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[54] HEAT RESISTANT ALLOY HAVING EXCELLENT HOT WORKABILITIES

[75] Inventors: Shozo Sekino; Mizuo Sakakihara; Shoji Murota, all of Fukuoka-ken, Japan
[73] Assignee: Nippon Steel Corporation, Tokyo, Japan

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[52] U.S. Cl. .................. 75/122, 75/171, 75/128 R, 75/128 B, 75/128 Z
[51] Int. Cl. .................. C22c 19/00, C22c 28/00
[58] Field of Search .......... 75/128 E, 128 F, 128 Z, 75/122, 171

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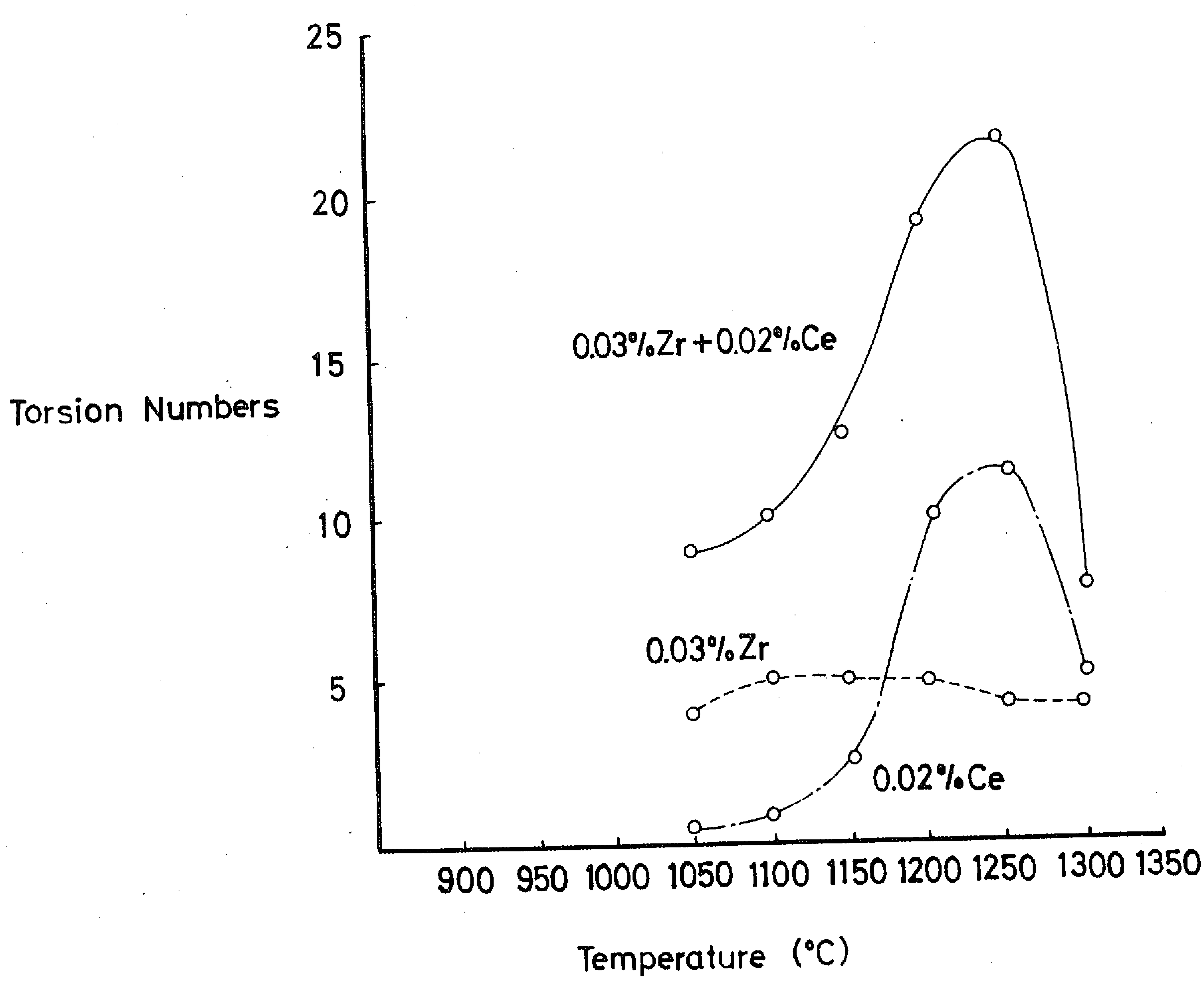
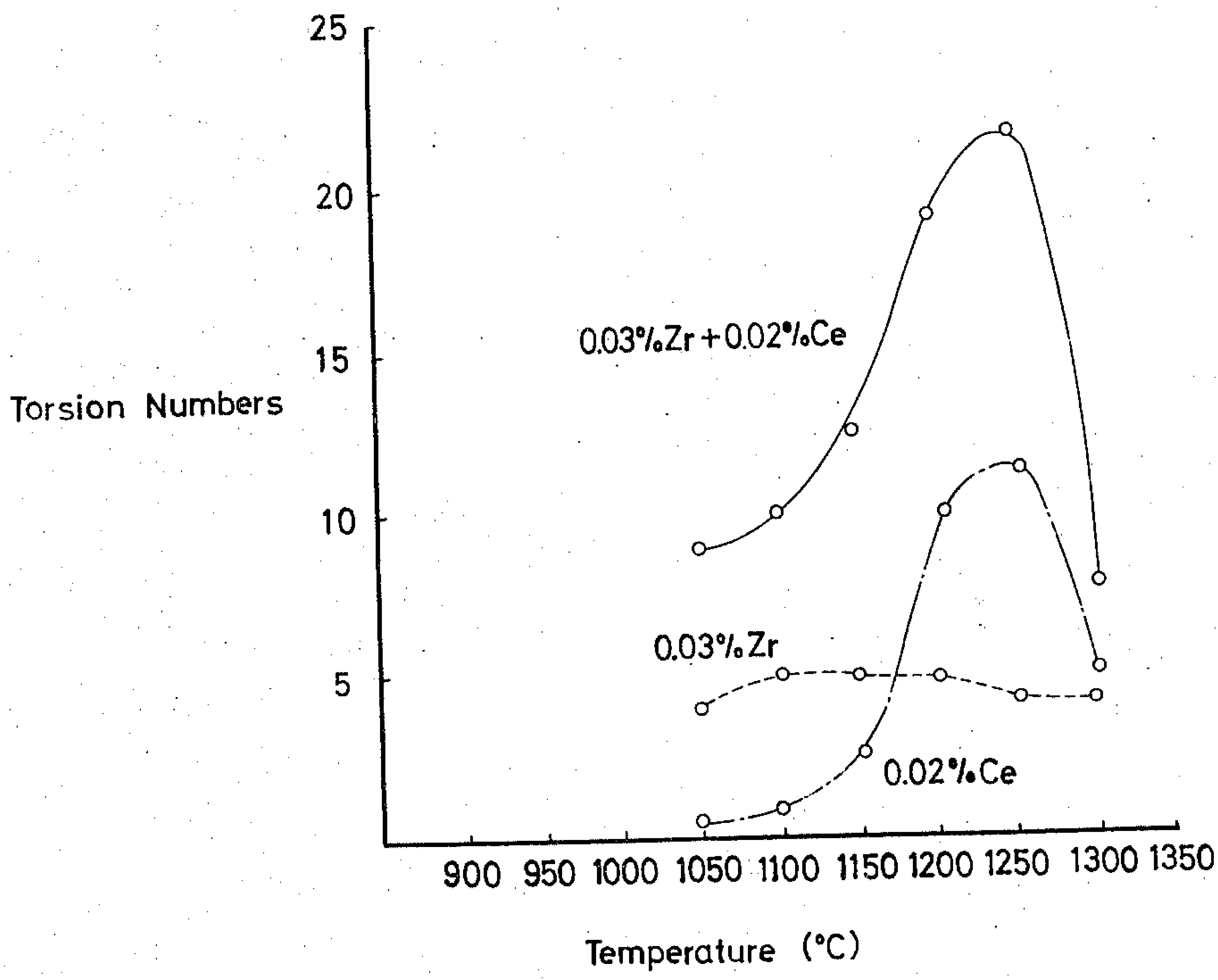
*Primary Examiner*—Hyland Bizot
*Attorney, Agent, or Firm*—Toren, McGeady and Stanger

[57] ABSTRACT

A heat resistant alloy having hot workability comprising 0.01 to 0.5% of C, 0.01 to 2.0% of Si, 0.01 to 3.0% of Mn, 22 to 80% of Ni and 10 to 40% of Cr as basic components together with one or both of 0.0005 to 0.20% of B and 0.001 to 6.0% of Zr and further one or more of 0.001 to 0.5% of Ce, 0.001 to 0.2% of Mg and 0.001 to 1.0% of Be, with the remainder being iron and unavoidable impurities.

3 Claims, 1 Drawing Figure




25
20
15
10
5
Torsion Numbers
0.03%Zr+0.02%Ce
0.03%Zr
0.02%Ce
900 950 1000 1050 1100 1150 1200 1250 1300 1350
Temperature (°C)

# HEAT RESISTANT ALLOY HAVING EXCELLENT HOT WORKABILITIES

The present invention relates to a heat resistant alloy having excellent hot workabilities.

Heat resistant alloys are used for applications such as furnace parts, burner nozzles, annealing boxes and protecting tubes for thermocouples and in recent years they have been widely used for components of atomic piles. These alloys are usually deformed at high temperatures (hot worked). Since the hot working is a working method which makes use of the character of the alloys that they soften at high temperatures, the hot working has an advantage that products of good dimentional accuracy can be easily obtained by small working power.

As one of the conventional heat resistant materials which have a suitable hot workability, an austenite steel containing 7 to 20% of nickel and 14 to 25% of chromium can be mentioned.

However, this conventional heat resistant steel and the like contain Si and W so as to increase hardness and tensile strength as well as wear resistance at high temperatures, and there are very few heat resistant alloys having intentionally improved hot workabilities.

In recent years, along the progress of the chemical industry and other industries, their plants have been enlarged, and large constructional heat resistant components have been demanded therefore. Further heat resistant steel materials used for such large constructional components are subjected to severe production conditions starting from a large alloy ingot to a wide and thin material. The conventional alloys have a vital defect that they are susceptible to hot work cracking during their production process or during their secondary working step for obtaining a predescribed form.

The present inventors have conducted various studies and experiments to overcome the defects and difficulties of the conventional alloys and have completed the present invention.

One of the objects of the present invention is to provide a heat resistant alloy having improved heat resistant properties, particularly hot workability.

Another object of the present invention is to provide a heat resistant alloy having excellent hot workability and an improved torsion property in a wide temperature range with addition of a small amount of selected alloying elements.

Other objects of the present invention will be clear from the following descriptions and attached drawings.

The attached drawing shows the synergistic effect of Zr and Ce in relation with the numbers of torsions.

The present invention is based on the discovery that when B, Zr, Ce, Mg and Be are selectively added in combination to a high-nickel and high-chromium austenite steel, the numbers of torsions can be increased in a wide range at high temperatures. The increase of the number of torsions represents improvement of the hot workability.

Thus, the present invention specifically covers:

1. a heat resistant alloy having hot workability comprising 0.01 to 0.5% of C, 0.01 to 2.0% of Si, 0.01 to 3.0% of Mn, 22 to 80% of Ni and 10 to 40% of Cr as basic components together with one or both of 0.0005 to 0.20% of B, and 0.001 to 6.0% of Zr and further one or more of 0.001 to 0.5% of Ce, 0.001 to 0.2% of Mg and 0.001 to 1.0% of Be, with the remainder being iron and unavoidable impurities,



2. a heat resistant alloy having excellent hot workability comprising 0.01 to 0.5% of C, 0.01 to 2.0% of Si, 0.01 to 3.0% of Mn, 22 to 80% of Ni, 10 to 40% of Cr as basic components, together with one or both of 0.0005 to 0.20% of B and 0.001 to 6.0% of Zr and further one or more of 0.001 to 0.5% of Ce, 0.001 to 0.2% of Mg and 0.001 to 1.0% of Be and still further one or more of 0.1 to 10.0% of Mo, 0.1 to 10.0% of W, 0.1 to 30.0% of Co, 0.05 to 10.0% of each of Ti, Nb, Ta, Al, V, Cu and Y (0.05 to 10.0% in total) with the remainder being iron and unavoidable impurities,

3. and the most preferable composition range of the present heat resistant alloy is: 0.01 to 0.45% of C, 0.01 to 0.15% of Si, 0.01 to 0.15% of Mn, 35 to 65% of Ni, 10 to 25% of Cr, as basic components together with one or more of 0.1 to 10% of Mo, 0.1 to 10% of Co, 0.1 to 10% of W, 0.001 to 0.03% of B, 0.01 to 1.0% of Zr, 0.01 to 0.1% of Ce, 0.001 to 0.01% of Mg, 0.001 to 0.1% of Be, 0.2 to 4.5% of Ti, 0.2 to 4.5% of Al, 0.05 to 0.1% of Y, 0.05 to 0.1% of Cu and still further one or more of Nb, V and Ta in an amount of 0.1 to 4.5 % for each.

The hot workability depends on the ductility of grain boundaries, ductility of the matrix, non-metallic inclusions, precipitates and so on. For improvement of the matrix ductility, 35 to 65% of Ni and 15 to 35% of Cr are most desirable, and for the improvement of the ductility of grain boundaries, it is necessary to decrease the segregations and precipitates at grain boundaries. Mn, Cu and Si segregate at grain boundaries and deteriorate workabilities of the alloy. The grain boundary segregation of these elements is smallest when nickel is present 35 to 65% and chromium is present 10 to 25%. When the nickel content is less than 35% segregation of copper becomes large while the nickel content is more than 65% segregation of manganese and silicon becomes large. Thus, 35 to 65% of Ni and 10 to 25% of Cr assure the smallest segregation in case of an ordinary solidification and the alloy of these composition ranges has a strong corrosion resistance in a neutral oxidizing or reducing gas atmosphere of such as Ar, He, CO, $H_2$which containing a small amount of impurities.

Detailed explanations will be made on the reasons for defining each of the elements of the present heat resistant alloy as above.

Carbon is effective to improve tensile strength, heat resistant properties, such as, creep strength and creep rupture strength as required for a heat resistant alloy, and at least 0.01% of carbon is required for the above improvement. This effect can be obtained when carbon is present together with carbide forming elements such as Mo, Ti and V and the carbides are present in a finely distributed state. An excessive content of carbon forms too large carbides which kill the above effect. Thus, the upper limit of the carbon content is defined at 0.5%. Silicon, when contained in an austenite alloy, remarkably reduces scaling at high temperature and improves tensile strength. These effects are obtained when silicon is present in an amount of 0.01% or more, but an excessive silicon content precipitates the ferrite and the austenite becomes unstable, lowering the heat resistance properties and the hot workabilities. A preferable range of the silicon content is not more 0.15%, but up to 2.0% of silicon is allowed to be present for obtaining the required strength.

When manganese is contained in an amount of 0.01% or more, it stabilizes the austenite and forms carbides to improve creep strength. Up to 3.0% of manganese may be contained for the above purpose. An excessive manganese content lowers the solubility of copper into the austenite and segregates Cu-riched phases of low melting point at the grain boundaries of the austenite, thus remarkably deteriotating hot workabilities and heat resistance properties. For this reason, a smaller amount of manganese is more desirable and a preferable range is 0.01 to 0.15%.

It is well known that nickel and chromium are indispensable for improving heat resistant properties at high temperatures and producing the austenite matrix. For example, many heat resistant alloys have been developed from an austenite 15Ni — 15Cr heat resistant steel. However, these conventional alloys have not been improved intentionally so as to withstand severe hot workings.

The ranges of nickel and chromium contents in the present invention are defined so as to maintain heat resistant properties as required for an heat resistant alloy and to obtain excellent hot workabilities. Namely, 22 to 80% of Ni and 10 to 40% of Cr form a stabilized austenite to give excellent hot workabilities.

In an austenite forming range out of the above ranges, the improvement of hot workabilities is small as compared with that obtained in the present inventive ranges or the remarkable effects on other heat resistant properties are not produced, although some improvement of hot workabilities is obtained.

As stated above, 35 to 65% of Ni and 10 to 25% of Cr are preferable against the intergranular segregation of Mn, Cu, Si, etc.

Heat resistant properties, particularly hot workabilities of the austenite produced by the above composition are already very excellent, but one or both of B and Zr and one or more of Ce, Mg and Be are contained in the present inventive alloys for giving hot workabilities enough to with-stand severe production conditions.

When B is contained in an amount of 0.0005% or more in an austenite heat resistant alloy, creep strength is improved as well as hot workabilities at high temperatures, particularly in a temperature range of 1,100° to 1,150°C are improved. But the content of B is beyond 0.2%, defects are formed and the above improvements are lowered. Thus the content of B is defined as 0.0005 to 0.2%, preferably 0.001 to 0.03%.

When Zr is contained in an amount of 0.001% or more, heat resistant properties are improved as in case of B addition. Particularly when Zr is present at grain boundaries, it reacts with carbon to form MC carbides to improve intergranular ductility and improve hot workabilities below 1,100°C. An excessive content of Zr forms large carbides and tends to kill the desirable effect of Zr addition. A Zr content of greater than 6.0% should be avoided. On the high-carbon side of the present invention, when Zr is contained in an amount of more than eight times the carbon content, the alloy shows tendencies toward embrittlement. Thus a preferable range of the Zr content is 0.01 to 1.0%.

Ce, Mg and Be prevent the effective elements such as Fe, Ni, and Mn from being sulfurated or oxidized during the steel making process and thus being partially wasted as impurities, and they are effective to clean the steel and decompose the sulfides remaining at the boundaries of solidifying grains and divide them into fine spheres, thus improving the hot workability above 1,100°C. These effects can be obtained when any of these elements is present in an amount of 0.001% or more, but an excessive contents of these elements reduces the above effects. Thus, the upper limit of these elements are defined as 0.5% for Ce, 0.2% for Mg, and 1.0% for Be. These elements may be added singles or in combination. The preferred ranges of these elements are stated herein before.

The alloy having the chemical composition defined according to the present invention does not crack under severe hot working conditions.

Further, one or more of Mo, W, Co, Ti, Nb, Ta, Al, V, Cu and Y may be added selectively to the alloy of the present invention. These elements form carbides nitrides or intermetallic compounds and improve heat resistant properties. Cu and Y, in particular, are effective to give the alloy corrosion resistance in addition. The effects of these elements are observed when Mo, W and Co are present in an amount of 0.1% or more, and when Ti, Nb, Ta, Al, V, Cu and Y are present in an amount of 0.05% (also 0.05% in total). An excessive amount of these elements forms too large cabides, nitrides or intermetallic compounds and lowers hot workabilities.

Thus, the upper limits of these elements are defined as 10% for Mo and W, 30.0% for Co, 10% for Ti, Al, Nb, Ta, V, Cu and Y in single and in combination.

Regarding Cu, Cu causes segregation at grain boundaries together with Mn and Si and deteriorates workabilities. Thus it is desirable to restrict the copper content as small as possible, and its preferred range is 0.05 to 0.1%.

Further, other elements such as P and S which are contained as unavoidable impurities should be maintained as low as possible because they damage heat resistant properties. The heat resistant alloy of the present invention can be produced by an ordinary production method which includes melting and refining in a converter or electric furnace, ingot-making, breaking-down, or continuous casting into slabs, hot rolling into wires or plates for commercial use. When the alloy of the present invention is produced by electro-slag refining, still further improved hot workabilities are obtained. The hot rolled wires and plates may be subjected to temper treatments or cold rolling in combination with temper treatments for final use.

One example of the present invention will be given here under.

Table 1 shows chemical compositions of 15mm thick plates produced by melting in an electric furnace, ingot-making, breaking-down and hot rolling, and heat resistant properties including hot torsion numbers to show hot workability at 1,100°C and creep rupture strength.

In the table, the alloys A, C, H and L are set forth as comparative to the present inventive alloys.

It is clear from the table that all of the present inventive alloys show remarkably improved heat resistant properties as compared with the comparative alloys.

Table I

| Designation of Alloys | Kind of Alloy | Chemical Compositions (%) C | Si | Mn | Ni | Cr | Fe | B, Zr | Ce,Mg,Be |
|---|---|---|---|---|---|---|---|---|---|
| A | Comparative | 0.40 | 0.95 | 1.50 | 20.0 | 25.0 | Balance | B: 0.003<br>Zr:0.07 | |
| B | Inventive | 0.40 | 0.95 | 1.50 | 20.0 | 25.0 | do. | B: 0.008 | Be: 0.30<br>Ce: 0.40 |
| C | Comparative | 0.20 | 0.50 | 0.80 | 50.0 | 30.0 | do. | | |
| D | | 0.20 | 0.50 | 0.80 | 50.0 | 30.0 | do. | | Be: 0.02 |
| E | Inventive | 0.20 | 0.50 | 0.80 | 50.0 | 30.0 | do. | Zr: 0.8<br>B: 0.03 | Ce: 0.07<br>Mg: 0.07 |
| F | | 0.20 | 0.50 | 0.80 | 50.0 | 30.0 | do. | Zr: 0.08 | Mg: 0.1<br>Be: 0.5 |
| G | | 0.20 | 0.50 | 0.80 | 50.0 | 30.0 | do. | B: 0.05<br>Zr: 0.04 | Mg: 0.03<br>Be: 0.09 |
| H | Comparative | 0.08 | 0.30 | 0.20 | 75.0 | 15.0 | do. | | Mg: 0.01<br>Ce: 0.02 |
| I | | 0.08 | 0.30 | 0.20 | 75.0 | 15.0 | do. | | Mg: 0.05 |
| J | Inventive | 0.08 | 0.30 | 0.20 | 75.0 | 15.0 | do. | B: 0.01 | Be: 0.07 |
| K | | 0.08 | 0.30 | 0.20 | 75.0 | 15.0 | do. | Zr: 0.07<br>Zr: 0.15<br>B: 0.015 | Be: 0.15<br>Ce: 0.1 |
| L | Comparative | 0.08 | 0.50 | 0.80 | 55.0 | 33.3 | 10.0 | Zr: 0.07 | |
| M | Inventive | 0.08 | 0.50 | 0.80 | 55.0 | 33.3 | 10.0 | Zr: 0.07<br>B: 0.003 | Ce: 0.02 |

| Designation of Alloys | Kind of Alloy | Chemical Composition (%) Mo, W, Co, Ti, Nb, Ta, Al, V, Cu, Y | Heat Resistant Properties: Hot Torsion Numbers at 1100°C | Creep Rupture Strength at 1000°C for 10 hrs.Kg/mm² |
|---|---|---|---|---|
| A | Comparative | Co: 0.5 | 10.0 | 1.5 |
| B | Inventive | Co: 0.5 | 19.5 | 1.8 |
| C | Comparative | Co: 1.00, Mo: 0.5 | 4.0 | 2.3 |
| D | | Co: 10.0, Mo: 0.5 | 6.3 | 2.4 |
| E | Inventive | Co: 10.0, Mo: 0.5 | 14.2 | 2.6 |
| F | | Co: 10.0, Mo: 0.5 | 17.7 | 2.3 |
| G | | Co: 10.0, Mo: 0.5 | 20.1 | 2.3 |
| H | Comparative | Co: 0.5, Mo: 1.0, Y:0.02, Nb:0.1 | 8.0 | 1.0 |
| I | | Co:0.5, Mo:1.0, Y:0.02, Nb:0.1 | 18.0 | 1.4 |
| J | Inventive | Co:0.5, Mo:1.0, Y:0.02, Nb:0.1 | 22.0 | 1.2 |
| K | | Co:0.5, Mo:1.0, Y:0.02, Nb:0.1 | 24.0 | 1.5 |
| L | Comparative | Mo:0.5, Al:0.4, Ti:0.4 | 3.5 | 2.8 |
| M | Inventive | Mo:0.5, Ti:0.003, Nb:0.15 | 13.3 | 3.0 |

What is claimed:

**1.** A heat resistant alloy having hot workability consisting essentially of 0.01 to 0.5% of C, 0.01 to 2.0% of Si, 0.01 to 3.0% of Mn, 22 to 80% of Ni and 10 to 40% of Cr as basic components together with one or both of 0.0005 to 0.20% of B, and 0.001 to 6.0% of Zr and further one or more of 0.001 to 0.5% of Ce, 0.001 to 0.2% of Mg and 0.001 to 1.0% of Be, with the balance being iron and unavoidable impurities.

**2.** A heat resistant alloy having excellent hot workability consisting essentially of 0.01 to 0.5% of C, 0.01 to 2.0% of Si, 0.01 to 3.0% of Mn, 22 to 80% of Ni, 10 to 40% of Cr as basic components, together with one or both of 0.0005 to 0.20% of B and 0.001 to 6.0% of Zr and further one or more of 0.001 to 0.5% of Ce, 0.001 to 0.2% of Mg and 0.001 to 1.0% of Be and still further one or more of 0.1 to 10.0% of Mo, 0.1 to 10.0% of W, 0.1 to 30.0% of Co, 0.05 to 10.0% of each of Ti, Nb, Ta, Al, V, Cu and Y (0.05 to 10.0% in total) with the balance being iron and unavoidable impurities.

**3.** A heat resistant alloy having excellent hot workability consisting essentially of 0.01 to 0.45% of C, 0.01 to 0.15% of Si, 0.01 to 0.15% of Mn, 35 to 65% of Ni, 10 to 25% of Cr, as basic components together with one or more of 0.1 to 10% of Mo, 0.1 to 10% of Co, 0.1 to 10% of W, 0.001 to 0.03% of B, 0.01 to 1.0% of Zr, 0.01 to 0.1% of Ce, 0.001 to 0.01% of Mg, 0.001 to 0.1% of Be, 0.2 to 4.5% of Ti, 0.2 to 4.5% of Al, 0.05 to 0.1% of Y, 0.05 to 0.1% of Cu and still further one or more of Nb, V and Ta in an amount of 0.1 to 4.5% for each with the balance being iron and unavoidable impurities.

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