United States Patent Office

3,723,196

Patented Mar. 27, 1973

1

3,723,196

AGE-HARDENING IRON-BASE ALLOY WITH IMPROVED TOUGHNESS

William J. Murphy and Gerald J. Spaeder, Monroeville Borough, Pa., assignors to United States Steel Corporation

No Drawing. Filed June 18, 1970, Ser. No. 47,611

Int. Cl. C22c *39/10, 39/50*

U.S. Cl. 148—31 7 Claims

ABSTRACT OF THE DISCLOSURE

A maraging steel alloy having, in the aged condition, a yield strength in the 200,000 to 300,000 p.s.i. range and a superior toughness, exhibiting Charpy V-notch values in excess of 100 ft.-lbs. at 80° F. The alloy essentially contains less than 0.005% each of carbon and sulfur, 15–20% nickel, 5–10% cobalt, 3–8% molybdenum, up to 1.5% titanium, up to 0.5% aluminum, and the balance iron with normal incidental impurities. In another embodiment, toughness can be increased appreciably with an insignificant sacrifice in strength by subsituting tungsten for molybdenum.

BACKGROUND OF THE INVENTION

The prior art is well familiar with a certain group of low-carbon, high-nickel martensitic wrought alloy steels known as "maraging steels." Unlike iron-carbon martensite, these iron-nickel martensitic alloys are relatively soft and ductile in the quenched condition, and became strong, hard and tough when tempered or aged. These alloys are therefore readily formable and weldable, and yet can be aged to exhibit yield strengths up to 300,000 p.s.i. and at the same time provide a relatively high degree of ductility and toughness. In addition to these physical properties, the maraging steel alloys have an exceptional resistance to stress-corrosion cracking, and can be easily welded in the high-strength aged condition.

The first maraging steel used commercially contained about 0.01% carbon, 20 or 25% nickel, and 1.5 to 2.5% titanium and 0.3% aluminum. The more recent improved maraging steels however contain 0.01 to 0.03% carbon, about 18% nickel, 7 to 8% cobalt, about 5% molybdenum, and less than 1% titanium. The latter is disclosed in U.S. Pat. 3,093,519, R. F. Decker et al., June 11, 1963.

Although the 18% nickel maraging steel does provide a superior combination of all the desirable physical properties, there has been continuing efforts to improve this alloy, particularly its impact toughness.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a new and improved maraging steel alloy which will exhibit a heretofore unattainable combination of physical properties. Specifically, the alloy of this invention can be aged to produce a greater degree of toughness, impact toughness and ductility with little sacrifice in strength and other desired properties. The alloy of this invention is therefore comparable in all respects to the prior art 18% nickel maraging steel except that it provides a substantially greater degree of toughness. Broadly, this improved maraging steel is substantially like the prior art 18% nickel maraging steel chemically except that carbon and sulfur must be critically controlled to levels below 0.005% each. In accordance with another embodiment, toughness can be increased appreciably without a significant sacrifice in strength by partially or completely substituting tungsten for the molybdenum in amounts of from 3 to 8%.

Since the commercial supply of molybdenum has been rather limited at times in the past several years, the second embodiment provides the added commercial and economic advantage of substituting more readily available tungsten for molybdenum.

2

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In its broad aspect, the maraging steel of this invention has a composition, in weight percentages, as follows:

	Percent
Carbon	Less than 0.005.
Sulfur	Less than 0.005.
Manganese	0.1 max.
Silicon	0.1 max.
Nickel	15 to 20.
Cobalt	5 to 10.
Molybdenum or tungsten	3 to 8.
Titanium	1.5 max.
Alumnium	0.5 max.
Iron	(1)

[1] Balance with incidental impurities.

As noted, the above composition differs essentially from the prior art 18% nickel maraging steel in critically limiting the carbon and sulfur contents to less than 0.005%. Although improvement in the steel's toughness is realized within the above composition range, it can be further optimized by completely substituting tungsten for the molybdenum. In addition to restricting the residuals carbon and sulfur, the alloy additives are preferably restricted to about 8.0% tungsten or molybdenum, about 18% nickel and about 10% cobalt as a compromise between optimum physical properties and economy.

In order to derive the benefits of this invention, it is essential that carbon as well as sulfur must be limited to amounts below a critical 0.005% each. The fact that sulfur is detrimental in the 18% nickel maraging steel has been documented in the prior art. Specifically, Novak and Diran, "What Are the Effects of Residual Elements in Maraging Steels?" Journal of Metals, March 1963, pp. 200–204, reported that sulfur will reduce the toughness of the maraging steel substantially in proportion to its concentration. They therefore conclude that maraging steels should contain less than 0.010% sulfur and preferably less than 0.007 or 0.005%. Carbon, on the other hand, in amounts up to 0.3%, has not been considered detrimental in the prior art maraging steels and, in fact, is reported to be beneficial in the 18% nickel maraging steel in amounts from 0.01 to 0.03%.

Although molybdenum and tungsten are equivalent alloying agents for some alloying purposes, tungsten has never been considered as a comparable substitute for molybdenum in maraging steels. On the contrary, a critical co-action between molybdenum and cobalt has always been deemed essential to achieve the superior properties characteristic of the newer improved maraging steels. Although pior art investigators have reported that tungsten in amounts up to 1.15% has essentially no effect on maraging steels, in larger concentrations tungsten is known to affect to the aging reaction and to increase strength, but at the expense of reducing toughness appreciably. As an example of such prior art teaching, see C. J. Novak and L. M. Diran, supra.

In contrast to the above prior art teachings, we have found that restricting carbon as well as sulfur to levels below 0.005% will improve the steel's toughness; and further that the substitution of tungsten for molybdenum in the 18% nickel maraging steel will not reduce toughness of the wrought and aged product, but will in fact substantially enhance toughness if the carbon content and sulfur content is maintained below 0.005% each. At the prior art carbon levels of 0.010 to 0.030%, tungsten in amounts exceeding 1.15% does indeed reduce the product's toughness. However, when carbon is below 0.005%, the combined effect of tungsten and low carbon will have an unexpected effect of increasing toughness. To appreciate this benefit, it is of course further essential that sulfur, like carbon, must be below 0.005%.

On an atomic weight basis, it would normally be expected that twice as much tungsten would be required to replace a given weight of molybdenum and attain a comparable strength level. Therefore, even if one should anticipate substitution of tungsten for molybdenum in a conventional 250-grade maraging steel having 3 to 6% molybdenum, it would require the use of 6 to 12% tungsten to effect a comparable job. Contrary thereto, the alloy of this invention contains only 3 to 8 weight percent tungsten, an amount equal to almost half the atomic weight percent molybdenum in the 250-grade maraging steel. For optimum results, i.e., optimum toughness with only minimal sacrifice in strength, the higher concentrations of tungsten are preferred, i.e., about 7 to 8%.

As in prior art maraging steels, elements frequently referred to as "auxiliary hardeners," e.g. titanium, aluminum, columbium and vanadium, may be added to the alloy to cooperate with the tungsten or molybdenum in providing strength. If present in excessive amounts, however, these elements may over-harden the alloy, thereby appreciably reducing ductility. Nevertheless, inclusion of these additives, particularly about 0.6 to 1.5% titanium and about 0.5% aluminum is preferable because optimum physical properties can be achieved at lower tungsten contents of about 5%.

To more graphically illustrate the advantages of this invention, a few of our tests, and the results thereof, are exemplified below.

In one test, two maraging steels were compared. Sample 1Mo was a conventional 250-grade maraging steel as is commercially available. The others, Samples 2W and 3W were substantially identical thereto, except that they contained tungsten in place of molybdenum. Each steel has the approximate composition as follows: 0.02% carbon, 0.05% manganese, 0.001% phosphorus, 0.005% sulfur, 0.06% silicon, 18% nickel, 9% cobalt, 0.4% titanium, and 0.05% aluminum (0.3% Sample 3W). In addition to the above, Sample 1Mo had 4.75% molybdenum, whereas Samples 2W and 3W had 5% tungsten. The steels were processed identically in accordance with prior art practices and aged for 3 hours at 900° F. Table I below gives the resulting mechanical properties for each sample.

TABLE I.—LONGITUDINAL MECHANICAL PROPERTIES OF SAMPLES 1Mo, 2W AND 3W

Sample	Yield strength (0.2% offset), k. s.i.	Tensile strength, k. s.i.	Elongation in 1 inch, percent	Reduction in area, percent	CVN energy at 80° F., ft.-lb.
1Mo	250	253	11.0	55.4	20, 21
2W	240	253	10.0	52.4	14, 12
3W	257	262	10.0	54.5	10, 17

It is readily seen from the above table that the mere substitution of tungsten for molybdenum in a conventional 250-grade maraging steel did not improve the mechanical properties. Yield strengths and tensile strengths were comparable, but toughness in the two tungsten containing samples was appreciably lower as expected.

In contrast to Table I above, the physical properties of the alloys of this invention are shown in Tables II and III below. Table II shows the physical properties of a 250-grade maraging steel having carbon and sulfur contents below 0.005% in accordance with the first embodiment of this invention. The samples in Table II all had substantially the same composition approximately as follows: 0.004% carbon, 0.02% manganese, 0.001% phosphorus, 0.0015% sulfur, 0.02% silicon, 17.5% nickel, 8% cobalt, 0.4% titanium, 0.08% aluminum and 4.8% molybdenum. The samples shown in Table III were identical to those shown in Table II except that they contained 5.1% tungsten instead of 4.8% molybdenum in accordance with the second embodiment of this invention. Except for variable annealing times as noted in the tables, all samples were processed identically.

TABLE II

Sample	Annealing time at 900° F., hours	Yield strength (.02% offset), k. s.i.	Tensile strength, k. s.i.	Elongation in 2 inches, percent	Reduction in area, percent	CVN Energy at 80° F., ft.-lb.
4Mo	0	107	145	[1] 19.5	83.9	N.D.
	1	229	239	15.0	67.5	86, 82
	3	246	257	12.0	60.5	65, 77, 67
	8	262	269	12.5	60.5	47, 32
	16	263	272	12.0	58.8	36, 30

See footnotes at end of Table III.

TABLE III

Sample	Annealing time at 900° F., hours	Yield strength (.02% offset), k. s.i.	Tensile strength, k. s.i.	Elongation in 2 inches, percent	Reduction in area, percent	CVN Energy at 80° F., ft.-lb.
5W	0	110	136	[1] 19.0	84.6	N.D.
	1	200	207	15.0	68.7	120, 124
	3	216	221	14.5	68.5	109, 112, 127
	8	226	232	14.0	68.0	105, 103
	16	226	236	14.0	68.0	97, 89

[1] Elongation in 1 inch (percent).

NOTE.—N.D.=Not Determined.

Comparing Table II with Table I, it is readily seen that the low carbon content, as taught herein, does substantially increase toughness, with little effect on strength. With a three hour anneal at 900° F., the low carbon samples had CVN values of 65, 77 and 67, as compared to 20 and 21 for the prior art steel.

Comparing Table III with Tables I and II, it is seen that the combination of low carbon and tungsten in place of molybdenum had an even greater effect in improving toughness. The three hour anneal samples at 900° F. had CVN values of 109, 112 and 127.

We claim:

1. A maraging steel alloy consisting essentially of 3 to 8% molybdenum, 15 to 20% nickel, 5 to 10% cobalt, less than 0.005% carbon, less than 0.005% sulfur and the balance essentially iron plus incidental impurities in

conventional residual amounts, said steel alloy, in the aged martensitic condition, characterized by a yield strength within the range 200 to 300 k.s.i. and a Charpy V-Notch Energy at 80° F. above 30 ft. lbs.

2. The maraging steel alloy of claim 1 containing about 8% molybdenum, about 18% nickel and about 10% cobalt.

3. The maraging steel alloy of claim 1 further containing up to 1.5% titanium and up to 0.5% aluminum.

4. A maraging steel alloy consisting essentially of 3 to 8% tungsten, 15 to 20% nickel, 5 to 10% cobalt, less than 0.005% carbon, less than 0.005% sulfur and the balance essentially iron plus incidental impurities in conventional residual amounts, said steel alloy, in the aged martensitic condition, characterized by a yield strength within the range 200 to 300 k.s.i. and a Charpy V-Notch Energy at 80° F. above 50 ft. lbs.

5. The maraging steel alloy of claim 4 containing about 8% tungsten, about 18% nickel and about 10% cobalt.

6. The maraging steel alloy of claim 4 further containing up to 1.5% titanium and up to 0.5% aluminum.

7. The maraging steel alloy of claim 6 containing about 6% tungsten.

References Cited

UNITED STATES PATENTS

3,093,519	6/1963	Decker	148—31
3,488,186	1/1970	Decker	75—123

OTHER REFERENCES

C. J. Novak and L. M. Diran, What Are the Effects of Residual Elements in Maraging Steels, Journal of Metals, March 1963, pp. 200–204.

R. F. Decker, J. T. Eash, and A. J. Goldman, 18% Nickel Maraging Steel, A.S.M. Trans., 1962, vol. 55, pp. 58–76; 1010–1015.

L. DEWAYNE RUTLEDGE, Primary Examiner

J. E. LEGRU, Assistant Examiner

U.S. Cl. X.R.

75—123 J, 123 K, 123 M