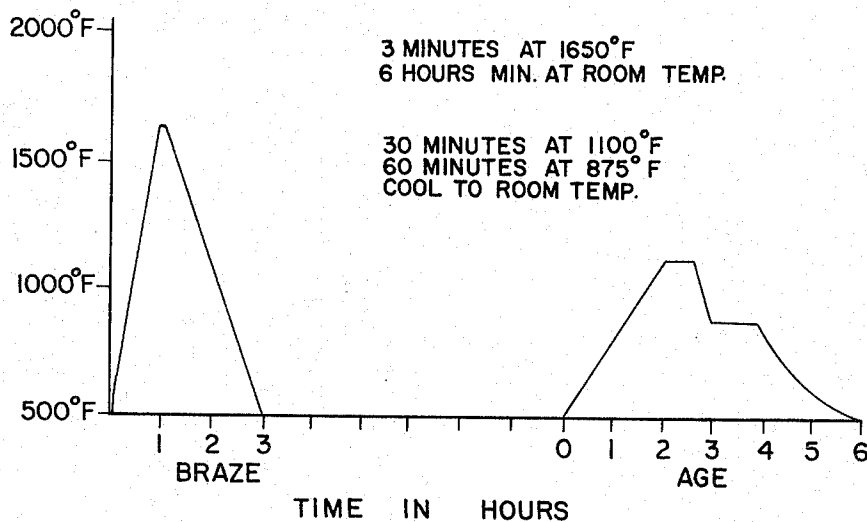


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STAINLESS STEELS  
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## METALLURGICAL CONDITIONING PROCESS FOR PRECIPITATION-HARDENING STAINLESS STEELS

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The present invention relates generally to heat treating processes for the metallurgical conditioning of stainless steels. More particularly the invention relates to a process for heat treating the precipitation hardening stainless steels of the semiaustenitic type which is operable to effect a substantial increase (on the order of 60%) in the ductility of such steels with substantially no change occurring in the object steel's ultimate tensile strength or other physical properties.

Presently known conventional conditioning processes which are directed to the same objective and disclosed in the prior art fall far short of the presently achieved effect and fail to accomplish the desired end result. The processes of the nearest known prior art, while citing incremental aging of the PH steels after low temperature hardening (by progressively lowering the temperature and holding time-at-temperature in at least two incremental steps and finally cooling to room temperature) broadly infer that beneficial results may accrue from aging in such stepped-down increments. However, this art fails to recognize the exact nature of these benefits nor is the hereafter described process disclosed by the art either generally or specifically. This is particularly evident from the fact that in all references where step aging is mentioned as a factor in the object process, martensitic transformation occurs at relatively low, sub-ambient temperatures, on the order of  $-100^{\circ}\text{F.}$ , prior to aging. Such low temperature treatment is unnecessary to the present process.

It is well known to those skilled in the art that the precipitation hardening stainless steels have an excellent combination of structural properties, particularly when employed in temperature environments up to  $700^{\circ}\text{F.}$  Such desirable characteristics as high strength-to-weight ratios, high modules of elasticity, good stress-rupture and creep properties and good fatigue properties are characteristic of these PH steels. Further, these alloys display similar properties in both the longitudinal and transverse directions and in both tension and compression. While two of the four better known PH stainless steels (Armco Steel Corporation's 17-7PH and PH 15-7 Mo, which are among the only ones recognized by those skilled in the art as being true precipitation hardening alloys) exhibit an acceptable ultimate tensile strength of approximately 200 k.s.i., when, for example, they are employed in brazed composite structures such as in stainless steel sandwich aircraft panels; such panels consisting of low density, high strength cellular core, upper and lower facing plates and edge closure components. However, such panel's ductility properly expressed in percentage elongation or reduction in cross-section values is usually deficient and is only marginal at best. This is particularly true in these brazed assemblies because flow temperature

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of the brazing alloy is below the annealing temperature of these semi-austenitic steels and above their optimum austenite conditioning temperature. As a result, a detrimental shift of the  $M_s$  temperature is experienced.

The process of the present invention, while not necessarily limited thereto, is directed primarily to conditioning of the two semiaustenitic alloys noted above which are considered to be true precipitation hardening steels. The composition of these semiaustenitic types is such that after annealing at temperatures near  $1950^{\circ}\text{F.}$  they remain austenitic on cooling; being relatively easy to fabricate in this form. Conventional treatment at  $1400^{\circ}\text{F.}$  or  $1725^{\circ}\text{F.}$  depletes the austenite of chromium and carbon to the extent that martensite begins to form on cooling to room temperature and will achieve maximum transformation after a long period of time or on refrigeration to  $-100^{\circ}\text{F.}$  Mechanical deformation may also result in transformation due to residual thermal growth. Final hardening is effected during the tempering treatment, as in the case of martensitic types. These alloys are initially hardened when the austenite transforms to martensite. Additional strengthening occurs during the conventional aging treatment, resulting from transformation of the retained austenite to martensite. It is therefore a primary object of the present invention to provide an improved metallurgical conditioning process for the true precipitation hardening stainless steels of the semiaustenitic type which substantially increases ductility in such steels without any significant loss of ultimate tensile strength.

Another object of the invention is to provide an improved metallurgical process of the above class and character which is particularly operable for conditioning brazed composite structures of the face plate to cellular core sandwich type and which employ semiaustenitic PH stainless steel as components thereof.

A further object is to provide an improved metallurgical process for heat treating the above steels which is operable to achieve an optimum relationship of ductility to tensile properties when hot forming an object workpiece at specified temperatures.

A still further object resides in the provision of a step aging process for precipitation hardening semiaustenitic stainless steel which is operable as a reprocessing heat treatment for such steels when they have exhibited poor physical properties due to the effect of previous heat treatment.

These and other objects and advantages of the invention will become apparent upon consideration of the following detailed description of the preferred application of the process, especially when taken in conjunction with the accompanying charts, test data and other graphic representations thereof.

To practice the process of the present invention, the object precipitation hardening steel of the semiaustenitic class, such for example as Armco's 17-7 PH or 15-7 Mo stainless steel, is subjected to an austenite conditioning temperature above  $1400^{\circ}\text{F.}$  and below  $1800^{\circ}\text{F.}$  for less than about two minutes and not more than about 15 minutes. The temperature of the workpiece is then lowered to some point below  $100^{\circ}\text{F.}$  and above  $32^{\circ}\text{F.}$ , generally indicated to be at room temperature, and then raised to a first aging temperature of  $1100^{\circ}\text{F.}$  for

15 minutes to 60 minutes. Subsequently, the temperature is dropped to a second aging temperature of about 875° F. for from one to twenty-four hours. This double, step aging process may be advantageously applied to brazing, hot forming and reprocessing operations when the elements, components or composite consists of, or embodies, stainless steel of the object class and character because the process may be interrupted at any point that may be advantageous to the processor, such as: (1) for hot forming—inasmuch as the object workpiece can be formed at 1100° F. at which point it is much more ductile, the remainder of the process being then completed after this fabrication; (2) for repair of a completed part—(a) when the part is already in the condition in which it would be following the 1100° F. step, where the 875° F–925° F. step would need to be applied; (b) when a part has lost a considerable part of its ductility, the 1100° F. step may be applied in order to somewhat lower the ultimate strength and to add considerably to the ductility, and then applying the 875° F. step in order to regain most of the original ultimate strength without disturbing the desired ductility previously achieved in the 1100° F. step; and (c) in cases where the part must go all the way through a reanneal and the entire present process, in which event, it is subjected to a temperature of 1050° F.–1075° F. for the first step of the aging because the response of a reworked workpiece to heat treatment is not quite as high as with a virgin part not previously processed.

The effects of exposure to 1400° F. to 1800° F. austenite conditioning temperature are well known and documented in the prior art. The 1100° F. step tempers the martensite to a lower ultimate tensile strength (about 170 k.s.i. but leaves ductility at a high level as well. The 1100° F. step while tempering the martensite, establishes equilibrium between the austenite that is in the process of being transformed into martensite and between the martensite that is in the process of reverting to austenite. The stabilized austenite, retained as a result of this balance, is somewhat greater in quantity than the austenite retained after transformation and subjected to a one hour period at room temperature. This makes any further effort to reduce the retained austenite by refrigeration, prior to the step age, unnecessary.

The hardening effect of the 875° F. aging treatment is due to a change in the intermetallic compounds at the grain boundaries. The grain size is finer after passing through this step and the structural change is accompanied by a very slight contraction in the object material. Further, such 875° F. aging increases the ultimate tensile strength of the steel to the order of 20 k.s.i. additional with no appreciable effect on the elongation gained in the 1100° step.

Dual step aging of semiaustenitic, precipitation hardening steels thus results in considerably more ductility than does the conventional single temperature aging process, as taught by the known art, to a nominal two times the ductility and ranging upward, as evaluated by percent elongation in two inch measurements. Corrosion resistance, creep, stress-rupture and other properties of the steel remain substantially unchanged. Thus, step aging according to the present invention, by effecting a pronounced increase in ductility of the object metal, makes its fabrication much easier and permits applications for such metals that were previously unfeasible because of poor ductility.

One such application is exemplified in a large structural panel employed on an advanced Mach 2+ aircraft, which panel was comprised of two 17-7 PH face plates, a 17-7 PH low density cellular core, and various edge and attachment member components. These were assembled and brazed to form a single, unitary structural composite. The large panels were aged at 1100° F. for only 15 minutes since the slower heating and cooling

rates due to heavy metal tooling produced substantially the same result as the 30 minute age for smaller parts.

The cooling rate between 1100° F. and the 875° F. step begins after the furnace door is closed and the part has recovered to 875° F.

A typical time at temperature cycle is shown by the graph of the figure.

Conventional nominal gage specimens of 17-7 PH, which were initially processed through a braze cycle and cooled to room temperature were subsequently processed in accordance with conventional procedure and with the process of the present invention as set forth above. These specimen were tested and compared as to basic structural properties. The results are shown below by Tables A and B respectively, wherein the numerical column designates specimen number, ad seriatim, column Y designates yield value, column U is ultimate tensile strength and column E is elongation. Values in columns Y and U are given in "k.s.i." (thousands of pounds per square inch) and values in column E are given in "percent elongation in two inches."

| A-Conventional Process                                            |              |              |               | B-Invented Process                                                         |              |               |
|-------------------------------------------------------------------|--------------|--------------|---------------|----------------------------------------------------------------------------|--------------|---------------|
| Minus 20° F. for 10 minutes. Aged 1,050° to 1,075° for 90 minutes |              |              |               | Held at room temperature for a minimum of 6 hours. Aged by step-age method |              |               |
| No.                                                               | Y,<br>k.s.i. | U,<br>k.s.i. | E,<br>Percent | Y,<br>k.s.i.                                                               | U,<br>k.s.i. | E,<br>Percent |
| 1                                                                 | 172.8        | 179.3        | 3.5           | 185.1                                                                      | 190.5        | 5.0           |
| 2                                                                 | 188.2        | 194.5        | 4.0           | 181.9                                                                      | 185.5        | 7.0           |
| 3                                                                 | 167.2        | 181.6        | 4.0           | 177.3                                                                      | 183.5        | 6.5           |
| 4                                                                 | 189.4        | 196.8        | 4.5           | 182.5                                                                      | 188.2        | 6.0           |
| 5                                                                 | 192.0        | 201.5        | 4.0           | 177.5                                                                      | 186.3        | 6.5           |
| 6                                                                 | 173.7        | 189.3        | 4.5           | 185.8                                                                      | 193.3        | 5.0           |
| 7                                                                 | 175.5        | 185.6        | 5.5           | 168.3                                                                      | 181.6        | 8.0           |
| 8                                                                 | 181.6        | 194.1        | 3.0           | 175.8                                                                      | 182.8        | 8.5           |
| 9                                                                 | 190.2        | 206.8        | 3.0           | 173.2                                                                      | 180.2        | 7.5           |
| 10                                                                | 176.5        | 184.4        | 5.0           | 171.5                                                                      | 180.3        | 7.5           |
| 11                                                                | 188.0        | 189.6        | 4.5           | 161.8                                                                      | 182.2        | 6.0           |
| 12                                                                | 188.9        | 195.5        | 4.0           | 180.1                                                                      | 180.9        | 7.0           |
| 13                                                                | 191.8        | 199.0        | 4.0           | 181.7                                                                      | 191.7        | 6.0           |
| 14                                                                | 174.5        | 186.6        | 4.0           | 177.9                                                                      | 185.5        | 6.5           |
| 15                                                                | 189.2        | 190.0        | 4.5           | 177.5                                                                      | 185.0        | 6.5           |
| Av                                                                | 182.6        | 191.6        | 3.7           | 177.2                                                                      | 185.2        | 6.6           |

NOTE: .008 nominal gage 17-7 PH, brazed at 1,650° to 1,690° F. for 3 to 15 minutes. Cooled to room temperature and processed as shown.

| A-Conventional Process                                            |              |              |               | B-Invented Process                                                         |              |               |
|-------------------------------------------------------------------|--------------|--------------|---------------|----------------------------------------------------------------------------|--------------|---------------|
| Minus 20° F. for 10 minutes. Aged 1,050° to 1,075° for 90 minutes |              |              |               | Held at room temperature for a minimum of 6 hours. Aged by step-age method |              |               |
| No.                                                               | Y,<br>k.s.i. | U,<br>k.s.i. | E,<br>Percent | Y,<br>k.s.i.                                                               | U,<br>k.s.i. | E,<br>Percent |
| 1                                                                 | 172.6        | 187.2        | 5.5           | 182.6                                                                      | 192.2        | 6.0           |
| 2                                                                 | 178.9        | 184.5        | 7.0           | 174.0                                                                      | 182.4        | 8.0           |
| 3                                                                 | 192.2        | 199.6        | 4.0           | 168.8                                                                      | 181.6        | 8.0           |
| 4                                                                 | 188.5        | 191.2        | 4.0           | 168.2                                                                      | 179.7        | 8.0           |
| 5                                                                 | 182.0        | 192.3        | 4.0           | 170.9                                                                      | 184.7        | 8.0           |
| 6                                                                 | 188.2        | 199.0        | 4.0           | 167.6                                                                      | 179.0        | 9.0           |
| 7                                                                 | 166.2        | 201.5        | 4.0           | 174.8                                                                      | 186.3        | 6.5           |
| 8                                                                 | 176.6        | 192.8        | 4.5           | 161.0                                                                      | 190.4        | 6.5           |
| 9                                                                 | 174.5        | 188.3        | 4.5           | 176.2                                                                      | 178.3        | 8.0           |
| 10                                                                | 176.2        | 185.5        | 4.5           | 173.2                                                                      | 190.8        | 6.0           |
| 11                                                                | 179.8        | 204.8        | 3.5           | 180.7                                                                      | 188.5        | 5.5           |
| 12                                                                | 181.3        | 208.7        | 2.5           | 186.0                                                                      | 189.7        | 6.0           |
| 13                                                                | 169.7        | 187.0        | 3.5           | 166.5                                                                      | 182.9        | 8.0           |
| 14                                                                | 161.6        | 177.9        | 5.0           | 173.7                                                                      | 190.4        | 8.0           |
| 15                                                                | 172.5        | 181.6        | 4.5           | 175.4                                                                      | 187.5        | 6.5           |
| Av                                                                | 177.4        | 192.1        | 4.3           | 174.0                                                                      | 185.6        | 7.2           |

NOTE: .010 nominal gage 17-7 PH, brazed at 1,650° to 1,690° F. for 3 to 5 minutes. Cooled to room temperature and processed as shown.

All test results shown in tables above are from tests conducted with 17-7 PH stainless steel.

Conventional flat tensile coupons of PH 15-7 Mo stainless steel were processed through the step-age cycle of the present invention with 17-7 PH brazed panels. Results are shown in table below.

| A. 17-7 PH |              |              |               | B. PH 15-7 Mo |              |               |  |
|------------|--------------|--------------|---------------|---------------|--------------|---------------|--|
| No.        | Y,<br>k.s.i. | U,<br>k.s.i. | E,<br>Percent | Y,<br>k.s.i.  | U,<br>k.s.i. | E,<br>Percent |  |
| 1.-----    | 174.8        | 190.4        | 6.5           | 187.1         | 193.6        | 6.3           |  |
| 2.-----    | 166.2        | 182.9        | 8.0           | 189.0         | 192.0        | 4.8           |  |
| 3.-----    | 173.2        | 180.2        | 7.5           | 188.8         | 192.5        | 5.0           |  |
| 4.-----    | 175.8        | 182.8        | 8.5           | 188.0         | 188.7        | 5.8           |  |
| 5.-----    | 168.3        | 181.6        | 8.0           | 190.7         | 193.6        | 4.6           |  |
| 6.-----    | 171.5        | 180.3        | 7.5           | 190.2         | 192.9        | 4.3           |  |
| 7.-----    | 174.4        | 186.8        | 8.0           | 190.9         | 194.2        | 4.0           |  |
| 8.-----    | 178.7        | 190.4        | 8.0           | 178.9         | 183.2        | 6.0           |  |
| Av.-----   | 172.9        | 184.4        | 7.7           | 187.3         | 191.3        | 5.1           |  |

NOTE: .010 nominal gage flat tensile specimens of 17-7 PH versus PH 15-7 Mo. Brazed 1,650° to 1,690° F. for 3 to 15 minutes. Cooled to room temperature and held for a minimum of 6 hours. Step aged. (Typical time-temperature cycle shown in Fig. A.)

Results of investigation and tests as shown above, of PH 15-7 Mo indicated that response to all processing was similar to the 17-7 PH response, with one exception. It was established that the optimum austenite conditioning temperature for PH 15-7 Mo was somewhat higher than that for 17-7 PH steel (id. 1400° F. minimum for PH 15-7 Mo).

The value of the present step-age conditioning process for semiaustenitic, precipitation hardening stainless steels is evident from data presented in the above tables. The process lends itself readily to variation of the time-at-temperature step and variation of the temperature in the first step, to the end that ductility of the object steel will be improved much more than the same steel when processed by the conventional single temperature aging procedure.

Utilization of the presently disclosed step-age process serves to make fabrication procedures of all heat treated stainless steels of the above class and character substantially easier, more economical and faster and will permit selection of the object alloys for many additional uses and applications that were heretofore precluded because of poor alloy ductility.

What we claim is:

1. An improved metallurgical conditioning process for treating semiaustenitic, precipitation hardening, stainless steel to produce a substantially more ductile alloy while retaining state-of-the-art tensile strengths and other desirable metallurgical characteristics, which process consists in the steps of:

exposing object workpiece to a temperature of from about 1400° F. to about 1700° F. for not less than about two (2) minutes and not more than about fifteen (15) minutes; then

decreasing said temperature to not more than about 80° F. and not less than about 60° F. and retaining at this temperature for at least about six (6) hours; then increasing said temperature to not more than about 1200° F. and not less than about 1000° F. for at least about fifteen (15) minutes; then

decreasing said temperature to not less than about 850° F. and not more than about 950° F. and retaining the object workpiece at such temperature for at least about one hour; and cooling to room temperature.

2. An improved metallurgical conditioning process for treating semiaustenitic, precipitation hardening, stainless steel to produce a substantially more ductile alloy while not deleteriously affecting conventional process achieved tensile strengths or other desirable metallurgical characteristics, which consists in the steps of first

exposing object workpiece to a temperature of from about 1500° F. to about 1600° F. for not less than about two (2) minutes and not more than about twelve (12) minutes; then

decreasing said temperature to not more than about 75° F. and not less than about 65° F. and retaining the workpiece at this temperature for at least about six (6) hours; then

increasing said temperature to not more than about 1150° F. and not less than about 1050° F. and maintaining workpiece at this temperature for at least about fifteen (15) minutes; then

decreasing said temperature to not less than about 860° F. and not more than about 925° F. and retaining workpiece at such temperature for at least about one hour; then

cooling to room temperature.

3. An improved metallurgical conditioning process for treating semiaustenitic, precipitation hardening, stainless steel to produce a substantially more ductile alloy while not deleteriously affecting conventional process achieved tensile strengths or other desirable metallurgical characteristics, which consist in the steps of:

exposing workpiece to a temperature of not more than about 1690° F. and not less than 1650° F. for a time period of not more than about ten (10) minutes and not less than about three (3) minutes; then said temperature being

decreased to not more than about 74° F. and not less than about 68° F. for at least about six (6) hours; then said temperature being

increased to not less than about 1075° F. and not more than about 1100° F. and workpiece retained at this temperature for at least about fifteen (15) minutes; then said temperature being

decreased to a temperature of not less than about 870° F. and not more than about 900° F. for a period of at least about one (1) hour; then

cooling to room temperature.

4. An improved metallurgical conditioning process for treating semiaustenitic, precipitation hardening, stainless steel to produce a substantially more ductile alloy while retaining state-of-the-art tensile strengths and other desirable metallurgical characteristics, which consists in the steps of:

exposing an object workpiece to a temperature of about 1675° F. for a time period of about five (5) minutes, then said temperature being

decreased to about 72° F. and there maintained for at least six (6) hours; then

increased to about 1090° F. and there maintained for at least fifteen (15) minutes; then again

decreased until a temperature of about 875° F. is reached and there maintained for at least about one (1) hour, and

cooling to room temperature.

5. An improved metallurgical conditioning process for semiaustenitic, precipitation hardening, stainless steel to produce a substantially more ductile alloy while retaining its tensile strength and other desirable metallurgical characteristics, which process consists in the steps of:

(a) exposing the object workpiece to a temperature of about 1400° F.-1600° F. for a period of about 2-15 minutes;

(b) lowering said temperature to about 60° F.-80° F. for a period of about 6 hours;

(c) elevating said temperature to about 1000° F.-1200° F. for a period of about 15 minutes;

(d) lowering said temperature to about 850° F.-950° F. for 1 hour; and then

(e) cooling to room temperature.

6. A process for materially increasing the ductility of semiaustenitic type, precipitation-hardening steels, while substantially having no adverse affect on its tensile properties, which comprises:

(a) a first step of subjecting the object steel to an austenite conditioning temperature of from about 1400° F. to about 1700° F. for a period of from about 2 minutes to about 15 minutes;

(b) lowering said temperature to substantially room temperature of from about 60° F. to about 80° F. and maintaining it thus for about 6 hours;

(c) elevating the temperature in a first aging step to

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not less than about 1050° F. and not more than about 1150° F. for a period of time not less than about 15 minutes and not more than about one (1) hour resultant to establish a substantial equilibrium between austenite being transformed into martensite and martensite reverting to austenite, wherein said austenite is greater in quantity than at the completion of said first and second steps to thereby impart ductility to object steel at the expense of its ultimate tensile strength property;

- (d) a second aging step, where temperature and time at temperature is respectively from about 850° F. to about 950° F. for a period of from about 1 hour to about 24 hours, whereby hardening is imparted by change in the intermetallic compounds at the

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grain boundaries, said grain size being finer, and ultimate tensile strength largely regained with the ductility already achieved remaining substantially unchanged from said first aging; and  
(e) cooling said steel to room temperature.

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