

[54] **HIGH TEMPERATURE LOW ALLOY STEEL**

[75] Inventors: **Tohru Mimino; Kazuhisa Kinoshita; Kelsuke Hattori,** Kawasaki-shi, Kanagawa-ken, Japan

[73] Assignee: **Nippon Kokan Kabushiki Kaisha,** Tokyo, Japan

[22] Filed: **Oct. 26, 1970**

[21] Appl. No.: **83,835**

[30] **Foreign Application Priority Data**

Nov. 19, 1969 Japan .....44/92413

[52] U.S. Cl. ....75/124, 75/126 C, 75/126 E, 75/126 J, 148/36

[51] Int. Cl. ....C22c 39/04, C22c 39/50

[58] Field of Search.....75/123, 123 B, 123 J, 123 N, 75/124, 126 E, 126 J; 148/36

[56] **References Cited**

**UNITED STATES PATENTS**

2,121,055 6/1938 Smith et al. ....75/123 B X

|           |         |                |            |
|-----------|---------|----------------|------------|
| 2,480,151 | 8/1949  | Malcolm .....  | 75/123 J X |
| 3,251,682 | 5/1966  | Wada .....     | 75/123 B X |
| 3,291,655 | 12/1966 | Gill .....     | 148/36     |
| 3,348,981 | 10/1967 | Goda .....     | 148/36     |
| 3,472,707 | 10/1969 | Phillips ..... | 148/36     |

*Primary Examiner*—Hyland Bizot

*Assistant Examiner*—J. E. Legru

*Attorney*—Flynn & Frishauf

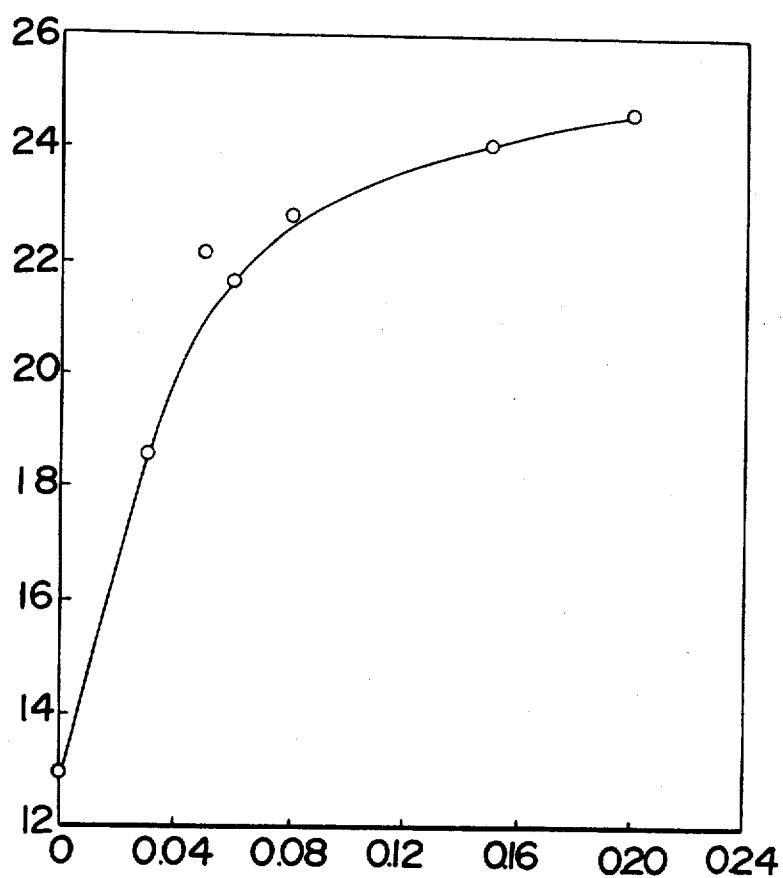
[57] **ABSTRACT**

A high temperature low alloy steel having a chemical composition consisting essentially of between about (i) 0.05 – 0.25% C, (ii) 0.05 – 0.80% Si, (iii) 0.40 – 1.30% Mn, (iv) 0.30 – 0.20% Mo, (v) 0.002 – 0.015% N in solid solution, (vi) less than 0.010% Sol. Al, (vii) 0 – 0.70% Cr, (viii) 0 – 0.10% V, and (ix) the balance being Fe + incidental impurities. The steel is preferably subjected to a normalizing heat treatment to obtain a high strength steel useful for extended service at temperatures between 400° and 500°C.

**8 Claims, 1 Drawing Figure**

PATENTED JAN 2 1973

3,708,280



## HIGH TEMPERATURE LOW ALLOY STEEL

The present invention relates to an inexpensive low alloy steel having high strength at temperatures within a range of 450° - 500°C. and has sufficient heat resistance and strength for use in petroleum refining processes, boilers and general chemical industrial use.

The recent tendency to apply high pressure conditions in thermal generation units, petroleum refining processes and other petroleum industries demands simplified apparatus. High temperature steel applied to such apparatus at temperatures of 450° - 500°C. is usually a 0.5% Mo steel in contrast to the carbon steel which is used at a temperature of 350° - 400°C.

trolled by limiting SolAl to less than 0.010% in order to effect solid solution of N sufficiently. 0.03 - 0.20% of Mo and 0.01 - 0.10% of V may be added as additive elements for the purpose of improving creep rupture strength. However, the amount of such expensive elements as Mo and V is so small that the cost is also low. In particular, 0.50 - 1.30% of Mn acts effectively to improve high tensile strength, but 0.20 - 0.70% of Cr is added to improve both creep rupture strength and high temperature tensile strength in the temperature range of 400° - 500°C.

Hereinafter, the chemical composition of the present invention steel and that of the conventional steel as a comparative data are shown in the following Table 1.

TABLE 1

|                  | Example 1 |       |       | Example 2 |       |       | Example 3 |  | The conventional steel |                |                |
|------------------|-----------|-------|-------|-----------|-------|-------|-----------|--|------------------------|----------------|----------------|
|                  | A         | B     | C     | D         | E     | F     | G         |  | Carbon steel           | 0.15% Mo steel | 0.50% Mo steel |
| C                | 0.19      | 0.18  | 0.13  | 0.19      | 0.17  | 0.16  | 0.21      |  | 0.20                   | 0.17           | 0.11           |
| Si               | 0.21      | 0.50  | 0.25  | 0.26      | 0.48  | 0.28  | 0.34      |  | 0.24                   | 0.21           | 0.22           |
| Mn               | 0.70      | 0.97  | 1.19  | 0.86      | 0.82  | 1.09  | 1.15      |  | 0.50                   | 0.49           | 0.49           |
| Cr               | 0.36      | 0.39  | 0.23  | 0.18      | 0.39  | 0.42  |           |  | 0.04                   | t <sub>r</sub> | 0.06           |
| Mo               | 0.38      | 0.11  | 0.10  | 0.12      | 0.07  | 0.07  | 0.07      |  | t <sub>r</sub>         | 0.12           | 0.53           |
| V                |           |       |       | 0.04      | 0.05  | 0.04  | 0.04      |  | t <sub>r</sub>         | t <sub>r</sub> | t <sub>r</sub> |
| Sol Al           | 0.003     | 0.006 | 0.002 | 0.001     | 0.003 | 0.007 | 0.003     |  | 0.003                  | 0.003          | 0.005          |
| N (total amount) | 0.008     | 0.007 | 0.007 | 0.007     | 0.008 | 0.007 | 0.007     |  | 0.007                  | 0.007          | 0.006          |

Although an 0.15% Mo steel has properties between those of an 0.5% Mo steel and carbon steel, such a steel is rarely used for various reasons.

In designing apparatus as described above, design stress at various temperatures is determined as the lowest value among the following values based upon Japanese Industrial Standards:

- 0.25 of the tensile strength.
- 0.625 of the proof strength.
- The mean value of stress causing 0.01 percent creep within 1,000 hours.
- 0.8 of the minimum value of stress causing rupture within 100,000 hours or 0.6 of the mean value of stress.

That is to say, (a) and (b) are the values of tensile testing at high temperatures for a short period of time and (c) and (d) use the smallest value in creep and creep rupture tests as design stress.

Carbon steel is not used for parts which require strength at a temperature of over 400°C. because of radical decrease in creep rupture strength and high temperature tensile strength. Although 0.15% Mo steel sees an increase of creep strength to a certain extent at a temperature of over 400°C., high temperature tensile strength is so low that design stress needs to be lowered. 0.5% Mo steel has high creep strength at a temperature of over 400° - 500°C., but has a low tensile strength at high temperatures, so that the design stress needs to be lowered for practical use.

The present invention aims to provide, a low cost, a low alloy steel with high design stress at temperatures of 450° - 500°C. by alloying carbon steel with several kinds of elements in small amounts thereby obtaining high temperature tensile strength and creep rupture strength.

More particularly, the alloy steel of the present invention consists essentially of 0.05 - 0.25% C and 0.05 - 0.80% Si in a killed steel. In this case, 0.002 - 0.015% of N dissolves in the alloy steel in the atmosphere. The present invention is characterized in that AlN is con-

The alloy steel of the present invention is normalized at a temperature of 800° - 950°C. and when the alloy steel is used in a boiler tube with a small diameter the cooling speed thereof being relatively fast, it shows a composition of ferrite and pearlite or a composition containing a small amount of bainite in pearlite. Therefore, the hardness is HV167 - 171, which is relatively low, and the cold working property is excellent. Accordingly, annealing is not required after normalizing as is the case of 0.5% Mo steel.

Tables 2 and 3 show high temperature tensile strength and creep rupture strength of the alloy steel of the present invention. Table 2 shows tensile strength at room temperature and high temperatures and Table 3 shows creep rupture strength at temperatures of 450° and 500°C. respectively.

TABLE 2

|                                    |                | Room Temperature   |                           |                           |                           |
|------------------------------------|----------------|--------------------|---------------------------|---------------------------|---------------------------|
|                                    |                | Kg/mm <sup>2</sup> | 400°C. Kg/mm <sup>2</sup> | 450°C. Kg/mm <sup>2</sup> | 500°C. Kg/mm <sup>2</sup> |
| The alloy of the present invention | A              | 52.5               | 53.1                      | 48.0                      | 42.6                      |
|                                    | B              | 55.7               | 57.5                      | 52.5                      | 46.6                      |
|                                    | C              | 55.4               | 58.0                      | 53.0                      | 47.8                      |
|                                    | D              | 56.3               | 51.6                      | 48.0                      | 43.3                      |
|                                    | E              | 54.6               | 51.8                      | 49.1                      | 44.0                      |
|                                    | F              | 55.2               | 52.5                      | 50.4                      | 47.2                      |
|                                    | G              | 56.7               | 57.2                      | 52.0                      | 45.1                      |
| the conventional steel             | carbon steel   | 46.3               | 44.6                      | 36.8                      | 29.7                      |
|                                    | 0.15% Mo steel | 45.2               | 41.1                      | 36.0                      | 29.3                      |
|                                    | 0.50% Mo steel | 43.8               | 47.3                      | 42.4                      | 38.0                      |

TABLE 3

|                                    |                | 450°C, 10 <sup>4</sup> hrs. creep rupture strength |      | 500°C, 10 <sup>4</sup> hrs. creep rupture strength |      |
|------------------------------------|----------------|----------------------------------------------------|------|----------------------------------------------------|------|
|                                    |                | A                                                  | B    | C                                                  | D    |
| the alloy of the present invention | A              | 26.1 Kg/mm <sup>2</sup>                            | 27.0 | 18.3                                               | 18.5 |
|                                    | B              | 27.0                                               | 29.8 | 18.3                                               | 20.2 |
|                                    | C              | 27.5                                               | 30.3 | 19.7                                               | 15.1 |
|                                    | D              | 28.6                                               | 24.3 | 15.1                                               | 7.5  |
|                                    | E              | 28.6                                               | 24.3 | 15.1                                               | 7.5  |
|                                    | F              | 28.6                                               | 24.3 | 15.1                                               | 7.5  |
|                                    | G              | 28.6                                               | 24.3 | 15.1                                               | 7.5  |
| the conventional steel             | carbon steel   | 13.5                                               | 13.5 | 13.5                                               | 13.5 |
|                                    | 0.15% Mo steel | 13.5                                               | 13.5 | 13.5                                               | 13.5 |

|       |                |      |      |
|-------|----------------|------|------|
| ional | 0.15% Mo steel | 21.2 | 14.0 |
| steel | 0.50% Mo steel | 35.0 | 24.2 |

It will be clear from Table 2 that the alloy steel of the present invention has a much higher tensile strength than the conventional steel at temperatures of 400° to 500°C. in every test piece. This results from the following facts: the effect of N, in a state of solid solution in the present low alloy steel, is limited by controlling the amount of Al to be used; the composite effect of N and solid solution and hardening by adding Mn and Cr in Examples 1 and 2 and the composite effect of Mn, N, solid solution and hardening by adding Mn in Example 3.

It will be clear from Table 3 that creep rupture strength of the alloy steel of the present invention is much higher than that of 0.15% Mo steel or Carbon steel but slightly lower than that of 0.50% Mo steel. The order of effective elements to be added in order to improve creep rupture strength for a long time is  $V > Mo > Cr$ , but when more than 0.1% of V is added, an extensive improvement of strength is not to be expected. The more the amount of Mo to be added increases, the more creep rupture strength improves, but as shown in the Tables a great improvement of creep rupture strength is not to be expected in case of a large addition. This is shown in the drawing in which the FIGURE is an explanatory chart of creep rupture showing the influence of the amount of Mo addition to the alloy steel of the present invention. The most efficient amount of Mo addition from an economical point of view is within a range of 0.04 - 0.12%. Cr scarcely contributes to the improvement of creep strength, but Cr addition can be increased because of low cost and in view of its effectiveness to prevent graphitization during the period of use at a high temperature.

As aforementioned, the alloy steel of the present invention has a remarkably high tensile strength at high temperatures and creep rupture strength, so that it is able to improve design stress of high temperature and high pressure apparatus at low cost and can be used in a wide range of fields requiring high strength at high temperatures of up to the extent of 500°C. Particularly, the alloy steel of the present invention is suitable for use in boilers, petroleum refining processes and as tube materials for heat exchangers and sheet materials for general chemical industries.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. High temperature low alloy steel suitable for service at temperatures between 400° and 500°C having a chemical composition consisting essentially of

|    |                                     |
|----|-------------------------------------|
| C  | 0.05 - 0.25%                        |
| Si | 0.05 - 0.80%                        |
| Mn | 0.40 - 1.30%                        |
| Cr | 0 - 0.70%                           |
| Mo | 0.03 - 0.20%                        |
| N  | 0.002 - 0.015%<br>in solid solution |

|                            |                  |
|----------------------------|------------------|
| Sol. Al                    | less than 0.010% |
| V                          | 0 - 0.10%        |
| Fe + incidental impurities | balance          |

2. The steel of claim 1 which after being subjected to a normalizing heat treatment at a temperature of 800° - 950°C retains said nitrogen in solid solution and has a microstructure of (i) ferrite and pearlite, or (ii) ferrite and pearlite containing a small amount of bainite.

3. The high temperature low alloy steel of claim 1 consisting of

|                            |                                                         |
|----------------------------|---------------------------------------------------------|
| C                          | 0.05 - 0.25%                                            |
| Si                         | 0.05 - 0.80%                                            |
| Mn                         | 0.40 - 1.30%                                            |
| Cr                         | 0.20 - 0.70%                                            |
| Mo                         | 0.03 - 0.20%                                            |
| N                          | 0.002 - 0.015%<br>in solid solution<br>less than 0.010% |
| Sol. Al                    |                                                         |
| Fe + incidental impurities | balance                                                 |

4. The steel of claim 3 which after being subjected to a normalizing heat treatment at a temperature of 800° - 950°C retains said nitrogen in solid solution and has a microstructure of (i) ferrite and pearlite, or (ii) ferrite and pearlite containing a small amount of bainite.

5. The high temperature low alloy steel of claim 1 consisting of

|                            |                                                         |
|----------------------------|---------------------------------------------------------|
| C                          | 0.05 - 0.25%                                            |
| Si                         | 0.05 - 0.80%                                            |
| Mn                         | 0.40 - 1.30%                                            |
| Cr                         | 0.20 - 0.70%                                            |
| Mo                         | 0.03 - 0.20%                                            |
| N                          | 0.002 - 0.015%<br>in solid solution<br>less than 0.010% |
| Sol. Al                    |                                                         |
| V                          | 0.01 - 0.10%                                            |
| Fe + incidental impurities | balance                                                 |

6. The steel of claim 5 which after being subjected to a normalizing heat treatment at a temperature of 800°C - 950°C retains said nitrogen in solid solution and has a microstructure of (i) ferrite and pearlite, or (ii) ferrite and pearlite containing a small amount of bainite.

7. The high temperature low alloy steel of claim 1 consisting of

|                            |                                                         |
|----------------------------|---------------------------------------------------------|
| C                          | 0.05 - 0.25%                                            |
| Si                         | 0.05 - 0.80%                                            |
| Mn                         | 0.40 - 1.30%                                            |
| Mo                         | 0.03 - 0.20%                                            |
| N                          | 0.002 - 0.015%<br>in solid solution<br>less than 0.010% |
| Sol. Al                    |                                                         |
| V                          | 0.01 - 0.10%                                            |
| Fe + incidental impurities | balance                                                 |

8. The steel of claim 7 which after being subjected to a normalizing heat treatment at a temperature of 800°C - 950°C retains said nitrogen in solid solution and has a microstructure of (i) ferrite and pearlite, or (ii) ferrite and pearlite containing a small amount of bainite.

\* \* \* \* \*