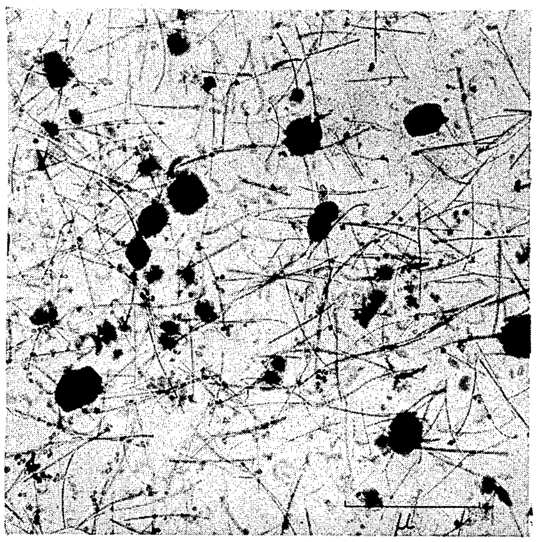
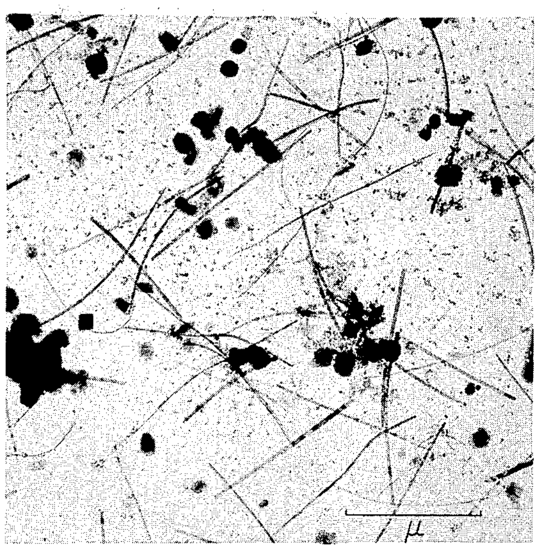
Fig. 1a



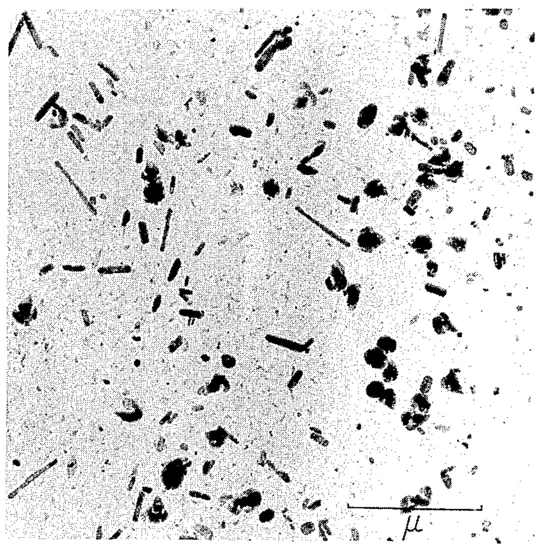
PERCENTAGE OF COLD ROLLING 0%

Fig. 1b



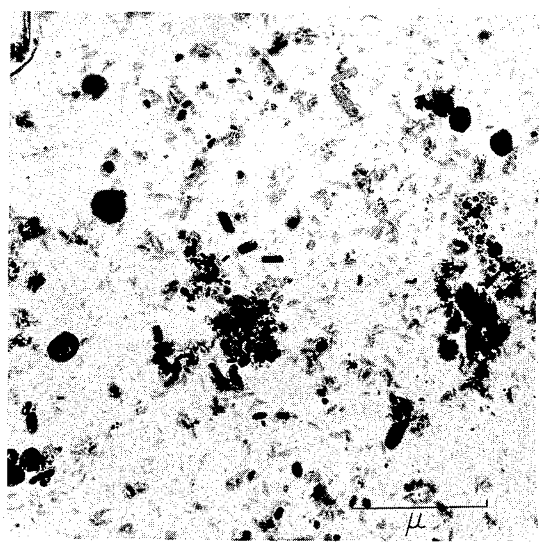
PERCENTAGE OF COLD ROLLING 10%

Fig. 1c



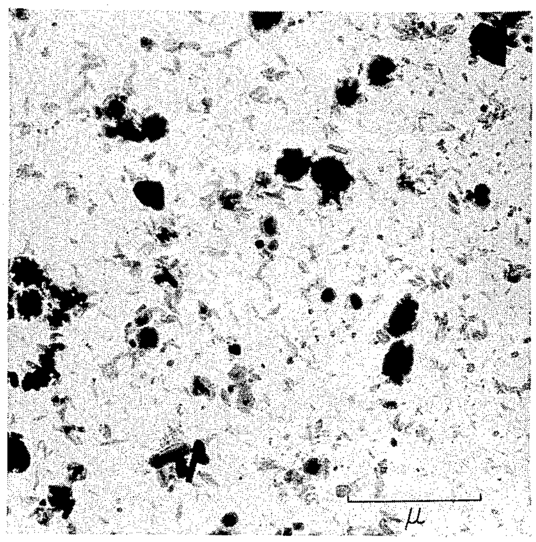
PERCENTAGE OF COLD ROLLING 15%

Fig. 1d



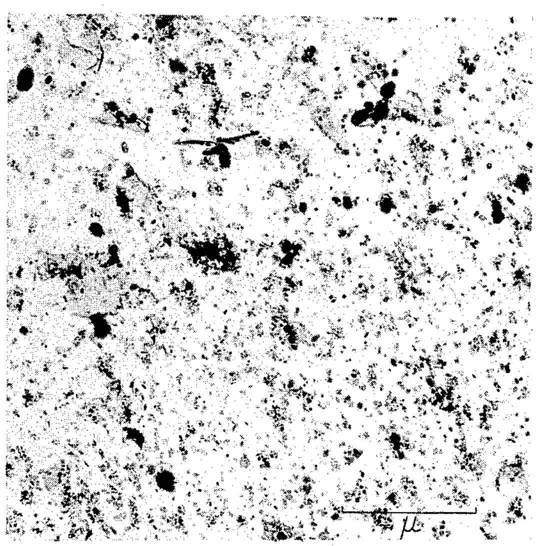
PERCENTAGE OF COLD ROLLING 30%

Fig. 1e



PERCENTAGE OF COLD ROLLING 50%

Fig. 1f



PERCENTAGE OF COLD ROLLING 70%

Fig. 2

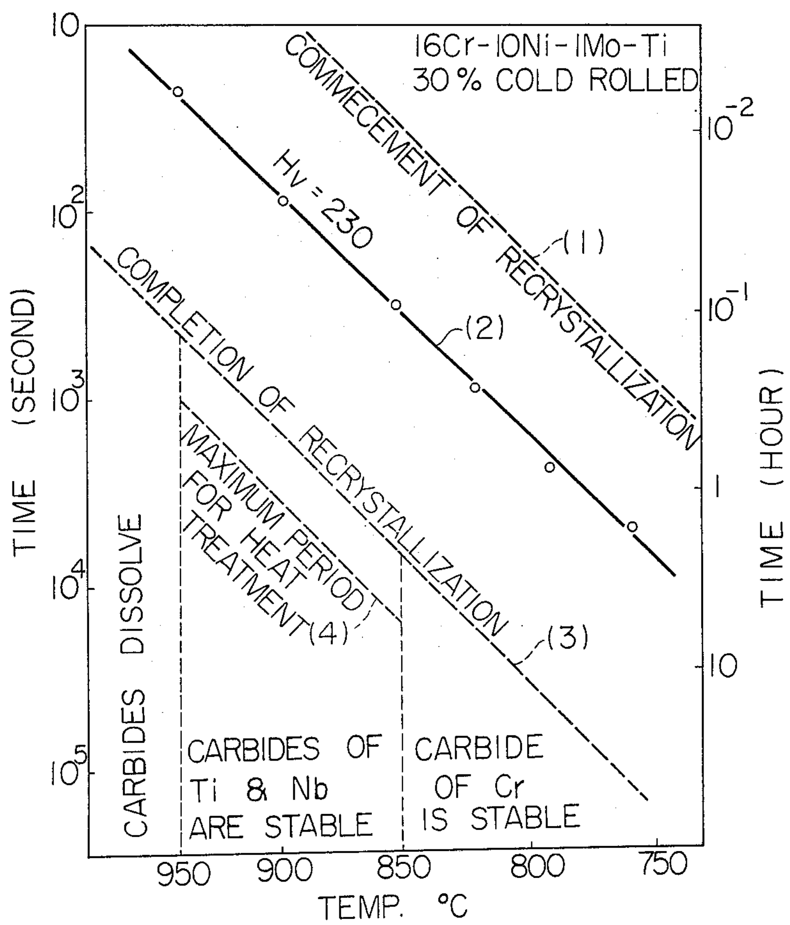

16Cr-10Ni-1Mo-Ti
30 % COLD ROLLED
COMMECEMENT OF RECRYSTALLIZATION
(1)
Hv = 230
(2)
COMPLETION OF RECRYSTALLIZATION
(3)
MAXIMUM PERIOD FOR HEAT TREATMENT
(4)
CARBIDES DISSOLVE
CARBIDES OF Ti & Nb ARE STABLE
CARBIDE OF Cr IS STABLE
TIME (SECOND)
10
10^2
10^3
10^4
10^5
TIME (HOUR)
10^{-2}
10^{-1}
1
10
950
900
850
800
750
TEMP. °C

Fig. 3

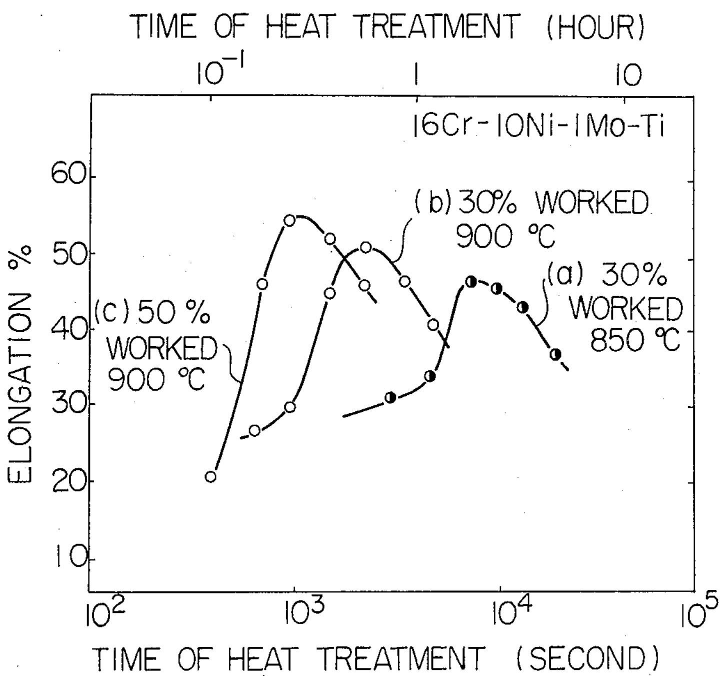

TIME OF HEAT TREATMENT (HOUR)
10⁻¹
1
10
16Cr-10Ni-1Mo-Ti
(b) 30% WORKED 900 °C
(a) 30% WORKED 850 °C
(c) 50 % WORKED 900 °C
ELONGATION %
60
50
40
30
20
10
10²
10³
10⁴
10⁵
TIME OF HEAT TREATMENT (SECOND)

Fig. 5

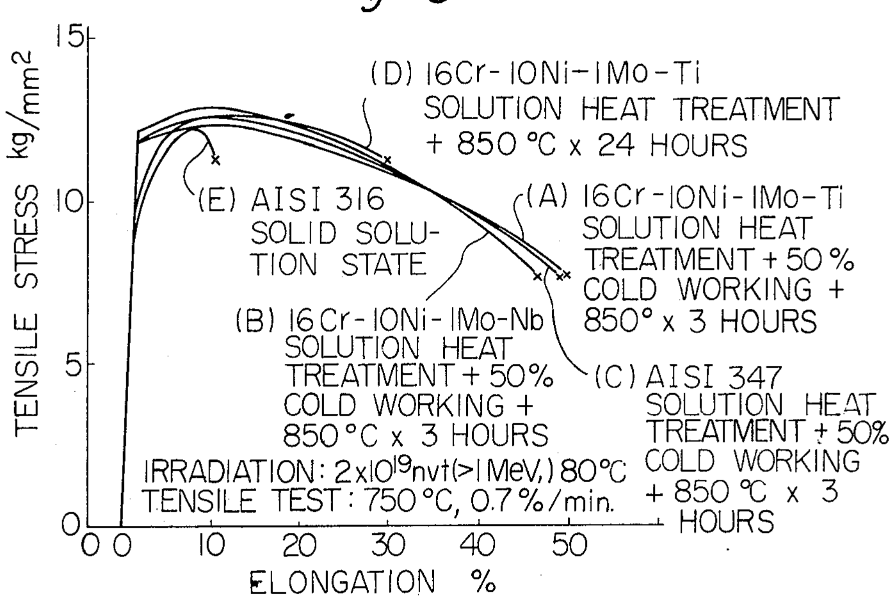
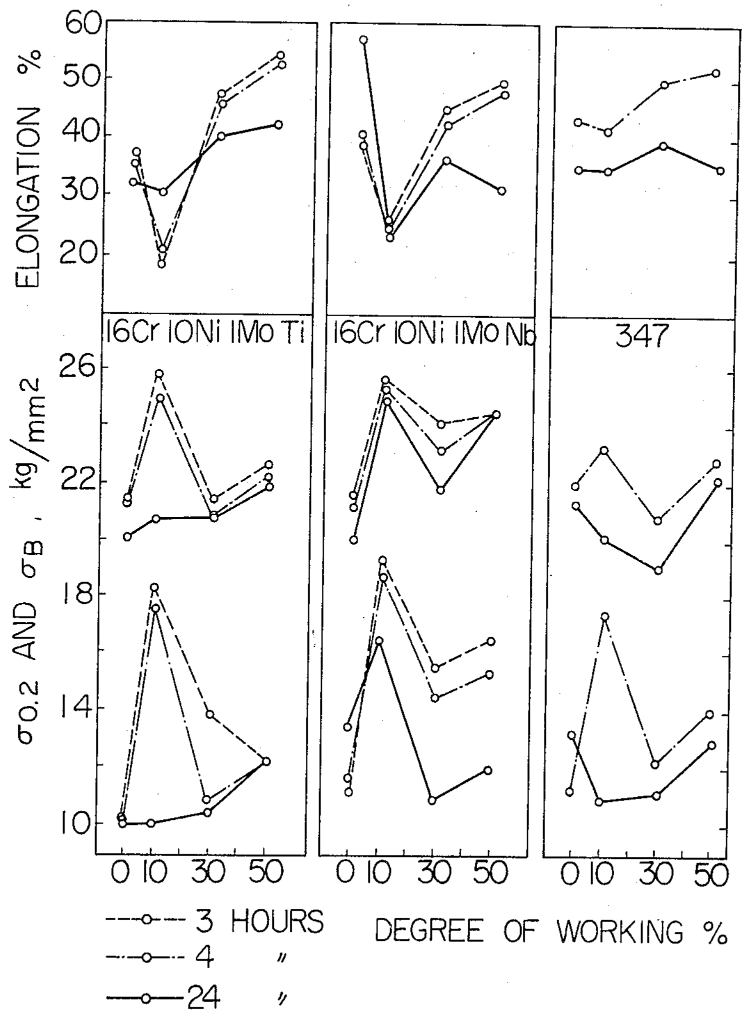

TENSILE STRESS kg/mm²
15
10
5
0
(D) 16Cr-10Ni-1Mo-Ti SOLUTION HEAT TREATMENT + 850 °C x 24 HOURS
(E) AISI 316 SOLID SOLU-TION STATE
(A) 16Cr-10Ni-1Mo-Ti SOLUTION HEAT TREATMENT + 50 % COLD WORKING + 850° x 3 HOURS
(B) 16Cr-10Ni-1Mo-Nb SOLUTION HEAT TREATMENT + 50% COLD WORKING + 850 °C x 3 HOURS
(C) AISI 347 SOLUTION HEAT TREATMENT + 50% COLD WORKING + 850 °C x 3 HOURS
IRRADIATION: 2x10¹⁹nvt(>1 MeV,) 80°C
TENSILE TEST: 750 °C, 0.7 %/min.
0
10
20
30
40
50
ELONGATION %

Fig. 4


ELONGATION %
60
50
40
30
20
16Cr 10Ni 1Mo Ti
16Cr 10Ni 1Mo Nb
347
σ0.2 AND σB , kg/mm2
26
22
18
14
10
0 10 30 50
0 10 30 50
0 10 30 50
DEGREE OF WORKING %
3 HOURS
4 〃
24 〃

United States Patent Office

3,669,759
Patented June 13, 1972

1

3,669,759

THERMOMECHANICAL TREATMENT FOR IMPROVING DUCTILITY OF CARBIDE-STABILIZED AUSTENITE STAINLESS STEEL

Tatsuo Kondo and Hajime Nakajima, Takai-Mura, and Ryukichi Nagasaki, Mito-shi, Japan, assignors to Japan Atomic Energy Research Institute, Tokyo, Japan

Filed Sept. 24, 1969, Ser. No. 860,683
Claims priority, application Japan, Sept. 27, 1968, 43/69,496
Int. Cl. C21d *1/00*
U.S. Cl. 148—12.3 11 Claims

ABSTRACT OF THE DISCLOSURE

An austenite stainless steel having superior ductility at high temperatures is obtained by subjecting the carbide-stabilized austenite stainless steel to solution heat treatment, cold-working said steel more than 15%, and annealing it at a temperature between 850° C. and 950° C. for less than four hours.

This invention relates to treatment of a class of austenite stainless steels of stabilized carbide type, that is, steels of AISI Type 321, 347, etc., of the AISI 300 series, in which a steel is first subjected to solution heat treatment, cold-worked, and then subjected to a further heat treatment for precipitating carbides and making the matrix recrystallize. The treatment diminishes brittleness, a defect in steels of this type, and provides new stainless steel materials which have high temperature tensile strength 20% or more higher than that of the conventional stainless steels, and elongation 30% or more greater than that of the conventional stainless steels.

In the prior art of stainless steel making, corrosion resistance was primarily aimed at, and therefore, the steel was supplied in the austenitic state, that is, in the state of solid solution, and cold working was depended upon for improving high temperature yield strength of the steel. In such prior art, however, ductility of the steel was sacrificed. Strength based on cold working cannot be retained at high temperatures and instability of mechanical properties of the steel is a problem.

Techniques for manufacturing stainless steels for use in fast neutron breeders are still in an inchoate stage in a world-wide sense. Although it is known that the carbide-stabilized austenite stainless steel can be advantageously used for fast breeder reactors and other high temperature nuclear reactors because reduction in ductility of said steel by irradiation of fast and thermal neutrons of more than 10^{19} nvt. at high temperatures is relatively little, but it has a defect that it becomes remarkably brittle by carbide stabilization treatment as long as the conventional treatment is concerned.

That is, the carbide-stabilized austenite stainless steel is, after solution treatment, subjected to the treatments to convert the dissolved carbon to carbide precipitates and further to coarsen the precipitated carbides. Because, in the austenite stainless steel in use for nuclear reactors, it has been believed that fine carbide precipitates tend to redissolve in the matrix by irradiation of neutrons, and it makes the matrix unstable; the aim has been to prevent redissolution of the carbide precipitates particles by coarsening them. However, in such a steel, reduction in ductility is remarkable because of the existence of the coarse carbides. Especially, this defect is fatal in steel containing titanium, and makes it less attractive as a reactor material.

2

In the carbide-stabilized austenite stainless steel in accordance with the prior art method, acicular carbide is precipitated during the carbide stabilization treatment (this carbide is identified as Cr_3C_2 by means of electron diffraction analysis, and its crystal form is orthorhombic). And the steel becomes brittle because of the anisotropic nature of this carbide pecipitate.

The purpose of this invention is to provide a new class of carbide-stabilized austenite stainless steels having a tensile strength 20% or more higher than that of the prior art stainless steel, elongation 30% or more higher than that of the prior art stainless steel and structural stability equivalent to or superior to that of the prior art steel by preventing reduction in ductility by a specific combination of degree of working and time and temperature of heat treatment. Brittleness that has been regarded as the most serious defect of the carbide-stabilized austenite stainless steels that is, steels of AISI Type 321, 347 etc. of the AISI 300 series, can now be diminished by a combination of cold working and heat treatment which comprises solution treatment, cold working, heat treatment for precipitation of carbides and recrystallization of the matrix. Therefore, this is a new method for obtaining austenite stainless steel materials of stabilized carbide type that have structural stability at high temperatures and improved ductility, further this method is easily applicable industrially. The stainless steel obtained in accordance with this invention is not only excellent as an industrial material for general use in the chemical industry but also is very useful as a material for fast breeders.

This invention has relation to the steel-making industry, especially manufacture of stainless steel tubes, manufacture of nuclear reactor materials and manufacture of nuclear fuel elements. The stainless steel of stabilized carbide type has been widely employed as the material usable at high temperatures in the chemical industry, since steel of this type has structural stability superior to that of the other stainless steels. However, this class of stainless steels has a fatal defect in that its mechanical properties, especially ductility are impaired by the alloying elements (Ti, Nb, etc.) added for stabilizing the carbides.

After an extensive study, we have found that if the carbide-stabilized austenite stainless steel is cold-worked at least 15% and as much as possible and then heated at a temperature in the range of 850–950° C., precipitation of acicular carbide is prevented and fine globular carbides (Tic, NbC etc.) preferentially precipitate and at the same time recrystallization of the matrix is completed and thus the crystal grains become fine.

As the degree of cold working increases (cold working may be repeated as explained hereinafter), carbide precipitates become more finely and more uniformly dispersed, and thus mechanical properties of the steel are remarkably improved. In the steel material manufactured in accordance with the particular combination of cold working and heat treatment of this invention, dislocations are well removed in its microstructure, and it is in the so-called annealed state, residual strain caused by the cold working does not remain, and therefore, it is less susceptible to sigma brittleness than the prior art steel. The carbide-stabilized austenite stainless steel in accordance with this invention, to whichever of the above-mentioned descriptions it may belong, is superior to the prior art steel of the same composition with respect to mechanical properties and micro-structural stability at high temperatures. There is no particular technical difficulty in the commercial practice of the method of the invention in comparison with the prior art method. Rather the method of this invention is superior to the prior art method in that dimensional accuracy is better maintained and oxidation loss is smaller since only stabilization treatment can be carried out after shaping, while in the prior art method, solution treatment and stabilization treatment must be carried out after shaping.

Now we explain this invention in detail by way of working examples referring to the attached drawings.

FIG. 1 (a) through (f) show the influence of cold working in the treatment of this invention.

FIG. 2 shows the relation between time and temperature in the heat treatment in accordance of this invention.

FIG. 3 shows the relation between conditions of the treatment and the obtained mechanical property (elongation).

FIG. 4 shows the relation between degree of working and time of heat treatment and the obtained mechanical properties.

FIG. 5 shows the post-irradiation mechanical properties of a stainless steel treated in accordance with this invention.

EXAMPLE 1

Specimens 95 x 15 x 1—2 mm. in dimension (thickness is selected by considering degree of cold working to undergo) are made of a heat of steel the analysis of which is as follows.

Component:	Weight percent
C	0.076
Si	0.57
Mn	1.17
Cr	16.17
Mo	1.07
B	0.0006
N	0.0161
P	0.023
S	0.004
Ni	10.04
Co	0.18
Ti	0.508
Fe	Balance

The specimens were subjected to solution heat treatment (heated at 1100° C. for 10 minutes and quenched in water), and thereafter they were cold-rolled respectively by 10%, 15%, 30%, 50% and 70% reduction. The cold-worked specimens were then, for the purpose of stabilizing carbide (precipitation of the carbide) and recrystallization, heated at 790° C., 810° C., 820° C., 850° C., 900° C. and 950° C. for 1 minute to 192 hours, and were quenched in water. The effects of the treatments were checked by means of electron microscope observation of carbide extraction replicas and thin foil of each specimen, X-ray diffraction, electron diffraction, optical microscope observation and measurement of Vickers hardness (H_v).

FIG. 1 (a) through (f) show the relation between amount of precipitated carbides and degree of working (reduction) resulting when the steel was subjected to carbide stabilization treatment at 850° C. for four hours. It was recognized that the acicular crystals seen in Photographs (a) and (b) are of Cr_3C_2, and the globular crystals seen in other photographs are of TiC by means of the above-mentioned tests. As seen here, it was established that carbides are fine and uniformly dispersed when the steel is subjected to cold working of 15% or more.

The relation between time and temperature of the treatment for precipitation and recrystallization and microstructures that were identified by the above-mentioned tests is shown in FIG. 2 as an example.

In this figure, the uppermost oblique (broken) line (1) represents the conditions under which recrystallization takes place, the next oblique (solid) line (2) represents the conditions under which the Vickers hardness reaches 230. In the area adjacent to this line, the mechanical properties of the treated steel vary remarkably in accordance with change in the conditions. The third (broken) line (3) shows the conditions for completion of recrystallization.

The area below the line of completion of recrystallization and right of the vertical straight broken line for 850° C. stands for an area in which carbide of chromium is stable. The area left of the same vertical line is an area in which carbides of Ti and Nb are stable. The area left of the vertical line for 950° C. is an area in which carbides dissolve. The steel which exhibits excellent properties in accordance with this invention must be in the area in which carbides of Ti and Nb are stable, and that must be in the area on the upper side of the line (4) indicated as maximum period for heat treatment in the figure, since if the heat treatment is prolonged, excellency in the mechanical properties is lost. The point at which the line of maximum period for heat treatment and the line for 850° C. intersect represents 4 hours.

This relation is shifted upward in the figure as the degree of working increases. This will be apparent from the following explanation pertaining to FIG. 3.

FIG. 3 shows the relation between conditions of the heat treatment and elongation, one of the mechanical properties concerned in this invention. Curve A tells that the steel which underwent 30% cold working and heat treatment at 850° C. shows remarkable change in its mechanical property (elongation) in the range 2–4 hours when heat-treated at 850° C. Curves B and C show a similar relation with respect to 30% and 50% working respectively at 900° C. By comparing Curves A, B and C, it is understood that as degree of working and temperature of heat treatment increase, the mechanical properties improve.

In FIG. 4 are shown the results of the high temperature tensile test at 650° C. of the specimens which was subjected to precipitation-recrystallization treatment at 850° C. after 10%, 30% and 50% working in comparison with the results with respect to the prior art treatment. In the prior art method, no mechanical working is applied before the stabilization treatment, or if it is applied, the carbide stabilization treatment is carried out over a prolonged time (24 hours for instance), and therefore, strength and ductility decrease.

The same specimens and a set of the specimens explained in the Example 3 which underwent solution heat treatment, 50% cold working, and precipitation-recrystallization treatment at 850° C. for 3 hours were irradiated with fast neutrons of 2×10^{19} nvt. in an irradiation hole (VT–1) of the Japan Research Reactor No. 2 (JRR–2) at the Tokai Establishment of Japan Atomic Energy Research Institute and then were subjected to tensile test at 750° C. The results are shown in FIG. 5.

In FIG. 5, (A) is a curve standing for a 16Cr-10Ni-1Mo-Ti specimen (the above-mentioned steel) which underwent 50% cold working, and heat treatment at 850° C. for 3 hours; (B) is a curve standing for a 16Cr-10Ni-1Mo-Nb specimen which underwent the same treatment; (C) is a similar curve for Steel AISI 347. These 3 kinds of steels fall within the scope of this invention. Curve (D) stands for the steel having the same composition as that of (A) which has been heat-treated at 850° C. for 24 hours without being subjected to cold working. Curve (E) stands for AISI 316 steel which simply underwent solution heat treatment. It is apparent that the steel materials of this invention have remarkably increased resistance to fracture.

EXAMPLE 2

The same steel as of Example 1 was subjected to solution heat treatment and was cold-rolled to 30% reduction. The specimen showed the following mechanical properties at 650° C.:

Tensile strength—32.5 kg./mm.^{2}
Yield strength—28 kg./mm.^{2}
Elongation—9%
Vickers hardness (room temperature)—311

The specimen was then heated at 850° C. for 2 minutes. The mechanical properties of the thus treated specimen were as follows at 650° C.:

Tensile strength—27 kg./mm.^{2}
Yield strength—22 kg./mm.^{2}
Elongation—20%
Vickers hardness (room temperature)—245

The specimen was then further cold-rolled to 50% reduction (61% in total reduction), and heated at 850° C. for 30 minutes. The thus treated specimen showed the following mechanical properties at 650° C.:

Tensile strength—23 kg./mm.^{2}
Yield strength—14 kg./mm.^{2}
Elongation—58%
Vickers hardness (room temperature)—160

The results show that repeated treatment further improves ductility of the material. In this case, the first heat treatment must be carried out under the condition that the material is partially relieved from the strain caused by the cold working and precipitation and recrystallization do not occur appreciably. And it has been established that softening (recovery from work hardening) must be limited to not more than 50%. Otherwise the accumulative effect of work hardening is diminished and there is less meaning in repetition of working.

EXAMPLE 3

The same treatment was repeated with respect to a steel having the following composition:

Component	Weight percent
O	0.082
Si	0.57
Mn	1.12
P	0.020
S	0.004
Ni	10.05
Cr	16.33
Mo	1.02
B	0.0005
N	0.0315
Co	0.16
Nb	0.88
Ti	0.011
Fe	Balance

The results are shown in FIGS. 4 and 5. The results are the same as in the cases with the above-mentioned species of steel, and the mechanism of improvement in ductility is the same whether the carbide stabilizing element is titanium or niobium.

The method of this invention is applied to steel species of the so-called carbide-stabilized type such as AISI 321, 347 and 348, that is, a class of steels the composition of which is in the range shown in Table 1.

TABLE 1

	Content	
	Minimum	Maximum
Component:		
Cr	12.0	25.0
Ni	6.0	25.0
C	0.03	2.0
Nb	0.30	5.0
Ti	0.15	5.0
Other elements	(1)	(1)
Fe	Balance	Balance

[1] As specified in AISI 300 series.

In the process of this invention, in order to prevent formation of acicular precipitates, the steel must be worked to not less than 15% as explained hereinbefore. Though there is no upper limit for the degree of working, the degree is practically limited by working conditions. The preferred working degree is between 30% and 50% for all steels of the class.

Temperature and time of precipitation-recrystallization treatment are defined as 850–950° C. and less than 4 hours respectively as seen in FIG. 2. At temperatures in excess of 950° C., carbides tend to dissolve in the matrix, or if they precipitate, they grow coarse. Temperatures lower than 850° C. are not only impractical because of the prolonged treatment time required but also undesirable because precipitation of carbide of chromium takes place in preference to that of TiC, NbC, etc. Practical conditions being considered, the preferred precipitation-recrystallization treatment time is 900–925° C. for all steels of the class.

Time required for precipitation-recrystallization treatment depends on treatment temperature, composition of steel, and degree of working. In any case, the satisfactory results are obtained when the heat treatment is finished within 4 hours.

When a steel of AISI Type 321 is treated in accordance with this invention, if it is cold-worked by about 30% and heat-treated at 900° C., the time required for the treatment is 25 minutes to 3 hours. If it is cold-worked by about 30% and heat-treated at 925° C., the time required for the treatment is 15 minutes to 2 hours. If it is cold-worked by about 50% and heat-treated at 900° C., the time required for the treatment is 3 minutes to 25 minutes. If it is cold-worked by about 50% and heat-treated at 925° C., the time required for the treatment is 2 minutes to 25 minutes. When a steel of AISI Type 347 is treated in accordance with this invention, if it is cold-worked by about 30% and heat-treated at 900° C., the time required for the treatment is 30 minutes to 3½ hours. If it is cold-worked by about 30% and heat-treated at 925° C., the time required for the treatment is 20 minutes to 2½ hours. If it is cold-worked by about 50% and heat-treated at 900° C., the time required for the treatment is 4 minutes to 30 minutes. If it is cold-worked by about 50% and heat-treated at 900° C., the time required for the treatment is 4 minutes to 30 minutes. If it is cold-worked by about 50% and heat-treated at 925° C., the time required for the treatment is 3 minutes to 25 minutes.

When the carbide-stabilized austenite stainless steel is treated in accordance with the thermomechanical heat treatment with repeated cold working of this invention, the annealing for removing the work hardening is carried out at a temperature between 850° C. and 950° C., preferably at the lowest temperature in this range. When a steel of AISI 321 is cold worked by about 30% and is annealed at 850° C., the time required for the annealing is not more than 7 minutes. If the steel is cold-worked by about 50% and annealed at 850° C., 3 minutes will suffice. When a steel of AISI Type 347 is cold-worked by about 30% and is annealed at 850° C., the time required for the annealing is not more than 9 minutes. If the steel is cold-worked by about 50% and annealed at 850° C., 4 minutes will suffice.

The stainless steel material of this invention is primarily intended to be used as the nuclear reactor material such as cladding of fuel elements, but it is not restricted to such use only. If a high frequency electric heating, for instance, is utilized, stainless steel material even of considerable size can be rapidly heat-treated with ease as is well known to those who skilled in the art.

We claim:

1. A process for manufacturing a carbide-stabilized austenite stainless steel which retains ductility at high temperature characterized in that carbide precipitates of the steel are stabilized in the form of fine particles comprising subjecting a carbide-stabilized austenite stainless steel to solution heat treatment, cold-working said steel not less than 15%, and heat-treating said steel at a temperaure between 850° C. and 950° C. for less than four hours.

2. The process as set forth in claim 1, in which said steel is cold-worked by about 30% to about 50%, and is heat treated at a temperature between 900° C. and 925° C.

3. The process as set forth in claim 2, in which the treated steel is a steel of AISI Type 321, the steel is cold-worked by about 30%, and the heat treatment is carried out at 900–925° C. for not more than 3 hours.

4. The process as set forth in claim 2, in which the treated steel is a steel of AISI Type 321, the steel is cold-worked by about 50%, and the heat treatment is carried out at 900–925° C. for not more than 25 minutes.

5. The process as set forth in claim 2, in which the treated steel is a steel of AISI Type 347, the steel is cold-worked by about 30%, and the heat treatment is carried out at 900–925° C. for not more than 3½ hours.

6. The process as set forth in claim 2, in which the treated steel is a steel of AISI Type 347, the steel is cold-worked by about 50%, and the heat treatment is carried out at 900–925° C. for not more than 30 minutes.

7. A process for manufacturing a carbide-stabilized austenite stainless steel which retains ductility at high temperature characterized in that after a carbide-stabilized austenite stainless steel is subjected to solution treatment; said steel is cold-worked by not less than 15% of the degree of working, said worked steel is annealed at a temperature between 850° C. and 950° C. until not more than 50% of the hardening by the working is removed, said cold working is repeated, again said steel is annealed at a temperature between 850° C. and 950° C. for less than 4 hours, and the above-mentioned working and annealing steps are repeated at least once.

8. The process as set forth in claim 7, in which the treated steel is a steel of AISI Type 321, the steel is cold-worked by about 30% and annealed at about 850° C. for not more than 7 minutes.

9. The process as set forth in claim 7, in which the treated steel is a steel of AISI Type 321, the steel is cold-worked by about 50% and annealed at about 850° C. for not more than 3 minutes.

10. The process as set forth in claim 7, in which the treated steel is a steel of AISI Type 347, the steel is cold-worked by about 50% and annealed at about 850° C. for not more than 9 minutes.

11. The process as set forth in claim 7, in which the treated steel is a steel of AISI Type 347, the steel is cold-worked by about 50% and annealed at about 850° C. for not more than 4 minutes.

References Cited

UNITED STATES PATENTS

2,528,638	11/1950	Clark, Jr.	148—136
2,536,033	1/1951	Clark, Jr.	148—136
2,536,034	1/1951	Clark, Jr.	148—136
3,441,406	4/1969	Bungardt et al.	148—12.3

FOREIGN PATENTS

780,384	3/1968	Canada	148—12.3

L. DEWAYNE RUTLEDGE, Primary Examiner

W. W. STALLARD, Assistant Examiner

U.S. Cl. X.R.

148—136