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[54] **HIGH TEMPERATURE BRAZE HEAT TREATMENT FOR PRECIPITATION HARDENING MARTENSITIC STAINLESS STEELS**
7 Claims, No Drawings

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[50] **Field of Search** 148/34, 37, 38, 125, 127, 135, 136; 29/497, 498, 504

[56] **References Cited**

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ABSTRACT: A brazing and heat treating cycle is described as applied to semiaustenitic stainless steel sheet material. The steps include a brazing operation, solution annealing, trigger annealing, subzero cooling and tempering. The brazed assembly exhibits good mechanical properties and good corrosion resistance.

HIGH TEMPERATURE BRAZE HEAT TREATMENT FOR PRECIPITATION HARDENING MARTENSITIC STAINLESS STEELS

The present invention was conceived during the performance of work in or under a U.S. Government contract with the Atomic Energy Commission identified as AT-11-1-GEN-14.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a heat treatment and braze cycle which is useful for producing good mechanical properties and good corrosion resistance in semiaustenitic stainless steels.

2. Description of The Prior Art

Semiaustenitic stainless steels have an attractive combination of mechanical and corrosion resistance characteristics which have been developed through control of the chemical composition of the steel, together with a specific processing related to such control of the chemical composition. Thus it is possible to develop a predetermined set of mechanical and corrosion resistance properties in a product of finished form by means of a given heat treatment.

Semiaustenitic stainless steel has found use in corrosive environments and one of the methods of fabricating said steel for use in such corrosive environment includes the step of brazing the material either to itself or to some other structural component. The temperature to which the semiaustenitic stainless steel is heated during such high-temperature brazing heat treatment of necessity alters the corrosion resistance and mechanical properties exhibited by such semiaustenitic stainless steel. Typically, these steels, as supplied, have a composition as set forth in U.S. Pat. No. 2,799,602 and contain up to about 0.15 percent carbon from about 12 to about 18 percent chromium from about 3.5 to about 7 percent nickel from about 2 to about 3 percent molybdenum up to about 0.5 percent silicon from about 0.25 to about 20 percent manganese and from about 0.5 to 0.15 percent nitrogen with the balance essentially all iron and incidental impurities.

Depending upon the heat treatment and chemistry, these steels may be characterized as being substantially completely austenitic in the annealed condition or their microstructure may contain up to about 30 percent delta ferrite with the balance being substantially all austenite when the material is cooled to room temperature from the prescribed annealing heat treatment. It has been found however that such annealing heat treatment must be limited to a temperature of about 2,000° F. because heating above such temperature may cause excessive grain growth regardless of the inclusion content. Moreover, excessive temperatures causes large amounts of delta ferrite to be formed and this material will not transform upon subsequent cooling regardless of the temperature to which the steel is cooled; consequently, the steel will exhibit poor mechanical properties which may be difficult to adjust in order to provide the proper balance of mechanical properties commensurate with the desired degree of corrosion resistance.

The brazing treatment to which the steel is usually subjected during fabrication includes a brazing at a temperature within the range between about 2,045° and about 2,150° F. depending upon the brazing alloy employed. While a short temperature excursion not exceeding about 5 minutes in duration to this temperature range will not produce significantly large amounts of delta ferrite in excess of that already present, nonetheless the mechanical properties exhibited by this steel will be far from optimum and as a result thereof it becomes necessary to re-heat treat this steel in order to reestablish the desired level of mechanical properties commensurate with the required degree of corrosion resistance and combine the same in the brazing cycle to which the steel undergoes.

SUMMARY OF THE INVENTION

The method of the present invention provides for the combination of a brazing and heat treatment cycle which is designed for improving the mechanical and corrosion resistance properties of the semiaustenitic stainless steels containing up to about 30 percent delta ferrite in their annealed condition at room temperature. During the brazing cycle the brazing assembly is rapidly heated to a temperature within the range between about 2,045° and about 2,150° F. for a time period of up to about 5 minutes. Following the high-temperature braze cycle the assembly is cooled to a temperature within the range between about 1,900° and about 1,925° F. in a time period of less than about 30 minutes. The assembly is held at the temperature range for a time period between about 50 minutes and about 70 minutes. The assembly in next step is cooled to a temperature within the range between about 1,700° and about 1,725° F. in a time period of less than about 30 minutes. The assembly is held within such trigger annealing temperature range for a time period between about 50 minutes and about 70 minutes. Thereafter the assembly is quenched to a temperature below about 1,100° F. in a time period not exceeding about 20 minutes and to room temperature within the time period not exceeding about 1 hour. Thereafter the assembly is subzero cooled, preferably within a 48-hour period of the completion of the quenching operation, to a temperature within the range between about −100° and about −125° F. for a time period between about 170 and 190 minutes. Thereafter the assembly is warmed to room temperature following which the assembly is tempered at a temperature within a range between about 985° and about 1,015° F. for a time period of between about 170 and about 190 minutes and thereafter cooled to room temperature. The foregoing treatment has been found to be effective for not only brazing material into its fabricated form but also for developing within the brazed structure an optimum combination between mechanical properties and corrosion resistance properties making the brazed structure suitable for use in a corrosive environment where the material is subject to cyclical stressing both at room temperature and at elevated temperatures.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The parts to be brazed are assembled in the desired manner with the interposition of a suitable brazing alloy between the surfaces to be joined. In this respect it has been noted that a composition which is sold under the trade name of AMDRY 100 and which contains between about 18.5 and about 19.5 percent chromium, about 9.8 to about 10.3 percent silicon, up to about 1 percent iron, up to about 1 percent manganese and the balance essentially nickel has proved to be quite useful in joining the semiaustenitic stainless steel surfaces into a joined structure. Such a brazing composition has a melting temperature of nominally 2,050° F. However, other brazing alloys can be used, such as those manufactured and sold under the trade name J-8100 and which are also a nickel-chromium-silicon-type brazing compositions with slightly higher melting points. In this respect it is preferred to maintain the brazing temperature as low as possible in order to minimize any grain growth as well as prevent the formation of excessive amounts of delta ferrite when the brazing assembly is heated to the required temperature. It has been found however that so long as a temperature of about 2,150° F. is not exceeded for a time period of up to about 5 minutes no significant grain growth occurs and the delta ferrite component of the microstructure is normally within acceptable limits to provide a required degree of mechanical properties commensurate with the required degree of corrosion resistance.

The assembly is then subjected to heat, that is, to a temperature within the range between about 2,045° and about 2,150° F. for a time period of up to about 5 minutes in order to join the surfaces in assembled relationship. Preferably, such brazing is performed in a regular brazing furnace which is provided with a controlled atmosphere to protect the surface of the semiaustenitic stainless steel. Any protective atmosphere can be employed and particular success has been had employing a hydrogen atmosphere having a dew point of not greater than about −90° F.

Following heating to a temperature within the range between 2,045° and 2,150° F., the assembly is cooled to a temperature within the range between about 1,900° and 1,925° F. in a time period of less than about 30 minutes. The brazed assembly is held at this temperature range between about 50 minutes and about 70 minutes. Once again it is preferred to employ a protective atmosphere while holding the brazed assembly at this temperature range for the time period indicated, such protective atmosphere preferably being hydrogen having a dew point of about less than −90° F. By holding the brazed assembly at this particular temperature range any thermal distortion or stresses induced resulting from a rapid heating to the brazing temperature as well as the rapid cooling therefrom are minimized and the same is accomplished without unduly altering the microstructure through inordinate grain growth or the production of untoward amounts of delta ferrite.

After holding at a nominal temperature of about 1,900° F., the brazed assembly is cooled to a temperature within the range between about 1,700° and about 1,725° F. and held at this so-called "trigger annealing" temperature range for a time period within the range between about 50 minutes and about 70 minutes. Once again the brazed assembly is subjected to a protective atmosphere and good success has been obtained with the utilization of dry hydrogen having a dew point of about −90° F. It is believed that by holding at the temperature range, that is between 1,700° and 1,725° F., an equilibrium amount of carbides will precipitate from the microstructure. Characteristically, these carbides form at the austenite-delta ferrite interface as well as within the austenite grain and as a result thereof, since the delta ferrite is discontinuous, such grain boundary carbides are also discontinuous thereby not adversely affecting the corrosion resistance of the steel. At the same time however the austenite becomes unbalanced to such a degree that M_s temperature is raised to approximately room temperature so that with subsequent treatment, as will be set forth hereinafter, the austenite can be transformed to martensite with its enhanced mechanical properties being developed thereby. It has been found that about 1 hour at the trigger annealing temperature range is usually sufficient time to approach the equilibrium amount of carbides being precipitated.

Following the holding period at the trigger annealing temperature range the brazed assembly is thereafter quenched to a temperature below about 1,100° F. in a time period not exceeding about 20 minutes and to room temperature within a time period not exceeding about 1 hour. It has been found that the quenching rate between about 1,700° and about 1,100° F. is very highly critical in that if the material, that is, the brazed assembly, is not cooled to a temperature below about 1,100° F. within a 20-minute time period, sufficient carbides and/or nitrides will precipitate which will adversely affect the corrosion resistance. In addition, the M_s temperature will be raised to a sufficiently high degree that with most of carbon and nitrogen being out of solution any transformation which does take place will not significantly improve the mechanical properties of the material from that exhibited by the material in the annealed condition. That is, the material will be in what may be referred to as an overaged condition having poor mechanical properties and poor corrosion resistance properties. It has been found that so long as the brazed assembly is quenched to a temperature below about 1,100° F. in a time period not exceeding that 20 minutes sufficient carbon and nitrogen will be retained within the austenitic component so that the proper mechanical properties can be developed together with enhanced corrosion resistance. It is highly desirable, in fact necessary, that the quenching be continued to room temperature and room temperature be achieved within the brazed assembly within the period not exceeding about 1 hour. While such quenching will be effective for preventing further carbide precipitation nonetheless the austenitic phase which is retained at room temperature is quite metastable.

After quenching and preferably within a period of 48 hours, the brazed assembly is subjected to a subzero cooling treatment. Subzero cooling treatment includes the treatment at a temperature within the range between about −100° and about −125° F. for a time period ranging between about 170 and about 190 minutes. Thereafter the brazed assembly is warmed to room temperature.

The attainment of a temperature range between about −100° about −125° F. can be accomplished in any number of ways including the immersion of the brazed assembly within a refrigerated chest or where desired a mixture of dry ice and acetone will usually produce a temperature within the desired range. During the subzero cooling treatment the metastable austenitic component of the microstructure is transformed to martensite, such martensitic transformation being accompanied by an increase in the strength characteristics exhibited by the alloy.

Following warming to the room temperature the brazed assembly is thereafter tempered at a temperature within the range between about 985° and about 1,015° F. for a time period of between about 170 and 190 minutes and thereafter the brazed assembly is cooled to room temperature. Such tempering treatment is preferably carried out in a vacuum, said vacuum being less than about 1×10^{14} millimeters of mercury. Once again it has been found desirable to cool the tempered assembly to a temperature of less than about 600° F. in a time period not exceeding about 1 hour. The tempering treatment is effective for optimizing the mechanical properties by decreasing the strength and increasing the ductility. Since the carbides have not been precipitated at the grain bounding the optimum combination of strength, ductility and corrosion resistance is achieved.

It has been found that due to furnace size limitations, the brazed assembly may be sufficiently large or the bulk of the material is of such size that the assembly cannot be cooled from a temperature of about 1,700° to a temperature of about 1,100° F. in less than 20 minutes. In such circumstance the 1-hour holding period at a temperature within the range between about 1,700° and about 1,725° is omitted and the alloy is allowed to cool directly from 1,900° F. to room temperature at a rate such that the cooling time through the temperature range between about 1,700° and about 1,100° does not appreciably exceed 20 minutes. When such cooling directly from 1,900° F. to room temperature is employed it is usually preferred to decrease the temperature of the subzero cooling treatment and a temperature as low as −320° F. can be employed to accomplish the transformation of the metastable austenite to martensite.

The process of the foregoing braze-heat treatment cycle is effective for producing sound brazed assemblies employing semiaustenitic stainless steel, such brazed assembly exhibiting the optimum mechanical properties developable within the semiaustenitic stainless steel commensurate with outstanding corrosion resistance. As an example of the effectiveness of the braze-heat treatment of the present invention, material given the designated heat treatment with the brazing done in hydrogen exhibited a room temperature tensile strength of about 185,000 p.s.i. and a yield strength of about 150,000 p.s.i. with an elongation of about 13 percent.

This material was heated in a brazing operation to 2,125° F. and held at said temperature for a period of 5 minutes. Thereafter the brazed assembly was furnace cooled to 1,900° F. and held for 60 minutes at 1,900° following which the assembly was furnace cooled to 1,710° F. and held at that temperature for 60 additional minutes. Thereafter the assembly was cooled to room temperature following which the assembly was subzero cooled to −100° F. and held at said temperature for 3 hours following which the brazed assembly was heated to room temperature and thereafter tempered at 1,000° F. for 3 hours and cooled to room temperature. Room temperature tensile testing revealed the following listed properties.

Tensile Strength	Yield Strength	Elongation
180 kpsi	150 kpsi	8%

Extensive in-pile and out-of-pile corrosion testing of material subjected to the braze-heat treatment disclosed herein has shown adequate corrosion resistance under various reactor environments from a standpoint of galvanic, stress and general corrosion.

I claim as my invention:

1. In the method of improving the mechanical and corrosion properties of a semiaustenitic stainless steel assembly in which the members are fabricated employing a high-temperature brazing cycle, the steps comprising:

a. rapidly heating the stainless steel braze assembly to a temperature within the range between about 2,045° and about 2,150° F. for a time period of up to about 5 minutes to effect a joining of the members,

b. cooling the braze assembly to a temperature within the range between about 1,900° and about 1,925° F. in a time period of less than about 30 minutes and holding said assembly at said temperature range for a time period of between about 50 minutes and about 70 minutes,

c. cooling the braze assembly to a temperature within the range between about 1,700° and about 1,725° F. in a time period of less than about 30 minutes and holding said assembly at said temperature range for a time period of between about 50 and about 70 minutes,

d. quenching the braze assembly to a temperature below about 1,100° F. in a time period not exceeding about 20 minutes and to room temperature within a time period not exceeding about 1 hour,

e. subzero cooling the braze assembly within 48 hours of the completion of step (d) to a temperature within the range between about −100° and −125° F. for a time period of between about 170 and about 190 minutes and thereafter warming to room temperature, and,

f. tempering the braze assembly at a temperature within the range between about 985° and about 1,015° F. for a time period of between about 170 minutes and about 190 minutes and thereafter cooling to room temperature.

2. The method of claim 1 in which each heat treatment step prior assembly the subzero cooling step (e) is performed in hydrogen having a dew point of not greater than −90° F.

3. The method of claim 1 in which the tempering treatment is performed in a vacuum of less than 1×10^{14} mm. of Hg.

4. The method of claim 3 in which the cooling from the tempering temperature in step (f) to a temperature of 600° F. is accomplished in less than 1 hour.

5. In the method of improving the mechanical and corrosion properties of a semiaustenitic stainless steel braze assembly in which the members are fabricated employing a high-temperature brazing cycle, the steps comprising,

a. rapidly heating the stainless steel braze assembly to a temperature within the range between about 2,100° and about 2,150° F. and holding for a time period of up to about 5 minutes,

b. cooling the braze assembly to a temperature within the range between about 1,900° and abut 1,925° F. in a time period of less than about 30 minutes and holding said assembly at said temperature range for a time period of between about 50 minutes and about 70 minutes,

c. quenching the braze assembly to room temperature through the temperature range between 1,710° F. and 1,100° F. in a time period not exceeding about 20 minutes and to room temperature within a time period not exceeding about 1 hour,

d. subzero cooling the braze assembly to a temperature within the range between about −100° and −125° F. for a time period of between about 170 and about 190 minutes and thereafter warming to room temperature, and,

e. tempering the braze assembly at a temperature within the range between about 985° and about 1,015° F. for a time period of between about 170 minutes and about 190 minutes and thereafter cooling to room temperature.

6. The method of claim 5 in which each heat treatment step prior to the subzero cooling step (e) is performed in hydrogen having a dew point of not greater than −90° F.

7. In the method of improving the mechanical and corrosion properties of a semiaustenitic stainless steel braze assembly in which the members are fabricated employing a high-temperature brazing cycle, the steps comprising,

a. rapidly heating the stainless steel braze assembly to a temperature within the range between about 2,100° and about 2,150° F. for a time period of up to about 5 minutes,

b. cooling the braze assembly to a temperature within the range between about 1,900° and about 1,925° F. in a time period of less than about 30 minutes and holding said assembly at said temperature range for a time period of between about 50 minutes and about 70 minutes,

c. cooling the braze assembly to a temperature of about 1,750° F. in a time period of less than about 30 minutes and holding said assembly at said temperature for a time period of between about 50 minutes and about 70 minutes,

d. quenching the braze assembly to a temperature below about 1,100° F. in a time period not exceeding about 20 minutes and to room temperature within a time period not exceeding about 1 hour,

e. subzero cooling the braze assembly within 24 hours of the completion of step (d) to a temperature within the range between about −100° and −1,250° F. for a time period of between about 170 and about 190 minutes and thereafter warmed to room temperature, and,

f. tempering the braze assembly at a temperature within the range between about 985° and about 1,015° F. for a time period of between about 170 minutes and about 190minutes and thereafter cooling to room temperature.

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