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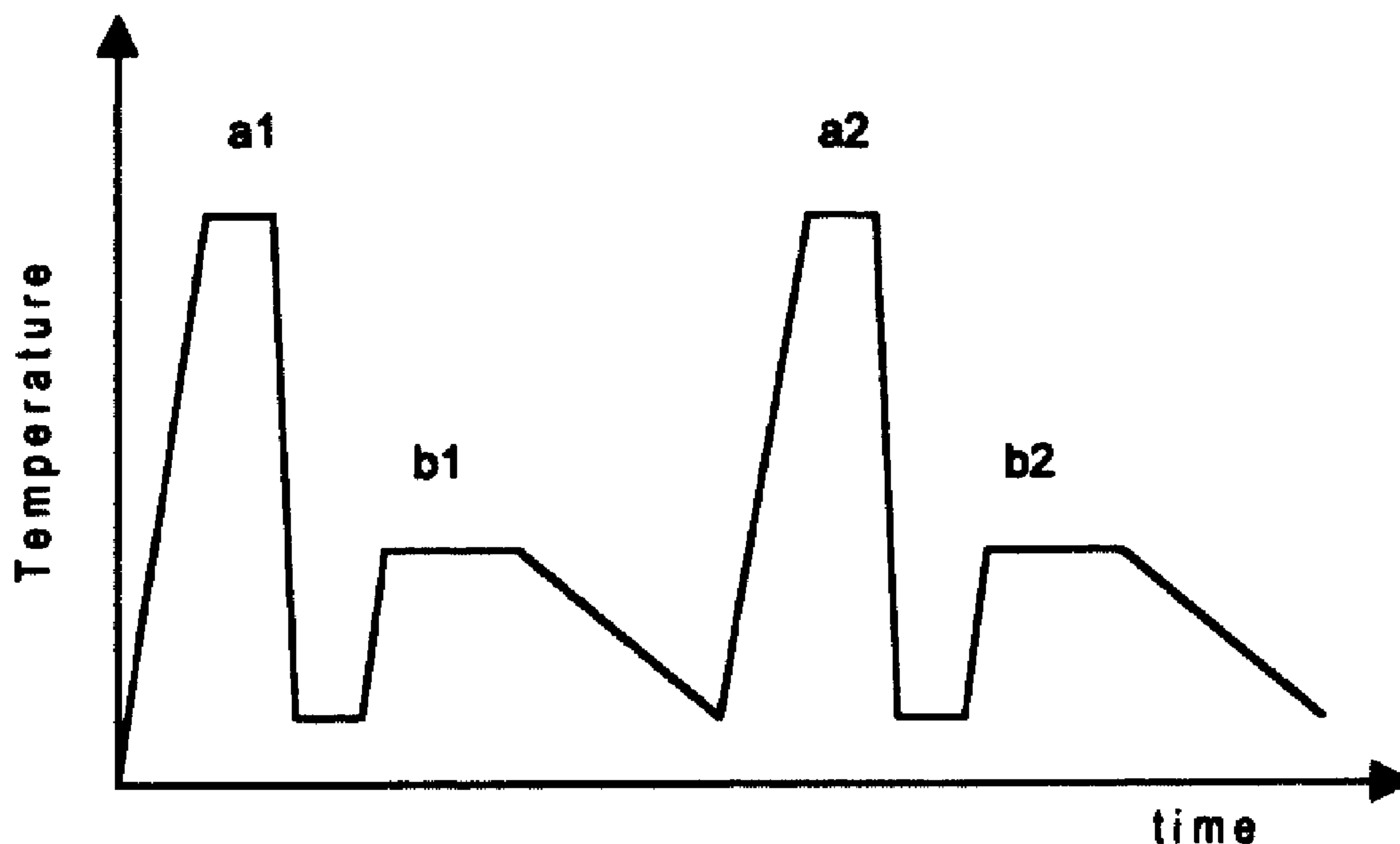
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(54) Titre : TUBE D'ACIER A HAUTE RESISTANCE A LA FISSURATION CAUSEE PAR LES CONTRAINTES DANS UN MILIEU CONTENANT DU SULFURE D'HYDROGENE ET METHODE DE PRODUCTION DUDIT TUBE

(54) Title: STEEL TUBE HIGHLY RESISTANT TO THE CRACKING DUE TO TENSIONS IN A MEDIUM CONTAINING HYDROGEN SULFIDE AND METHOD TO PRODUCE SUCH TUBE



(57) **Abrégé/Abstract:**

The present invention is related to a steel product, particularly a steel product such as a seamless steel tube, with high mechanical resistance and an excellent resistance to the cracking caused by tension in the media containing hydrogen sulfides. The chemical composition of the steel used allows to obtain a product with high mechanical resistance and high cracking resistance caused by tension in media containing hydrogen sulfides and with high fracture toughness. The invention is characterized by the fact that to manufacture it a low alloy steel bar is used with the following composition, in % by weight, apart from Fe: C between 0.20 and 0.26; P a maximum of 0.02; S a maximum of 0.005; Mo between 0.40 and 0.85; Cr between 0.90 and 1.10; Al between 0.01 and 0.05; Mn between 0.3 and 0.5 of Mn; maximum hydrogen when casting of 2 ppm, Cu + 8 Sn $\leq$ 30%; Si + Mn $\leq$ 0.9%. Total maximum O, 20 ppm and total maximum N 80 ppm; and because it comprises a heat treatment consisting in a double quenching and tempering or a double quenching followed by one tempering.

A B S T R A C T

The present invention is related to a steel product, particularly a steel product such as a seamless steel tube, with high mechanical resistance and an excellent resistance to the cracking caused by tension in the media containing hydrogen sulfides. The chemical composition of the steel used allows to obtain a product with high mechanical resistance and high cracking resistance caused by tension in media containing hydrogen sulfides and with high fracture toughness. The invention is characterized by the fact that to manufacture it a low alloy steel bar is used with the following composition, in % by weight, apart from Fe: C between 0.20 and 0.26; P a maximum of 0.02; S a maximum of 0.005; Mo between 0.40 and 0.85; Cr between 0.90 and 1.10; Al between 0.01 and 0.05; Mn between 0.3 and 0.5 of Mn; maximum hydrogen when casting of 2 ppm, Cu + 8 Sn $\leq$ 30%; Si + Mn $\leq$ 0.9%. Total maximum O, 20 ppm and total maximum N 80 ppm; and because it comprises a heat treatment consisting in a double quenching and tempering or a double quenching followed by one tempering.

**STEEL TUBE HIGHLY RESISTANT TO THE CRACKING DUE TO
TENSIONS IN A MEDIUM CONTAINING HYDROGEN SULFIDE AND
METHOD TO PRODUCE SUCH TUBE**

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FIELD OF THE INVENTION

The present invention relates to a steel product, particularly a steel product such as a seamless steel tube with high mechanical resistance and an excellent resistance to cracking caused by tension in media containing hydrogen sulfide. This steel product is characterized by a combination of a specific chemical composition, a steel production process and a heat treatment of the material.

15

BACKGROUND OF THE INVENTION

The presence of hydrogen sulfide (H_2S) in the fluids of the oil wells imposes severe restrictions to the use of steel tubes due to their degradation resulting from a phenomenon known as Sulfide Stress Cracking (SSC). The growing development of deep wells containing hydrogen sulfide demands the use of high mechanical resistance tubes and an excellent resistance to SSC.

25 The SSC phenomenon has been studied for many years, cf. G.

Presouyre, I. Berstein, Acta Met. 27, 1979, p89 y cfr. D. Sponseller, R. Garber y J. Straatmann, ASTM STP 792 Micon 82, 1982, p172.

5 In carbon steels, the inclusion of hydrogen, as a result of the reaction between hydrogen sulfide and iron, causes a noticeable reduction of the fracture toughness of the material. This reduction becomes even more pronounced when the mechanical resistance of the steel is higher., cf. Corrosion in the Petrochemical Industry,
10 ASM, p264 and cf. Internal Report CINI 748/94, C. Pampillo, 1994.

Due to economic reasons, mainly all research and development works in this field are focused on high mechanical resistance and low alloy carbon steels, cf. E. Anelli, L. Cariboni, F. Leone, A. Mascanzoni, 3rd Int.
15 Conf. on Steel Rolling, Japón, 1985, p637. and cfr. M. Watkins, R. Ayer, Corrosion 95, Paper 50.

The National Association of Corrosion Engineers (NACE), has standardized some of the most used tests for this kind of materials under Standard NACE TM0177.

20

In this Standard 4 tests are presented, among which is the so-called Method D, it is an arrest type fractomechanical test. A double cantilever beam type sample (DCB) is used to evaluate the resistance to cracking propagation due to SSC and to quantify it
25 through the critical stress intensity factor in the medium (K_{ISSC}).

5 There is also the so called Method A, which consists in the application of a tension load by means of a metallic ring to a test sample of the material to be tested, submerged in a medium consisting in an aqueous saturated solution. It is then determined whether the test sample is fractured. This means that this method can obtain two results: positive or negative.

10 It can be noticed that Method A has been commonly used to evaluate SSC resistance, although this test does not allow to obtain any property of the material that could be used as a design parameter.

Application of Method D has spread in the last years due to its quantitative character and the possibility of applying the results obtained to the design.

15 To carry out the present invention, the SSC resistance of several low-alloy carbon steels has been determined by means of the application of the DCB test. Likewise the effect of chemical composition and heat treatments on steel behaviour when faced to the SSC phenomenon has been studied.

20 The steps and metallurgical characteristics necessary to meet the mechanical requirements of this type of steels resistant to

5 corrosion have been extensively analyzed in the literature, cf. Sour Grade
C110, Liane Smith, Intetech, June 1999, private report.

Both the experience in the field and the laboratory tests have demonstrated
that there is a hardness limit above which the SSC phenomenon appears.
This fact represents a great dilemma, due to the need to combine high
10 resistance with relatively low hardness values. This means that this kind of
steels, in a stage after the heat treatment, must have a high relationship
between yield and tensile stress. This indicates that the most adequate steels
for those requirements are quenched and tempered steels.

The previous results have been deeply analyzed through the job prepared by
15 CSM, Rome; cf "110SSG: Status dell'attivit di sviluppo" CSM, Rome,
January 2000, private report.

Likewise, there is a document of a Mexican Patent Publication No.
MX9708775A, where Kondo et al disclose a process to produce a seamless
steel tube resistant to sulfide stress cracking by controlling the chemical
20 composition in a fairly wide range and applying a rolling process and a
specific heat treatment.

This document discloses the effect of chemical elements such as C, P, S, Mo,
Cr, Mn, O, N, Al, Ti, Ni, Si, Va, Ca, W, B and Zr establishing content ranges
technologically unfeasible even in the

most restricted ranges.

When the carbon effect is mentioned, a range of 0.15% to 0.50% of the total weight of the heat is mentioned.. As the shortest interval
5 a range of 0.20% to 0.35% is considered. It has been demonstrated that heats containing 0.35% carbon, quenched with water, have shown cracks, even before being in contact with media containing sulphydric acid.

10 The different metallurgical factors influencing the capacity of steels to resist to SSC are well known. The mechanical resistance level, the micro-structure, the hardness, the segregation and the level content of non metallic inclusions are very important, cf
"Mejoramiento de la resistencia a la iniciación y propagación de
15 SSC de tubos para OCTG de alta resistencia a través del control de la microestructura y las precipitaciones" G. López Turconi et al. NACE 2001.

However, in spite of all that information, the problem of manufacturing seamless tubes highly resistant to SSC, has not
20 been fully solved and there is not enough information about the levels of the parameters above indicated, as well as about the qualitative and quantitative composition of said steels.

25 OBJECTIVE OF THE INVENTION

The main objective of this invention is to provide a chemical composition of the steel used for manufacturing seamless tubes and a manufacturing process, permitting to obtain a product with
5 high mechanical resistance.

Another objective of the invention is to meet the requirements of the previous objective, in a product also presenting high resistance to SSC.

10

Still another objective is to make possible a product with high fracture toughness values.

Other objectives and advantages of the present invention will be
15 apparent from the analysis of the following description and the illustrative, but no limitative, examples indicated in the present description.

BRIEF DESCRIPTION OF THE INVENTION

20

Briefly, in one of its modalities, the present invention is related with the qualitative and quantitative composition of steel. Extensive studies were carried out about a manufacturing process to obtain seamless steel tubes with high mechanical resistance and
25 high resistance to the SSC, which shown that compositions of the

state of the art could not solve the posed problem. By subjecting the material to a two continuous quenching and tempering cycles or double quenching followed by tempering, it is possible to obtain a material with high K_{ISSC} values measured through the NACE
5 TM0177 Method D test.

Steel microstructure, the level of its residual stresses and its mechanical resistance depend on its chemical composition and on the manufacturing thermo-mechanical treatments; this leads to
10 consider microstructure, chemical composition and thermo-mechanical treatments as factors depending on the material itself.

As a result of the research carried out, it has been possible to design a new process to manufacture seamless steel tubes wherein
15 such tubes are obtained from a low-alloy steel bar having the following content of elements by weight percentage: C between 0.20 and 0.26; P a maximum of 0.02; S a maximum of 0.005; Mo between 0.40 and 0.85; Cr between 0.90 and 1.10; Al between 0.010 and 0.050; Mn between 0.30 and 0.50 of Mn; maximum
20 hydrogen when casting of 2 ppm, $Cu + 8 Sn \leq 0.30\%$ (The percentage of the copper content plus eight times the tin content must be less than or equal to 0.30%); $Si + Mn \leq 0.9\%$ (The percentage of silicon added to the percentage of manganese must be below 0.9%).

Following is the description of the effect that each of the elements added has on the properties of the material claimed in the present invention.

5

Carbon effect

Carbon is needed to increase the hardenability of the material, and in this way, increase the steel resistance. The content of C (between 0.18 and 0.30%) does not modify the resistance to SSC.

10 This is valid in case the remaining variables are kept constant, in particular the material's yield stress. The contents of C shall be kept under 0.26 % to avoid cracks during water quench. And it must be above 0.20% to obtain an acceptable martensitic transformation.

15

Manganese effect

The marked increase of hardenability produced by Manganese addition, added to its low cost, makes it a usually used alloy element, with contents higher than 0.30%.

20

The increases in manganese content tend to raise the susceptibility to SSC. Manganese reduces the cohesion of the limits of austenitic grains and pushes P to segregate to the grain boundaries. That is the reason why it is preferable addition of Mn to be below 0.50 %
25 by weight.

Silicon effect

The silicon, like manganese, promotes the segregation of P to grain boundaries, whereby it results harmful and it must be kept at
5 the lowest possible level, preferably under 0.40 % by weight.

Chromium effect

Chromium produces hardening by solid solution and increases the hardenability of the material, thus increasing the resistance to
10 SSC. This is the reason why a minimum content of 0.90% is desired, but since an excess of hardenability also means cracking problems during quenching in water, it is recommendable to maintain a maximum value of 1.10% by weight.

15 As it is well know, quenching in other type of refrigerating medium will mean complications in the equipment to recover released gases or in the formation of inert atmospheres.

Molybdenum effect

20 The molybdenum, increasing the hardenability of steel, allows to increase the tempering temperature, thus preventing the segregation of brittleness generating elements to the austenitic grain boundaries. Therefore, its addition improves the SSC resistance. The percentage to be added ranges between 0.40 and
25 0.85, below this level its effect is not enough and moreover it

would unnecessarily increase the price of the process.

Phosphorus effect

Phosphorus exists as an unavoidable element in steel, and a
5 content above 0.02 % produces segregation in the grain
boundaries, which reduces the SSC resistance.

Sulfur effect

Like phosphorus, sulfur is inevitably found in steel, and a content
10 of more than 0.005% reduces the toughness and hardenability of
material.

Oxygen effect

Oxygen exists inevitably in steel, as well as sulfur and phosphorus
15 in a quantity above 20 ppm can cause a reduction in the toughness
of the material and also generate an inclusionary content
worsening the steel resistance to SSC.

Hydrogen effect

20 The content of hydrogen in the steel has to be kept below 2 ppm, in
order to avoid the formation of cracks at the time of steel's
solidification.

Nitrogen effect

25 The nitrogen exists necessarily in the steel as well as phosphorus,

sulfur and oxygen. It must be kept below 80 ppm to obtain a steel containing precipitate that do not reduces material toughness and do not generate ageing efects during the tempering process.

- 5 Studies on the state of the art allow to find out that the segregation of P on grain boundary has a strong influence on SSC resistance.

10 It is also known that the direct measurement of this segregation presents difficulties, making necessary indirect measurement in the chemical composition of the elements originating such segregation.

Therefore, as a parameter of this measurement the following expression has been used:

15

$$A\text{-value} = (Mn + 4.3 P + 17.0 (Mn * P))$$

Where Mn and P correspond to the Manganese and Phosphorus content respectively expressed in % by weight. It has been found, and this makes part of the state of the art, that the lower the parameter A-value, the better the performance of the material is to SSC.

20

After multiple tests carried out in our laboratories we found out that an optimum value is 0.6 or lower. A lower parameter level is

25

difficult since Mn is an element necessary in our steel and is practically impossible to reduce the content of P to zero.

Meeting this requirement , it is found out that the K_{ISSC} value of
5 the material expressed in MPa m^{1/2} is placed between 24 and 50 for the products reproducing the teachings of the present invention.

In another of its aspects, the invention consists in a steel manufacturing process that is carried out according to a clean
10 steel practice (low contents of sulfur and oxygen) with the purpose of guaranteeing a maximum steel cleanliness level of 2 fine series according to standard ASTM E45. At the same time, the clean steel practice permits to achieve cleanliness levels with a content of oversize inclusions not bigger than 30 µm.

15

These inclusion levels are guaranteed by controlling total oxygen, limiting it to a maximum of 20 ppm.

The clean steel manufacturing process is mainly characterized by
20 the points hereinafter detailed:

The practice of secondary metallurgy, assuring the floatation of inclusions and impurities in the ladle furnace or LF, by means of an adequate inert gases bubbling process. The generation of fluid slag
25 able to absorb impurities and inclusions, permits to obtain a highly

cleaned steel, as well the modification of inclusions by means of the addition of Si Ca.

As a step of the present process, a solid steed bar is obtained,
5 preferably of a circular section, by using a continuous casting machine.

Another important aspect of the present invention is the heat treatment to be applied to the steel to obtain the desired
10 properties.

It is considered that steels with a tempered martensite type structure are the most resistant to SSC.

15 The heat treatment procedure of this invention is characterized by the performance of a process that permits to widely improve the properties of steel to resist SSC.

When a steel tube with the specified chemical composition is
20 subjected to the heat treatment described in this invention, a structure is obtained that contains a fine dispersion of cementite particles, which improves the work of the material in media containing hydrogen sulfurs.

25 It is known that smaller prior austenitic grain size improves the

resistance to SSC. It is also known that this grain size is modified when changing the temperature and / or time of the austenitisation process, which imposes the performance of a strict control during the process.

5

An adequate tempering process, preferably carried out by means of simultaneous cooling in the inside and in the outside of the steel tube, preferably with water, is necessary to obtain a high cooling speed and to promote the martensite formation.

10

We have surprisingly discovered that there is a beneficial effect of carrying out a multiple heat treatment of austenitisation and quenching for the refinement of the prior austenitic grain. The application of double quenching is effective for the grain refinement, and particularly effective is the refinement obtained thanks to the second quenching.

The tempering temperature has an important influence on the steel's mechanical resistance, as well as on the final microstructure and segregation.

20

Besides, high tempering temperatures will be convenient to achieve an adequate recovery and recrystallization, which improves the resistance to SSC.

25

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 corresponds to a Cartesian axis diagram, in which the axis
5 of the ordinates corresponds to the temperature and the axis of the
abscissa corresponds to the time, thus showing the cycle of heat
treatment of the seamless steel tube, with a heat treatment
consisting in a double quenching and tempering process.

10 Figure 2 corresponds to a Cartesian axis diagram, in which the axis
of the ordinates corresponds to the temperature and the axis of the
abscissa corresponds to the time, thus showing the cycle of heat
treatment of the seamless steel tube, consisting in a double
continuous quenching followed by the tempering process.

15

DETAILED DESCRIPTION OF THE INVENTION

In the aspect of the invention related to the heat treatment, said
20 treatment is made up of a double cycle of quenching and tempering
or continuous double quenching followed by the tempering and can
be described through figures 1 and 2.

Both heat treatments described in the present invention allow to
25 obtain a fine dispersion of the cementite particles and permit the

grain size refinement, which together with the achievement of a minimum content of 95% of martensitic structure, can assure a better performance of the material SSC.

5 Since tempering is an important process affecting the characteristics of the final product, it is necessary to determine an optimal tempering temperature according to the desired characteristics of the final product. The steel tube must be kept at a uniform temperature so determined. The differences in the
10 tempering temperatures can be in the utmost of 20°C, preferably 10°C.

The best way to carry out the invention is described in the following steps:

15

Selecting a steel which adequate chemical composition above described, in order to assure a structure with a minimum martensite content of 95 %.

20 Keep the carbon content in the interval of 0.20-0.26 % by weight since lower values generate the formation of softer martensites and higher carbon contents can generate cracks during quenching in water.

25 Reducing as much as possible content of impurities such as P and

S and residual elements such as O, N and H (See "Brief description of the invention")

Carry out a multiple heat treatment in order to homogenize and
5 refine the austenitic structure.

Precisely controlling the effective temperature of material in the tempering phase, preferably within the interval of tempering temperature $\pm 10^{\circ}$ C, in order to constrain hardness variability.

10

EXAMPLES

In this section , application examples of the present invention, related to the chemical composition aspect of the invention are presented, organized in tables.

15

Table 1 determines the different compositions and their effects in the A-value, table 2 establishes the effect of such composition with the two heat treatments indicated, in the mechanical properties of the product, and table 3 shows the effect of such compositions also
20 with the heat treatment indicated, on the resistance to SSC.

The effect of the chemical composition and the examples developed are included in Table 1 and the heat treatments selected assure the properties to resist SSC claimed in the present invention. This
25 can be observed in the examples mentioned in tables 1, 2 and 3.

All cases referred by the same letter: "A", "B", etc. have the same composition and the same heat treatment.

5 The invention has been sufficiently described such that any person with an average level of knowledge about the subject can reproduce it and obtain the results mentioned herein. However, any knowledgeable person in the art of the present invention can be capable of making modifications not described in the present
10 application, but if for the application of those modifications in a given material or in the manufacturing process to obtain it, the subjects claimed in the following claim are applied, such material and the process shall be comprised within the scope of the present invention.

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20

25

Table 1. Chemical composition

Material	C:	Mn	Si	P	S	Mo	Cr	Cu	Al	Sn	O (ppm)	N (ppm)	N (ppm)	Cu + 8Sn	Si + Mn	A-value
A	0.23	0.42	0.26	0.009	0.001	0.54	1.07	0.14	0.018	0.009	17	79	1	0.21	0.68	0.52
B	0.26	0.38	0.25	0.011	0.001	0.49	1	0.09	0.02	0.008	12	75	1	0.15	0.63	0.50
C	0.21	0.48	0.25	0.007	0.002	0.48	1.02	0.15	0.019	0.008	19	71	1	0.21	0.73	0.57
D	0.25	0.37	0.25	0.008	0.002	0.75	0.96	0.08	0.017	0.004	18	68	1	0.11	0.62	0.45
E	0.25	0.41	0.25	0.005	0.002	0.76	0.97	0.085	0.027	0.006	17	59	1	0.13	0.66	0.47
F	0.25	0.38	0.22	0.008	0.002	0.76	0.95	0.092	0.016	0.006	18	61	1	0.14	0.60	0.47
G	0.23	0.38	0.19	0.009	0.002	0.72	0.98	0.13	0.016	0.009	17	72	1	0.20	0.57	0.48
H	0.24	0.36	0.22	0.009	0.001	0.73	1	0.17	0.023	0.012	18	70	1	0.27	0.58	0.45
I	0.23	0.49	0.23	0.008	0.003	0.77	1.02	0.1	0.02	0.007	16	72	1	0.16	0.72	0.59

Table 2. Mechanical properties

Material	Heat treatment	Yield Stress		Tensile Stress	
		MPa	ksi	MPa	ksi
A	TRTR	599	86.9	736	106.7
B	TTR	605	87.7	701	101.7
C	TRTR	647	93.8	758	109.9
D	TTR	728	105.7	810	117.7
E	TTR	736	106.9	819	118.9
F	TRTR	755	109.7	793	115.2
G	TRTR	770	111.7	862	124.9
H	TRTR	800	116.0	890	129.0
I	TTR	815	118.3	879	127.5

TRTR: Double cycle of quenching and tempering .

TTR: Double cycle of quenching followed by one tempering.

5

Table 3. Fracture toughness ($K_{I\text{SSC}}$ measured by Method D)

Material	$K_{I\text{SSC}}$ (Mpa m ^{1/2})
A	48.1
B	44.0
C	43.4
D	36.6
E	35.2
F	36.4

21

G	29.9
H	30.2
I	31.1

C L A I M S

We claim:

1. A process of manufacturing a steel product featuring high mechanical resistance and high resistance to cracking caused by tension in media containing hydrogen sulfide, the process comprising:

selecting a low alloy steel bar containing alloy elements with the following chemical composition expressed in % by weight

C between 0.20 and 0.26,

P a maximum of 0.02,

S a maximum of 0.005,

Mo between 0.40 and 0.85,

Cr between 0.90 and 1.10,

Al between 0.01 and 0.05,

Mn between 0.3 and 0.5,

H a maximum when casting of 2 ppm,

$\text{Cu} + (8 * \text{Sn}) \leq 0.30$,

$\text{Si} + \text{Mn} \leq 0.9$,

O a maximum of 20 ppm, and

N a maximum of 80 ppm; and

heat treating the low alloy steel bar according to a heat treatment process consisting of a double cycle of quenching and tempering, or double quenching followed by tempering.

2. The process of claim 1, wherein the step of selecting comprises the low alloy steel bar meeting the following condition

$$A - \text{value} \leq 0.6,$$

where

$$A - \text{value} = (\text{Mn} + 4.3\text{P} + 17.0 (\text{Mn} * \text{P})).$$

3. The process of claims 1 or 2, comprising using a continuous casting machine to obtain the low alloy steel bar.

4. The process of claim 3, comprising producing the low alloy steel bar with a circular section.

5. The process of any one of claims 1 to 4, wherein the step of heat treating comprises precisely controlling an effective temperature during the tempering within $\pm 10^\circ\text{C}$ in order to constrain hardness variability.

6. A steel product made according to the process of any one of claims 1 to 5.

7. The steel product of claim 6, characterized by a steel cleanliness level of maximum 2 fine series according to ASTM E45 standard.

8. The steel product of claims 6 or 7, characterized by a content of oversize inclusions in the steel product does not exceeding a dimension of 30 μm .

9. The steel product of any one of claims 6 to 8, characterized by a minimum martensite content of 95% by volume.
10. A seamless steel tube product made according to the process of any one of claims 1 to 5.
11. The seamless steel tube product of claim 10, characterized by a steel cleanliness level of maximum 2 fine series according to ASTM E45 standard.
12. The seamless steel tube product of claims 10 or 11, characterized by a content of oversize inclusions in the steel product does not exceeding a dimension of 30 μm .
13. The seamless steel tube product of any one of claims 10 to 12, characterized by a minimum martensite content of 95% by volume.

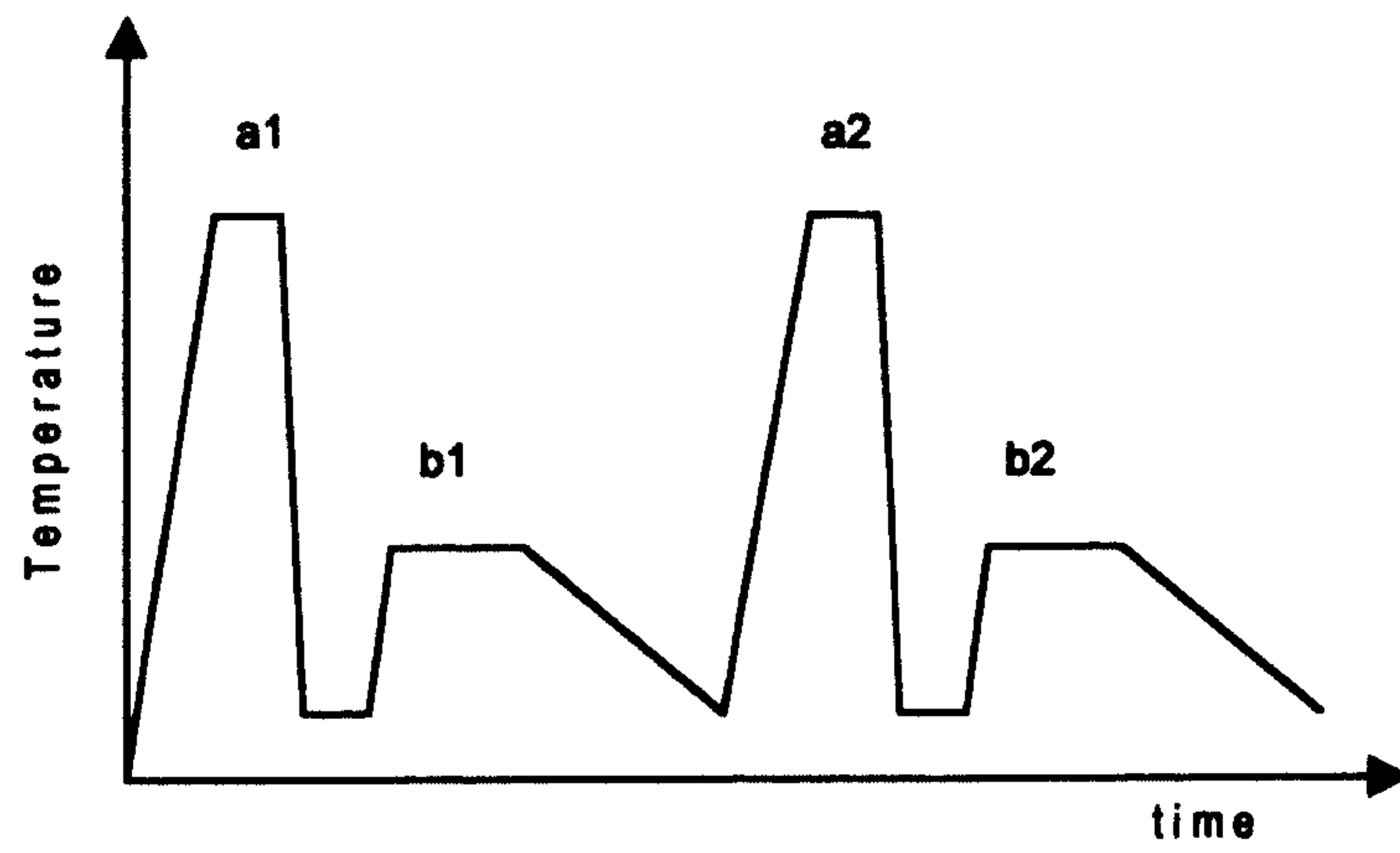


Figure 1

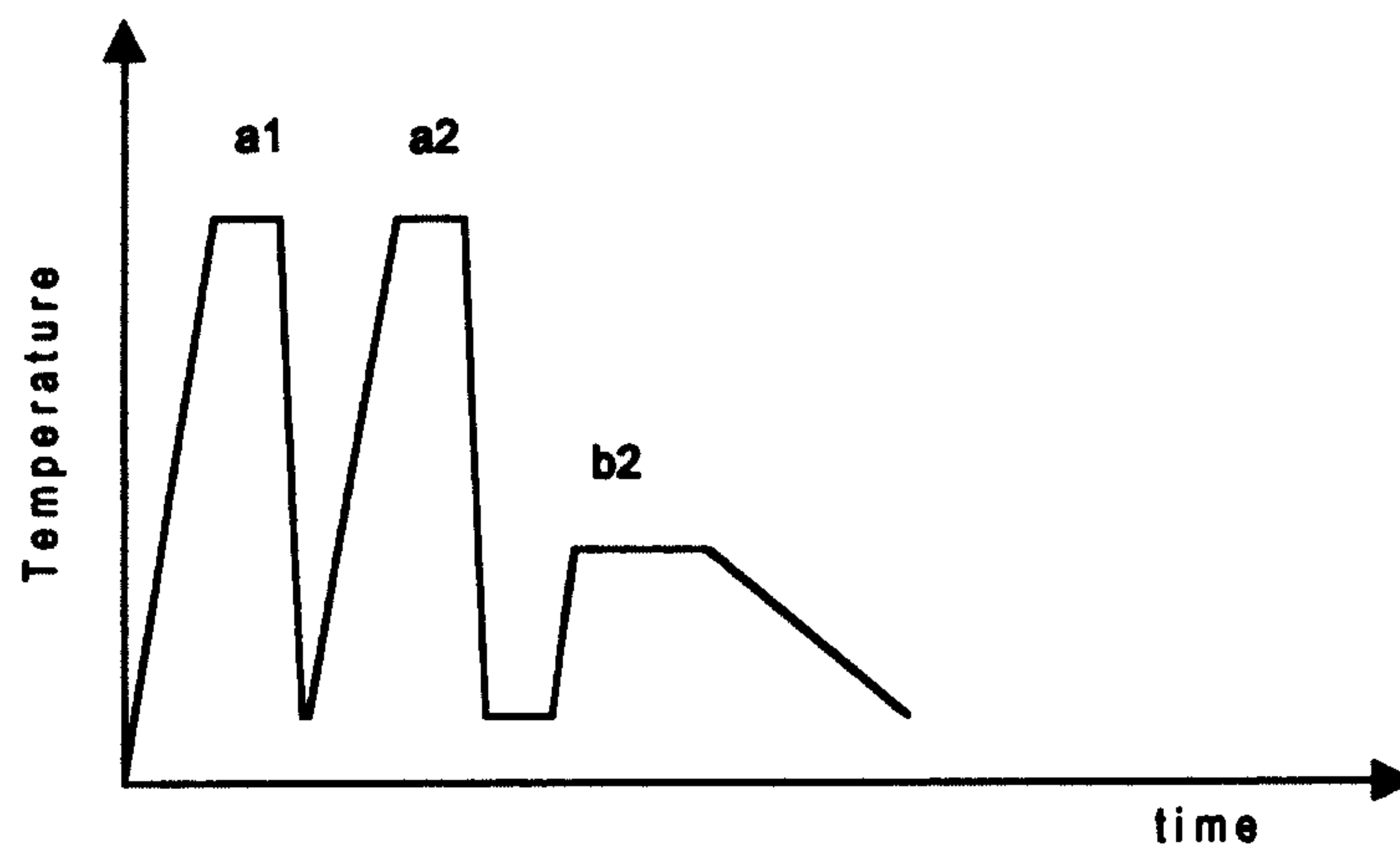


Figure 2

