

1

2,959,480

**CORROSION RESISTANT NICKEL-MOLYBDENUM ALLOYS**

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The present invention relates to corrosion resistant alloys and, more particularly, to nickel-molybdenum alloys characterized by a high degree of resistance to corrosive media such as hydrochloric, sulphuric phosphoric and other acids.

It is well known that nickel-molybdenum-alloys are widely used for the manufacture of chemical plant and equipment which is required to withstand corrosive attack by hydrochloric, sulphuric, phosphoric and other acids. Broadly, the alloys contain from 10 to 40% molybdenum and from 2 to 25% iron, the balance being nickel and small amounts of carbon, silicon and manganese. Alloys of this kind at present on the market contain from 26 to 30% molybdenum, from 4 to 7% iron, from 0.1 to 1.5% silicon and from 0.1 to 1.0% manganese, the balance being nickel and impurities.

As will be readily recognized by those skilled in the art, these alloys frequently have to be fabricated by welding. The fabrication operation entails localized heating of the parts to be joined to the temperature of fusion, and has the unfortunate result that the material in a zone adjacent or nearly adjacent to the fused zone is rendered susceptible to intergranular corrosion in some corrosive media, especially in hot, strong hydrochloric acid, so that the equipment becomes useless for the purpose for which it was intended.

A review of the literature, e.g., U.S. Patents Nos. 1,375,082 and 1,375,083, indicates that alloys containing about 80% to 90% nickel, 10% molybdenum and up to 10% iron were considered useful for the purpose of resisting the corrosive attack of acids. According to the disclosure set forth in U.S. Patent No. 1,710,445, the corrosion resistance could be enhanced by broadening the molybdenum content to about 15% to 40% of the alloy. The latter alloy optionally included up to 4% manganese, up to about 1.5% silicon for purposes of fluidity, about 0.3% vanadium as a scavenger and up to about 0.5% carbon. Such alloys were apparently considered unsatisfactory because they required a heat treating operation as indicated in U.S. Patent No. 1,836,317. In this latter patent it was proposed that the necessity of employing a heat treating operation was obviated if the carbon content of the alloys was kept below 0.6%, e.g., less than 0.2%. However, the patentee indicated that the alloys were susceptible only to a moderate amount of working, e.g., forging or rolling.

The prior art apparently still considered such alloys unsatisfactory. For example, in U.S. Patent No. 2,109,285 it is disclosed that the silicon and carbon contents usually employed lessened the corrosion resistance and that the contents thereof should be kept below 0.10% and 0.05%, respectively. It was considered that iron, chromium, manganese, copper and vanadium did not enhance corrosion resistance. In U.S. Patent No. 2,196,699 it was proposed to incorporate 0.08% to 6% antimony in the prior art alloys for the purpose of increasing the corrosion resistance properties thereof. After a period of twenty years and many proposals, the art was still confronted with the problem of commercially providing a satisfactory alloy capable of exhibiting the desired re-

2

sistance to corrosive effects of acids in heat affected zones.

As mentioned hereinabove, the metallurgist now appreciates that the corrosion resistance of such alloys was seriously impaired because of deleterious intergranular corrosion resulting from fabrication operations. As far as applicant is aware, the only known way of overcoming this problem is described in U.S. Patent No. 2,237,872, and consists of a special heat treating process comprising heat treating the alloys for upwards of 2 hours but not exceeding 72 hours within the range of 900° C. and 1175° C. Such heat treatment is, however, difficult to apply in practice owing to the practical problems involved in heat treating large fabricated pieces of equipment and the distortion developed during heat treatment. In fact, as referred to hereinabove with respect to U.S. Patent No. 1,836,317, it is commercially desirable to avoid heat treating operations which must be applied to the fabricated commercial equipment to be used for handling hot, strong acids such as hydrochloric acid.

In addition to the problem of intergranular corrosion described hereinbefore, other problems have confronted the art such as those involved in hot working proposed alloys prior to the fabrication of equipment therefrom. Many alloys were so susceptible to cracking during hot working as to be useless for practical, commercial use in wrought forms.

Thus, hitherto, there still existed the demand for and need of an alloy characterized not only by a high degree of resistance in corrosive media such as hydrochloric acid, sulphuric acid, etc., but which (1) could be hot worked without the incurrance of cracking, (2) could be easily fabricated, as by welding, such that when subjected to the action of corrosive acids the alloy would not undergo the deleterious intergranular corrosion in heat affected zones which characterized fabricated equipment made from alloys of the prior art, and (3) did not require cumbersome, tedious and expensive heat treatments to condition fabricated equipment made of the alloy against the intergranular corrosive attack described hereinabove.

Although attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as I am aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that nickel-molybdenum alloys containing special amounts of vanadium are highly resistant to corrosive media such as hydrochloric acid, sulphuric acid, phosphoric acid and other acids, are hot workable, are easily fabricated as by welding, and do not require heat treatment subsequent to fabrication to minimize intergranular corrosive attack in heat affected zones when subjected to a corrosive environment.

It is an object of the present invention to provide nickel-molybdenum alloys which are resistant to the influence of corrosive media such as hydrochloric acid, sulphuric acid, phosphoric acid, etc.

Another object of the invention is to provide corrosion-resistant nickel-molybdenum alloys which can be hot worked, e.g., by forging or rolling.

The invention still contemplates providing nickel-molybdenum alloys which do not undergo deleterious intergranular corrosion in heat affected zones when used as fabricated chemical processing equipment and subjected to attack of corrosive media such as hot hydrochloric acid.

It is a further object of the invention to provide nickel-molybdenum alloys which do not require heat treatment to resist intergranular corrosive attack in heat affected zones when used as chemical processing equipment.

The invention further contemplates providing hot workable, nickel-molybdenum alloys capable of withstanding in heat affected zones the intergranular corrosive attack of corrosive media such as hydrochloric acid, sul-

phuric acid, phosphoric acid and other acids without requiring heat treatment to minimize intergranular corrosive attack.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention provides nickel-molybdenum alloys containing special amounts of vanadium and which are highly resistant to corrosive media such as hydrochloric acid, sulphuric acid, phosphoric acid and other acids, are hot workable, and do not undergo deleterious intergranular corrosion in heat affected zones when used as fabricated structures in chemical processing equipment. These alloys contain by weight about 20% to about 35% molybdenum, up to about 15% iron, vanadium in an amount of 1.2% to 2.3%, the balance being essentially nickel. The vanadium content should be not less than 1.1% and particularly good results are obtained concerning both corrosion resistance and hot workability in accordance with the invention with alloys containing 26% to 30% molybdenum, up to 7% iron, vanadium in an amount of 1.2% to 2.3%, e.g., 1.8% to 2.1%, the balance being nickel.

The molybdenum content of these vanadium-containing alloys according to the invention is between 20 and 35%. With less than 20% molybdenum the general corrosion resistance of the alloy is very poor. As the molybdenum content increases the corrosion resistance increases, but so does the difficulty of hot-working the alloys, and the upper limit of 35% is imposed by the extreme difficulty of forging the alloys with higher molybdenum contents with an economic yield. The best combination of corrosion resistance and forgeability is obtained with from 26 to 30% molybdenum.

Chromium has an adverse effect on forgeability, so the alloys are preferably chromium-free, although a little chromium, i.e., up to 5%, can be tolerated.

Some silicon is commonly present, as it is added as a deoxidiser, but silicon also has an adverse effect on forgeability, and the silicon content should not exceed 1.0%. Preferably it does not exceed 0.8%.

If each of the elements molybdenum, vanadium, silicon and chromium is present simultaneously in an amount at or close to the maximum value given above, the alloy may still be virtually unforgeable. It is therefore necessary to impose a further limitation and specifically to ensure that the value of the expression

$$2(\% \text{ Mo}-20)+5(\% \text{ V}-1.2)+10(\% \text{ Si}-0.2)+\% \text{ Cr}$$

does not exceed 30.

Some of the molybdenum may be replaced by an equal percentage of tungsten, since tungsten is beneficial in increasing the resistance to corrosion after welding. However, tungsten renders the alloy more difficult to forge, and it should not amount to more than 10% of the alloy.

When tungsten is present the expression defining the overall limitation in the composition of the alloy is modified, and in fact the expression

$$2(\% \text{ Mo}+\% \text{ W}-20)+5(\% \text{ V}-1.2)+10(\% \text{ Si}-0.2)+\% \text{ Cr}$$

must not exceed 30. Subject to the limitations expressed above the vanadium content should be as high as possible.

The iron content of the alloys should be low, as the corrosion resistance falls with increasing amounts of iron in the alloys. It is convenient to use ferro-alloys in making the alloys of the invention, so iron is commonly present, but for best results there should not be more than 7% iron. However, good corrosion resistance is obtained with 10% and reasonably good resistance up to a maximum of 15% iron.

Cobalt may be present as an impurity in the nickel, and larger amounts up to 5% may replace part of the nickel.

The carbon content is preferably as low as possible since the corrosion resistance falls off rapidly with increasing carbon content. It should not exceed 0.15%, though 0.25% may be tolerated if a lower level of corrosion resistance is acceptable, that is to say, if the alloy is not to be subjected in use to highly corrosive attack.

Manganese is another element commonly used as a deoxidizer and therefore generally present. The manganese content may be up to 3%, but is preferably from 0.1 to 0.5%.

Aluminium may be used as a deoxidiser and may then be present in the resultant alloy in amounts of 0.1 to 0.2%. It may be present up to 2.0% without harm.

Traces of other elements, such as calcium, added to deoxidise and improve the workability of the alloys may be present. Copper, which has a very deleterious effect upon workability, should so far as possible be absent, but can be tolerated up to 0.5%.

The balance of the alloy except for impurities and residual deoxidisers is nickel.

I have also found that the resistance to intergranular corrosion produced by the vanadium increases with increase in the molybdenum content, and to some extent also with increase in the silicon content. By using molybdenum contents in the upper part of the preferred range, therefore, we can obtain substantially the optimum results with rather less vanadium than would otherwise be required.

The improvement brought about by means of the invention is clearly shown by the results obtained with alloys treated to simulate the effect of welding. In this treatment one end of a forged round bar of the alloy 4 inches long by 1/2 inch diameter was fused in an oxy-acetylene flame, the bar being exposed to the flame for about 15 seconds and the metal fused for about 3 seconds, and then air-cooled. A test piece 1/2 inch long and 3/8 inch in diameter was then machined from the heated end, immersed in a boiling 10% hydrochloric acid solution and then sectioned longitudinally. Some specimens were immersed for 28 days and others for 61 days. The depth of penetration of the corrosive attack was measured from each side, giving two values for each specimen. In all the alloys tested the rate of corrosion under similar conditions in regions not affected by the heat is less than 0.001 inch in 28 days.

Some of the alloys thus treated and tested were free from or contained too little vanadium. These are identified by the letters A, B, and C. Others were in accordance with the invention and are identified by numbers. The compositions of the alloys and the results obtained were as follows:

No.	Composition—Percent					Depth of Corrosion (Inches) After—			
	Mo	Fe	Si	C	V	28 days		61 days	
A.....	26.8	5.15	0.31	0.01	-----	0.029	0.028	-----	-----
B.....	27.6	5.23	0.40	0.02	0.52	0.021	0.016	0.033	0.030
C.....	27.8	5.11	0.39	0.01	0.96	0.014	0.009	-----	-----
1.....	28.0	5.27	0.41	0.02	1.48	0.005	0.002	0.010	0.009
2.....	26.1	5.25	0.48	0.02	2.05	0.004	0.003	0.008	0.008
3.....	25.4	5.00	0.07	0.02	2.00	0.007	0.004	0.023	0.022
4.....	28.9	2.04	0.34	0.02	1.97	0.002	0.002	0.009	0.009
5.....	30.0	1.95	0.25	0.02	2.03	N11	N11	0.004	0.003

The beneficial effect of increase in the molybdenum content is shown by comparison of alloys Nos. 3, 4 and 5, and that of silicon by comparison of alloys Nos. 2 and 3, particularly by the figures of corrosion after 61 days.

The fabricated and welded plant or equipment made from our alloys is not heat-treated after being welded, since the vanadium content renders this unnecessary. Thus such plant or equipment made from welded alloys is used in the as-welded state in contact with hydrochloric acid or other corrosive medium known normally to produce intergranular corrosion in the absence of heat-treatment.

The alloys may, however, advantageously be subjected to a carbide-coarsening heat-treatment before being welded in order to render the molybdenum carbide less readily taken into solution on the subsequent welding operation. Such a heat treatment may comprise heating the alloy to a temperature above 1175° C. and below the solidus temperature (approximately 1315° C.), cooling to a temperature within the range 1150° C. to 900° C. and maintaining within this temperature range long enough to allow the carbon in solution to re-precipitate on existing carbide particles. The alloy should be reasonably quickly cooled from the latter temperature e.g., by air cooling.

For example the alloy may be heated at 1250° C. for 20 minutes, cooled in the furnace to 1000° C. and air-cooled to room temperature. Alternatively, the alloy after heating at 1250° C. may be rapidly cooled to a temperature within the range 1150° C. to 900° C. and maintained at this temperature for a period of time e.g., 1 hour, long enough to coarsen the carbides and then cooling, e.g., in air or water.

A further alternative consists in oscillating the temperature of the furnace in which the alloy is being treated to values above 1175° C. and then to values within the range 1150° C. to 900° C. Finally the alloy is air cooled or otherwise quickly cooled from the latter temperature.

On the other hand any heat treatment serving to precipitate carbides in a finely dispersed state, e.g., heating to 1200° C. followed by air-cooling, should be avoided.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A corrosion-resistant, hot-workable alloy suitable for use in chemical plant equipment, said alloy being further characterized in that it does not undergo deleterious intergranular corrosion in heat affected zones when subjected in the as-welded condition to attack by corrosive media, said alloy consisting essentially of 26% to 30% molybdenum, up to 10% iron, 1.8% to 2.1% vanadium, up to 0.8% silicon, 0.01% to 3% manganese, up to 0.25% carbon, up to 5% cobalt, and the balance essentially nickel.

2. A new and improved nickel-base alloy characterized by the properties of corrosion resistance, hot workability and resistance to deleterious intergranular corrosion in heat affected zones when used in the as-welded condition and subjected to attack by corrosive media, said alloy consisting essentially of 26% to 30% molybdenum, up to 15% iron not less than 1.1% and up to 2.3% vanadium, up to 1% silicon, up to 3% manganese, up to 0.25% carbon, and the balance essentially nickel.

3. A corrosion-resistant, hot-workable alloy suitable for use in chemical plant equipment, said alloy being further characterized in that it does not undergo deleterious intergranular corrosion in heat affected zones

when subjected in the as-welded condition to attack by corrosive media, said alloy consisting essentially of about 20% to about 35% molybdenum, up to about 15% iron, 1.2% to 2.3% vanadium, up to 1% silicon, up to 3% manganese, up to 0.25% carbon, up to 5% cobalt, up to 5% chromium, up to 2% aluminum, and the balance essentially nickel, the molybdenum, vanadium, silicon and chromium being present in such amounts that the relationship expressed by the following formula is satisfied:

$$2(\% \text{ Mo}-20)+5(\% \text{ V}-1.2)+10(\% \text{ Si}-0.2)+\% \text{ Cr}$$

equals a numerical value not exceeding 30.

4. A corrosion-resistant, hot-workable nickel-base alloy suitable for use in chemical plant equipment and being further characterized in that it resists intergranular corrosion in heat affected zones when subjected in the as-welded condition to attack by corrosive media, said alloy consisting essentially of about 20% to about 35% molybdenum, up to about 15% iron, 1.2% to 2.3% vanadium, up to 1% silicon, up to 3% manganese, up to 0.2% carbon, up to 5% cobalt, and the balance essentially nickel.

5. A corrosion-resistant, hot-workable alloy suitable for use in chemical plant equipment, said alloy being further characterized in that it does not undergo deleterious intergranular corrosion in heat affected zones when subjected in the as-welded condition to attack by corrosive media, said alloy consisting essentially of about 20% to about 35% molybdenum plus tungsten, the amount of tungsten not exceeding 10%, up to about 15% iron, 1.2% to 2.3% vanadium, up to 1% silicon, up to 3% manganese, up to 0.25% carbon, up to 5% cobalt, up to 5% chromium, up to 2% aluminum, and the balance essentially nickel, the molybdenum, tungsten, vanadium, silicon and chromium being present in such amounts that the relationship expressed by the following formula is satisfied:

$$2(\% \text{ Mo}+\% \text{ W}-20)+5(\% \text{ V}-1.2)+10(\% \text{ Si}-0.2)+\% \text{ Cr}$$

equals a numerical value not exceeding 30.

6. A method of improving the resistance to intergranular corrosion of an alloy consisting essentially of about 26% to about 30% molybdenum, up to 7% iron, 1.2% to 2.3% vanadium, up to 0.8% silicon, up to 0.5% manganese, up to 0.15% carbon and the balance essentially nickel, which comprises heating said alloy at a temperature above about 1175° C. and below the solidus temperature of said alloy, cooling to a temperature of between about 1150° C. to about 900° C. and maintaining this temperature condition for a period sufficient for the carbon in solution to re-precipitate on existing carbide particles, and then further cooling said alloy.

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