

STEEL STRIP FOR FLAPPER VALVES

TECHNICAL FIELD

The invention relates to a steel strip for flapper valves in compressors and other reed
5 valve applications.

BACKGROUND OF THE INVENTION

Flapper or reed valves are used in various types of applications where a specific type of
compression cycle is regulated for a specific purpose. It can be a refrigeration cycle in a
10 hermetic reciprocating compressor working uninterrupted in a refrigerator or in the air
conditioner of a car. A flapper valve is basically a spring made from a pre-hardened
steel strip. In its simplest form, the flapper valve has a tongueshaped reed, where one
end is fixed and the opposite end hangs free and regulates the liquid or gas flow in the
compressor. The flapper valve reed (called “valve reed” in the following) suffers from
15 both cyclic bending stresses and cyclic impact stresses during its service. Usually, these
cyclic stresses eventually cause fatigue failure. Accordingly, the fatigue properties are
of the utmost importance for the flapper valve reed material.

A valve reed made of a steel strip of this invention has its fatigue properties optimized
20 by the combined effect of modifications to the chemical composition and the heat
treatment of the steel, plus superior control of non-metallic inclusion size, volume
fraction and prevalent specie.

Compressor OEMs require new materials that have a higher fatigue life than prior art
25 materials in order to improve the compressor’s performance and life.

Furthermore, there is a growing interest in the industry to develop more energy efficient
and quieter compressors. The coefficient of performance (COP) can be increased by
increasing the valve lift and by reducing the thickness of the valve reeds. Compressor
30 designers therefore require valve materials that have enhanced fatigue strength. Bending
stresses occur when the flapper valve opens and impact stresses when it closes.

Accordingly, hardened and tempered high carbon steel strips are commonly used for flapper valves due to their good bending and impact fatigue strength.

5 The 1 % carbon unalloyed steel of the type ASTM 1095 or EN Nr.: 1.1274 has in the past been the standard choice for non-stainless applications and various attempts have been made in order to improve the fatigue properties of said steel. JPS60128241 describes such an attempt by specifying the average size of the spheroidal carbides in the hot rolled strip. US2015/0030870 A1 discloses a steel strip having a limited area ratio of carbides not less than 0.5 μm in the metallographic structure. WO2007/129979
10 A1 is directed to the improvement of the fatigue life by providing a coating on at least one side of the steel strip.

However, increasing industry demands and resulting performance requirements mean that future valve reeds will increasingly need to be made out of very thin strip steel with
15 an increased fatigue life expectancy.

DISCLOSURE OF THE INVENTION

The general object of the present invention is to provide a pre-hardened steel strip for flapper valve reed having an optimized combination of properties such that it can be
20 manufactured by conventional methods of valve production and subsequently be used to produce more efficient and reliable compressors. A particular object is to provide a steel strip having improved bending fatigue strength.

The foregoing objects, as well as additional advantages are achieved to a significant
25 measure by providing a cold rolled, hardened and tempered martensitic steel strip having a composition, microstructure and physical properties as set out in the claims.

The invention is defined in the claims.

30 DETAILED DESCRIPTION

The importance of the separate elements and their interaction with each other as well as the limitations of the chemical ingredients of the claimed alloy are briefly explained in

the following. All percentages for the chemical composition of the steel are given in weight % (wt. %) throughout the description. The amounts of microstructural phases are given in volume % (vol. %). Upper and lower limits of the individual elements can be freely combined within the limits set out in the claims.

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The arithmetic precision of the numerical values can be increased by one or two digits. Hence, a value given as e.g. 0.1 % can also be expressed as 0.10 % or 0.100%.

Carbon (0.90 - 1.10 %)

- 10 Carbon is to be present in a minimum content equal to or greater than 0.9 %, preferably at least 0.95 % for obtaining the desired mechanical properties after hardening. The upper limit for carbon is equal to or less than 1.10 % and may be set to 1.05 %.

Silicon (0.10 - 0.50 %)

- 15 Silicon is used for deoxidation. Si is a strong ferrite former and increases the carbon activity. Si is also a powerful solid-solution strengthening element and strengthens the steel matrix. This effect appears at a content of about 0.1 % Si and preferably the amount of Si is equal to or greater than 0.10 % Si and equal to or less than 0.50%. The lower limit may be set to 0.15, 0.20, 0.25 or 0.30 %. The upper limit may be set to
20 0.45, 0.40, 0.35 or 0.30 %.

Manganese (0.20 - 0.80 %)

- Manganese is an austenite stabilizer and contributes to improve the hardenability of the steel. Manganese shall therefore be present in a minimum content equal to or greater
25 than 0.20 %, preferably at least equal to or greater than 0.30 or equal to or greater than 0.35 or equal to or greater than 0.40 %. When the content of Mn is too large the amount of retained austenite after finish tempering may be too high. The steel shall therefore preferably have a Mn content that is equal to or less than 0.80 % Mn, more preferably equal to or less than 0.60 %.

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Chromium (0.05 – 0.30 %)

Cr contributes to improve the hardenability of the steel. Therefore, Cr is present at a content equal to or greater than 0.05 %, preferable equal to or greater than 0.10 %.

However, if more than 0.30 % is added then there is a risk for the undesired formation of pearlite, so preferably the amount of Cr is equal to or less than 0.30 %.

Molybdenum (0.15 – 0.40 %)

Mo may optionally be added to the steel. Mo is a ferrite stabilizer and is known to have a very favourable effect on the hardenability. Molybdenum can be used for improving the secondary hardening response during tempering. The minimum content is preferably equal to or greater than 0.15 % and more preferably equal to or greater than 0.25 %.

Molybdenum is strong carbide forming element and also a strong ferrite former. The maximum content of molybdenum is therefore preferably equal to or less than 0.40 %.

Vanadium (0.05 - 0.20 %)

Vanadium forms evenly distributed fine precipitated carbides, nitrides and carbonitrides of the type V(N,C) in the matrix of the steel. Vanadium shall therefore preferably be present in an amount equal to or greater than 0.05 % and less than or equal to 0.20 %.

The upper limit may be equal to or smaller than 0.18, 0.16, 0.14 or 0.12 %. The lower limit may be equal to or greater than 0.06, 0.07, 0.08, 0.09 or 0.10 %.

Niobium (0.02 - 0.09 %)

Niobium is similar to vanadium in that it forms carbonitrides of the type M(N,C) and may in principle be used to replace part of the vanadium but that requires the double amount of niobium as compared to vanadium. In addition, Nb(C,N) are much more stable than V(C,N) and may therefore not be dissolved during austenitising. The minimum amount of Nb preferably is equal to or greater than 0.02, 0.03, 0.04 or 0.05 % and maximum amount is equal to or less than 0.09, 0.08, 0.07 or 0.06 %.

V+0.5Nb (0.10 - 0.16 %)

The combined amount of V and Nb preferably may be restricted to fall within the range according to the equation $V+0.5Nb$ is equal to or greater than 0.10 % and equal to or less than 0.16 % in order to optimize the amount of primary precipitated hard phases.

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Nitrogen (0.01 - 0.15 %)

Nitrogen is an optional element which may be deliberately added to the steel. N is a strong austenite former and also a strong nitride former. N is restricted to be equal to or less than 0.15% in order to obtain the desired type and amount of hard phases, in particular MX, wherein M is mainly V and Nb but other metals like Cr and Mo may be present to some extent. X is one or both of C and N.

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However, a high nitrogen content may lead to work hardening, edge cracking and/or a high amount of retained austenite. When the nitrogen content is properly balanced against the contents of V and Nb, carbonitrides of the above type will form. These may be partly dissolved during the austenitizing step and then precipitated during the tempering step as particles of nanometre size. The thermal stability of vanadium-carbonitrides and, in particular, niobium-carbonitrides is considered to be better than that of the corresponding carbides. Therefore, the resistance against grain growth at high austenitizing temperatures may be enhanced by a deliberate addition of nitrogen.

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However, if nitrogen is not deliberately added then it may only be present at the impurity content level of N. The impurity content should then preferably be limited to less than or equal to 0.03 %. The upper content of N as an impurity may be set to 0.02, 0.015 or 0.01 %.

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25 **Aluminium** (≤ 0.05 %)

Aluminium may optionally be used for deoxidation in combination with Si and Mn. The upper limit is restricted to being less than or equal to 0.05% to avoid precipitation of undesired phases such as AlN and hard, brittle Alumina inclusions. Preferably, Al is not deliberately added to the steel but is only present at the impurity level.

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Ti, Zr and Ta (≤ 0.02 % each)

These elements are carbide formers and may be present in the alloy in the claimed ranges for altering the composition of the hard phases. However, normally none of these elements are deliberately added.

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Boron (≤ 0.01 %)

B may be used in order to further increase the hardness of the steel. The amount is limited to being equal to or less than 0.01 %, preferably ≤ 0.005 or even ≤ 0.001 %.

10 **Ca and REM** (Rare Earth Metals)

These elements may be added to the steel in the amounts of $\text{Ca} \leq 0.009$ and $\text{REM} \leq 0.2$ in order to further improve the hot workability and to modify the shape of non-metallic inclusions.

15 **Impurity elements**

P and S are the main impurities, which can have a negative effect on the mechanical properties of the steel strip. P may therefore be limited to equal to or less than 0.04 %, preferably equal to or less than 0.02 %. S may be limited to being equal to or less than 0.03 % or ≤ 0.01 , or ≤ 0.008 or ≤ 0.001 or ≤ 0.0005 %.

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Retained austenite $0 \leq 10\%$

Austenite is undesirable and the amount of retained austenite is less than or equal to 10%, preferably less than or equal to 5%, more preferably is less than or equal to 3% and most preferably is zero (measured by XRD according to ASTM E975-13).

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The present inventors have systematically investigated the effect of a modified chemical composition and a modified heat treatment on the mechanical properties of the flapper valve reed material. The modifications made to the chemical composition relative to the conventional material were mainly focused on increases in the contents of vanadium,

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niobium and molybdenum. The tensile strength of the steel strip depends on the thickness of the strip. A thinner strip will have a higher tensile strength than a thicker strip. Accordingly, one can expect a thinner strip to also have a higher bending fatigue

strength. The lower limit of the tensile strength may be equal to or greater than 1700, 1750, 1800, 1850, 1900, 1950 or 2000 MPa. The lower limit of the bending fatigue strength may be equal to or greater than 950, 1000, 1020 or 1040 MPa.

5 EXAMPLE

In this example two steel strips (No. 1 and No. 2) according to the invention are compared to the nominal compositions of the conventional steel strip UHB 20C and a commonly used equivalent National specification ASTM 1095. The composition (in wt %) of the investigated steels was as follows:

		ASTM 1095	UHB 20C	No. 1	No. 2
10	C	0.90 – 1.03	0.97	1.01	1.03
	Si	Not specified	0.25	0.29	0.29
	Mn	0.30 – 0.50	0.46	0.43	0.42
	Cr	Not specified	0.15	0.17	0.17
15	V	Not specified	< 0.01	0.10	0.10
	Nb	Not specified	< 0.001	0.07	0.06
	Mo	Not specified	< 0.01	0.03	0.31
	N	Not specified	0.011	0.008	0.008
	Al	Not specified	0.011	0.006	0.006
20	P	≤0.040	0.0055	0.012	0.011
	S	≤0.050	0.001	0.001	0.001

Fe and impurities balance.

The cold rolled strips used in these trials were produced from a route that is also the intended production route for the inventive product. It included:

- Melting, including but not limited to: Si and or Al deoxidation, use of calcium-aluminate slag with a low oxygen potential, ladle degassing and stirring with inert gas
- Casting, including pouring within an inert gas shroud and the use of an exothermic hot-top when ingot cast.

- Hot rolling to strip from temperature range of 1100 to 1250°C, finishing with coiling in the range of 400 to 700°C.
- Annealing of the hot rolled strip in the temperature range 720 to 770°C
- Descaling
- 5 • Depending on final thickness, a number of cold rolling and sub-critical annealing cycles (temperature range 690 to 720°C for 1 hr plus equalisation time)
- Final cold rolling with a minimum of 20% reduction.

Wherever prior processing is thought to have any potentially significant influence on
10 the performance of the inventive materials, the key parameters have been listed in the following.

The cold rolled strips used for the trials all had a thickness of 0.381 mm and a width of 330 mm. The strips were subjected to martempering (hardening and tempering) in a continuous hardening line by austenitizing at 850 - 870 °C for approximately 3.5
15 minutes followed by quenching in a lead bath to around 350 °C and thereafter in an oil bath to approximately 200 °C followed by cooling between water cooled plates down to room temperature. The strips were thereafter subjected to an inline single tempering step, at temperatures ranging between 400 - 500°C for 2 minutes with the aim of achieving a target Rm of 1860 MPa ± 100MPa (Tested in accordance with ISO 6892).
20 This target tensile level was chosen as the level typically used for this application, at this thickness.

After hardening and tempering, the material was slit to the desired width to carry out laser-based empirical flatness checks to confirm the suitability of the resulting strips to fulfil the demands of the final product.

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It was found that both the inventive steels achieved the target mechanical properties and flatness for a number of the iterations within the reported trial temperature ranges.

The hardened and tempered microstructures of the trial materials all consisted of
30 approximately 4 – 7.5% retained secondary carbides with a mean diameter of 0.60 – 0.85µm (measured by image analysis based optical microscopy @x1000 magnification

and confirmed by EBSD) with no measurable retained austenite (measured by XRD according to ASTM E975-13).

5 Subsequent reverse bending fatigue testing (R-1, staircase method designed according to ISO 12107 using a 2 000 000 cycle run-out) revealed that, at the same nominal tensile strength as the conventional steel, the reverse bending strength was increased by between 10% and 20% relative to a standard level of ~900MPa that is typically achieved using this test method (10% Probability of failure, with 95% Confidence level) on the conventional steel.

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This improvement in bending fatigue properties was the result of changes in the microstructure that were consequent on the modification of the chemical composition. The changes in chemical composition have had the effect of reducing the martensitic grain size without significantly changing the prior austenite grain size, whilst
15 significantly increasing the area fraction of secondary carbides (all measured by EBSD)

INDUSTRIAL APPLICABILITY

The inventive steel strip can be used for producing flapper valve reeds for compressors
20 having improved fatigue properties.

CLAIMS

1. A cold rolled and pre-hardened martensitic steel strip for flapper valve reeds in compressors, wherein the steel strip has:
- a) a composition consisting of, in weight %,:
C 0.9 - 1.1
Si 0.1 - 0.5
Mn 0.2 - 0.8
Cr 0.05 – 0.3
V 0.05 - 0.20
Nb 0.02 - 0.09
optionally
Mo 0.15 – 0.40
N 0.01 - 0.15
Al ≤ 0.05
Ti ≤ 0.02
Zr ≤ 0.02
Ta ≤ 0.02
B ≤ 0.01
Ca ≤ 0.009
REM ≤ 0.2
Fe and impurities balance,
- b) a matrix comprising tempered martensite,

- c) a tensile strength of, 1600 – 2400 MPa, preferably 1760 -1960 MPa,
- d) a thickness of 0.07- 3.5 mm and a width of 7 - 450 mm.

5 2. A strip according to claim 1 fulfilling at least one of the following requirements:

- a) a composition consisting of in weight %:

	C	0.9 – 1.1
10	Si	0.2 - 0.4
	Mn	0.3 - 0.6
	Cr	0.1 – 0.2
	V	0.07 - 0.15
	Nb	0.03 - 0.07
15	optionally	
	Mo	0.25 – 0.35
	Al	≤ 0.01

wherein the impurity contents of P and S fulfils the following requirements

20	P	≤ 0.02
	S	≤ 0.006

- b) a matrix comprising at least 85 volume % tempered martensite,

- 25 c) a thickness of 0.1 - 1.5 mm.

3. A strip according to claim 1 or 2 wherein the strip has a thickness of up to 0.2 mm and fulfils at least one of the following requirements:

a tensile strength (R_m) of 2000-2300 MPa,

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a yield strength ($R_{p0.2}$) of 1740-2200 MPa,

a ductility A50 of 3-6 %,

wherein all values are in accordance with ISO 6892.

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4. A strip according to any of the preceding claims, fulfilling at least one of the following requirements:

- a) a composition consisting of in weight %:

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C 0.95 – 1.05

Si 0.25 - 0.35

Mn 0.3 - 0.6

Cr 0.1 – 0.2

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V 0.07 - 0.15

Nb 0.03 - 0.07

Mo 0.25 – 0.35

Al ≤ 0.01

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- b) a matrix consisting at least 90 volume % tempered martensite,

c) a thickness of 0.1 - 1.0 mm.

5. A strip according to any of the preceding claims wherein the amount of (V+0.5Nb) is equal to or greater than 0.10 % and equal to or less than 0.16%.

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6. A strip according to any of the preceding claims wherein the matrix comprises up to 8 vol. % carbides, wherein the area fraction of carbides is measured by image analysis based optical microscopy @x1000 magnification.

10 7. A strip according to any of the preceding claims wherein matrix consist of tempered martensite and an area fraction 4.5 – 7.5 % carbides with a range of mean carbide diameters of 0.60 to 0.85 μm , measured by image analysis based optical microscopy @x1000 magnification, wherein the diameter is expressed as the equivalent circular diameter and the mean value is the arithmetical mean value.

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8. A strip according to any of the preceding claims wherein the strip has reverse bending fatigue strength of at least 950 MPa.

20 9. A strip according to any of the preceding claims wherein the strip has reverse bending fatigue strength of at least 1000 MPa.

10. A strip according to any of the preceding claims wherein the strip has reverse bending fatigue strength of at least 1040 MPa.

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11. A strip according to any of the preceding claims wherein the amount of retained austenite is less than or equal to 10%, preferably less than or equal to 5%, more preferably is less than or equal to 3% and most preferable is zero when measured by XRD according to ASTM E975-13.

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