

Description

Nickel-based brazing foil and process for brazing

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The invention relates to a nickel-based brazing foil and a process for brazing two or more parts.

Soldering is a process for joining metal or ceramic
10 parts using a melted filler material referred to as solder. The melting temperature of the solder is lower than that of the parent metals to be joined, which are wetted but not melted by the solder. A characteristic property of solders is their low melting range, i.e.
15 the range between the solidus temperature and the liquidus temperature, and the resulting processing temperatures which typically lie 10°C to 50°C above the liquidus temperature.

20 A distinction is made between soft soldering and hard soldering, or brazing, depending on the processing temperature of the solder. Soft solders are processed at temperatures below 450°C, whilst hard solders, or brazes, are processed at temperatures above 450°C.

25 Brazes are used in applications in which high mechanical stability of the soldered joint and/or high mechanical stability at high operating temperatures is desired.

30 Parts made of stainless steel and Ni- and Co-alloys are frequently joined using Ni-based brazes. These Ni-based brazes may also have a certain chromium content which results in improved corrosion resistance. In addition they may contain the metalloid elements silicon, boron
35 and phosphorus which result in a reduction in the

melting temperature and consequently the processing temperature of the braze. These elements are also referred to as glass-forming elements.

5 Ni-Cr-braze alloys are typically available in the form of solder powders produced using atomizing processes, or in the form of solder pastes in which the atomized powders are mixed with organic binding agents and solvents.

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When brazing solder pastes, the binding agents and solvents are decomposed. This can lead to inadequate flow and wetting behaviour and consequently to a poor joint. These problems can be avoided by using a braze
15 in the form of a ductile foil, whereby a solder seam can be produced more reliably. Ni-based brazing foils which can be produced in the form of ductile foils are known from US 4,316,572, for example. These ductile brazing foils can be produced by means of rapid solidification
20 processes and are at least partially amorphous.

It is, however, desirable to further reduce the costs of brazing foils and to further increase the reliability of the joints produced with brazing foils.

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The object of the invention is therefore to specify a nickel-based braze which can be produced as a ductile and at least partially amorphous foil at favourable cost. Furthermore, the joints made with the brazing
30 foil should be more reliable.

This object is achieved by the subject matter of the
35 independent claims. Advantageous developments are detailed in the corresponding dependent claims.

The invention specifies an amorphous, ductile brazing foil with a composition consisting essentially of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2
5 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent.

10 The invention specifies an alternative amorphous, ductile brazing foil with a composition consisting essentially of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d\text{CeX}_f\text{Y}_g$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic
15 percent; 0 atomic percent $\leq d \leq 14$ atomic percent; 0 atomic percent $\leq e \leq 5$ atomic percent; 0 atomic percent $< f \leq 5$ atomic percent; 0 atomic percent $\leq g \leq 20$ atomic percent, incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic
20 percent $\leq b + c + d \leq 25$ atomic percent, and where X is one or more of the elements Mo, Nb, Ta, W and Cu, and Y is one or both of the elements Fe and Co.

In the invention the brazing foil contains the glass-
25 forming elements P and B. In one embodiment the brazing foil is silicon-free and in an alternative embodiment the brazing foil contains silicon, the Si content being d 0 atomic percent $< d \leq 14$ atomic percent.

30 In the invention the phosphorus content c in atomic percent is greater than the boron content b in atomic percent which is greater than the phosphorus content c in atomic percent divided by 15, i.e. where $c > b > c/15$. The sum of the Si, P and B contents lies within
35 a range of 10 atomic percent $\leq (c + d + e) \leq 25$ atomic percent.

This sum of the metalloids Si, B and P and the ratio between the P content and the B content of the nickel-based brazing foil according to the invention specify a
5 amorphous, ductile foil in long lengths and with small geometrical variations along the length of the foil.

Due to the increased length of the foil it is possible to reduce production costs. In addition, the
10 reliability of the solder seams produced with the brazing foil is increased as the geometry of the foil is uniform.

Known Ni-Cr-P-based braze alloys such as those
15 described as solder materials NI107 und NI112 in DIN EN 1044 (Filler metals) and as BNi-7 and BNi-12 in US AWS A5.8/A5.8M:2004 (Specification for Filler Metals for Brazing and Braze Welding) cannot be produced as amorphous foils with continuously stable geometry over
20 long lengths in a mass production context. Hard phases which interfere with the casting process can be precipitated during production of the amorphous Ni-Cr-P foils.

25 As solid particles these hard phases damage the casting nozzle and thereby interfere with sheet production and have a negative influence on geometric sheet quality. As a result, sheet quality deteriorates continuously as the casting process progresses and it is impossible to
30 take counter-measures during casting. This means that the casting process must be interrupted after a short period in order to clean and overhaul the casting nozzle. Each time the casting process is interrupted, the continuous amorphous foil is broken, making it
35 impossible to produce long amorphous foil strips.

This is undesirable since an economic production process and the possibility of further industrial processing require foils of this type, i.e. foils with lengths of more than 100 m (metres) which maintain a stable foil geometry along their entire lengths. Furthermore, processing short foil pieces of less than approx. 100 m in length is disadvantageous in the further machining of the foils.

The variations and irregularities which can occur with the known Ni-Cr-P-based brazing foils are also disadvantageous in terms of the further industrial use of the brazing foils since the amount of solder supplied to the joint is determined primarily by the foil thickness. Large variations in solder quantity can lead to variations in the soldering result, which can in turn lead to the failure of components.

The problems of short lengths and large geometrical variations can be avoided by means of the compositions according to the invention. It is found that a small boron content in an Ni-Cr-P-based alloy based on the $c > b > c/15$ rule permits the production of amorphous foils with stable sheet geometry over long lengths. The alloys according to the invention also have a liquidus temperature of below 1080°C and good corrosion resistance due to the Cr content.

The composition according to the invention does not have the aforementioned disadvantages of significant geometrical variations since the use of the ratio according to the invention between the P, B and C content suppresses the formation of damaging hard phases.

It is possible to produce continuous foil lengths of several thousand metres which have only very small

fluctuations in thickness of less than 20% of nominal sheet thickness. In addition, the brazing foils according to the invention have a liquidus temperature of less than 1080°C and can thus be processed at
5 temperatures of under 1100°C. It is possible to maintain the sheet quality within the desired quality criteria even at these foil lengths.

The amorphous, ductile brazing foil according to the
10 invention can thus be produced in long lengths with small geometrical variations. This is advantageous in the further processing of the brazing foil.

The further processing of amorphous brazing foils
15 typically takes the form of slitting, cross-cutting, continuous etching, stamping or laminating. These further processes require the provision of long foil lengths of stable geometry in order to fulfil economic requirements. These requirements can be met with the
20 brazing foil according to the invention.

Amongst other techniques, soldering applications for amorphous brazing foils involve winding the foil around a long cooling pipe in order to solder the pipe
25 continuously to a continuous spiral cooling fin around its periphery. These pipes, up to 30 m in length, are used as cooling pipes in steam generators, for example.

In industrial applications such as this one it is
30 desirable to provide continuous foil lengths of more than 100 m which have a stable foil geometry in order to be able to apply a fixed layer of solder continuously to such long pipes. In general, industrial assembly processes also benefit from or require the use
35 of long foil lengths in order to avoid uneconomic frequent machine downtimes of assembly plant.

These requirements can also be met with the brazing foil according to the invention.

In one embodiment the brazing foil has a Cr content of
5 16 atomic percent $< a \leq 30$ atomic percent. This higher chromium content provides a brazing foil with improved corrosion resistance. Such a brazing foil can be used for applications involving corrosive media. For
10 example, this brazing foil with its higher Cr content can be used in motor vehicle exhaust gas recirculation systems.

The reduction of emission values in motor vehicle construction leads to an increased demand for
15 corrosion-resistant soldered joints using stainless steels such as, for example, DIN EN 1.4404 or 1.4539 to resist sulphurous, nitrous and high-chloride media.

In applications in which the components require very
20 high corrosion resistance, such as EGR (Exhaust Gas Recirculation) coolers for the motor vehicle industry, for example, the formation of coarse grains is undesirable since in addition to reducing mechanical properties it also reduces the corrosion resistance of
25 the components. For this reason it is, in addition, desirable to achieve a soldering temperature of below 1100°C .

In further embodiments the brazing foil has a B content of 1 atomic percent $\leq b \leq 8$ atomic percent and/or a P
30 content of 5 atomic percent $\leq c \leq 18$ atomic percent.

Should the brazing foil contain one or more of the elements Mo, Nb, Ta, W or Cu, in a further embodiment the content f of this element/these elements may be in
35 the range 0 atomic percent $< f \leq 3$ atomic percent.

Should the brazing foil contain one or more of the elements Fe or Co, the content g of this element/these elements may be within the range $0 \text{ atomic percent} < g \leq 5 \text{ atomic percent}$ or $0 \text{ atomic percent} < g \leq 1 \text{ atomic percent}$.

The brazing foil as according to one of the preceding embodiments may contain silicon or be silicon-free, i.e. may have a Si content of $0 \text{ atomic percent} < b \leq 14 \text{ atomic percent}$ or a Si content of $d = 0 \text{ atomic percent}$.

In one embodiment the brazing foil is at least 50% amorphous, preferably at least 80% amorphous.

The brazing foils can have a thickness D of $15 \mu\text{m} \leq D \leq 75 \mu\text{m}$. Furthermore, they may have a width B of $0.5 \text{ mm} \leq B \leq 300 \text{ mm}$ or a width B of $30 \text{ mm} \leq B \leq 150 \text{ mm}$. The brazing foils according to the invention can thus be produced in dimensions appropriate for a plurality of applications.

In further embodiments the brazing foil has a length L of at least 200 m with a thickness variation of less than 25% over the length of the foil and a length L of at least 5000 m with a thickness variation of less than 10% over the length of the foil. The brazing foil is provided in the form of a sheet which can be cut up in order to create a plurality of smaller foils of the desired size and/or shape.

The brazing foil according to the invention can be produced in lengths of several thousand metres. This has the advantage that the production costs can be reduced since the quantity of brazing foil with small geometrical variation and which can be produced from one casting run is increased.

The brazing foil can also be produced reliably with small thickness variations. In further embodiments the brazing foil has a thickness variation from the mean thickness of less than 20% over a length of 100 m, a
5 thickness variation of less than 25% over a length of 200 m and a thickness variation of less than 10% over a length of 5000 m. In a further embodiment the foil has a thickness variation of less than 15 μm over a length of 100 m. These foils fulfil the criteria set out in
10 AWS A5.8.

This uniform geometry is advantageous since the solder seams produced from the foil are reliable. Variations in thickness can lead to gaps in the solder seam and
15 consequently to an unreliable joint. This problem can be avoided since the brazing foil according to the invention has small thickness variations.

In further embodiments the brazing foils have a
20 liquidus temperature of less than 1100°C, less than 1080°C and less than 1050°C respectively. This is desirable since the maximum soldering temperature for many industrial soldering processes, in particular for joining stainless steel parent metals, is limited to
25 approx. 1200°C. As a general rule, the lowest possible soldering temperature is best since undesirable coarse grain formation takes place in the parent metal from a temperature of 1000°C. This undesirable coarse grain formation leads to a reduction in the mechanical
30 stability of the parent metal which is critical for many technical applications such as heat exchangers, for example.

The invention also specifies a brazed object with a
35 first part and a second part. The first part is joined by fusion to the second part by a solder seam produced using a brazing foil as according to one of the

preceding embodiments. The object thus has a solder seam produced by means of a brazing foil as according to the invention.

- 5 It also specifies an exhaust gas recirculation cooler and a heat exchanger with a first part and a second part in which the first part is joined by fusion to the second part by a solder seam produced using a brazing foil as according to one of the preceding embodiments.

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In one embodiment, the first part and the second part are made of a stainless steel. The stainless steel may, for example, be an austenitic stainless steel or have ferritic or mixed joints. Alternatively, the parts may
15 be made of a Ni-alloy or a Co-alloy.

The solder seam located between the parts may have a thickness of more than 15 μm .

- 20 It also specifies processes for joining two or more parts by fusion. In one process a brazing foil as according to one of the preceding embodiments is inserted between two or more parts to be joined. The parts to be joined have a higher melting temperature
25 than the brazing foil. The solder joint is heated to a temperature above the liquidus temperature of the braze and below the melting temperature of the two parts. The solder joint is then cooled between the parts to be joined, thereby forming a brazed joint.

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The parts to be joined may be parts of a heat exchanger or an exhaust gas recirculation cooler or an oil cooler or components of a heat exchanger or an exhaust gas recirculation cooler or an oil cooler.

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The invention also discloses processes for producing an amorphous ductile brazing foil. In a first embodiment a

molten mass consisting of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent. An amorphous ductile brazing foil is produced by rapid solidification of the molten mass on a moving cooling surface with a cooling speed of more than approx. $10^5^\circ\text{C}/\text{sec}$.

In a further embodiment of this process an amorphous, ductile brazing foil is produced from a molten mass consisting essentially of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d\text{CeX}_f\text{Y}_g$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; 0 atomic percent $\leq e \leq 5$ atomic percent; 0 atomic percent $< f \leq 5$ atomic percent; 0 atomic percent $\leq g \leq 20$ atomic percent, incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent, and where X is one or more of the elements Mo, Nb, Ta, W and Cu, and Y is one or both of the elements Fe and Co.

This invention discloses a process for joining by fusion two or more parts comprising the following steps:

- provision of a molten mass consisting of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent.

- production of an amorphous brazing foil by rapid solidification of the molten mass on a moving cooling surface with a cooling speed of more than approx. 10^5 °C/sec;
- 5 - formation of a solder joint by insertion of the brazing foil between the metal parts to be joined;
- heating of the solder joint to a temperature above the liquidus temperature of the brazing foil;
- cooling of the solder joint to form a joint between
10 the metal parts to be joined.

A further process for joining by fusion two or more parts comprises the following steps:

- provision of a molten mass consisting of
15 $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d\text{CeX}_f\text{Y}_g$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; 0 atomic percent $\leq e \leq 5$ atomic percent; 0 atomic percent $< f \leq 5$ atomic percent; 0 atomic percent $\leq g \leq 20$ atomic percent, incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent, and where X is one or more of the elements Mo, Nb, Ta, W and Cu, and Y is
20 one or both of the elements Fe and Co;
- production of an amorphous brazing foil by rapid solidification of the molten mass on a moving cooling surface with a cooling speed of more than approx. 10^5 °C/sec;
- 30 - formation of a solder joint by the insertion of the brazing foil between the metal parts to be joined;
- heating of the solder joint to a temperature above the liquidus temperature of the brazing foil;
- cooling of the solder joint to form a joint between
35 the metal parts to be joined.

In one embodiment the heating of the solder joint to a temperature above the liquidus temperature of the brazing foil is carried out in inert gas. This simplifies the soldering process as the use of a vacuum furnace can be avoided. In particular, the use of a vacuum furnace to carry out the soldering process can be avoided if the processing temperature is below 1100°C.

10 In a further embodiment the heating of the solder joint to a temperature above the liquidus temperature of the brazing foil is carried out in a continuous furnace. This process is simplified if it can be carried out in inert gas. The use of a continuous furnace has the advantage that the soldering process can be carried out continuously. This reduces the time lost during the process.

The invention is explained in greater detail below with reference to the drawings and embodiments.

Fig. 1 shows a thickness measurement across the sheet cross-section of a comparison foil.

25 Fig. 2 shows a thickness measurement across the sheet cross-section of a brazing foil as according to the invention.

30 The invention specifies an amorphous, ductile brazing foil which has a composition consisting essentially of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; incidental impurities ≤ 0.5 atomic percent; rest Ni.

The brazing foil contains the glass-forming elements P and B, the phosphorus content c in atomic percent being greater than the boron content b in atomic percent which is greater than the phosphorus content c in atomic percent divided by 15, i.e. $c > b > c/15$.

Furthermore the content of the glass-forming elements P and B, and Si in the event that it is used as a third glass-forming element, is in the region of 10 atomic percent $\leq b + c + d \leq 25$ atomic percent.

Brazing foils with this composition can be produced in sheet lengths of over 200 m with small thickness variations.

The compositions of the brazing foils according to the invention and the compositions of comparison brazing foils are detailed in Table 1. The liquidus temperature and $L_{\max}$ value of the various brazing foil sheets are also given in Table 1.

The value $L_{\max}$ describes the foil length which can be produced as a continuous sheet without interruption with the absolute minimum and maximum geometric variations from the mean sheet thickness not exceeding 25%.

The foils are produced in the form of sheets by means of rapid solidification technology. To produce the sheets a molten mass of the desired composition is prepared. The molten mass is rapidly solidified on a moving cooling surface with a cooling speed of over approx. 10^5 °C/sec in order to produce an amorphous, ductile foil sheet.

Alloys 1 to 5 and 12 in Table 1 are comparison alloys and are not according to the invention.

Alloys 1 to 3 each contain P but not B as the glass-forming element, and alloys 4 and 5 each contain P and Si but not B as glass-forming elements. Alloy 12 contains P, B and Si. However, alloy 12 has a Cr
5 content of 32 atomic percent which is above the maximum limit of the brazing foil according to the invention.

Alloys 1, 2, 4, 5 and 12 each have a value $L_{\max}$ of 50 m or less. These alloys do not permit the production of a
10 brazing foil of the commercially desired length with the desired stable geometry.

Alloy 3 is produced with a value $L_{\max}$ of 5000 m, but has no Cr content. Consequently the corrosion resistance of
15 this alloy is insufficient for many applications. Alloy 3 is not according to the invention.

Alloys 6 to 11 and 13 to 22 are according to the invention.

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Alloy 6 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{20}\text{B}_4\text{P}_{10}\text{Si}_7$, a liquidus temperature of 1010°C and $L_{\max}$ of 2000 m. Alloy 7 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{20}\text{B}_8\text{P}_{10}$, a liquidus temperature of 1020°C and $L_{\max}$ of 5000 m. Alloy 8 has a composition of
25 $\text{Ni}_{\text{rest}}\text{Cr}_{16}\text{B}_4\text{P}_9\text{Si}_7\text{Mo}_1\text{Cu}_1$, a liquidus temperature of 1050°C and $L_{\max}$ of 5000 m. Alloy 9 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{20}\text{B}_3\text{P}_{10}\text{Si}_8\text{Fe}_{10}$, a liquidus temperature of 1020°C and $L_{\max}$ of 4000 m. Alloy 10 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{16.5}\text{B}_3\text{P}_{17.1}$, a liquidus temperature of 890°C and $L_{\max}$
30 of 5000 m. Alloy 11 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{16.5}\text{B}_{1.5}\text{P}_{17.1}$, a liquidus temperature of 895°C and $L_{\max}$ of 5000 m. Alloy 13 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{20}\text{B}_4\text{P}_9\text{Si}_7\text{Co}_{10}$, a liquidus temperature of 1050°C and $L_{\max}$ of 4000 m. Alloy 14 has a composition of
35 $\text{Ni}_{\text{rest}}\text{Cr}_{14}\text{B}_{1.2}\text{P}_{17}$, a liquidus temperature of 900°C and $L_{\max}$ of 30 5000 m. Alloy 15 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{17}\text{B}_3\text{P}_{10}\text{Si}_{10}$, a liquidus temperature of 1025°C and

$L_{\max}$ of 3000 m. Alloy 16 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{18}\text{B}_4\text{P}_{17}$, a liquidus temperature of 930°C and $L_{\max}$ of 5000 m. Alloy 17 has a composition of $\text{Ni}_{\text{res}}\text{Cr}_{18}\text{B}_{2.5}\text{P}_{13}\text{Si}_3$, a liquidus temperature of 980°C and
5 $L_{\max}$ of 5000 m. Alloy 18 has a composition of $\text{Ni}_{\text{res}}\text{Cr}_{18}\text{B}_{2.5}\text{P}_{13}\text{Si}_3\text{Cu}_4$, a liquidus temperature of 990°C and $L_{\max}$ of 5000 m. Alloy 19 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{18}\text{B}_{2.5}\text{P}_{13}\text{Si}_3\text{Mo}_1$, a liquidus temperature of 1010°C and $L_{\max}$ of 5000 m. Alloy 20 has a composition of
10 $\text{Ni}_{\text{rest}}\text{Cr}_{20}\text{B}_{2.5}\text{P}_{14}$, a liquidus temperature of 1000°C and $L_{\max}$ of 5000 m. Alloy 21 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{22}\text{B}_{2.5}\text{P}_{14}$, a liquidus temperature of 1000°C and $L_{\max}$ of 5000 m. Alloy 22 has a composition of $\text{Ni}_{\text{rest}}\text{Cr}_{22}\text{B}_{2.5}\text{P}_{13}\text{Si}_3$, a liquidus temperature of 1010°C and $L_{\max}$ of 5000 m.

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In the invention the brazing foil contains Cr, P and B, the elements P and B each having a content selected such that $c > b > c/15$. Furthermore, the content of the glass-forming elements Si, P and B lies in the range 10
20 atomic percent $\leq b + c + d \leq 25$ atomic percent.

This percentage of glass-forming elements and the ratio between the P and the B content permits the production of sheets in long lengths with small geometric
25 variations. $L_{\max}$ is thus increased. It is assumed that the formation of brittle hard phases is suppressed during rapid solidification so that it is possible to produce the foil sheet in long lengths with small thickness variations.

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Alloys 6 to 11 and 13 to 22 in Table 1 fulfil these criteria and are according to the invention. The table indicates that the alloys according to the invention are produced in the form of sheets each with a value
35 $L_{\max}$ of 2000 m or more. Alloys 7, 8, 10, 11, 14 and 16 to 22 are each produced with a value $L_{\max}$ of 5000 m, the ends of which are constitutional.

Alloys 7, 10, 11, 14, 16, 20 and 21 each have P and B as glass-forming elements and are silicon-free. Alloys 6, 15, 17 to 19 and 22 each have P, B and Si as glass-forming elements.

In addition to the glass-forming elements, alloys 6, 7, 10 and 11 contain only Ni and Cr and no further elements. In addition to the glass-forming elements, alloy 8 contains Ni, Cr, 1 atomic percent Mo and 1 atomic percent Cu. In addition to the glass-forming elements, alloy 9 contains Ni, Cr and 10 atomic percent Fe. In addition to the glass-forming elements, alloy 13 contains Ni, Cr and 10 atomic percent Co. These alloys each have a value $L_{\max}$ of 2000 m or more. In addition to the glass-forming elements, alloy 18 contains P, B and Si, Ni, Cr and 4 atomic percent Cu. In addition to the glass-forming elements, alloy 19 contains P, B, Si, Ni, Cr and 1 atomic percent Mo.

Fig. 1 shows a thickness measurement across the sheet cross section of comparative alloy 1 in Table 1 at a sheet length of 200 m. The variations in minimum and maximum sheet thickness from the mean value are shown in the figure. Fig. 1 illustrates that in this example the variations are above 50%. Such variations are undesirable for mass produced products and also unacceptable for many applications.

Fig. 2 shows a thickness measurement across the foil cross section of alloy 10 as according to the invention at a sheet length of 200 m. Fig. 2 illustrates that the variations in minimum and maximum sheet thicknesses from the mean value lie below 10%. The variations in thickness of the brazing foil according to the invention are much smaller than the variations in thickness measured with comparative alloy 1 shown in

Fig. 1. The foil geometry of the brazing foil according to the invention is more uniform over long sheet lengths.

Claims

1. Amorphous, ductile Ni-based brazing foil with a composition consisting essentially of
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$$\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$$
with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; incidental impurities ≤ 0.5 atomic percent; rest Ni, wherein $c > b > c/15$ and
10 10 atomic percent $\leq b + c + d \leq 25$ atomic percent.
2. Amorphous, ductile Ni-based brazing foil with a composition consisting essentially of
15
$$\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d\text{CeX}_f\text{Y}_g$$
with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; 0 atomic percent $\leq e \leq 5$
20 atomic percent; 0 atomic percent $< f \leq 5$ atomic percent; 0 atomic percent $\leq g \leq 20$ atomic percent, incidental impurities ≤ 0.5 atomic percent; rest Ni, wherein $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent, X is one or more of
25 the elements Mo, Nb, Ta, W and Cu and Y is one or both of the elements Fe and Co.
3. Amorphous, ductile brazing foil in accordance with claim 1 or claim 2,
30 characterised by a Cr content of 16 atomic percent $< a \leq 30$ atomic percent.
4. Amorphous, ductile brazing foil in accordance with
35 one of the preceding claims, characterised by

a B content of 1 atomic percent $\leq b \leq 8$ atomic percent.

- 5 5. Amorphous, ductile brazing foil in accordance with one of the preceding claims, characterised by a P content of 5 atomic percent $\leq c \leq 18$ atomic percent.
- 10 6. Amorphous, ductile brazing foil in accordance with one of the preceding claims, characterised by a Si content of $d = 0$ atomic percent.
- 15 7. Amorphous, ductile brazing foil in accordance with one of claims 1 to 5, characterised by a Si content of 0 atomic percent $< b \leq 14$ atomic percent.
- 20 8. Amorphous, ductile brazing foil in accordance with one of claims 2 to 7, characterised in that 0 atomic percent $< f \leq 3$ atomic percent.
- 25 9. Amorphous, ductile brazing foil in accordance with one of claims 2 to 8, characterised in that 0 atomic percent $< g \leq 5$ atomic percent.
- 30 10. Amorphous, ductile brazing foil in accordance with claim 9, characterised in that 0 atomic percent $< g \leq 1$ atomic percent.
- 35 11. Amorphous, ductile brazing foil in accordance with one of the preceding claims,

characterised in that
the brazing foil is at least 80% amorphous.

- 5 12. Amorphous, ductile brazing foil in accordance with
one of the preceding claims,
characterised by
a thickness D of $15\text{ }\mu\text{m} \leq D \leq 75\text{ }\mu\text{m}$.
- 10 13. Amorphous, ductile brazing foil in accordance with
one of the preceding claims,
characterised by
a width B of $0.5\text{ mm} \leq B \leq 300\text{ mm}$.
- 15 14. Amorphous, ductile brazing foil in accordance with
claim 13,
characterised by
a width B of $30\text{ mm} \leq B \leq 150\text{ mm}$.
- 20 15. Amorphous, ductile brazing foil in accordance with
one of the preceding claims,
characterised by
a variation in thickness from a mean thickness of
less than 25% over a length of 200 m.
- 25 16. Amorphous, ductile brazing foil in accordance with
one of the preceding claims,
characterised by
a variation in thickness from a mean thickness of
less than 20% over a length of 100 m.
- 30 17. Amorphous, ductile brazing foil in accordance with
one of the preceding claims,
characterised by
a variation in thickness from a mean thickness of
35 less than 10% over a length of 5000 m.

18. Amorphous, ductile brazing foil in accordance with one of the preceding claims, characterised by a variation in thickness from a mean thickness of less than 15 μm over a length of 100 m.
19. Amorphous, ductile brazing foil in accordance with one of the preceding claims, characterised by a liquidus temperature of less than 1100°C.
20. Amorphous, ductile Brazing foil in accordance with claim 19, characterised by a liquidus temperature of less than 1080°C.
21. Amorphous, ductile brazing foil in accordance with claim 20, characterised by a liquidus temperature of less than 1050°C.
22. An exhaust gas recirculation cooler having a first part and a second part, the first part being joined fast to the second part by a solder seam produced using a brazing foil in accordance with one of claims 1 to 21.
23. An exhaust gas recirculation cooler in accordance with claim 22, characterised in that both the first part and the second part are made of a stainless steel.
24. An exhaust gas recirculation cooler in accordance with claim 22 or claim 23, characterised in that the solder seam $> 15 \mu\text{m}$.

25. A heat exchanger having a first part and a second part, the first part being joined fast to the second part by a solder seam produced using a
5 brazing foil in accordance with one of claims 1 to 21.
26. A heat exchanger in accordance with claim 25, characterised in that
10 both the first part and the second part are made of a stainless steel.
27. A heat exchanger in accordance with claim 25 or claim 26,
15 characterised in that the solder seam is $> 15 \mu\text{m}$.
28. A brazed object having a first part and a second part, the first part being joined fast to the
20 second part by a solder seam produced using a brazing foil in accordance with one of claims 1 to 21.
29. A brazed object in accordance with claim 28,
25 characterised in that both the first part and the second part are made of a stainless steel.
30. A brazed object in accordance with claim 28 or claim 29,
30 characterised in that the solder seam is $> 15 \mu\text{m}$.
31. Process for producing an amorphous ductile brazing
35 foil comprising the following steps:
- provision of a molten mass consisting of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$ with 2 atomic percent $\leq a \leq 30$

- atomic percent; $0.5 \text{ atomic percent} \leq b \leq 14$
atomic percent; $2 \text{ atomic percent} \leq c \leq 20$ atomic
percent; $0 \text{ atomic percent} \leq d \leq 14$ atomic
percent; incidental impurities ≤ 0.5 atomic
percent; rest Ni, where $c > b > c/15$ and 10
atomic percent $\leq b + c + d \leq 25$ atomic percent,
- production of an amorphous ductile brazing foil
by rapid solidification of the molten mass on a
moving cooling surface with a cooling speed of
more than approx. 10^5 °C/sec.
32. Process for producing an amorphous ductile brazing
foil comprising the following steps:
- Provision of a molten mass consisting of
 $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d\text{CeX}_f\text{Y}_g$ with $2 \text{ atomic percent} \leq a \leq 30$
atomic percent; $0.5 \text{ atomic percent} \leq b \leq 14$
atomic percent; $2 \text{ atomic percent} \leq c \leq 20$ atomic
percent; $0 \text{ atomic percent} \leq d \leq 14$ atomic
percent; $0 \text{ atomic percent} \leq e \leq 5$ atomic percent;
 $0 \text{ atomic percent} < f \leq 5$ atomic percent; 0 atomic
percent $\leq g \leq 20$ atomic percent, incidental
impurities ≤ 0.5 atomic percent; rest Ni, where c
 $> b > c/15$ and $10 \text{ atomic percent} \leq b + c + d \leq 25$
atomic percent, and where X is one or more of the
elements Mo, Nb, Ta, W and Cu and Y is one or
both of the elements Fe and Co,
- production of an amorphous ductile brazing foil
by rapid solidification of the molten mass on a
moving cooling surface with a cooling speed of
more than approx. 10^5 °C/sec.
33. Process for joining by fusion two or more parts
comprising the following steps:
- insertion of a brazing foil in accordance with
one of claims 1 to 21 between two or more parts
to be joined, the parts to be joined having a
higher melting temperature than the brazing foil;

- heating of the solder joint to a temperature above the liquidus temperature of the braze;
- cooling of the solder joint, thereby forming a brazed joint between the parts to be joined.

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34. Process for joining by fusion two or more parts comprising the following steps:

- provision of a molten mass consisting of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; incidental impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent,,
- production of an amorphous ductile brazing foil by rapid solidification of the molten mass on a moving cooling surface with a cooling speed of more than approx. $10^5^\circ\text{C}/\text{sec}$;
- formation of a solder joint by the insertion of the brazing foil between the parts to be joined;
- heating of the solder joint to a temperature above the liquidus temperature of the brazing foil;
- cooling of the solder joint, thereby forming a brazed joint between the parts to be joined.

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35. Process for joining by fusion two or more parts comprising the following steps:

- provision of a molten mass consisting of $\text{Ni}_{\text{rest}}\text{Cr}_a\text{B}_b\text{P}_c\text{Si}_d\text{Ce}_e\text{X}_f\text{Y}_g$ with 2 atomic percent $\leq a \leq 30$ atomic percent; 0.5 atomic percent $\leq b \leq 14$ atomic percent; 2 atomic percent $\leq c \leq 20$ atomic percent; 0 atomic percent $\leq d \leq 14$ atomic percent; 0 atomic percent $\leq e \leq 5$ atomic percent; 0 atomic percent $< f \leq 5$ atomic percent; 0 atomic percent $\leq g \leq 20$ atomic percent, incidental

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- impurities ≤ 0.5 atomic percent; rest Ni, where $c > b > c/15$ and 10 atomic percent $\leq b + c + d \leq 25$ atomic percent, and where X is one or more of the elements Mo, Nb, Ta, W and Cu and Y is one or
- 5 both of the elements Fe and Co,
- production of an amorphous ductile brazing foil by rapid solidification of the molten mass on a moving cooling surface with a cooling speed of more than approx. 10^5 °C/sec;
 - 10 - formation of a solder joint by insertion of a brake foil between the parts to be joined;
 - heating of the solder joint to a temperature above the liquidus temperature of the brazing foil;
 - 15 - cooling of the solder joint, thereby forming a brazed joint between the parts to be joined.
36. Process for joining by fusion two or more metal parts in accordance with one of claims 33 to 35,
- 20 characterised in that the parts to be joined are parts of a heat exchanger or an exhaust gas recirculation cooler or components thereof.
- 25 37. Process in accordance with one of claims 33 to 36, characterised in that the heating of the solder joint to a temperature above the liquidus temperature of the brazing foil is carried out in inert gas.
- 30 38. Process in accordance with one of claims 33 to 37, characterised in that the heating of the solder joint to a temperature above the liquidus temperature of the brazing foil
- 35 is carried out in a continuous furnace.

39. Use of a brazing foil in accordance with one of claims 1 to 21 for brazing two or more parts of a heat exchanger or exhaust gas recirculation cooler or oil cooler.

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40. Use of a braze in accordance with one of claims 1 to 21 for joining by fusion two or more parts made of austenitic stainless steel or a Ni-alloy or a Co-alloy.

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