(19) DANMARK

(10) **DK/EP 1065285 T4**

Patent- og Varemærkestyrelsen

(12) Oversættelse af ændret europæisk patentskrift

(51) Int.Cl.: ***C 21 D 8/04 (2006.01)*** ***C 21 D 9/48 (2006.01)***

(45) Oversættelsen bekendtgjort den: **2016-04-18**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om opretholdelse af patentet i ændret form: **2016-01-13**

(86) Europæisk ansøgning nr.: **00401868.5**

(86) Europæisk indleveringsdag: **2000-06-30**

(87) Den europæiske ansøgnings publiceringsdag: **2001-01-03**

(30) Prioritet: **1999-07-01 FR 9908414**

(84) Designerede stater: **AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE**

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(54) Benævnelse: **STÅLPLADE MED LAVT INDHOLD AF CARBON BEROLIGET MED ALUMINIUM TIL EMBALLAGE**

(56) Fremdragne publikationer:
EP-A- 0 360 955
DE-C- 19 622 164
FR-A- 2 472 021
GB-A- 2 086 425
PATENT ABSTRACTS OF JAPAN vol. 006, no. 044 (C-095), 19 mars 1982 (1982-03-19) & JP 56 158822 A (NIPPON STEEL CORP), 7 décembre 1981 (1981-12-07)
US-A- 4 698 103

Description

The present invention relates to the field of steels for application in the field of food, non-food or industrial metal packaging.

Steels produced for uses specific to metal packaging differ from thin sheet metal especially in their physical characteristics.

The thicknesses of steel sheets for packaging vary from 0.12 mm to 0.25 mm for the very great majority of uses but can reach greater thicknesses, up to 0.49 mm for very particular applications. This is the case, for example, for certain non-food packaging materials such as, for example, certain aerosols or for certain industrial packaging materials. The thicknesses may also be as low as 0.08 mm, for example in the case of food trays.

Steel sheets for packaging are customarily coated with a metal coating (tin, remelted or not, or chrome) on top of which there is usually deposited an organic coating (varnishes, inks, plastic films).

In the case of two-piece packaging materials, these are made by deep-drawing using a blank holder, or by deep-drawing/finish-drawing for beverage containers, and are usually cylindrical or frustum-shaped, axially symmetrical containers. However, packagers are showing an ever greater interest in steels of ever thinner thicknesses, of from 0.12 mm to 0.075 mm, and, with the aim of setting themselves apart from the competition, they are seeking to innovate with ever more complex shapes. We are therefore now finding containers of original shapes manufactured from low-thickness steel sheets which, although exhibiting greater difficulties in forming, must meet the criteria for use (mechanical resistance of the packaging, resistance to the axial load to which they are subjected during storage in stacks, resistance to the internal overpressure to which they are subjected during heat sterilisation treatment and to the internal partial vacuum pressure to which they are subjected after cooling) and therefore must have very high mechanical strength.

Accordingly, the utilisation and performance of those packaging materials depend on a certain number of mechanical characteristics of the steel:

- the planar anisotropy coefficient ΔC aniso,
- the Lankford coefficient,

- the yield strength Re,
- the ultimate tensile strength Rm,
- the elongation A%,
- the uniform elongation Ag%.

In order to give the packaging equivalent mechanical resistance at lower steel thickness, it is indispensable that the steel sheet has a higher ultimate tensile strength.

For producing packaging materials it is known to use standard low-carbon and low-manganese, aluminium-killed steels.

The carbon content customarily sought for this type of steel is between 0.020 % and 0.040 %, because contents greater than 0.040 % lead to less favourable mechanical characteristics for deep-drawing and contents less than 0.015 % bring about a propensity to natural aging of the sheet metal despite aging by annealing.

The manganese content is reduced as much as possible because of an unfavourable effect of that element on the value of the Lankford coefficient for non-vacuum-degassed steels. Accordingly the sought manganese content is between 0.15 and 0.25 %.

Those steel sheets are produced by cold-rolling a hot strip, with a degree of cold-rolling of between 75 % and more than 90 %, followed by continuous annealing at a temperature between 640 and 700°C, and a second cold rolling with a degree of elongation in the course of that second cold rolling which can vary between 2 % and 45 %, depending on the level of ultimate tensile strength Rm sought.

However, for aluminium-killed low-carbon steels, enhanced mechanical characteristics are associated with a low elongation capacity. This poor ductility, besides the fact that it is unfavourable for forming the packaging, brings about a thinning of the walls during that forming which will be unfavourable for the performance of the packaging.

Accordingly, for example, an aluminium-killed low-carbon steel having an ultimate tensile strength Rm of the order of 550 MPa will have a degree of elongation A% of the order of only 1 to 3 %.

GB-A-2 086 425 shows a process for manufacturing a sheet of cold-rolled steel having an excellent deep-drawing capability and excellent resistance to aging, wherein there is produced a slab comprising from 0.01 to 0.03 % carbon, from 0.05 to 0.30 % manganese, from 0.020 to 0.100 % soluble aluminium, not more than 0.0050 % nitrogen, the remainder being iron and inevitable impurities; the slab is hot-rolled and, after coiling the hot-rolled steel, it is cold-rolled and, in a continuous annealing line, the steel is held at a temperature between the A_1 and A_3 transformation points for more than 10 seconds; it is cooled down from temperatures above 650°C at a cooling rate of more than 200°C per second and accelerated aging is carried out by holding it at temperatures of between 300 and 500°C for more than 30 seconds.

The present invention is aimed at proposing a sheet of aluminium-killed low-carbon steel for packaging, which has, at a level of ultimate tensile strength which is equivalent to that of aluminium-killed low-carbon steels from the prior art, a higher degree of elongation A%.

In order to obtain those characteristics, the invention relates to a process for manufacturing a strip of aluminium-killed low-carbon steel for packaging, in which:

- a hot-rolled strip of steel comprising by weight between 0.022 and 0.035 % carbon, between 0.15 and 0.25 % manganese, between 0.040 and 0.070 % aluminium, between 0.0035 and 0.0060 % nitrogen, the remainder being iron and inevitable residual impurities is provided,
- a first cold-rolling of the strip is carried out,
- the cold-rolled strip is subjected to annealing,
- optionally, a secondary cold-rolling is carried out,

characterised in that the annealing is a continuous annealing, the cycle of which comprises increasing the temperature up to a temperature above the starting temperature of pearlite transformation Ac_1, holding the strip above that temperature for a period greater than 10 seconds, and rapidly cooling the strip down to a temperature less than 350°C at a cooling rate between 100 and 500°C/s.

In accordance with other characteristics of the process of the invention:

- during the annealing the strip is held at a temperature between Ac_1 and 800°C, for a period of from 10 seconds to 2 minutes;
- the strip is cooled at a rate of more than 100°C per second down to ambient temperature.

The invention relates also to a sheet of killed-aluminium low-carbon steel for packaging, comprising by weight between 0.022 and 0.035 % carbon, between 0.15 and 0.25 % manganese, between 0.040 and 0.070 % aluminium, between 0.0035 and 0.0060 % nitrogen, the remainder being iron and inevitable residual impurities, manufactured in accordance with the above process, characterised in that it has, in the aged state, a degree of elongation A % satisfying the relationship:

$$(670 - Rm)/14 < A\ \% < (720 - Rm)/17$$

Rm being the ultimate tensile strength of the steel, expressed in MPa.

In accordance with other characteristics of the sheet, the steel includes carbon in the free state and/or some carbides precipitated at low temperature, and has a number of grains per mm^2 which is greater than 20000.

The characteristics and advantages will appear more clearly from the description which follows, given solely by way of example and with reference to the accompanying Figures.

Figures 1 and 2 are diagrams showing the influence of the annealing temperature on the ultimate tensile strength Rm.

Figure 3 is a diagram showing the influence of the cooling rate on the ultimate tensile strength Rm.

Figure 4 is a diagram showing the influence of the cooling rate on the ultimate tensile strength Rm and degree of elongation A%.

Figure 5 is a diagram showing the influence of the cooling rate on the HR30T hardness.

A number of tests were carried out, firstly in the laboratory and then under industrial conditions, in order to validate the characteristics of the invention. The full results of two of those tests will now be described.

These tests relate to two cold coils of aluminium-killed low-carbon steel, the characteristics of which are reproduced in Table 1 hereinbelow.

Table 1

	Contents (10^{-3} %)				Hot-rolling			Cold-rolling	
	C	Mn	Al	N	TFR (°C)	Tcoil (°C)	Thickn. (mm)	Deg. of reduction (%)	Thickn. (mm)
A	23	186	50	3.6	860/880	530/565	1.97	89.8	0.20
B	25	203	58	4.6	860/880	530/565	2.00	87	0.28

The first column shows the coil designation; the second to fifth columns contain the contents, in terms of 10^{-3} % by weight, of the main constituents of importance. The sixth to eighth columns relate to the hot-rolling conditions: the sixth column gives the final temperature of hot-rolling; in the seventh column, the coiling temperature; in the eighth column, the thickness of the hot strip. Finally, columns nine and ten relate to the cold-rolling conditions: the ninth column gives the degree of reduction of cold-rolling, and the tenth column the final thickness of the cold strip.

These two standard strips were subjected to different annealing operations followed by second cold-rolling operations which were also different.

The holding temperatures during annealing were varied from 650°C to 800°C, the cooling rates were varied from 40°C/s to 400°C/s, and the degrees of elongation on second rolling were varied from 1% to 42%.

In addition to the micrographic examinations, characterisation of the metal obtained in these different tests consisted, on the one hand, of performing tensile strength tests on ISO 12.5x50 test-pieces in the rolling direction and in the cross-direction, in the fresh state and in the aged state following aging at 200°C for 20 minutes and, on the other hand, determining the HR30T hardness also in the fresh state and aged state.

These tests allowed it to be demonstrated that it is possible to considerably increase the ultimate tensile strength Rm for the same aluminium-killed low-carbon steel at the same degree of elongation in the second cold-rolling, if between the two cold-rollings there is performed continuous annealing in accordance with the conditions of the invention.

In other words, these tests allowed it to be demonstrated that it is possible to considerably increase the ductility A% for the same aluminium-killed low-carbon steel, at the same ultimate tensile strength Rm, if between the two cold-rollings continuous annealing in accordance with the conditions of the invention is performed, because the same level of Rm is achieved with a lower degree of elongation in the course of the second rolling. Accordingly, it becomes possible to produce grades of aluminium-killed low-carbon steel having a level of Rm of the order of 380 MPa without requiring a second rolling after annealing except for, perhaps, a light cold-working operation known as a skin pass which makes it possible to prevent the yield-strength plateau present in the metal when discharged from annealing.

Influence of the composition of the steel

As indicated hereinbefore, the invention is not to be found in the composition of the steel, which is a standard aluminium-killed low-carbon steel.

As with all aluminium-killed low-carbon steels, it is essentially the carbon and manganese contents which are important:

- the carbon content customarily sought for this type of steel is between 0.022 % and 0.040 %, because contents greater than 0.040 % lead to less favourable characteristics for deep-drawing. For contents less than 0.022 % there is no pearlite transformation on cooling, and this pearlite transformation is necessary and desired;
- the manganese content is reduced as much as possible because of an unfavourable effect of this element on the value of the Lankford coefficient for non-vacuum-degassed steels; accordingly, the manganese content sought is between 0.15 and 0.25 %.

Nitrogen and aluminium are also two elements which it is appropriate to control. Nitrogen is included in excess if it is desired to obtain a hard and aging steel. Generally it is between 0.0035 and 0.0060 %.

Aluminium is used in order to kill the steel. Generally between 0.040 and 0.070 % is included.

Influence of the hot-denaturing conditions

Continuously annealed aluminium-killed low-carbon steels are rolled at a temperature greater than Ar_3.

The essential parameter is the temperature of coiling, and cold coiling is preferred, between 500 and 620°C. Indeed, hot coiling, at a temperature greater than 650°C, has two drawbacks:

- it gives rise to heterogeneities in the mechanical characteristics linked to the differences in cooling rates between the core and the extremities of the strip;
- it causes a risk of abnormal grain growth, which can occur for certain combinations (final temperature of rolling, coiling temperature) and can constitute an unacceptable defect both in hot sheet and in cold sheet.

Nevertheless, hot coiling can be carried out by performing, for example selective coiling: the temperature being higher at the extremities of the strip.

Influence of the cold-rolling conditions

Owing to the low final thicknesses to be achieved, the range of degrees of cold reduction extends from 75 % to more than 90 %.

The main factors which come into play in defining the degree of cold reduction are very obviously the final thickness of the product - and on this point there is scope for varying the thickness of the hot product - and also metallurgical considerations.

The metallurgical considerations are based on the influence of the degree of cold reduction on the microstructural state and, consequently, on the mechanical characteristics after recrystallisation and annealing. Accordingly, the more the degree of cold reduction increases, the lower the recrystallisation temperature, the less grains, and the higher the Re and Rm. In particular, the degree of reduction can have a very great influence on the Lankford coefficient.

If there are requirements in terms of deep-drawing spurs it is appropriate, for example, to optimise the grade of steel, and especially the carbon content, and the degree of cold-rolling reduction with the hardness or desired mechanical characteristics in order to obtain a metal referred to as "spur-free metal".

Influence of the annealing

An important characteristic of the invention is to be found in the annealing temperature. It is important that the annealing temperature is greater than the starting point of pearlite transformation Ac_1 (of the order of 720°C for this type of steel).

Another important characteristic of the invention is to be found in the cooling rate, which must be between 100 and 500°C/s.

In the course of the strip being held at a temperature greater than 720°C, carbon-rich austenite is formed. The rapid cooling of this austenite allows a certain amount of carbon to be maintained in the free state and/or precipitation of fine, disperse carbides at low temperature. This carbon in the free state and/or these carbides formed at low temperature promote the blocking of dislocations, which makes it possible to achieve high levels of mechanical characteristics without necessitating a high degree of reduction in the course of the second cold-rolling which follows.

It is therefore important to carry out rapid cooling, by between 100 and 500°C/s at least down to a temperature less than 350°C. If the rapid cooling is stopped before 350°C, the free carbon atoms will be able to combine and the sought effect will not be obtained. It is clear that rapid cooling down to ambient temperature is possible.

It is also possible to carry out cooling at a rate greater than 500°C/s but the Applicant has found that above 500°C/s the influence of an increase in the cooling rate is no longer very significant.

Figures 1 and 2 show the influence of the annealing temperature at constant cooling rate (100°C targeted and actually 73 to 102°C/s in Figure 1; 300°C targeted and actually 228 to 331°C/s in Figure 2) on the ultimate tensile strength Rm.

From these Figures there can be see a clear increase in Rm for an identical degree of elongation during the second rolling in the case of steels annealed at 740°C and at 780°C compared to the same steels annealed at 650°C and at 680°C.

However, this influence of the annealing temperature on the ultimate tensile strength Rm is not very perceptible for degrees of elongation on second cold-rolling which are less than 3 %. It only becomes truly significant starting from 5 % elongation on second cold-rolling.

A temperature which is too high, higher than 800°C, causes at least partial precipitation of the nitrogen in the form of aluminium nitrides. This precipitated nitrogen no longer participates in the hardening of the steel, which has the effect of lessening the ultimate tensile strength Rm. There are indications of this phenomenon in Figure 2, where there can be seen, for degrees of elongation greater than 10 %, a lessening of the increase in ultimate tensile strength Rm between the sample annealed at 750°C and the sample annealed at 800°C.

The time for holding the strip between 720°C and 800°C must be sufficient to return all the carbon corresponding to equilibrium to solution. Holding it for 10 seconds is sufficient for ensuring that the amount of carbon corresponding to equilibrium is returned to solution for steels whose carbon content is between 0.020 and 0.035 % and holding it beyond 2 minutes, although possible, is of no benefit and is costly.

Figures 3 and 4 show the influence of the cooling rate at constant annealing temperature (750°C) maintained for 20 seconds.

As can be seen in Figure 3, at 10 % elongation on second cold-rolling, the ultimate tensile strength Rm of the steel is equal to about 520 MPa if the cooling rate is 100°C/s, whereas it reaches only 440 MPa if the cooling rate is 50°C/s.

It is accordingly possible to produce an aluminium-killed low-carbon steel whose Rm value is 520 MPa with only 10 % elongation on second cold-rolling if the cooling rate is 100°C/s, whereas it is necessary to carry out second cold-rolling with a degree of elongation of 25 % if the cooling rate is only 50°C/s.

This lower degree of elongation on second cold-rolling makes it possible for the ductility of the steel to be reduced less. Accordingly, it can be seen in Figure 4 that the steel whose Rm is 520 MPa has a ductility A % of 14 when the cooling rate is 100°C/s, whereas it is 3.5 when the cooling rate is 50°C/s.

This finding is also valid for the hardness of the steel. As can be seen in Figure 5, given the same degree of elongation on second cold-rolling, the hardness of the steel increases if the cooling rate is 100°C/s. This increase in hardness is due to a free carbon content which is higher and/or due to the presence of fine, disperse precipitates.

From the micrographic analysis of the samples it has been possible to determine that the number of grains per mm^2 is higher (more than 20000) and that the carbides, when they are formed, are intergranular cementite.

This manufacturing process accordingly makes it possible to produce an aluminium-killed low-carbon steel for packaging, comprising by weight between 0.022 and 0.035 % carbon, between 0.15 and 0.25 % manganese, between 0.040 and 0.070 % aluminium, between 0.0035 and 0.0060 % nitrogen, the remainder being iron and inevitable residual impurities, which has, in the aged state, a degree of elongation A % satisfying the relationship:

$$(670 - Rm)/14 < A\ \% < (720 - Rm)/17$$

Patentkrav

1. Fremgangsmåde til fremstilling af et stålbånd med et lavt indhold af carbon beroliget med aluminium til emballage, hvori:

- man tilvejebringer et varmvalset stålbånd omfattende vægtmæssigt mellem 0,022 og 0,035% carbon, mellem 0,15 og 0,25% mangan, mellem 0,040 og 0,070% aluminium og mellem 0,0035 og 0,0060% nitrogen, idet resten udgøres af jern og uundgåelige resturenheder,
- man udfører en første koldvalsning af båndet,
- man udsætter det koldvalsede bånd for en genopvarmning,
- man udfører en eventuel anden koldvalsning,

kendetegnet ved, at genopvarmningen er en kontinuerlig genopvarmning, hvor cyklussen omfatter en temperaturstigning til en temperatur større end temperaturen svarende til stålets eutektoid, en holdetid af båndet over denne temperatur i mere end 10 sekunder og en hurtig afkøling af båndet til en temperatur mindre end 350°C ved en afkølingshastighed mellem 100°C/sek. og 500°C/sek.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** båndet under genopvarmningen holdes ved en temperatur på mellem 720°C og 800°C i fra 10 sekunder til 2 minutter.

3. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** båndet afkøles ved en hastighed, der er større end 100°C/sek., til omgivelsestemperatur.

4. Stålplade med lavt indhold af carbon beroliget med aluminium til emballage omfattende vægtmæssigt mellem 0,022 og 0,035% carbon, mellem 0,15 og 0,25% mangan, mellem 0,040 og 0,070% aluminium og mellem 0,0035 og 0,0060% nitrogen, idet resten udgøres af jern og uundgåelige resturenheder, fremstillet ifølge fremgangsmåden ifølge krav 1 til 3, **kendetegnet ved, at** den i ældet tilstand har en forlængelsesgrad A%, der tilfredsstiller ligningen:

$$(670 - Rm) / 14 \leq A\% \leq (720 - Rm) / 17$$

hvor Rm er den maksimale brudmodstand af stål udtrykt i MPa.

5. Stålplade ifølge krav 4, **kendetegnet ved, at** stålet omfatter carbon i fri tilstand og/eller nogle carbider udfældet ved lav temperatur og har et antal korn pr. mm^2, der er større end 20.000.

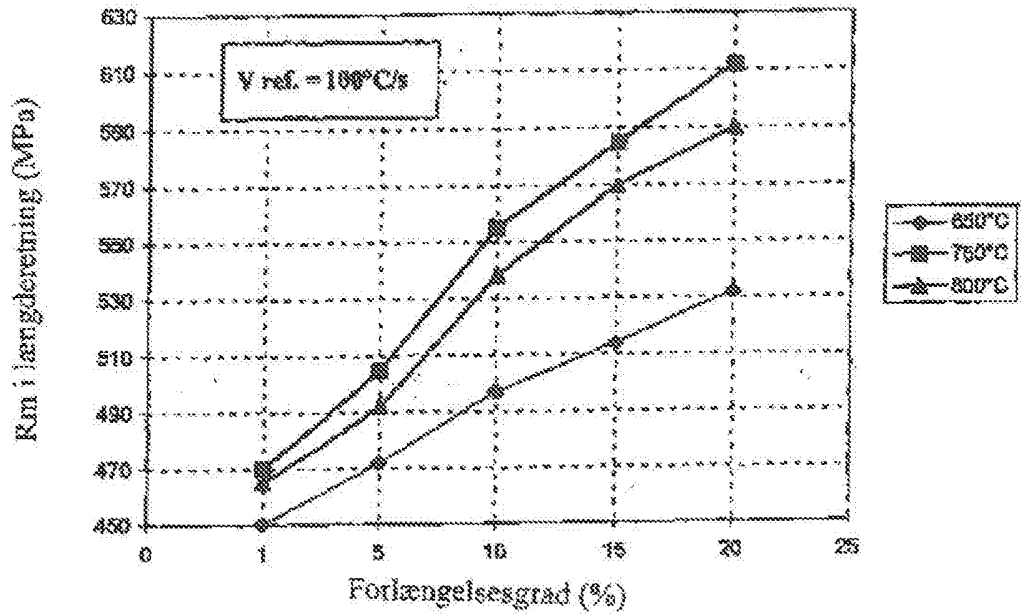
V ref. = 100°C/s
Rm i længderetning (MPa)
Forlængelsesgrad (%)
650°C
750°C
800°C

FIG. 1

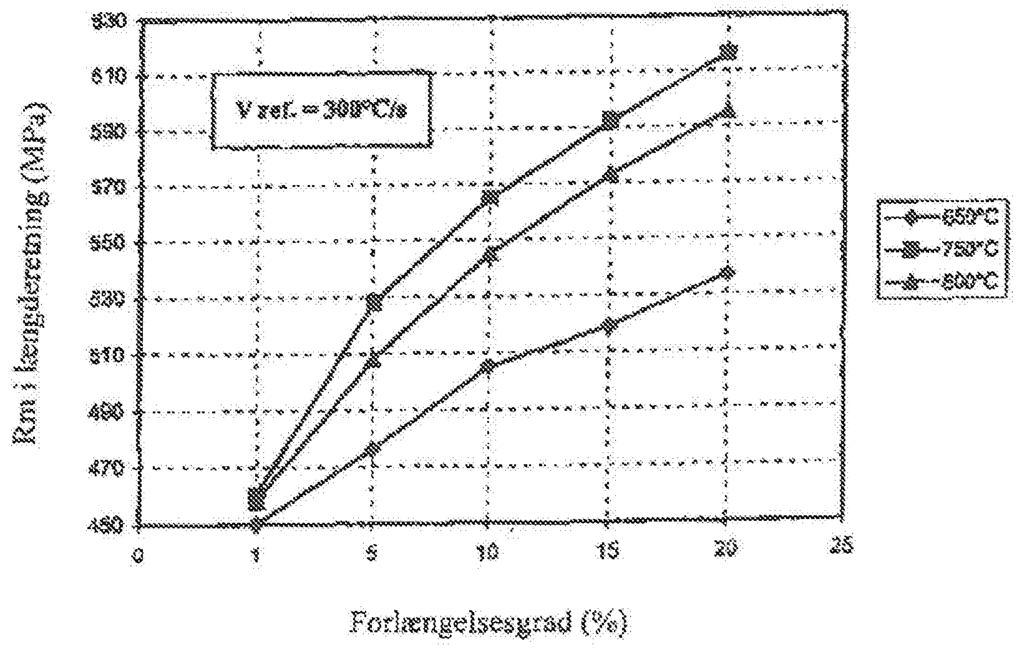
V ref. = 300°C/s
Rm i længderetning (MPa)
Forlængelsesgrad (%)
650°C
750°C
800°C

FIG. 2

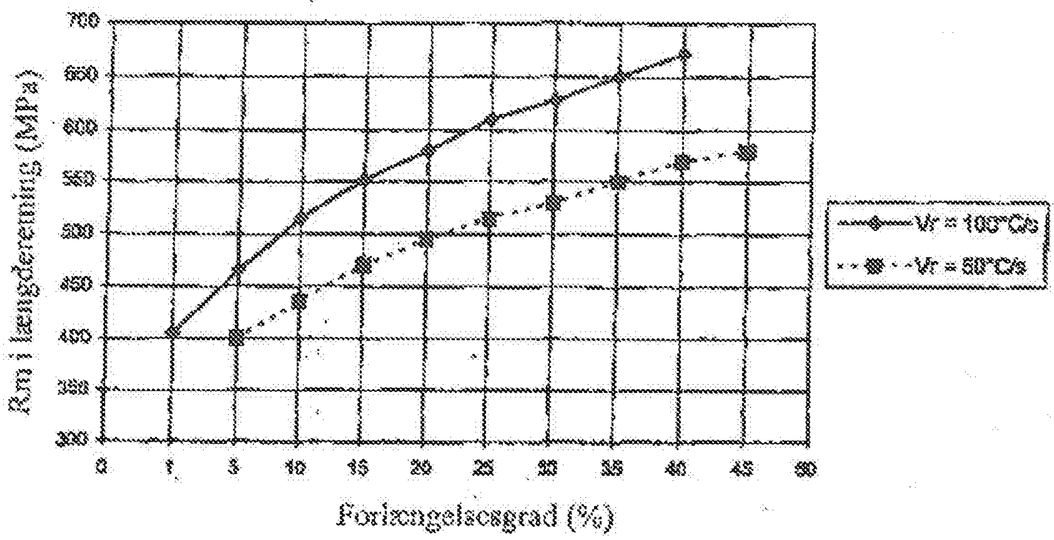
Rm i længderetning (MPa)
700
650
600
550
500
450
400
350
300
0
1
3
10
15
20
25
30
35
40
45
50
Forlængelsesgrad (%)
Vr = 100°C/s
Vr = 50°C/s

FIG. 3

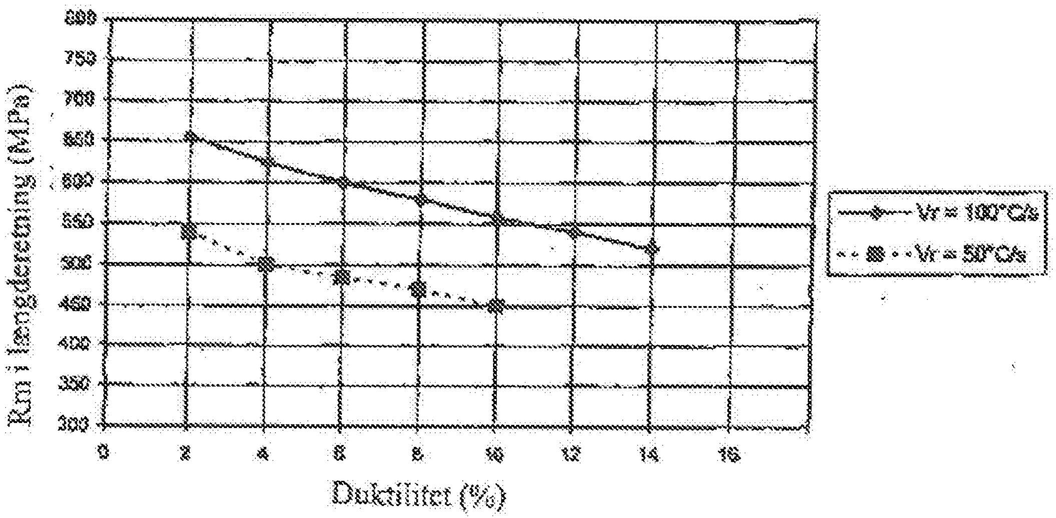
Rm i længderetning (MPa)
800
750
700
650
600
550
500
450
400
350
300
0
2
4
6
8
10
12
14
16
Duktilitet (%)
Vr = 100°C/s
Vr = 50°C/s

FIG. 4

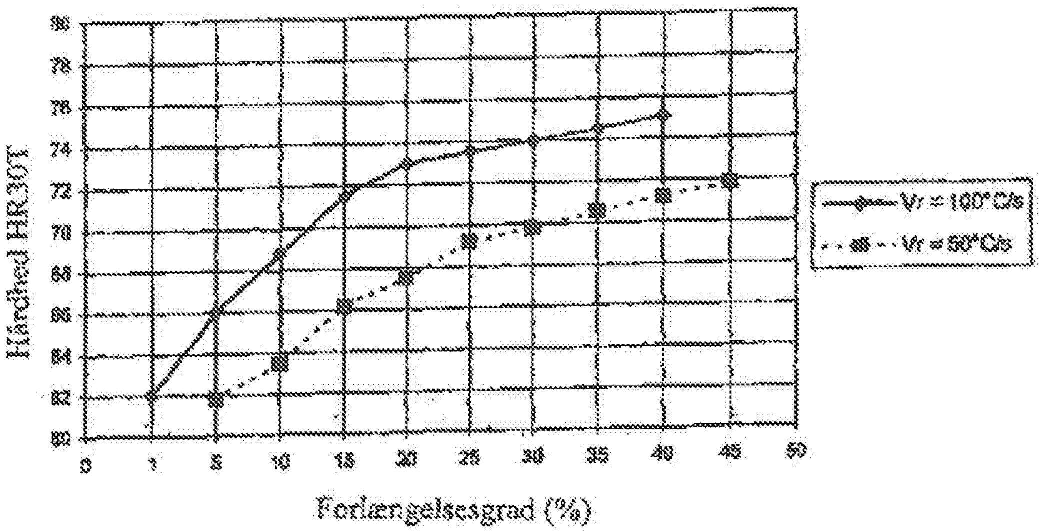

FIG. 5