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HEAT TREATMENT

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This invention relates to a method of heat treating corrosion resistant nickel-base alloys containing molybdenum.

Nickel-base alloys containing about 10% to 40% molybdenum, which alloys sometimes contain one or more additional elements such as chromium, tungsten, vanadium, and iron in proportions up to 5% or 10%, are resistant to corrosion, and are widely used in the fabrication of articles and apparatus required to resist corrosion, for example, by hydrochloric acid. Ordinarily, alloys of this type are annealed by rapidly cooling them from a temperature which depends to some extent on the composition of the alloy but is above about 1100° C. and are used in the annealed condition.

It has been observed that when nickel-molybdenum alloys are exposed, even for a short period of time, to temperatures within the range of about 300° C. to 700° C., after having been annealed, the corrosion resistance of the alloys is seriously detrimentally affected. The effect of exposure to this range of temperatures is well illustrated where a weld has been made in such alloys. If a joint is made between two plates of the material, using as filler material an alloy of the same composition, the deposited weld metal is resistant to corrosive attack, but those portions of the plates on either side of the weld and adjacent to it which have been heated by conduction to about 300° C. to 700° C. are severely attacked, while those portions of the plates remote from the weld are resistant to attack. This effect of elevated temperatures on the corrosion resisting properties of the alloy presents a serious problem.

It is an important object of this invention to treat alloys of the class described to improve their resistance to corrosion and to decrease or prevent loss of corrosion resistance upon exposure to elevated temperatures. Another object of the invention is to provide a heat treatment which prevents excessive corrosion adjacent to welds in welded articles fabricated from alloys of this type. A further object is to heat treat such alloys to improve their physical properties not only at ordinary temperatures, but also upon and after exposure to temperatures within the range of 300° C. to 700° C.

These and other objects are achieved by the present invention which is based on the discovery that if fully annealed alloys which normally are detrimentally affected by exposure to the detrimental temperature range between 300° C. and 700° C. are heated to a temperature (intermediate between annealing temperatures and the detrimental temperature range) between about 900° C. and 1175° C. for about 2 to 72 hours they become "stabilized," their physical and corrosion-resisting properties no longer being subject to deterioration on exposure to elevated temperatures.

Accordingly, the invention is a method of heat treating such alloys, for example nickel-molybdenum alloys containing about 10% to 40% (preferably 15% to 30%) molybdenum, with or without minor amounts of other alloying elements, which comprises heating the alloys at an elevated stabilizing temperature between 900° C. and 1175° C., for 2 to 72 hours. The heated alloys may be cooled in air. Preferably, the temperature employed is between 1020° C. and 1065° C., and the material is maintained at such temperature for from 2 to 24 hours. When a temperature near the lower end of the range is chosen, the alloy or article being treated should be heated for a longer time than if a temperature near the higher end of the range is chosen, and relatively large articles should be maintained at the treating temperature for a longer time than smaller articles. When the alloys are stabilized by sufficient exposure to stabilizing temperatures, the effect on corrosion resistance of either previous or subsequent exposure to temperatures within the range of 300° C. to 700° C. is counteracted.

The invention also includes a corrosion-resistant welded article fabricated from a nickel-base alloy containing molybdenum, such article being resistant to preferential corrosion in the weld zone, its corrosion resistance being substantially uniform over the welded surface and the surface adjacent the weld zone.

Tests have been made on nickel-molybdenum alloys of several different compositions in which the specimens under test were exposed to boiling concentrated hydrochloric acid. Certain of the specimens were tested in the annealed condition. Others were tested after they had been annealed and then exposed to temperatures within the damaging range. Still other specimens were annealed, given the heat treatment of the invention, and then subjected to temperatures between 300° C. and 700° C. It was found by such tests that alloys which had not been given the heat treatment of the invention but had been exposed to elevated temperatures suffered a loss in weight of as much as nine times the loss in weight of similar alloys not exposed to those temperatures, while alloys which had been heat treated and

then subjected to temperatures between 300° C. and 700° C. were fully as corrosion resistant as alloys which had not been subjected to those temperatures. Further, the corrosion-resistance of heat treated specimens which had not been subjected to elevated temperatures before test was better than that of specimens not heat treated. The results of these tests are given in Table I.

TABLE I

Corrosion rates, mg./sq. cm./hr. in boiling concentrated HCl after preliminary heat treatment and subsequent holding for one week at temperature. Air cooling except where otherwise noted as W. Q. (=water quenched)

Preliminary heat treatment	Room temp.	300° C.	400° C.	500° C.
Composition A—20% Mo., 20% Fe, 0.3% V, rest principally Ni:				
W. Q. from 1160° C.	1.54	1.92	4.0	14.3
W. Q. from 1160° C., 6 hr. at 1020°C.	0.73	0.87	0.81	0.69

	600° C.	700° C.
Composition B.—30% Mo, 5% Fe, 0.3% V, rest principally Ni:		
W. Q. from 1160° C.	0.17	0.37
W. Q. from 1160° C., 6 hr. at 1020° C.	0.11	0.17

Tensile tests of samples of a nickel-base alloy containing 20% molybdenum and 20% iron conducted at 500° C., after the test pieces had been held at that temperature for one week, indicated that the physical properties of such alloys are considerably improved by the heat treatment of the invention. Results of such tests are shown in Table II. Specimen A was annealed by water quenching from 1160° C. Specimen B was annealed in the same manner and was then heated at 1020° C. for 6 hours and air cooled. Both specimens were then held for one week at 500° C.

TABLE II

Results of tensile tests conducted at 500° C. of Ni-base alloys containing 20% Mo and 20% Fe

	Yield point	Tensile strength	Elongation	Reduction of area
	P. s. i.	*P. s. i.*	*Percent*	*Percent*
Specimen A	40,000	76,500	16	20.2
Specimen B	37,000	98,000	29.5	26.8

It is an important advantage of the invention that articles may be fabricated by welding from nickel-base alloys containing molybdenum without the danger of such articles suffering a loss of corrosion resistance in the vicinity of the welds. When apparatus is to be made from such alloys by welding, it is preferable first to fabricate the apparatus and then to heat treat it as a whole. However, where this is impracticable the various parts of the article or apparatus may be heat treated before they are welded, and, in such case, no heat treatment of the welded article is necessary. If such apparatus is fabricated from annealed alloys, it is unnecessary to anneal the apparatus.

While in the above examples of the invention, specific reference has been made to nickel-molybdenum alloys, the presence of chromium or tungsten or both does not substantially alter the effect of the heat treatment described. Chromium may be included in such alloys up to about 20% and tungsten may also be included up to about 7%. If chromium is present, the maximum proportion preferable is 15%, and if tungsten is present, the maximum proportion preferable is 5%. Alloys containing chromium or tungsten or both should be heat treated near the higher limits of the temperature range defined. Iron may be included in the alloys as a diluent in proportions up to about 25%, preferably between 5% and 20%. Minor proportions of manganese, silicon, vanadium, carbon, zirconium, tantalum, columbium, and titanium may also be included in the alloys with little effect on the benefit derived from the heat treatment.

I claim:

1. Method of treating nickel-base alloys containing 10% to 40% molybdenum which comprises heating such alloys, after they have been fully annealed, at a temperature between 900° C. and 1175° C. for about 2 to 72 hours.

2. Method of treating nickel-base alloys containing 10% to 40% molybdenum which comprises heating such alloys, after they have been fully annealed, at a temperature within the range of 1020° C. to 1065° C. for about 2 to 24 hours.

3. Method of treating nickel-base alloys containing 10% to 40% molybdenum which comprises fully annealing such alloys and then heating the annealed alloys at a stabilizing temperature between 900° C. and 1175° C. for about 2 to 24 hours.

4. Method of treating nickel-base alloys containing 10% to 40% molybdenum which comprises rapidly cooling such alloys from a temperature above 1100° C. and then heating the alloys at an annealing temperature within the range of 1020° C. to 1065° C. for about 2 to 24 hours.

5. A corrosion-resistant welded article fabricated from a nickel-base alloy containing 10% to 40% molybdenum, said article being in the condition produced by heating within the range of stabilizing temperatures between 900° C. and 1175° C., and the corrosion resistance of such article being substantially uniform over the welded surface and the surface adjacent the weld zone.

6. A welded article farbricated from a nickel-base alloy containing about 10% to 40% molybdenum, such article being in the condition produced by heating at stabilizing temperatures within the range of 900° C. to about 1065° C. and being resistant to preferential corrosion at the areas adjacent the weld zones when subjected to corrosive media which normally would cause corrosion to take place at a more rapid rate at such areas than at areas remote from the weld zones.

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