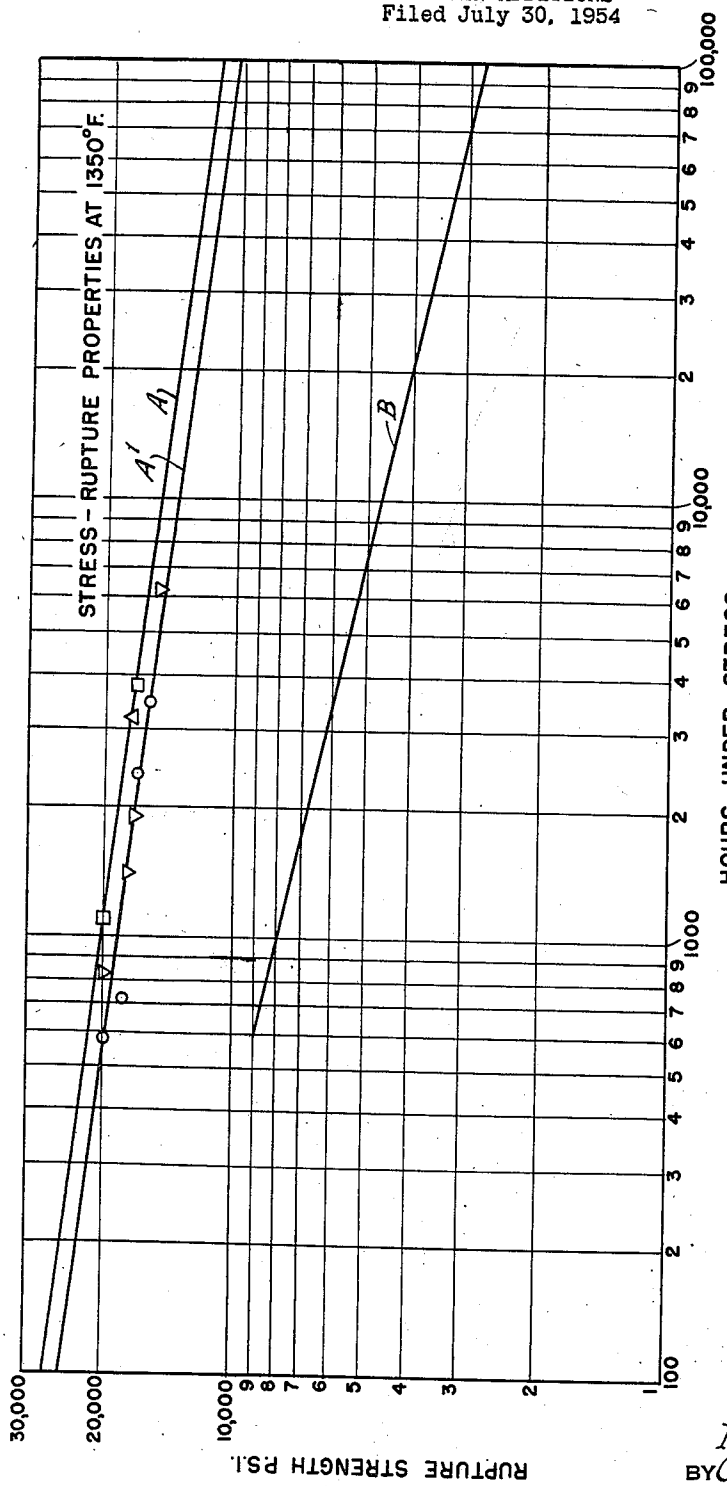
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FORGEABLE HIGH STRENGTH AUSTENITIC ALLOY WITH MOLYBDENUM, TANTALUM, COLUMBIUM-TANTALUM, AND NITROGEN ADDITIONS

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FORGEABLE HIGH STRENGTH AUSTENITIC ALLOY WITH MOLYBDENUM, TANTALUM, COLUMBIUM-TANTALUM, AND NITROGEN ADDITIONS

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This invention relates to forgeable alloy steels having enhanced stress rupture strength, corrosion resistance, and freedom from embrittlement in extended service, at elevated temperatures and stresses, and, more particularly, to a fully austenitic chrome-nickel-iron alloy steel attaining the foregoing properties with a minimum total alloy content.

For a number of years there has been a steady increase in the superheater outlet temperatures and pressures of vapor generators, with a resulting increase in the efficiency and economy of turbines driving electric generators. These temperature and pressure increases required alloy steels to be used in the superheaters, such as stainless steels of the columbium and titanium bearing 18Cr—8Ni AISI types 347 and 321. With superheater outlet temperatures of 1050° F., the pressures involved are frequently substantially in excess of 2000 p. s. i.

With pressures of this order, the superheater tubing must have wall thicknesses of up to 5/8" for such 18–8 alloys to remain within their allowable working stresses. Such wall thicknesses are undesirable, not only from the standpoint of fabrication problems but also from the standpoints of heat transfer and thermal stress gradients across the wall of the tubing. As a consequence, the increase in superheater outlet temperatures recently has been arrested at substantially the 1100° F. level.

Any further substantial increase in superheater outlet temperatures requires steel alloys capable of practical fabrication into tubing having wall thicknesses acceptable from the fabrication, heat transfer, and thermal stress gradient standpoints, and having long-time strength and corrosion resistance at temperatures in excess of 1350° F. and pressures substantially in excess of 2000 p. s. i. In addition, considering the large quantities of such tubing required in modern vapor generator installations, such alloys must have a low total alloy content in order to be economically feasible for use as superheater tubing.

There are known alloys which have long-time strength at high temperatures but which either have too high an alloy content to be economically practical for use as superheater tubing or are substantially non-forgeable, difficult to forge, or characterized by a loss of desirable properties when exposed for long times to temperatures used in superheater service.

The present invention is, accordingly, directed to a steel alloy capable of economically practical use as tubing operating at temperatures in excess of 1350° F. and pressures in excess of 2000 p. s. i., and having the lowest possible alloy content, being particularly low or "lean" in strategically important elements. The invention is particularly directed to such an alloy meeting the following requirements:

(1) Stress-rupture strength, at 1350° F., at least twice that of AISI type 304 alloys, the most economical steel alloys commercially available for use at such elevated temperatures;

(2) Adequate resistance to corrosion by superheated vapor and combustion gases at 1350° F.;

(3 Adequate hot plasticity, for fabrication into tubing;

(4) Favorable mechanical properties;

(5) Weldability; and

(6) Freedom from serious embrittlement in long-time service at such high temperatures.

To meet these requirements, the invention alloy has the following base composition:

	Percent
Cr	15.00–20.00
Ni	12.00–18.00
C	0.02–0.15
Mn	0.25–2.50
Si	0.10–1.00

Balance iron with the usual impurities.

This base composition is a fully austenitic iron-chrome-nickel steel alloy of relatively low carbon and silicon content. The chromium content is sufficiently high for adequate oxidation and corrosion resistance at temperatures of the order of about 1500° F., and yet sufficiently low to suppress sigma-phase formation. The nickel content is sufficient to maintain the alloy structure fully austenitic over a wide range of variation in alloying additions. The fully austenitic, or face-centered lattice, structure is important for maximum sustained high-temperature strength, the low carbon content assures hot plasticity and weldability, and the low silicon content is adequate insurance against micro-fissuring in welding.

The creep-rupture strength of this base composition is raised by suitable alloy addition designed to produce age hardening processes in the base composition by forming complex carbides or intermetallic compounds which are soluble in the base composition at very high temperatures but insoluble or of limited solubility therein at lower temperatures in the general vicinity of the contemplated use temperature; i. e. of the order of 1350° F., or higher.

In accordance with the present invention, the creep-rupture strength of the base composition is very substantially increased by adding thereto Mo from 2.00% to 3.00%, Ta(Cb—Ta) from 1.00% to 2.00%, and N from 0.15% to 0.25%. The invention alloy may be classed generally as a 15Cr—15Ni—2.5Mo—1.5a(Cb—Ta—.15N steel alloy.

In the drawing, the single figure is a graphical comparison, at 1350° F., of the creep rupture strength of the invention alloy and an AISI type 304 18Cr—8Ni steel alloy.

In the invention alloy, the chromium content selected had to be high enough to insure adequate resistance to oxidation and scaling at a contemplated maximum use temperature of 1350° F. to 1450° F., and low enough to inhibit or minimize the formation of embrittling sigma phase. A chromium content of 15% to 17% is suitable for effecting these results. It is advisable to hold the chromium content on the low side since chromium as well as most of the other element available for strengthening the base composition, is a ferrite former promoting the weak, body-centered cubic lattice structure which has to be compensated by suitably increased additions of the relatively expensive and strategically important, austenite forming nickel. The nitrogen addition aids in stabilizing the strong austenitic structure and is also significant in the age hardening reaction.

With a chromium content of 15% to 17%, a nickel content of 15% is sufficient to "neutralize" the ferrite forming tendencies of chromium and the precipitate producing and strengthening additions. A chromium content of 15% to 17% with a nickel content of about 15% is advantageous from the standpoint of creep strength, as investigations demonstrate that an increase in nickel content above 8% and 10%, required to achieve a fully austenitic structure in a 20% chrome-iron alloy, does not improve the creep strength in any significant degree.

Similarly, if the nickel content in such an alloy is held at 15%, an increase in the chromium content from 15% to 25% does not add materially to the creep strength.

The carbon content of the invention alloy is carefully selected to assure a high enough carbon content for strengthening the alloy through formation of complex carbides yet not so high as to affect adversely forgeability and lead to seams in tubing formed from the alloy. For this purpose, the carbon content has a maximum of 0.12% and preferably is held between 0.03% and 0.05%.

Manganese has a beneficial effect upon hot working properties due to its action upon oxygen and sulphur. It is also desirable as an ingredient due to its tendency to form austenite, although its potency, in this respect, is inferior to that of nickel. Hence, the preferred manganese content is 1.75%, which is near the upper end of the range of manganese commonly found in 18–8 type alloys.

Silicon is a strong ferrite former, and should be kept at a low value where it is desired to promote austenite formation. On the other hand, silicon participates in the formation of strengthening compounds, such as silicides, with columbium and tantalum. It is also a powerful deoxidizer, and enhances resistance to oxidation, at high temperatures, by forming a tightly adherent protective scale, being much more effective than chromium in this respect. By combining a low-range chromium content with a high range silicon content, satisfactory scaling resistance, with a minimum tendency to sigma-phase embrittlement, is assured. For these reasons, a silicon content of substantially 0.75% is preferred.

As stated, the base composition is strengthened by alloy additions designed to produce age hardening processes. For this purpose, the invention alloy, including such additions, is solution heat treated at a high temperature, such as 2200° F. to 2300° F., followed by an aging treatment, or by use, at a lower temperature, such as 1350° F. With suitable alloy additions, a fine dispersion of precipitated compounds in the lattice structure of the matrix is achieved. This fine dispersion resists or retards plastic deformation under stress at elevated temperatures, and thus produces high load carrying ability at such elevated temperatures.

In accordance with the present invention, it has been found that, of available strengthening alloy additions, tantalum, columbium-tantalum and molybdenum are most potent in improving the rupture strength, at elevated temperatures, of the base composition. It also appears that pure columbium, in this respect, is not as effective as tantalum and columbium-tantalum. Nitrogen has been found to be notably effective as a strengthening additive when used in combination with tantalum, columbium-tantalum, and molybdenum.

It has been found further that the strengthening effect of individual additives is not additive and does not even correlate with the relative individual potencies when the additives are added in combination to the base composition. There appears to be an optimum concentration for each element which appears to differ for different combinations of additives.

Within the composition range previously tabulated, a preferred composition of a forgeable, high-strength-at-high-temperature alloy embodying the invention, and which is lean in alloy content and economically practical for superheater tubing, is as follows:

	Percent
Cr	17.00 maximum
Ni	15.00 maximum
C	0.12 maximum
Mn	2.00 maximum
Si	0.75 maximum
Mo	2.00–3.00
Ta	1.00–2.00
N	0.15–0.25

Balance iron with the usual impurities.

The preferred Mo, Ta(Cb—Ta) and N contents are, respectively, 2.50%, 1.50% and 0.15%.

Alloys of substantially this preferred composition have been compounded, solution heat-treated at 2200° F.–2300° F. and aged at temperatures of the order of 1300° F.–1500° F. These alloys have then been subjected to stress rupture tests at 1350° F. for over 10,000 hours. In the accompanying drawing, the stress-rupture curve, plotted on a logarithmic scale with rupture strength in p. s. i. as ordinates and hours under stress as abscissae, is given with actual values up to the 6,000 hours point, and extrapolated to 100,000 hours, the test temperature being 1350° F.

Curves A and A′ represent the stress-rupture values of alloys embodying the invention, while curve B represents those of an AISI type 304 18Cr—8Ni alloy. It will be observed that, at 1000 hours, the stress-rupture strength of the invention alloys is 18,750–20,000 p. s. i., over twice the strength of the type 304 alloy. At 10,000 hours, the stress-rupture strength of the invention alloys is 15,000–16,000 p. s. i. as compared to about 4700 p. s. i. for the type 304 alloy. At 100,000 hours, the indicated rupture strength of the invention alloys is 10,100–11,100 p. s. i., approximately four (4) times the 2700 p. s. i. value for the type 304 alloy. The values for the AISI type 304 alloy are taken from ASTM–ASME Spec. Tech. Publ. No. 124.

It will be noted that the invention alloys have stress-rupture strengths, at 1350° F., over twice that of the type 304 alloy. Consequently, they can be used to form tubing suitable for prolonged service at such temperature and having reduced wall thicknesses acceptable from the fabrication, thermal stress gradient, and economy standpoints, while having a prolonged stress resistance at least equal to that of tubing formed from the type 304 alloys.

The alloys embodying the invention and represented by curves A and A′ of the drawing have percentage compositions within the following ranges:

	Percent
Cr	16.25–18.00
Ni	12.00–15.00
C	0.08– 0.12
Mn	0.80– 1.75
Si	0.30– 0.75
Mo	2.00– 3.00
Ta(Cb—Ta)	1.00– 2.00
N	0.10– 0.18

Balance iron with the usual impurities.

While a specific embodiment of the invention has been shown and described in detail to illustrate the application of the invention principles, it will be understood that the invention may be embodied otherwise without departing from such principles.

What is claimed is:

1. A forgeable austenitic steel alloy having superior stress resistance and corrosion resistance properties, and freedom from impact embrittlement, in extended service under stress at temperatures of the order of 1300° F.; said alloy having the following composition:

	Percent
Cr	15.00–20.00
Ni	12.00–18.00
C	0.02–0.15
Mn	0.25–2.50
Si	0.10–1.00
Mo	2.00–3.00
Ta (Cb—Ta)	1.00–2.00
N	0.15–0.25

Balance iron with the usual impurities,

said alloy having a rupture-strength, after 1000 hours under stress at 1350° F., of at least 18,750 p. s. i., and, after 5000 hours under stress at 1350° F., of at least 15,000 p. s. i.

2. An alloy as claimed in claim 1 which has been solution heat treated at 2250° F.

3. A forgeable austenitic steel alloy having superior stress resistance and corrosion resistance properties, and freedom from impact embrittlement, in extended service under stress at temperatures of the order of 1300° F.; said alloy having the following composition:

	Percent
Cr	17.00 maximum
Ni	15.00 maximum
C	0.12 maximum
Mn	2.00 maximum
Si	0.75 maximum
Mo	2.00–3.00
Ta (Cb—Ta)	1.00–2.00
N	0.15–0.25

Balance iron with the usual impurities,

said alloy having a rupture-strength, after 1000 hours under stress at 1350° F., of at least 18,750 p. s. i., and, after 5000 hours under stress at 1350° F., of at least 15,000 p. s. i.

4. An alloy as claimed in claim 3 which has been solution heat treated at 2250° F.

5. A forgeable austenitic steel alloy having superior stress resistance and corrosion resistance properties, and freedom from impact embrittlement, in extended service under stress at temperatures of the order of 1300° F.; said alloy having the following composition:

	Percent
Cr	17.00 maximum
Ni	15.00 maximum
C	0.12 maximum
Mn	2.00 maximum
Si	0.75 maximum
Mo	2.50
Ta (Cb—Ta)	1.50
N	0.15

Balance iron with the usual impurities,

said alloy having a rupture-strength, after 1000 hours under stress at 1350° F., of at least 18,750 p. s. i., and, after 5000 hours under stress at 1350° F., of at least 15,000 p. s. i.

6. An alloy as claimed in claim 5 which has been solution heat treated at 2250° F.

7. A forgeable austenitic steel alloy having superior stress resistance and corrosion resistance properties, and freedom from impact embrittlement, in extended service under stress at temperatures of the order of 1300° F.; said alloy having the following composition:

	Percent
Cr	16.25–18.00
Ni	12.00–15.00
C	0.08–0.12
Mn	0.80–1.75
Si	0.30–0.75
Mo	2.00–3.00
Ta (Cb—Ta)	1.00–2.00
N	0.10–0.18

Balance iron with the usual impurities,

said alloy having a rupture-strength, after 1000 hours under stress at 1350° F., of at least 18,750 p. s. i., and, after 5000 hours under stress at 1350° F., of at least 15,000 p. s. i.

8. An alloy as claimed in claim 7 which has been solution heat treated at 2250° F.

References Cited in the file of this patent

FOREIGN PATENTS

670,555	Great Britain	Apr. 23, 1952
929,727	France	Jan. 6, 1948
478,014	Italy	Feb. 12, 1953