PATENT INFORMATION ANALYSIS
MOCK CERTIFICATION EXAMINATION

Paper B

Engineering

This paper comprises:

- Part 1: General questions
- Part 2: Case A, Patentability
- Part 3: Case B, Invalidity
  - Abstracts and claims of the delivered patent
  - Documents D1-D7
  - Table to be used
General instructions for preparing answer papers

(1) Candidates will give their answers in English.

(2) Candidates shall accept the facts given in the examination paper and limit themselves to those facts. Whether and to what extent those facts are used shall be the responsibility of each candidate. Candidates shall not use any special knowledge they may have of the technical field of the invention.
Part 1: General questions

1. In a world-wide perspective, is the following patentable? Motivate (5 points)
   a) Computer Programs
   b) Methods for doing Business
   c) A vase with a nice shape without further technical contribution
   d) Anti-personnel mines
   e) A cosmetic treatment involving surgery or therapy

2. What date determines the term of a patent if (4 points)
   a) The patent has a priority date from a previously filed patent application?
   b) The patent is a divisional patent claiming priority from a previously filed patent application?
   c) The patent originates from an International patent application (PCT application)?
   d) The patent is a U.S. patent filed in 1994?

3. Which patent claim has the broadest scope of protection? Explain your reasoning. (3 points)
   i) Apparatus characterized by features A or B
   ii) Apparatus characterized by features A and B

4. During a novelty search you discover two relevant documents. The first document discloses an apparatus with feature A and the second document discloses an apparatus with feature B. Argue for each claim i) and ii), whether it is novel and/or inventive starting from each document that you discovered.

5. What is a Provisional Patent Application? (3 points)

6. A screwdriver, with a handle made of rubber, is previously known. Are the following screwdrivers novel? Explain your reasoning. (3 points)
   a) A screwdriver with a handle made of polyurethane rubber.
   b) A screwdriver with a handle made of an elastic material.

7. Which are the main differences between a utility model and a patent? (3 points)

8. During a novelty search you discover a document with the number DE 9406143 U. What does the kind code “U” indicates? (1 point)

9. An EP-patent with application date on February 2000, is claiming priority from a Canadian patent with application date on April 1999. What date should be considered during an invalidation search? Please comment why. (3 points)

10. What are the possible grounds for invalidation of a patent in force? (3 points)

11. List the major differences for delivery of a Patent by the US patent office in view of the European Patent office praxis. Name at least three. (4 points)

12. What is considered possible public availability except printed published documents? (2 points)
12. A "product" has been presented orally by his inventor at a commercial meeting with a customer. This presentation was not recorded, nor included in a published paper. 9 months later a PCT patent application describing the “product” is filed by the inventor at the WIPO designating EP. Could you use testimony of this presentation to invalidate the final EP patent? Motivate the answer (3 points)

13. What kind of documents should be included in a Freedom To Operate search? (2 points)

14. Which parts of a patent document are of interest for an Freedom To Operate search and why? (3 points)

15. Which documents of which patent authorities do you have to include if you have to do an infringement search for Germany? (3 points)

16. A client contacts you and has a product release within short time and a he has a limited budget. The company acts in Europe and the intention is to sell the product in the whole of Europe. If you have to limit your Freedom To Operate search due to budget constraints, what would you recommend the customer to focus on? (5 points)
Part 2: Case A, Patentability

Company Z wants to continue the prosecution of a patent by filing a European Patent Application for an invention, validly claiming priority from a French Application with a filing date of 27 November 2007. P works in the R&D department of company Z and is under obligation of secrecy according to his work contract. However, P is informed that he/she will not be promoted and he/she decides to leave the company in February 2008 and harm it.

The following claims will be filed before the EPO on the day before priority expires:

- Claim 1: Product.
- Claim 2: Product of claim 1 comprising feature A and preferably feature B.
- Claim 3: Method of making the product.
- Claim 4: Method of claim 3 comprising step C.

The priority application contained only a description of the product and the product including A and preferably B. In view of general common knowledge the priority application was enabling for the product.

Company Z turns to you and requests a patentability search and analysis to be done. This occurs one month before filing before the EPO. Company Z tells you that P was involved in the development and that P left the company in February 2008.

After performing the searches, you discover the following documents:

- D1, a European patent application, filed in March 2007 and published in September 2008, disclosing the product and the method for making the product.
- D2, a sales document showing the product, distributed at an annual conference in April 2007.
- D3, a document published by P at an annual conference in March 2008, describing the product in which feature A was added and details of the method for making the product including the feature A and which method included the steps of claim 3.
- D4, patent application, published in September 2007, disclosing the usefulness of feature A for a class of products including but not mentioning the product of claim 1. It also described the effect of step C in the technical field of the method, showing embodiments different from the method of claim 3.

Questions (25 p)

Argue for each claim, whether it is novel and/or inventive departing from each document that you discovered.
Part 2 Case 2 – Invalidity / Presentation & Questions

In this paper, candidates should assume that a European patent has been delivered with the three (3) independent claims presented.

The following documents D1 – D7 Opponent Documents
D1: PCT document A
D2: PAJ Japanese Abstracts
D3: US document A
D4: EP document A
D5: Engineering journal article
D6: US document A
D7: US document A

Question 1 (5 p)
Please quote the different features described in the independent Claim 1 (similar features appears in independent claims M and N of the invention). You could either use a separate paper or use the table provided.

Question 2 (20 p)
If possible, use the support of the document D1-D7 to find a way to invalidate the patent. For each argument please localize inside the document, using the line number, all the elements which support your opinion. The candidate should select the most suitable method to invalidate the claims of this patent in accordance with the EPO praxis. In order to justify his/her point of view she/he should select among the documents provided the most suitable elements for supporting his assertions and provide a detailed explanation of the invalidation process by employing standard X, Y & A categorization and associated arguments. However, no detailed attorney-like analysis is required.

If multiple alternatives for invalidation are identified, indication of all strategies that may support the invalidation based upon legal ground should be presented in order to achieve full marks.
Part 2 Case 2 - Invalidity / Abstract and Claims of the delivered Patent

Abstract

Preformed articles of an amorphous metal foil which are particularly adapted to be used in the manufacture of an assembly having brazed joints, especially a heat exchanger. Methods for the manufacture of a heat exchanger or other assembly having brazed joints, which method includes the process step of providing a preformed article formed of a brazing foil composition of an amorphous metal alloy in contact with one or more elements of said heat exchanger or other assembly.

Independent claims of the Patent (3)

Independent Claim 1: A preformed article formed of an amorphous metal brazing foil having an irreversibly deformed, non-planar, three dimensional configuration including a primary planar face with at least one perforation passing therethrough, said article being adapted for use in the manufacture of an assembly having brazed joints, said manufacture comprising the brazing of a plurality of tubes to at least one plate, and the brazing of said plate to a shell encasing said plurality of tubes and said at least one plate.

Independent Claim M: A method for the manufacture of a heat exchanger or other assembly having brazed joints, which method includes the process steps of: providing a preformed article formed of an amorphous metal brazing foil in contact with one or more elements of said heat exchanger or other assembly, said brazing foil having an irreversibly deformed, non-planar, three dimensional configuration including a primary planar face with at least one perforation passing therethrough, said preformed article being in contact with said one or more elements of said heat exchanger or other assembly during the fabrication thereof; and subsequently subjecting the heat exchanger or other assembly to suitable conditions in order to effectuate at least partial melting of said preformed article in order to produce brazed joints between elements of said heat exchanger or other assembly.

Independent Claim N: A heat exchanger or other assembly having brazed joints manufactured by a method which includes the process step of providing a preformed article formed of an amorphous metal brazing foil in contact with one or more elements of said heat exchanger or other assembly, said brazing foil having an irreversibly deformed, non-planar, three dimensional configuration including a primary planar face with at least one perforation passing there through.
In a plate heat exchanger, having double-walled plate formed heat transfer elements (1, 2), adjacent such heat transfer elements are permanently brazed together by means of three different and spaced brazing joints. A first brazing joint surrounds an area, which covers the heat transfer portions (3, 4) of the heat transfer elements and first inlet openings and outlet openings (8, 9) communicating with a flow passage (6) that is formed between said heat transfer portions. A second joint and a third joint surround respective inlet openings and outlet openings (10, 11), which are closed from communication with said flow passage (6). Leakage areas (16-19; 39), which communicate with the surrounding of the plate heat exchanger, are formed between said first joint and each one of said other joints.

Plate heat exchanger The present invention relates to a plate heat exchanger for heat transfer between a first fluid and a second fluid, in which plate heat exchanger plate formed heat transfer elements are permanently joined together to a plate package and between themselves delimit in alternate interspaces first flow passages for said first fluid and second flow passages for said second fluid, respectively; each heat transfer element comprises two plates abutting against each other and having throughopenings aligned with each other; and said throughopenings in the plates of the heat transfer elements form a first inlet channel and a first outlet channel through the plate package, which channels communicate with said first flow passage and are closed from communication with said second flow passages, and a second inlet channel and a second outlet channel through the plate package, which channels communicate with said second flow passages and are closed from communication with said first flow passages.

Plate heat exchangers in which every plate formed heat transfer element consists of two plates abutting against each other are previously known. A conventional openable plate heat exchanger of this kind is shown for instance in US XXXXXXX. Owing to the fact that each heat transfer element comprises two plates it is achieved a safety against getting the two heat exchange fluids, flowing on respective sides of the heat transfer element, mixed with each other within the plate heat exchanger, if a hole would be formed through one of the plates. A leakage of one of the fluids through a hole of this kind makes the fluid in question flowing out into the space between the plates and further therethrough to and past the edges of the plates, where the leakage can be observed. So that the heat exchange fluids during normal operation of the plate heat exchanger shall not flow out into the spaces between the plates in the respective heat transfer elements the plates in each heat transfer element have to seal against each other around their said through-openings. Sealing of this kind can be obtained for instance through welding, brazing or gluing. Even plate heat exchangers having permanently joined heat transfer elements, each comprising two plates abutting against each other, are previously known. A drawback with these known brazed plate heat exchangers is that the double-walled heat transfer elements are brazed together with each other in a conventional manner, i.e. in the same manner as single-walled heat transfer elements in a brazed plate heat exchanger. The adjacent heat transfer elements are, thus, joined with each other by means of a single continuous brazing joint, and if this brazing joint is not close or does not keep tight, there is a risk that the heat exchange fluids despite the double-wall arrangement are mixed with each other in the plate heat exchanger without this being noticed.

The object of the present invention is to provide a plate heat exchanger having permanently joined double-walled heat transfer elements, which is safer than previously known plate heat exchangers of this kind against mixing of the heat exchange fluids in the plate heat exchanger without this being noticed. This object is obtained according to the invention by the adjacent heat transfer elements being joined together in each of said interspaces by means of three different and spaced joints, a first joint of which...
surrounds an area covering the flow passage that is delimited in the interspace as well as the inlet channel and the outlet channel through the plate package, which channels communicate with the flow passage, whereas a second one and a third one of said joints surrounds the one of said inlet channels and the one of said outlet channels, respectively, which constitute by-pass channels and are closed from communication with the flow passage in the interspace, and by leakage areas in said interspace, which are situated between said first joint and the respective one of said second and third joints, communicating with the surrounding of the plate heat exchanger. The invention concerns plate heat exchangers in general, having permanently joined heat transferring elements. For the joining of the heat transfer elements it is possible to use for instance welding, brazing or gluing.

In practice, the heat transfer elements of a brazed plate heat exchanger are often rectangular and pressed in a way such that relatively large plane corner portions thereof are brazed together in pairs around each one of those inlet channels and outlet channels which extend through the plate package. A special embodiment of the invention therefore concerns a brazed plate heat exchanger, in which said adjacent heat transfer elements have plane surfaces in said interspace, which are facing each other and delimit between themselves said leakage areas as well as at least parts of said three joints, the joints being constituted by brazing joints or gluing joints and being formed by a connection or bonding material, and the leakage areas being free of bonding material. When a leakage area is to be delimited in this way by and between two plane portions of two heat transfer elements, facing and abutting against each other, which plane portions should simultaneously be partly brazed or glued together by means of a bonding material, at least one of the plane portions opposite to the leakage area may be covered on its surface with a substance preventing the surface from being wetted by said bonding material when the latter is in a liquid state. Brazing technique for making possible such partial brazing together of two plane surfaces facing each other is known from previous publication.

In a plate heat exchanger according to the invention one of said leakage areas may extend between said first joint and one of said second and third joints from one part to another of the edge surrounding each one of the adjacent heat transfer elements. However, it is preferred that the leakage areas extend around the respective ones of said by-pass channels.

Within the scope of the invention a leakage area of the above said kind may be delimited by different parts of two adjacent heat transfer elements. One possibility is that it is delimited by and between the two plates of the heat transfer elements situated closest to each other. In this case the leakage area may communicate with the surrounding of the plate heat exchanger either in a way such that part of the leakage area extends out to the edges of the heat transfer elements, or through a hole in at least one of said plates and, thus, through the space between this plate and the further plate of the same heat transfer element.

Another possibility is that the leakage area is delimited by and between the plates of the two heat transfer elements, situated most remote or farthest from each other. In this case these two plates have throughopenings which are smaller than the aligned openings of the two plates of the heat transfer elements, which are situated closest to each other. Furthermore, in this case the plates situated farthest from each other are sealingly connected directly or indirectly with each other around their said openings, the leakage area being formed and extending around the connection area. Even in this case the leakage area communicates with the surrounding of the plate heat exchanger through the space between the plates in at least one of the two heat transfer elements.

It shall be noticed that the above said space between the two Plates in each heat transfer element may be microscopically thin, i.e. it need not be larger than the interspace that is formed between two plane plates abutting closely against each other. The invention is described in the following with reference to the accompanying drawings, in which figure 1 shows a number of double-walled heat transfer elements arranged as in a plate heat exchanger according to the invention but spaced from each other, figure 2A and 2B show two plates, which are to be included in one and the same double-walled heat transfer element of the kind shown in figure 1, figure 2C shows a thin foil of a bonding or brazing material intended for joining of two heat transfer elements according to figure 1, figure 3
shows a special embodiment of a plate to be included in one heat transfer element, figure 4 shows a section through several heat transfer elements, some of which comprise a plate formed in accordance with figure 3, figures 5-10 show sections through parts of heat transfer elements formed in different ways in accordance with the invention, and figure 11 shows a section through a plate heat exchanger, comprising heat transfer elements in accordance with figure 10.

Figure 1 shows five rectangular double-walled heat transfer elements 1, 2 having corrugated heat transfer portions 3, 4 and a plane end plate 5. The latter is intended to form together with the heat transfer elements 1, 2 a part of a plate package to be included in a permanently joined so called brazed plate heat exchanger. In the plate heat exchanger there are delimited between the heat transfer elements 1, 2 alternating first flow passages 6 and second flow passages 7 for the respective ones of two fluids, between which heat is to be transferred through the heat transfer elements. The flow passages 6 and 7 are formed owing to the corrugations of the heat transferring portions 3, 4 of the heat transfer elements 1, 2 forming ridges and valleys, the ridges of adjacent heat transfer elements crossing and abutting against each other.

For access of the fluids to the flow passages 6 and 7, respectively, the heat transfer elements 1, 2 have in their corner portions through openings 8-11, which form inlet channels and outlet channels through the plate package. Even the end plate 5 has corresponding openings aligned with the openings 8-11. The openings 8 and 9 in the heat transfer elements 1, 2 form inlet channels and outlet channels, respectively, for one of said fluids. These inlet channels and outlet channels communicate with said first flow passages 6 but are closed from connection with said second flow passages 7. The openings 10 and 11 form inlet channels and outlet channels, respectively, for the second fluid, which inlet channels and outlet channels communicate instead with the flow passages 7 but are closed from connection with the flow passages 6. The flow paths described here through the plate heat exchanger according to figure 1 are formed owing to the heat transfer elements 1, 2 being brazed together in the following manner. Two adjacent heat transfer elements 1, 2, which delimit between themselves a flow passage 6, are brazed together around their edge portions. Furthermore, they are brazed together around their respective openings 10 and 11, which are formed in the corner portions of the two heat transfer elements. These corner portions are situated in the same plane as the crests of the corrugation ridges of the two heat transfer elements, which cross and abut against each other in the flow passage 6.

In a corresponding way two adjacent heat transfer elements, which between themselves delimit a flow passage 7, are brazed together. In this case, however, the heat transfer elements are instead brazed together apart from along their edges -around their respective openings 8 and 9. Figures 2A and 2B show two plates 12 and 13, which abutting against each other shall form a double-walled heat transfer element 1 of the kind shown in figure 1. As can be seen from the figures 2A and 2B the plates 12 and 13 have the same press pattern of ridges and valleys, so that when these plates come to abutment against each other there will be formed a surface contact between them. Preferably, the plates have been pressed simultaneously in contact with each other, so that surface contact comes up between them across the hole of their surfaces facing each other.

The plates 12 and 13 have aligned openings 8a-11a. In annular areas 8b- 11b around the openings 8a-11a the plates are intended to be brazed together, so that fluids flowing through channels in the plate heat exchanger formed by the openings 8a-11a, cannot flow out between the plates 12, 13. The plates 12 and 13 are not brazed together at other places than around the openings 8a-11a. In figure 2A the numerals 14 and 15 designate the corner portions of the plate 12, through which the plate 12 is intended to be brazed together with a plate in an adjacent heat transfer element. By dash-dot lines 16 and 17 there are illustrated in figure 2A two annular surfaces on the corner portions 14, 15, which extend around the openings 10a and 11a, respectively, and through which the plate 12 shall not be brazed together with the just mentioned plate in an adjacent heat transfer element. Even along a further surface 18 of the plate 12, which extends from the surface 16 to the edge of the plate 12, the plate 12 is to be free from brazing connection with said adjacent heat transfer element. A
similar further surface 19 exists in connection with the annular surface 17. The edge portions of the plates 12 and 13, which are bent in the same direction, are designated 20 and 21, respectively, in the figures 2A and 2B.

Figure 2C shows a thin foil 22 of a brazing material, which is formed and intended for brazing together of a heat transfer element consisting of the plates 12 and 13 with a further heat transfer element situated closest to the plate 13. It is thus the plate 13 which is to be brazed together with one of the plates in the further heat transfer element. Then, surfaces corresponding to the surfaces 16-19 are to be present in connection with the openings 8a and 9a of the plate 13, which is illustrated in figure 2C in a way such that brazing material is missing in small areas 23 and 24.

Before brazing together of the heat transfer elements 1, 2 there is applied onto said surfaces 16-19 in every second interspace, and onto the corresponding surfaces in the other interspaces - at least on one of the plates to be brazed together - a substance having the effect that the plates on these surfaces cannot be wetted by the brazing material used, when this is in a liquid state. Hereby, the plates will remain free of brazing material and, thus, will not be brazed together with each other through these surfaces when the brazing material has solidified.

In a brazed plate heat exchanger of the kind now described with reference to the figures 1 and 2A-C adjacent heat transfer elements will be brazed together by means of three separate and spaced brazing joints.

Thus, in an interspace, in which a flow passage 6 is delimited, a first brazing joint will extend around the edges of the heat transfer elements. A second brazing joint will extend around the openings 10 and a third brazing joint around the openings 11. Between the heat transfer elements there will be left opposite to the surfaces 16-19 areas in which there will be no brazing material. These areas separate the first brazing joint from the second brazing joint as well as from the third brazing joint. Thanks to this arrangement of brazing joints a fluid, which for some reason leaks through or past one of said brazing joints close to one of the openings 10 and 11, will flow furtheron through one of said areas, that is free from brazing material, to and past the edges of the heat transfer elements to the surrounding of the plate heat exchanger.

Figure 3 shows a part of a heat transfer element formed differently than according to the figures 2A and 2B. An annular surface 25 extends around and closest to an opening 8c, and thereafter extends a further annular surface 26. Around the surface 26 there is a surface 27 covering the whole of the corner portion of the heat transfer element around the surface 26. The shown heat transfer element is intended to be brazed together with an adjacent heat transfer element through the surfaces 25 and 27, whereas the surface 26 is intended to be free of brazing material and, thus, delimit an annular area between the two heat transfer elements which are brazed together. This area is free of brazing material and can receive and conduct a flow of liquid which for some reason has leaked past one of the brazing joints opposite to the surfaces 25 and 27.

Instead of being conducted further to the edges of the heat transfer elements a liquid flow of this kind is conducted in this case through a hole 28 in one of the plates in the heat transfer element shown in figure 3. Since the two plates of the heat transfer element are not brazed together more than at a narrow annular surface around each opening, corresponding to the surface 25, liquid flowing through the hole 28 will be able to flow furtheron between the plates to and past their edges to the surrounding of the plate heat exchanger. Figure 4 shows a section through parts of six double-walled heat transfer elements, of the kind shown in figure 3, which are brazed together in pairs around their openings 8c.

Figure 5 illustrates a further embodiment of the invention. A first heat transfer element comprising two plates 29, 30 is brazed together with a second heat transfer element comprising two plates 31, 32. The plate 29 has a through-opening 33 (corresponding to for instance the opening lla in the plate 12 in figure 2A) and the plate 31 has a corresponding opening 34 of the same size. Corresponding openings in the plates 30 and 32 are larger than the openings 33 and 34 and are designated in figure.
5 by the numerals 35 and 36, respectively. The openings 33, 34 and 35, 36 have a common centre axis 37. The space hereby formed between the plates 29 and 31 is partly filled out, closest to the openings 33, 34, by a ring 38 that is brazed together around the openings 33, 34 with the plate 29 as well as the plate 31. The rest of said space forms a leakage area 39 between the adjacent heat transfer elements. The leakage area 39 extends around the ring 38 and is delimited by, apart from the ring 38 and the plates 29, 31, the edges of the plates 30, 32. The plates 30, 32 are brazed together along these edges.

In the arrangement according to figure 5 the brazing joint between the plates 30 and 32 delimits a flow passage (not shown) for a first fluid between the heat transfer elements 29, 30 and 31, 32, whereas the plates 29 and 31, the ring 38 and the brazing joints between the ring 38 and the plates 29 and 31 delimit an inlet channel or an outlet channel through the plate heat exchanger for a second fluid. If one of said brazing joints would prove not to be tight, one of said fluids will flow through or past the leaking brazing joint out into the leakage area 39. From there, the fluid will flow furtheron between the plates 29, 30 and/or between the plates 31, 32 in spaces 40, 41 formed between these plates.

The fluid will flow furtheron in one or both of the spaces 40, 41 to the surrounding of the plate heat exchanger across the edges of the plates. Figure 6 shows an embodiment of the invention similar to the one shown in the figures 3 and 4. A groove is formed in one of the heat transfer elements, so that an annular leakage space 42 is formed, extending around the through-openings 43-46 in the four plates 47-50 included in the heat transfer elements. Figures 7 and 8 show embodiments of the invention, which are of principally the same kind as the embodiment according to figure 5. The same numerals as used in figure 5 have been used, therefore, in the figures 7 and 8 with the addition of the letters -a and 12, respectively, for details corresponding to each other in the different figures.

One difference is that the ring 38 according to figure 5 is missing in the figures 7 and 8 and that, instead, the two plates 29a, 31a and 29b, 31b, respectively, which are situated farthest from each other, are brazed together directly with each other around their openings 33a, 34a and 33b, 34b, respectively.

The embodiment according to figure 8 differs from the one in figure 7 in that the plates 29b and 31b have been provided with annular depressions 51 and 52, respectively, opposite to the leakage space 39b. The purpose of these depressions is that the leakage space 39b shall be able to receive some liquid brazing material without this causing blockage of the connections between the leakage space 39b and the spaces 40b, 41b between the plates 29b, 30b and the plates 31b, 32b, respectively.

As can be seen, the plates 30b, 32b around their openings 35b, 36b have edge portions extending a distance into the leakage area 39b. Figure 9 shows a further development of the embodiment according to figure 8. Thus, the plates 29b and 31b have been provided with protuberances 53 on their sides turned away from each other. The protuberances 53, which are several in each plate, are situated between the leakage area 39b and the openings 33b, 34b and are distributed with mutual interspaces around the openings 33b, 34b. Protuberances 53 formed on adjacent heat transfer elements and facing each other are brazed together. Figure 10 shows another further development of the embodiment according to figure 8. As can be seen the annular depression 52a in the plate 31b has been made deeper than the depression 51a in the plate 29b, so that even more liquid brazing material could be collected in the leakage area 39b without risk for blocking of its connection with the spaces between the plates 29b, 30b and 31b, 32b, respectively. As illustrated at 54 the foil of brazing material has further been formed in a way such that the risk for an access of brazing material should be collected in the leakage area 39b has been reduced. Figure 11 shows a section through part of a brazed plate heat exchanger comprising double- walled heat transfer elements of the kind shown in figure 10.

The heat transfer elements are arranged between two end plates 55 and 56. The end plate 55 has an inlet pipe 57 for a first fluid and an outlet pipe 58 for a second fluid. These pipes are connected aligned with the respective through-openings of the heat transfer elements, which openings form an inlet channel and an outlet channel, respectively, through the plate heat exchanger. A reinforcing member
59 which is brazed together with both the end plate 56 and with the inlet pipe 57, extends through the inlet channel for said first fluid. A similar reinforcing member 60 extends through the outlet channel for said second fluid and is brazed together with the end plate 56 and the outlet pipe 58. The reinforcing members 59 and 60 are needed to keep together the package of heat transfer elements, since each one of the heat transfer elements comprises two plates which are joined with each other through brazing only in the areas around the heat exchange fluid inlet channels and outlet channels through the plate heat exchanger. The various heat transfer elements, however, are brazed together - in addition to around their edges - at a lot of places across their corrugated heat transfer portions.

[Figures 1, 2A, 2B, 2C]
Part 2 - Case 2 - Invalidity / Document D2

[ABSTRACT]
PURPOSE: To provide the production of a laminated heat exchanger having high productivity and no possibility of leakage.

CONSTITUTION: Each hollow cubic side walled material 5 is placed on left/right both end part 2a of a rectangular plate 2, a brazing filler metal sheet 7 of Ni base amorphous foil is placed on the upper surface of the plate 2 sandwiched by the hollow cubic side walled material 5, further, a corrugated fin 37 directed its groove parallel to the hollow cubic side walled material 5 is placed on thereon, the brazing filler metal sheet 7 is placed on the corrugated fin 3 and then placing other plate 2. And the corrugated fin and hollow cubic side walled material 5 as well as the corrugated fin 4 and hollow cubic side walled material 6 with changing its direction by right angle are placed on the second plate 2. These works are repeated at plural times and then welding is executed on the contact point between the end part of the hollow cubic side walled material 6 and plate 2, the plate 2 to corrugate fins 3, 4, and the plate fin 2 to hollow cubic side walled materials 5, 6 are subjected to brazing.

[DRAWINGS]
Disclosed is an interlayer for brazing and diffusion bonding, having a portion as a continuous stratum with an amorphous structure. The amorphous stratum of the interlayer, being ductile, imparts structural integrity to the otherwise brittle alloy composition. Thus, forming and shaping of the interlayer to faying surfaces are improved. In the joining process, the interlayer melts, and on solidifying by cooling or interdiffusion of elements, is converted to a crystalline solid metallurgically bonded to the workpiece. Preferred are flat ribbons with a continuous amorphous surface stratum comprising at least 30 volume percent, and up to 100 percent, of the interlayer.

The field of the invention is joining of metals. More particularly, the invention is concerned with brazing and liquid phase diffusion bonding of metal workpieces using metal interlayers between the faying surfaces. Brazing is a method of joining metals wherein a lower melting point material is interposed as a filler between two higher melting point metal surfaces. Through the application of heat, the brazing material is caused to melt and, by capillary action, to fill the space between the metals. After melting occurs, the assembly is cooled. Usually, there is a slight degree of alloying at the braze-base metal interface. Phase diffusion bonding (PDB) has been shown to be a useful method of joining superalloys. As in brazing, a thin alloy filler, or interlayer, is interposed between the surfaces to be joined. After heating to cause melting of the interlayers, the assembly is held above the melting temperature to promote interdiffusion between the base metal and filler. Among other phenomena, elements such as boron, which are typically used as melting point depressants in the interlayer, are caused by atomic diffusion to migrate into and throughout the base metal, thereby causing solidification of the joint. While the detail methods of brazing, PDB bonding and other analogous liquid phase joining processes differ with respect to the heating cycle and solidification phenomena, the filler alloys used for joining superalloys often have many similarities. Alloys of the desired composition for fillers are typically nickel-base and contain mostly chromium, cobalt, iron, silicon, and boron. To carry out the objects of the PDB bonding method, compositions are more precisely controlled and tailored to the types of superalloys being joined than when brazing is the object. During mass production using brazing or PDB bonding, it is common practice to preplace the filler material. One way this is achieved is by forming the filler alloy into a suitable shape, called a preform, and inserting it between or adjacent to the surfaces to be joined before heating. It is desirable that the preform by formable to the nominal shape of the faying surface of the joint. Because if the preform cannot assume the necessary contour, the faying surfaces may be unduly kept apart; provision must either be made to move the surfaces together or to supply additional filler material to the joint during bonding to avoid an imperfect, unfilled joint. Both preventive actions are undesirable. Another problem arises if the preform does not have a surface area which substantially matches the area of the faying surfaces; an undesirable surplus or deficiency of filler material may result. For many joint configurations, particularly those having contoured surfaces, it is desirable that the preform be supplied in a sheet or foil, 0.05 to 0.25 mm thick. One method of achieving this is to adhere particulate filler material to a thermoplastic carrier sheet which volatilizes prior to melting of the alloy. Not only are there potential problems with the carrier residue, but the low effective density of filler engenders the previously mentioned problems attending poor preform configuration. Most suitable are thin metal foil preforms, cut to the joint area and complying to the joint contour, either by stamping or in situ forming. However, a characteristic of many high temperature filler alloys of the types described above is that they tend to be very hard and brittle, due to the enrichment in melt depressants such as boron, and therefore are not readily rolled or formed into thin foils. One method of overcoming this problem is indicated in, U.S. Pat. No. X,XXX,XXX, wherein formable alloy in thin foil form is modified in composition by the surface addition of a melting point depressant element, such as boron. The interlayer so formed has a ductile interior and brittle exterior, allowing it to be die stamped to a complex shape. However, the interlayer formed in such a manner is costly to fabricate and is
limited to certain core compositions. Further, the boron is not evenly distributed through the interlayer and the local melting point varies.

Another approach is to introduce the filler as a coating on one of the faying surfaces. However, this approach is limited in that the incorporation of a multiplicity of elements in the interlayer is not convenient, and usually at the most, three elements are included. Further, there can be adverse economics. Thus, interlayer foils currently appear most attractive. But there is a need for an improved superalloy bonding and brazing interlayer foil, having a desired multi-element homogeneous composition but capable of being economically produced and readily formed for complex joints.

Common braze and PDB foils, like most metals of common experience have a crystalline metal structure. Actually, little attention has been given to their microstructures heretofore, other than to obtain general homogeneity. It has been evident for sometime that certain metal alloys can exist in a metastable amorphous solid state. As such, they are characterized by an absence of the long-range atomic ordering characteristic of the more familiar crystalline state. Amorphous metals also called glassy metals, evidence substantially different properties from the same compositions in the crystalline state. Amorphous metals are formed by methods such as rapid quenching of liquid metals and physical or chemical deposition. While they have long been known to exist, in recent years more attention has been given to the development of useful amorphous materials. Various amorphous metal ribbons are currently obtainable commercially.

Compositions of, and methods for making amorphous metals are described in the technical literature, including a number of patents. A review of this literature shows a recent trend towards novel materials for specialized applications. For example, alloys for resisting radiation damage and corrosion, and alloys having low electrical resistivity; among uses suggested are reinforcing elastomers and plastics, forming electromagnets, and the like. Other more recent patents describe refractory element containing alloys for applications as diverse as razor blades and magnetostriuctive devices. For a metal to be convertible to an amorphous solid it must have a particular composition and liquid state structure. It is said that the more readily formed amorphous alloys are mixtures of two transition metals or are transition or noble metals containing about 20 atomic percent metalloid, e.g., silicon, boron and phosphorous. Nonetheless, whether a particular composition can be made amorphous, and the conditions necessary to attain same, are largely a matter of experiment.

Generally amorphous metals are characterized by very high tensile strengths and hardnesses. It is these properties, coupled with the retention of a modicum of ductility, which make them most appealing for mechanical design concepts. Of course, any amorphous property advantages are lost as soon as a material is heated above the temperature at which the metastable phase converts to a crystalline structure. Typically, this transition temperature is approximately half the melting point. Thus, it has been an object of past development to devise new composition alloys with higher transition temperatures. And when an existing composition alloy is considered for use in its amorphous form, it has been obvious that the only suitable uses are those where it is maintained below its transition temperature. Therefore, since braze and PDB alloys are by their nature put into use by heating to high temperatures, and since amorphous metals are by nature not usable as such at high temperature, prior to the invention herein there was no obvious useful connection.

SUMMARY OF THE INVENTION

An object of the invention is to provide an improved method and interlayer foil for brazing and bonding. A further object is to provide ductile and formable interlayers suitable for joining complex alloys. The present invention embraces the concept that an interlayer foil with an amorphous metal structure produces an improved brazed or diffusion bonded structure, even though all trace of the amorphous structure is destroyed in making the final joined product. Hereafter, the designations MPV (Metastable Phase Variational) bonding and MPV interlayer are used when referring to processes and articles of the invention. As previously mentioned, there was no appreciation heretofore that an amorphous
atomic structure would be of utility in a product or process wherein heating above the metastable phase transition temperature was inherent and amorphous properties were lost.

According to the invention, an improved MPV interlayer for joining metal workpieces is formable as a separate element with amorphous metal structure, is melttable at a temperature lower than the metals being joined, and is adapted to be solidified as a metallurgically bonded and crystalline solid between the faying surfaces of the workpieces. MPV interlayers in accord with the invention have at least 30 percent amorphous structure, thereby making them capable of being formed and shaped for joining purposes, even though they contain embrittling elements. As stated, MPV interlayers may be fully amorphous throughout. But MPV bonding desirably does not require interlayers of such character. Fully amorphous interlayers are more difficult to make when substantial thickness is required. When only a portion of the MPV interlayer is amorphous, the amorphous portion will be a continuous layer on at least one surface of the interlayer. Thus, such an interlayer will have a ductile amorphous stratum to which a crystalline stratum is integrally attached. Alternatively, amorphous strata may be on either side of the interlayer with a crystalline core.

In a preferred embodiment, an interlayer for joining superalloys has a nickel-base and a boron content. An alternate embodiment interlayer has substantially the composition of the superalloys for which it is usable, but lacks aluminum, titanium and carbon, while including a melting point depressant, such as boron. Preferred MPV interlayers typically have melting points about 60° C. less than the melting point of any workpiece on which they are used.

An advantage of the invention is that homogeneous interlayers can be formed from normally brittle materials, and the interlayers can be conveniently shaped and formed as by stamping, punching, bending, and the like. In addition, the general handling of the interlayers is made easier. To practice the invention it is not necessary to be limited to particular alloy compositions and interlayer configurations which are entirely convertible to an amorphous state, but those which are only partially convertible are usable as well. The workpieces joined according to the invention will have stable high performance metallurgical structures. But with more formable amorphous structured interlayers, the ease for forming sound joints by brazing and bonding is improved, and the cost is lowered. The invention is particularly suited to the joining of high temperature nickel base superalloys but is adaptable to other metallurgical systems as well.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment is described in terms of joining nickel-base superalloys of the types which are used in gas turbine engines, although as will be apparent the invention will be equally applicable to other base alloys, and in any joining process where it is desirable to have an interlayer alloys suitable for brazing and bonding cast nickel-base alloys could be found among:

- AMS (Aerospace Materials Specification) : mostly used as brazing alloys,
- UT (United Technologies) designations are more prevalently used for diffusion bonding.

It will be noted that generally the AMS alloys contain silicon and boron, will small quantities of phosphorous and carbon. The UT alloys mostly contain only boron as the melting point depressant, and have on the whole a lower metalloid content. As a result, the UT alloys will tend to have somewhat higher melting points than the AMS alloys. The alloys in Table 1, and other alloys for brazing and bonding, are commercially procurable or readily fabricated as ingots by conventional melting, pouring and casting techniques. ##TABLE1##

Based on the foregoing, a generalization of the properties required of MPVM interlayers can be made. These properties include a composition which is mechanically and chemically suited for use in conjunction with the workpieces being joined and a composition which produces a melting point which is less than that of the metals which are being joined. Typically, for joining iron and nickel base alloys, a desired interlayer will be a nickel alloy with a liquidus of 60° C. or more below the solidus of the workpieces. A narrower melting point difference might be acceptable in the case of some alloys, but generally it is necessary that the interlayer liquify sufficiently to flow and fill the joint at a temperature
which does not adversely affect the base metals. In other circumstances, the interlayer melting point may have to be substantially less than that of the workpieces to avoid deleterious effects on the workpiece microstructure. Another characteristic required of the interlayer is that it be capable of forming a metallurgical bond with the workpieces upon the solidification from the melt. This is required because if there is no metallurgical bond, then the joint will have insufficient strength, whether it be a brazed or diffusion bonded joint.

The composition of a MPV interlayer must make it suited for conversion to an amorphous state. As stated previously, the characteristics of readily convertible alloys are not amenable to precise definition, and are largely a matter of experiment. Fortunately, known nickel brazing and bonding alloys have shown by experiment the desired characteristics. The invention will be usable with other base alloy systems and interlayers when experiment shows that interlayer alloys have all the necessary characteristics enumerated above.

As the previously referenced patents state, for diffusion bonding a preferred interlayer for superalloys contains up to 5% boron. A further preferred practice is that the interlayers have a composition substantially similar to that of the superalloy but excluding or limiting aluminum, titanium and carbon, when boron is used as the melting point depressant. Although silicon is not commonly used as a melting point depressant for diffusion bonding it is quite common in AMS braze alloys. In specialized applications, silicon and phosphorous might be used in diffusion bonding interlayers as well. As should be evident from the general discussion herein, any alloy which is suitable for brazing or diffusion bonding is also suitable for MPV bonding if it can be made amorphous.

Interlayer Fabrication

As the summary indicates, a MPV interlayer in accord with the invention is in part comprised of at least a portion with an amorphous structure. This portion is present as a continuous, relatively ductile stratum which imparts integrity to the otherwise brittle interlayer. The following describes how such interlayers may be formed. The subsequent section describes more particularly the structure which must be present in a MPV interlayer. In this discussion, it is presumed that a desired interlayer foil has a particular thickness, length, and width. This is conceived as being most easily obtained by forming a random length ribbon of a particular cross section, and then shearing or stamping the ribbon to the exact foil size desired. However, it is also contemplated that the initial formation of a filament may be followed by further processing, as by machining or forming, to alter the cross section.

To convert an ingot of an interlayer alloy into a foil with amorphous structure, the metal may be melted and then resolidified with cooling of the melt at a high rate to form the desired solid shape. Several techniques are available for achieving this, and they mostly involve contacting the liquid metal with a smooth cool surface, such as copper maintained below 100° C. Most simply a small quantity of molten metal can be squeezed into a thin foil between two cool anvils. Alternatively, physically deposited particles may be accreted as a film. More desirably, continuous filament casting techniques revealed in various U.S. patents are usable, with suitable modification to resist molten super alloy attack and form the desired cross section. Of course, to obtain amorphous atomic structure in any portion of a filament formed from a liquid, the liquid must be cooled at a sufficiently rapid rate. For the nickel base interlayer alloys this is of the order of 10.sup.5 ° C. per second. Thus, only apparatus and processes adapted to achieve such conditions in filaments of the desired dimensions will be suitable for directly making MPV interlayers as they are further described below. While the invention is discussed in terms of ribbons, flat filaments and foils, in particular instances interlayers which have other lower aspect ratio cross sections, such as circular, are within contemplation.

The presence of the amorphous state in a filament or foil is typically determined by examination of the X-ray diffraction pattern. Optical and electron transmission microscopy can also be used to verify the absence of longrange crystallographic ordering which is characteristic of amorphous metals. For purposes of this specification, a portion of metal alloy characterized as amorphous may have within it isolated islands of crystalline metal structure material which are comprised of either impurities or elements of the metal alloy.
Further information regarding the techniques for rapidly quenching liquid metals in order to convert them into an amorphous atomic structure and details of the techniques for analyzing such material are obtainable by reference to literature. Our preferred mode of practicing the invention is to form the interlayer foil from the liquid with an amorphous stratum being created during the solidification process. The thickness and width of interlayers may vary considerably. Desired thicknesses may range from 0.02 to 0.25 mm while widths may vary from 2 to 25 mm or more. The maximum thickness will be limited by the apparatus cooling rate capability and the necessary amorphous-crystalline structure balance described below. The width will be limited by the capability of the apparatus. Of course, multiple thin pieces may be used to build up a desired total interlayer thickness or width for a particular joint.

Interlayer Structure
A MPV interlayer of the invention must have at least a portion which has an amorphous structure. Inasmuch as the preferred manufacture of interlayers entails rapidly quenching liquid metals into ribbons, the portion of the foil which is in contact with the heat extraction surface or medium will be that which experiences the highest cooling rate and therefore, will most likely be amorphous. By way of example, if the interlayer is formed in an apparatus or method wherein heat is extracted from one side of the ribbon then that side will more easily be rendered amorphous. The rate of heat extraction is of course dependent upon the particular method used to rapidly quench the interlayer alloy. The degree to which a particular interlayer alloy foil has an amorphous structure will be further influenced by its thermal and physical characteristics and thickness. The degree of ease of amorphous structure obtained will be enhanced by lowered thickness, specific heat, heat of fusion, and density and increased thermal conductivity. Generally, since the cooling rates required for forming an amorphous structure are exceedingly high, it is difficult to fully quench a relatively thick nickel alloy foil, e.g., one of the order of 0.2 mm. Thus, it is a desirable feature of the invention that MPV interlayers need not be fully amorphous, as disclosed below.

We have not run controlled experiments to determine the limiting structural configurations of interlayer foils, as they will be dependent on the cross section and the direction in which they are bent with respect to the crystalline-amorphous strata. And of course, the desired limits will be dependent on the end application of the interlayer foil with regard to the degree of formability which is required. But on the whole, our more significant conclusion is that an interlayer foil having at least a portion which is amorphous will exhibit an ability to be shaped and formed with greater resistance to the brittle fracture which is characteristic of interlayer with no amorphous structure whatsoever. Based on our observations, we believe that the amorphous portion of the interlayer should be at least about 30% of the thickness (or volume) of the foil when the foil is a nickel base boron containing alloy. A lower volume percent, e.g., 10, may be usable in special instances where the alloy has different properties or the application is less demanding than those we typically conceive for the manufacture of gas turbine components. Of course, it should be evident that foils which are in greater proportion amorphous, up to 100%, will be equally satisfactory as MPV interlayers.

Cross sectional structure of a foil wherein the amorphous atomic structure is present in two strata one on each principal surface, with a crystalline portion contained between. Such an interlayer would be produced by a method in which heat is extracted from both surfaces of the ribbon. Since there are two ductility lending strata, it would be anticipated that a lower thickness of each strata would be adequate to impart formability to the interlayer foil. Accordingly, our judgment is that the same total volume percent of amorphous structure, namely 30%, divided between the two strata will be most often adequate to achieve the objects of the invention in an interlayer. The rectangular cross sections shown in the figures are for exemplary purposes only and it should be apparent the foregoing descriptions are applicable to other cross sections as well.

MPV Joining Process
The following describes the practice of MPV bonding. An interlayer is provided having the following characteristics: a melting point less than the metals being joined; at least one continuous surface stratum with an amorphous metal structure which imparts formability to the interlayer; and an amorphous phase comprising 30 volume percent or more of the interlayer. The interlayer is then shaped as by stamping, shearing, machining, or otherwise, to the shape which conforms to the faying surfaces. The interlayer is then placed between the faying surfaces of the workpieces and the workpieces are positioned so that the faying surfaces are as close as feasible. (In particular instances, it may be desirable to supply surplus interlayer alloy to the joint; in such cases, the interlayer foil would have greater surface area than that of the faying surfaces of the workpieces.) If the faying surfaces are contoured, then as the workpieces are pressed together the interlayer foil will be bent accordingly if it has not been otherwise preformed to the contour.

The amorphous stratum in the interlayer will impart compliance to the interlayer to allow it to contour itself to the faying surfaces, beyond that which would be expectable for a purely crystalline interlayer where fracturing and possible mislocation might result. Next the assembly of workpieces and interlayer is heated, as by a furnace or induction heater, typically in a controlled atmosphere or vacuum. In other instances, fluxes and oxidizing heat sources might be used. The temperature is raised above the melting point of the interlayer, at a rate, and to a degree, sufficient to cause the interlayer to liquify within the joint. Usually the assembly is held at temperature for a period of time to obtain metallurgical interaction between the interlayer and the workpieces. Generally, this interaction entails dissolution of minor surface films on the workpiece and interlayer and a degree of alloying between the interlayer and the workpiece. Usually this occurs in a matter of minutes. In brazing, solidification of the interlayer is obtained by cooling the assembly. Typical cooling rates are 5°C per second or less. As the joint often has relatively small exposed surface area compared to the workpieces, this may mean that heat extraction from the interlayer will be through the workpiece and epitaxial solidification from the workpiece surface will often take place. Of course, non-epitaxially solidified braze joints can be quite satisfactory as well.

In transient liquid phase diffusion bonding, after the interlayer melts, the temperature is sustained usually constantly at a point above the interlayer melting point—as high as the workpiece materials will endure without adverse effect—for a period of time sufficient for interdiffusion of elements to take place between the interlayer and the workpiece. As is disclosed in the references, this interdiffusion leads to solidification of the interlayer due to its changing composition. The phenomena in the joint region are such that the interdiffused interlayer will solidify epitaxially from the faying surfaces of the workpieces, which of course typically have crystalline metal structures. Thus, a common feature of MPV joining is that a crystalline metal structure results in the joints, most usually one which is epitaxial with the workpieces.

An interlayer must produce a sound metallurgical structure with good bonding to the workpieces. This is determinable by mechanical testing. Even more conveniently, metallographic inspection of a good workpiece joint will show it to be substantially free of voids, oxide films, and concentrated precipitates formed during joining. An interlayer must also have a composition which produces a joint with the capability of resisting the thermal stresses associated with cooling of the assembly. Properties which affect its performance are its elevated temperature strength and ductility, thermal expansion, shrinkage on solidification, and solidus-liquidus temperature differential.

A particularly useful application of MPV bonding is for the joining of cast single crystal superalloys. In such instances it is an object to have the single crystal structure extended across the joint region of a workpiece assembly. To achieve this, the crystal structures of the workpieces are essentially aligned to within a tolerance which experiment shows will avoid creation of a discontinuity after joining. The MPV interlayer is interposed and the diffusion bonding process is carried out as generally above, to ensure epitaxy. It will be found that a single crystal joined assembly will be the result from the epitaxial solidification.
[DRAWINGS]
[ABSTRACT]
A flexible multilayered brazing material is disclosed comprising at least one layer of ductile brazing foil defining a core body having two major surfaces and at least one minor surface, and at least one layer of ductile brazing foil substantially covering said two major surfaces and at least one minor surface. In particular, the layer(s) and the covering foil are each at least about 50% amorphous, with the covering foil being, most preferably, helically wrapped around the layers. The multilayered brazing materials enable brazing of large gaps and wide gaps formed by juxtaposed parts to be brazed. Processes for producing the flexible multilayered brazing material are also disclosed.

[DETAILS]
The present invention relates to brazing of metal parts and, in particular, to brazing filler metals useful for brazing gaps of thickness greater than about 100um and width of several inches or more. Brazing is a process for joining metal parts, often of dissimilar composition, to each other. Typically, a filler metal that has a melting point lower than that of the metal parts to be joined is interposed between the parts to form an assembly. The assembly is then heated to a temperature sufficient to melt the filler metal. Upon cooling, a strong, preferably corrosion resistant joint is formed. Conventional brazing filler materials exist in a wide variety of forms which are characteristic of metallic materials, namely: powders, pastes formed from powders, foils, strips and rods. Among these forms, strips and foils of brazing filler metals offer the most promise in the formation of uniformly brazed joints because of the relative ease of placement of the brazing filler metals into the assembly to be brazed. Recently, a variety of alloys have been developed which can be cast into homogeneous, ductile, thin brazing foils by, for example, the casting process disclosed in U.S. XXXXXXX. This casting process, known as planar flow casting, involves solidification of molten metal into a thin foil by casting onto a rapidly moving quenching surface. Alloys suitable for casting into such foils are disclosed, for example, in U.S. XXXXXXX. However, homogeneous ductile brazing foil materials produced thus far do not exceed about 0.035 in (90 m) in thickness. In many applications, however, the brazing gap thickness is greater than about 100 um and/or wider than about 250 mm (4 0 in.) Accordingly, it has been necessary to individually place a plurality of the foils into the joint to be brazed, either in a stacked and/or side-by-side configuration. Unfortunately, problems are created in maintaining the layers in proper alignment with each other and, as a result, the use of a plurality of individual layers has not gained commercial acceptance. It is known to consolidate a number of layers of at least 50% amorphous ribbon by the process disclosed in U.S. XXXXXXX. Also, attempts have been made to use adhesives to consolidate multiple layers of these materials. In the former instance, however, copper-phosphorus and nickelboron-silicon-base brazing foils become brittle on consolidation and, therefore, would have extremely limited use in brazing joints of complex shape. In the latter instance, use of adhesives produces the unacceptable result of unwanted residue or porosity in the brazed joint. As a result, non-uniform and, in many instances, unacceptably weak joints are produced. There remains a need in the art for thick and/or exceptionally wide, flexible brazing foils which can accommodate brazing of large parts such as tail pipes of aircraft turbine engines.

SUMMARY OF THE INVENTION
In accordance with the invention, there is provided a flexible multilayered brazing material suitable for use in brazing joints having a gap thickness greater than about 100 km and/or a width in excess of the width of a single foil. The flexible multilayered brazing material comprises, in combination, at least one layer of ductile
brazing foil defining a core body having two major surfaces and at least one minor surface, and at least one layer of ductile brazing foil substantially covering said two major surfaces and at least one minor surface of said core body. More particularly, the core body and cover layer are each composed of metastable material which is at least about 50% amorphous.

BRIEF DESCRIPTION OF THE DRAWINGS
Figure 1 illustrates the simplest form of a product of the present invention, with the cover layer having been folded over the core body. Figure 2 illustrates the simplest form of the most preferred product of the present invention, with the cover layer helically wrapped around the core body. Figure 3 illustrates the production of exceptionally wide strip by arranging a plurality of layers in side-by-side relationship to define a core body which is then wrapped in the cover layer. Figure 4 is a side view of apparatus useful for producing multilayered product of the type illustrated in Figure 1. Figure 5a is a sectional view taken across the line A-A in Figure 4 showing the general construction of the forming die near the inlet end thereof.

Figure 5b is a sectional view taken across the line B-B of Figure 4 illustrating the general construction of the forming die near the outlet end thereof. Figure 6 is a top view of the forming die illustrated in Figure 4 showing the folding regimen of the cover layer as it travels through the forming die. Figure 7 is a top view of an apparatus useful for producing the product of the type illustrated in Figures 2 and 3. Figure 8 is a side view of the apparatus illustrated in Figure 7.

DETAILED DESCRIPTION OF THE INVENTION
The present invention is illustrated, in its simplest form, in Figures 1 and 2. Figure 1 shows a multilayered brazing strip in accordance with the present invention consisting of a single layer of brazing material defining a core body 1 encased in a covering layer 2. In this embodiment, the cover layer 2 is formed by folding a single strip of brazing foil having a width equal to about 21 + 2d, where "I" is the width of the core body 1 and "d" is the thickness of core body 1, about the core body 1 such that the edges of the cover layer 2 contact to form a seam 3 along one surface of the multilayered product. Figure 2 shows an alternate, more preferred embodiment of the present invention wherein the core layer 1' is helically wrapped along its length with a cover layer 2'. In the embodiment of Figure 2, the width of the cover layer need not be related to the width of the core body because the angle of wrapping will control the formation of a continuous cover and the seam 3. In either embodiment, it is very desirable to avoid any significant overlap of edges of the cover layer in order to maintain substantial uniformity of the thickness of the final product. In the present invention, the thickness of the multilayered product can be controlled by providing more than one layer to define the core body or, similarly, more than one cover layer. However, regarding in the latter, one cover layer is most preferred. Another embodiment of the present invention is illustrated in Fig. 3. In this embodiment, a plurality of layers 1", 1 O" are arranged in side-by-side relation to define the core body and thereported wrapped in a cover layer 2" to produce wide, thick strip. With this embodiment, the width of the strip is, in a practical sense, limited only by the capabilities of the equipment available to properly wrap the core layers. Although the present invention is conceptionally quite simple, it offers a number of advantages over prior art products.

First, alignment problems associated with individually stacked multiple layers in a gap are overcome. Second, elimination of problems associated with using adhesives to bond multiple layers together to form a preformed multilayered product is avoided. Third, brazing is uniform, i.e., non-uniformity in brazement thickness as ordinarily occurs with pastes, powders and rod feed are eliminated. Fourth, thick brazing metal material formed of at least 50% amorphous ductile foils can be produced which heretofore was unavailable for brazing large components. Fifth, flexible multilayered brazing materials formed from at least 50% amorphous ductile foils can be produced which are particularly useful in the production of uniformly brazed joints having complex shapes. The brazing foils employed to produce
the multilayered products of the present invention must be ductile. That is, the core layer must consist of brazing foil having sufficient flexibility to enable it to be bent to a radius of about 10 times the thickness of the foil without breaking. In addition, the cover layer must be sufficiently flexible such that it can be bent to a radius equal to or slightly less than the thickness of the core body without breaking.

Suitable foils useful for the core body material and cover layer are at least about 50% amorphous foils disclosed, for example, in U.S. Patent No XXXXXXX. As a result of the use of ductile foils in the core body and as the cover layer. The multilayered product will exhibit sufficient flexibility such that it can be bent to a radius equal to about the width of the multilayered product without breaking and without causing substantial displacement of the core body relative to the cover layer upon returns to the unbent condition. The products of the present invention can be produced by a variety of techniques employing a wide range of equipment. Figures 4-6 illustrate a preferred process for continuous manufacturing of multilayered flexible brazing strips from a plurality of ductile, brazing foils. Figures 7 and 8 illustrate the most preferred process for continuous manufacturing of multilayered flexible brazing strip from a plurality of ductile brazing foils. According to the process illustrated in Figure 4, a first ductile brazing foil 1 is continuously dispensed from a first guide roll 10 past a first grade roll 11 into a forming die 12. Simultaneously, a second ductile brazing foil 2 is continuously dispensed from a second feed roll 10a past a second guide roll 11a into forming die 12. As described heretofore, the second foil has a width equal to about 21 + 2d. In the process illustrated in Fig. 4, the second foil is fed beneath the first foil to produce a multilayered preform as illustrated in Fig. 5a. Forming die 12, illustrated in detail in Figures 5a, 5b and 6, consists of a generally flat bottom portion 120 and angular side walls 121,122. The angular side walls 121, 122 gradually change shape from the input end 12a of the forming die 12 to the output end 12b of the forming die 12, thereby causing the second foil to be deformed in such a manner as to gradually fold over the major and minor side surface(s) of the first strip. This gradual folding process is more clearly illustrated by reference to Figure 6, referring to lines 21, 22 which represent the edges of second foil 2. Referring again to Figure 4, the multilayered perform is then subjected to cold rolling, at cold rolling mill 13, sufficient to cause permanent deformation of the second strip (cover layer) necessary to produce the final product illustrated in Figure. 1.

Ordinarily, the degree of permanent (plastic) deformation or cold rolling is about 1-2%, and should not exceed about 396. The cold rolled, flexible, multilayered brazing strip is then wound onto a take up roll 13. It should be readily apparent that the above described process includes only the basic steps necessary to produce products of the present invention of the type illustrated in Figure 1. Products of the type wherein the core body consists of multiple stacked layers or multiple layers in side-by-side relationship are readily producible by using the above described process, modified to provide additional feed rolls or feed rolls which supply multiple strips. It should also be readily apparent that the forming step can be accomplished by any of a wide variety of equipment other than the above described forming die such as, for example, rolling equipment arranged in the direction of travel of the strips which effects the folding regimen illustrated schematically in Fig. 6. Moreover, it should be apparent that additional apparatus features such as guiding and aligning rolls and drive mechanisms have been omitted from the illustration because they are not necessary for a complete understanding of the present invention and because it understood by those skilled in the art to include the same. The most preferred process for production of products of the present invention is illustrated by the apparatus shown in Figures 7 and 8.

As is readily apparent, the embodiment illustrated therein is employed for the production of products of the type described heretofore with reference to Figures 2 and 3. According to Figure 7, the core body 1’ is fed through the open center of closed loop 70 driven, for example, by a drive ear 71 attached to a motor 72. Associated with the loop 70 is a feed roll 73 mounted on a roll holder 74 arranged at an angle relative to the plane of rotation of the loop 70 to effect a helical wrapping of the core body 1’ with the cover layer 2’. The helically wrapped preform then passes through guide rolls 75 and 76 (bottom rolls 75 and 76’ illustrated in Figure 8) to a cold rolling mill 77 (employing cold rolling rolls 78 and 79 as shown in Figure 8) plastically deform the cover layer to produce the final form of the multilayered
brazing strip illustrated in Figure 2. From the cold rolling mill, the flexible multilayered product is fed to a take-up roll 80. As described with respect to Figures 4-6, the apparatus illustrated in Figures 7 and 8 has been simplified so as to convey the basic features necessary to enable one skilled in the art to make and use the invention. It will be readily apparent that basic changes in the product construction can be effected, for example, by changing the angle of offset between the plane of rotation of the loop 70 and the roll holder 74. (As the angle e approaches go', significant overlap of the cover layer can occur: alternatively, as the angle becomes more obtuse, gaps in the cover layer can be created.) Further, in order to produce products of the type illustrated in Figure 3, it is readily apparent that multiple strips forming the core body would be fed in side-by-side relation through the apparatus illustrated in Figures 7 and 8. The following examples are presented to illustrate the production of products within the scope of the present invention. They are not intended to limit the scope of the invention defined by the appended claims in any respect.

EXAMPLE -1
A multilayered, flexible brazing material having a width of about 25mm (= 1 inch), a thickness of about 150 um (= 6 mil) and a length of about 15 m (~ 45 feet) was produced using an amorphous alloy having nominal composition (in weight percent) Cr7Fe3Si4.5Co.6B 3.2NiBaTi. The multilayered brazing product was produced by continuously drawing two foils, one 50mm (about 2 inch wide and about 50 um (2 mil) thick and one about 25mm (one inch) wide and about 50 um (2 mil) thick simultaneously using a specially designed die followed by cold rolling (schematically illustrated in Figures 4-6). During the drawings, the wide foil folds onto the narrow foil, effectively encasing the narrow foil. The multilayered foil was cold rolled at a 60m/min (=180'/min) production rate under a pressure of about 25 kPa to produce a rolled strip of about 150um (= 6 mil) thick. Production rate was controlled by regulating the rotation speed of the cold rolling mill and the take-up roll which is positioned after the cold rolling mill (shown in Figure 4).

EXAMPLE 2
A 160mm wide and 150 um thick flexible multilayered brazing product is produced from amorphous foil having a nominal composition as recited in Example 1. The production technique consists of laying up, in side-by-side fashion, three amorphous foils of about 50 mm in width and about 50 Lm in thickness and thereafter helically wrapping a covering foil of about 50mm width and about 50 bm thickness to form a flat helicoid surrounding the three side-by-side foils forming the core body.

Afterwards, the wrapped foil is rolled through a two roll cold rolling mill. (As schematically illustrated in figures 7 and 8). As a result, a flat multilayered product of substantially rectangle cross-section is produced. Having described the invention in full clear concise and exact terminology so as to enable one skilled in the art to make and use the same, the full scope of the invention is defined by the appended claims.
Mock Certification Exam for Patent Information Professionals 2011

[DRAWINGS]
Part 2 - Case 2 - Invalidity / Document D5

[ABSTRACT]
The potential of a photofabrication process involving photolithography and electrochemical milling has been established for the production of accurate holes in a range of sheet materials (10-500μm thick), including molybdenum, platinum, Pt-IORh, sterling silver, carat gold and silver- and palladium-based alloys. Based on scanning electron microscopy, the new technique shows its unique capability of producing high quality components in materials which were hitherto considered to be difficult or impossible to fabricate. Furthermore, the technique does not involve the use of any highly toxic or aggressive chemicals: a non-passivating neutral solution of sodium chloride is used as the electrolyte. Details of the type, concentration and application of the electrolyte are discussed. The technique appears to be potentially attractive to the manufacturers of fine apertures and similar intricate shapes of industrial components and jewellery items.

[DRAWINGS]

Fig 18 SEM picture (45° tilt) of aperture in platinum foil produced by present photoelectrochemical technique (670× magnification)
Brazing of metal parts employing a homogeneous, ductile, filler metal foil is disclosed. The brazing foil, useful for brazing cobalt based alloys, has a composition consisting essentially of 0 to about 4 atom percent iron, 0 to about 26 atom percent chromium, 0 to about 20 atom percent nickel, 0 to about 4 atom percent tungsten, 0 to about 4 atom percent molybdenum, 0 to about 20 atom percent boron, 0 to about 12 atom percent silicon, 0 to about 2 atom percent carbon and the balance essentially cobalt and incidental impurities. In addition to containing the foregoing elements within the above-noted composition ranges, the composition must be such that the total of iron, chromium, nickel, tungsten, molybdenum and cobalt ranges from about 75 to 85 atom percent and the total of boron, silicon and carbon ranges from about 15 to 25 atom percent. The ductile foil permits fabrication of preforms of complex shapes which do not require binders and/or fluxes necessary for brazing powders presently used to braze cobalt and nickel base alloys.

Brazing is a process for joining metal parts, often of dissimilar composition, to each other. Typically, a filler metal that has a melting point lower than that of the metal parts to be joined together is interposed between the metal parts to form an assembly. The assembly is then heated to a temperature sufficient to melt the filler metal. Upon cooling, a strong, corrosion resistant, leak-tight joint is formed.

Nickel and cobalt based alloys are conventionally joined by means of hydrogen, inert gas or vacuum brazing techniques. Such methods are employed to maintain low levels of contamination in the joint area. For high service temperature applications, nickel or cobalt based brazing filler alloys, having American Welding Society designation BNi or BCo compositions, per AWS A5.8, are used. These alloys produce brazed joints with high temperature strength and corrosion ad oxidation resistance.

The brazing alloys suitable for use with cobalt and nickel based alloys contain a substantial amount (about 3 to 11 weight percent) of metalloid elements such as boron, silicon and carbon. Consequently, such alloys are very brittle and are available only as powder, powder-binder pastes, powder-binder tapes and bulky cast preforms. Powders are generally unsuitable for many brazing operations, such as dip brazing, and do not easily permit brazing of complex shapes. Although some powders are available as pastes employing organic binders, the binders form objectionable voids and residues during brazing.

Some brazing alloys are available in foil form. However, such materials are either fabricated only through a costly sequence of rolling and careful heat-treating steps or are prepared by powder metallurgical techniques. Rolled foil is not sufficiently ductile to permit stamping of complex shapes therefrom. Powder metallurgical foil is not homogeneous and employs binders, which form objectionable voids and residues during brazing.

Ductile glassy metal alloys have been disclosed in U.S. Pat. No. XXXXXXX, issued Dec. 24, 1974 to H. S. Chen et al. These alloys include compositions having the formula Ma Yb Zc, where M is a metal selected from the group consisting of iron, nickel, cobalt, vanadium and chromium, Y is an element selected from the group consisting of phosphorus, boron and carbon, and Z is an element selected from the group consisting of aluminum, silicon, tin, germanium, indium, astatine and beryllium, ‘a’ ranges from about 60 to 90 atom percent, ‘b’ ranges from about 10 to 30 atom percent and ‘c’ ranges from about 0.1 to 15 atom percent.

Also disclosed are glassy wires having the formula Ti Xj, where T is at least one transition metal and X is an element selected from the group consisting of phosphorus, boron, carbon, aluminum, silicon, tin, germanium, indium, beryllium and antimony, ‘i’ ranges from about 70 to 87 atom percent and ‘j’ ranges from about 26 to 85 atom percent.
from about 13 to 30 atom percent. Such materials are conveniently prepared by rapid quenching from the melt using processing techniques that are now well -known in the art.
No brazing composition are disclosed therein, however. There remains a need in the art for a homogeneous, cobalt based brazing material that is available in ductile foil form.

SUMMARY OF THE INVENTION
In accordance with the invention, there is provided a homogeneous, ductile brazing foil useful as a filler metal for a brazed metal article. The brazing foil is composed of metastable material having at least 50 percent glassy structure, and has a thickness ranging from about 20 MU m (0.0008 inch) to 90 MU m (0.0035 inch).
It has been found that use of a cobalt based brazing foil that is flexible, thin and homogeneous, as described above, improves braze joint strength, enhances joining precision and reduces process time.

More specifically, the brazing foil has a composition consisting essentially of 0 to about 4 atom percent iron, 0 to about 26 atom percent chromium, 0 to about 20 atom percent nickel, 0 to about 4 atom percent tungsten, 0 to about 4 atom percent molybdenum, 0 to about 20 atom percent boron, 0 to about 12 atom percent silicon, 0 to about 2 atom percent carbon and the balance essentially cobalt and incidental impurities. In addition to containing the foregoing elements within the above-noted composition ranges, the composition must be such that the total of iron, chromium, nickel, tungsten, molybdenum and cobalt ranges from about 75 to 85 atom percent and the total of boron, silicon and carbon constitutes the remainder, that is, about 15 to 25 atom percent.

The homogeneous brazing foil of the invention is fabricated by a process which comprises forming a melt of the composition and quenching the melt on a rotating quench wheel at a rate of at least about 105 (degree) C./sec.

The filler metal foil is easily fabricable as homogeneous, ductile ribbon, which is useful for brazing as cast. Advantageously, the metal foil can be stamped into complex shapes to provide braze performs. Further, the homogeneous, ductile brazing foil of the invention eliminates the need for binders and pastes that would otherwise form voids and contaminating residues. Also, the filler material provided by the invention enables alternative brazing processes of cobalt and nickel based alloys, e.g., dip brazing in molten salts, to be employed.

DETAILED DESCRIPTION OF THE INVENTION
In any brazing process, the brazing material must have a melting point that will be sufficiently high to provide strength to meet service requirements of the metal parts brazed together. However, the melting point must not be so high as to make difficult the brazing operation. Further, the filler material must be compatible, both chemically and metallurgically, with the materials being brazed. The brazing material must be more noble than the metal being brazed to avoid corrosion. Ideally, the brazing material must be in ductile foil form so that complex shapes may be stamped therefrom. Finally, the brazing foil should be homogeneous, that is, contain no binders or other materials that would otherwise form voids or contaminating residues during brazing.

In accordance with a preferred embodiment of the invention a homogeneous, ductile cobalt based brazing material in foil form is provide. The brazing foil has a composition consisting essentially of 0 to about 4 atom percent iron, 0 to about 26 atom percent chromium, 0 to about 20 atom percent nickel, 0 to about 4 atom percent tungsten, 0 to about 4 atom percent molybdenum, 0 to about 20 atom percent boron, 0 to about 12 atom percent silicon, 0 to about 2 atom percent carbon and the balance essentially cobalt and incidental impurities.

The composition is such that the total of iron, chromium, nickel, tungsten, molybdenum and cobalt ranges from about 75 to 85 atom percent and the total of boron, silicon and carbon comprises the balance, that is about 15 to 25 atom percent. These compositions are compatible with and more noble than cobalt based alloys and are suitable for brazing nickel as well as cobalt base alloys.
By homogeneous is meant that the foil, produced, is of substantially uniform composition in all dimensions. By ductile is meant that the foil can be bent to a round radius as small as ten times the foil thickness without fracture. Examples of brazing alloy compositions within the scope of the invention are set forth below.

The brazing temperature of the brazing alloys of the invention ranges from about 1,035 (degree) C. to 1,300 (degree) C. The brazing foils of the invention are prepared by cooling a melt of the desired composition at a rate of at least about 105 (degree) C./sec, employing metal alloy quenching techniques well-known to the glassy metal alloy art; see, e.g., U.S. Pat. No. XXXXXXX, discussed earlier, the purity of all compositions is that found in normal commercial practice. A variety of techniques are available for fabricating continuous ribbon, wire, sheet, etc. Typically, a particular composition is selected, powders or granules of the requisite elements in the desired portions are melted and homogenized, and the molten alloy is rapidly quenched on a chill surface, such as a rapidly rotating metal cylinder.

Under these quenching conditions, a metastable, homogeneous, ductile material is obtained. The metastable material may be glassy, in which case there is no long range order. X-ray diffraction patterns of glassy metal alloys show only a diffuse halo, similar to that observed for inorganic oxide glasses. Such glassy alloys must be at least 50% glassy to be sufficiently ductile to permit subsequent handling, such as stamping complex shapes from ribbons of the alloys. Preferably, the glassy metal alloys must be at least 80% glassy, and most preferably substantially (or totally) glassy, to attain superior ductility.

The metastable phase may also be a solid solution of the constituent elements.

In the case of the alloys of the invention, such metastable, solid solution phases are not ordinarily produced under conventional processing techniques employed in the art of fabricating crystalline alloys. X-ray diffraction patterns of the solid solution alloys show the sharp diffraction peaks characteristic of crystalline alloys, with some broadening of the peaks due to desired fine grained size of crystallites. Such metastable materials are also ductile when produced under the conditions described above.

The brazing material of the invention is advantageously produced in foil (or ribbon) form, and may be used in brazing applications as cast, whether the material is glassy or a solid solution. Alternatively, foils of glassy metal alloys may be heat treated to obtain a crystalline phase, preferably fine-grained, in order to promote longer die life when stamping of complex shapes is contemplated. Foils as produced by the processing described above typically are about 20 to 90 MU m (0.0008 to 0.0035 inch) thick, which is also the desired spacing between bodies being brazed. Such spacing maximizes the strength of the braze joint.

Further, no fluxes are required during brazing, and no binders are present in the foil. Thus, formation of voids and contaminating residues is eliminated. Consequently, the ductile brazing ribbons of the invention provide both ease of brazing, by eliminating the need for spacers, and minimal post-brazing treatment.

The brazing foils of the invention are superior to various powder brazes of the same composition in providing good braze joints. This is probably due to the ability to apply the brazing foil where the braze is required, rather than depending on capillarity to transport braze filler from the edge of surfaces to be brazed.

EXAMPLE 1

Ribbons about 6.5 mm (0.25 inch) wide and about 40 to 60 MU m (about 0.0010 to 0.0035 inch) thick were formed by squirting a melt of the particular composition by overpressure of argon onto a rapidly rotating copper chill wheel (surface speed about 1,000 to 2000 m/min). Metastable, homogeneous
ribs of substantially glassy alloys having compositions listed in weight percent and atom percent were produced.

EXAMPLE 2

Tensile test specimens were cut from Haynes Alloy 188 (‘Haynes’ is a registered trademark of Cabot Corporation, Kokomo, Ind.), in strip form the composition of Haynes Alloy 188 is given.

The thickness was 0.16 cm (0.063 inch). A brazing alloy of the invention, a glassy, ductile ribbon of nominal composition of Sample No. 1 and having dimensions 46 MU m (0.0018 inch) thick by 6.3 mm (0.25 inch) wide, was used to braze the test specimens.

The tensile specimens were dimensioned and fabricated as lap shear specimens per AWS C3.2-63. The specimens were cut perpendicularly to the length direction.

Brazing specimens were degreased with warm benzene. Lap joints containing brazing ribbons of the invention were assembled with the ribbons side-by-side the length of the lap joint. In the case of these brazing alloys, the ribbons acted as the spacers. A single spot weld was used to hold the assembly together, as is common industrial practice.

Brazing was done in a vacuum furnace which was evacuated to a pressure of 1.33 * 10^-2 Pa (10^-4 Torr). The furnace was held at 1,300 (degree) C. for 15 minutes. Upon brazing, three shear specimens were subjected to tensile shear testing, with the following results:

<table>
<thead>
<tr>
<th>Shear Strength GPa (psi)</th>
<th>Tensile Strength GPa (psi)</th>
<th>Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-A 0.113 (16,320)</td>
<td>0.338 (48,960)</td>
<td>Base metal</td>
</tr>
<tr>
<td>1-B 0.112 (16,267)</td>
<td>0.336 (48,800)</td>
<td>Base metal</td>
</tr>
<tr>
<td>1-C 0.120 (17,333)</td>
<td>0.359 (52,000)</td>
<td>Base metal</td>
</tr>
</tbody>
</table>

All brazes were observed to fail in the base metal and not in the braze; therefore, the values reported are lower bounds.

EXAMPLE 3

Tensile test specimens of Haynes Alloy 188 were prepared for brazing as in Example 2. A brazing alloy of the invention, a glassy ductile ribbon of nominal composition of Sample No. 2 and having dimensions 46 MU m (0.0018 inch) thick by 6.3 mm (0.25 inch) wide was used to braze three test specimens.

Brazing was done in a vacuum furnace which was evacuated to a pressure of 1.33 * 10^-2 Pa (10^-4 Torr). The furnace was held at 1,300 (degree) C. for 15 minutes. The brazed joints evidenced the following joint strengths.

<table>
<thead>
<tr>
<th>Shear Strength GPa (psi)</th>
<th>Tensile Strength GPa (psi)</th>
<th>Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-A 0.052 (7573)</td>
<td>0.313 (45440)</td>
<td>Joint</td>
</tr>
</tbody>
</table>
EXAMPLE 4

Tensile test specimens of Haynes Alloy 188 were prepared for brazing as in Example 2. A brazing alloy of the invention, a glassy ductile ribbon of nominal composition of Sample No. 3 and having dimensions 46 MU m (0.0018 inch) thick by 3.2 mm (0.125 inch) wide was used to braze one test specimen. Brazing was done in a vacuum furnace which was evacuated to a pressure of 1.33 * 10^-2 Pa (10^-4 Torr). The furnace was held at 1,300 (degree) C. for 15 minutes. The brazed joints evidenced the following joint strengths:

<table>
<thead>
<tr>
<th>Shear Strength</th>
<th>Tensile Strength</th>
<th>Area of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 3</td>
<td>GPa (psi)</td>
<td>GPa (psi)</td>
</tr>
<tr>
<td>0.047 (6880)</td>
<td>0.287 (41280)</td>
<td>Joint</td>
</tr>
</tbody>
</table>

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EXAMPLE 5

Tensile test specimens of Haynes Alloy 188 were prepared for brazing as in Example 2. A brazing alloy of the invention, a glassy ductile ribbon of nominal composition of Sample No. 4, and having the dimensions 41 MU m (0.0016 inch) thick and 6.3 mm (0.25 inch) wide was used to braze two test specimens. Brazing was done in a vacuum furnace evacuated to 1.33 * 10^-2 Pa (10^-4 Torr). The furnace was held at 1,200 (degree) C. for 15 minutes. The brazed joints evidenced the following joint strengths.

<table>
<thead>
<tr>
<th>Shear Strength</th>
<th>Tensile Strength</th>
<th>Area of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 4</td>
<td>GPa (psi)</td>
<td>GPa (psi)</td>
</tr>
<tr>
<td>0.051 (7413)</td>
<td>0.301 (44,480)</td>
<td>Joint</td>
</tr>
<tr>
<td>0.052 (7627)</td>
<td>0.316 (45,760)</td>
<td>Joint</td>
</tr>
<tr>
<td>0.042 (6133)</td>
<td>0.254 (36800)</td>
<td>Joint</td>
</tr>
</tbody>
</table>
Nickel-Chromium-Silicon alloys of the nominal composition, Ni(45-78) Cr(16.34) Si(6.21) in the form of thin foil are made ductile by the presence of appreciable amounts of an amorphous phase and a metastable, solid solution, microcrystalline single phase and are especially suitable for preplacement as preforms in a joining operation such as brazing. Up to about 40 atomic percent of the nickel is replaceable with palladium.

The nickel-chromium-silicon alloys in the nickel-rich corner of the Ni-Cr-Si ternary triangle such as the composition specified in Aeronautical Material Specification 4782, (Ni62.3 Cr18.9 Si18.8) have been used in the form of powders, pastes and less than 100 percent dense foil fabricated from powder, because of the brittle nature of these alloys when these alloys have a silicon content greater than 6 atomic percent.

The disadvantages of using powder and pastes is that the alloy when molten, has to flow into the joint and fill up the gap between the mating parts. The flow of the molten alloy is strongly sensitive to the brazing environment and under non-ideal conditions the alloy may not flow through the joint gap. Also the organic binders in the pastes leave a residual contamination which alter the properties of the brazed joint. The use of sintered foil which has a density of less than 100 percent will result in voids in the brazed joint.

U.S. Pat. No. XXXXXXX discloses a wire product where alloys are represented by the formula Ti Xj wherein T is a transition metal and X is Al, Sb, Be, B, Ge, C, In, P, Si or Sn. The transition metals include metals from Groups IB, IIIB, IVB, VB, VIB, VIIB and VIIIB of the periodic table. The patent also teaches that the alloys contain at least 50 percent amorphous phase. As is apparent from that description, about 280 binary alloys are disclosed and an infinite number of alloys when mixtures of metals are used for T and X. The only alloys specifically disclosed are Pd77.5 Cu6 Si16.5 and Ni40 Pd40 P20. The patent also discloses ternary alloys of the formula Ma Yb Zc in sheet, ribbon and powder form wherein M is Ni, Fe, Cr, Co or V, Y is P, C or B and Z is Al, Si, Sn, Sb, Ge, In or Be.

It is believed that a 100 percent dense foil of the Ni-Cr-Si alloys which are ductile in nature and is therefore suited for fabricating into brazing preforms of a required geometry, by conventional stamping or photo etching techniques, without cracking would be an advancement in the art.

The advantages of the present invention over the present techniques is the ability to make ductile foil which would be normally brittle if made by conventional techniques. The process of making ductile foil also results in foil of uniform composition which is highly desirable for obtaining brazed joints with a high degree of reproducibility.

Such a ductile foil is especially suitable for fabricating into brazing preforms of required geometry.

SUMMARY OF THE INVENTION
In one aspect of this invention there is provided an alloy in the form of a brazing foil having a thickness of from about 0.0005 to about 0.005 inches and consisting essentially of from about 45 to about 78 atomic percent of nickel, from about 16 to about 34 atomic percent of chromium and from about 6 to about 21 atomic percent of silicon. Optionally up to about 40 atomic percent of the nickel can be replaced with palladium.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS
For a better understanding of the present invention, together with the other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above description of some of the aspects of the invention.
U.S. Pat. No. XXXXXXXX claims that additions of silicon aid in the formation of the amorphous phase. However, the sole purpose of additions of silicon to the alloy of this invention is for its effect of depressing the melting range, as commonly used in nickel-base brazing alloys. Up to 40 atomic percent of the nickel is replaceable with palladium to depress the melting range further than that provided by silicon.

In the nickel-chromium-silicon system, alloys of a silicon content greater than about 6 atomic percent form nickel and chromium silicides which embrittle the alloy and do not allow for fabricating into thin foil by conventional casting and rolling techniques.

The formation of silicides is well documented in the description of the Ni-Cr-Si ternary system as described by Knotek, Lugscheider and Eschnauer in Hartlegierungen Zum Verschleiss--Schutz, P. 30, Verlag Stahleisen MBH, Dusseldorf, 1975.

It is known that rapid cooling of a molten metal will in some instances form amorphous materials instead of crystalline phases. Some techniques for rapid quenching are disclosed in U.S. Pat. Nos. XXXXXXXX; XXXXXXXX; XXXXXXXX and XXXXXXXX. In the practice of this invention it is preferred to use a metal stream from an orifice to impinge upon a rotating drum having its external surfaces cooled by an internal cooling medium such as water. The metal stream upon solidifying forms a sheet-like material that is projected from the drum by centrifugal force.

Depending on the cooling rate during the rapid quenching, the resulting structure consists of a combination of an amorphous phase, new phases not obtainable under equilibrium conditions and a solid solution with solubility limits extended beyond their equilibrium values as described by Pol Duwez, R. H. Willens in Transactions of the Metallurgical Society of AIME, Volume 227 p. 362, April 1963.

The amorphous phase is intrinsically ductile because the glassy structure allows for slip in all possible directions. Additional ductility results from the presence of a microcrystalline single phase metastable solid solution which has a large grain-boundary area.

A rapid cooling rate of about 105 (degree) C./sec to 106 (degree) C./sec would prevent the formation of these embrittling silicides and extend the solubility of silicon in the Nickel-Chromium binary system. At the same time such high rates of cooling would create an appreciable amount of amorphous phase which has a disordered glassy structure. Above about 10 percent amorphous phase is preferred.

The alloy of this invention can be fabricated into thin foil containing appreciable amounts of amorphous phase and a metastable, micro-crystalline, solid solution, single phase, by the available rapid quenching techniques such as, melt extraction, melt-spin, vapor deposition or sputtering with cooling rates of about 105 (degree) C./sec to 106 (degree) C./sec.

An alloy fabricated in such manner is ductile and allows for fabrication of performs of intricate geometry, for preplacement in a brazing operation. The ductile foils of this invention have a thickness of from about 0.0005 to about 0.005 inches with thicknesses of from about 0.0015 inches to about 0.004 inches being preferred.

While alloys having the composition, Ni(45-78) Cr(16-34) Si(6-21) can be prepared in accordance with this invention in the form of a ductile brazing foil, preferred materials are Ni(60-65) Cr(17-20) Si(18-20) with AMS 4782 alloy having the composition, Ni62.3 Cr18.9 Si18.8 being especially preferred. If desired up to about 40 atomic percent of the nickel present in the alloys can be replaced with palladium.

While there has been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.
### Part 2 - Case 2 - Invalidity / Table

<table>
<thead>
<tr>
<th>Feature ref.</th>
<th>Features description</th>
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<tbody>
<tr>
<td>a)</td>
<td></td>
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<td>b)</td>
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<td>c)</td>
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