0	≤1.5
N	0.32-0.45	0.24-0.32

C	≤0.1	≤0.03
REM	0.0001-1.0 (at least 50% Ce)	≤0.2 (mainly La and/or Ce)
Ca	≤0.5	≤0.02
Mg	≤0.5	≤0.02
Al	≤1.0	≤0.040
Ta	≤0.5	
Nb	≤0.5	
Ti	≤1.0	
Zr	≤1.0	
Sn	≤1.0	
In	≤1.0	
B	≤0.1	≤0.02
Cu	≤3.0	≤2.0
PREW:	40-67(*)	≥40 (**)
[MM+Al][0+S]:		-
	$0.1x10^{-5}$ to $2000x10^{-5}[\%]^2$ or	-
	$1.0x10^{-5}$ to $5000x10^{-5}[\%]^2$	

(*) PREW=wt%Cr+3.3(wt%Mo+0.5wt%W)+30wt%N

(**) PREW=wt%[Cr]+3.3(wt%[Mo]+0.5wt%[W])+16wt%[N]

As can be seen, the elemental ranges for Cr, Ni, Mo, W, Si, Mn, C, Ca, Mg, Al, B and Cu of the known steel completely fall within the claimed ranges. As to the nitrogen content, a point-like overlap exists for the claimed lower limit of 0.32% which represents the upper limit for nitrogen of the steel known from D1.

It is also apparent from the comparative table that the formula for calculating the pitting corrosion equivalent (PREW) featuring in claim 1 slightly differs for nitrogen by the factor of 30 compared to the formula disclosed in D1 including 16wt% [N]. Applying

the claimed formula for the PREW to the exemplifying steel compositions 19, 22, 24, 25, 29, 35, 40 given in document D1, Table 1, which all comprise REMs within the claimed range, however shows that these examples actually satisfy the claimed proviso of $40 \leq PREW \leq 67$.

Turning to the solubility product [MM+Al][0+S] defined in claim 1, document D1 fails to disclose the actual oxygen content [O] dissolved in the individual exemplified steel alloys. Hence the solubility product cannot be accurately calculated. Since however the range claimed for the solubility product in the present application is extremely broad, it can be duly assumed that the steels disclosed in document D1 likewise fall within the claimed range of 0.1×10^{-5} to $2000 \times 10^{-5}[\%]^2$ or 1.0×10^{-5} to $5000 \times 10^{-5}[\%]^2$, respectively. This finding has not been disputed by the appellant at the oral proceedings.

3.2 The appellant's position is correct that document D1 does not explicitly disclose the composition of the claimed rare earth metal (REM) which is defined to comprise at least 50% Ce. The appellant further argued that D1 did not disclose the teaching of the present application that additions of REM to the duplex stainless steel helps either to suppress the formation or at least to reduce the precipitation speed of sigma- and khi-phases and thus improves weldability, high temperature oxidation resistance and high temperature workability (A1 publication paragraphs [0044], [0045]). To support its argument, the appellant referred to Figure 16 showing the effect of Ba and REM additions to the steel's microstructure and the mechanism which is

responsible for retarding the formation of the secondary phases provided by REM.

3.3 As to the composition of REM, it is noted that rare earth metals commonly used in metallurgy encompasses an unintentional alloy which is mainly composed of Ce and includes further elements such as La, Nd, and Pr as well as possibly very low amounts of the Pm, Sm etc. Despite this lack of an explicit disclosure in D1 with respect to this issue, no fundamental difference is seen between the composition of the claimed REM and the REM (mainly composed of La and/or Ce) referred to in document D1, page lines 43 to 46, contrary to the appellant position.

The additional effect attributed to the addition of REM as described in the application is not disputed. It is however noted that the REM according to the application and the REM in document D1, if added in the same concentration to the (same) steel composition, alone or in combination with Ca, Mg and B, are expected to react in the same way and thus exhibit the same effect on the physical and mechanical properties of the steel. As described in document D1, all these constituents essentially contribute to improve the steel's hot workability mainly by fixing sulfur and oxygen.

Turning to the additional effect provided by REM on the formation and precipitation speed of σ- and χ-phase, D1 explicitly notes that the known duplex stainless steels have a significantly improved thermal stability due to an extremely slow precipitation speed of hard and brittle intermetallic compounds such as sigma-phase and similar phases (D1, page 12, line 55 to page 13,

line 11). Hence, the REM added alone or in combination with the other constituents by their interaction with these elements will bring about exactly the same technical effect on the technical properties of the known steels as the effect described in the application (A1 publication, paragraph [0013]). Despite the appellant's arguments on that point, a fundamental difference between the technical effect achieved by the addition of REM according to the application and the REM according to D1 could not be identified.

3.4 Referring to the relatively high pitting potential (mVvsSCE) disclosed for the known steels in document D1, Table 2, the appellant further argued that the claimed steel exhibited a better resistance to pitting corrosion due to the presence of nitrogen in amounts ranging from 0.32 to 0.45%.

With respect to the steel's resistance to "pitting", document D1 discloses on page 13, lines 25 to 27 that by adhering to the high value for PREW of ≥ 40 calculated by the formula in D1, page 6, lines 1 and 2 and including [N], the resistance to pitting of the known steels can be greatly improved to a degree which is comparable or even superior to prior art super duplex steels.

More importantly, however, the patent application fails to prove that increased amounts of nitrogen in the claimed range of 0.32 to 0.45% actually do contribute to an improved resistance to pitting corrosion, as alleged by the appellant: to the contrary, compared to the examples comprising high amounts of nitrogen, the exemplified steels 19, 22, 23, 27 to 29, 31 to 34 in

Table 1, all comprising rather low nitrogen contents in the range of 0.23 to 0.32% (and thus falling within the nitrogen range given in D1) did not generate pitting corrosion as well. Consequently, the appellant's allegation that nitrogen in the preferred range of 0.32 to 0.35% results in an improved pitting corrosion potential is unfounded.

3.5 In view of these considerations it is concluded that, compared with the teaching of document D1, the use of REM ≥ 50%Ce and the addition of nitrogen in the claimed amount are not associated with a particular technical effect on the steel's properties or, put the other way, the technical features, referred to by the appellant, do not exhibit an effect unknown from the prior art D1.

4. Given this situation, claim 1 does not comprise technical features involving an inventive step vis-à-vis the technical disclosure of document D1.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

V. Commare T. Kriner