

US010260129B2

(12) **United States Patent** (10) Patent No.: US 10,260,129 B2
Baker et al. (45) Date of Patent: Apr. 16, 2019

(54) ULTRA SUPERCRITICAL BOILER HEADER ALLOY AND METHOD OF PREPARATION

- (71) Applicant: **Huntington Alloys Corporation**, Huntington, WV (US)
- (72) Inventors: Brian A. Baker, Kitts Hill, OH (US); Gaylord D. Smith, Huntington, $\overline{W}V$ (US); Ronald D. Gollihue, Grayson, KY (US)
- (73) Assignee: **Huntington Alloys Corporation**, $\frac{6,106,767 \text{ A} * 8/2000 \text{ Kennedy} \dots \dots \dots \dots \dots \text{ C22C 30/00}}{420/448}$
- (*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days. JP H 08/188841 * 7/1996
- (21) Appl. No.: 16/051,874 OTHER PUBLICATIONS
-

(65) **Prior Publication Data**

US 2018/0340242 A1 Nov. 29, 2018

Related U.S. Application Data

- (63) Continuation of application No. 12/420,251, filed on \overrightarrow{A} his Apr. 8, 2009, now Pat. No. 10,041,153.
- (60) Provisional application No. 61/043,881, filed on Apr. 10, 2008.
- (51) Int. Cl.

(45) Date of Patent: Apr. 16, 2019

- (52) U . S . CI . CPC C22C 19 / 055 (2013 . 01) ; C22C 19 / 05 (2013.01); C22C 19/058 (2013.01); C22F 1/10 (2013.01); F22B 37/22 (2013.01)
- (58) Field of Classification Search None See application file for complete search history.

(56) References Cited

U.S. PATENT DOCUMENTS

420/448

UP H 08/188841 * 7/1996 C22C 19/05

(22) Filed: **Aug. 1, 2018** English translation of JPH 08/188841 (Year: 1996).*

* cited by examiner

Primary Examiner — Yoshitoshi Takeuchi

(74) Attorney, Agent, or $Firm$ - Burris Law, PLLC

ABSTRACT

A high temperature, high strength Ni-Co-Cr alloy is provided. The alloy includes, in weight percent (wt. %): 23.5 to 25.5% Cr, 15.0 to 22.0% Co, 1.1 to 2.0% Al, 1.0 to 1.8% Ti, 0.95 to 2.2% Nb, less than 1.0% Mo, less than 1.0% Mn, up to 0.24% Si, less than 3.0% Fe, less than 0.3% Ta, less than 0.3% W, 0.005 to 0.08% C, 0.01 to 0.3% Zr, 0.0008 to 0.006% B, up to 0.05% rare earth metals, and a balance of Ni plus trace impurities .

17 Claims, 3 Drawing Sheets

 $FIG. 1$

FIG. 2

FIG. 3

patent application Ser. No. 12/420,251 filed on Apr. 8, 2009, age-hardening potential of the alloy, thereby developing
which claims the benefit of U.S. Provisional Patent Appli- high strength at elevated temperatures. Howe cation No. 61/043,881 filed Apr. 10, 2008, both of which are ¹⁰ chromium not only degrades the strengthening mechanism incorporated herein by reference.

a high temperature, high strength nickel (Ni)-cobalt (Co)-
chromium (Cr) alloy for long-life service at 538° C. to 816° C. that offers a combination of strength, ductility, stability, stability, SUMMARY toughness and fissure-free weldability as to render the alloy 20 range uniquely suitable for the header pipe in ultra-superrange uniquely suitable for the header pipe in ultra-super-

In one form of the present disclosure, a high temperature,

critical boiler applications where essentially fissure-free high strength Ni—Co—Cr alloy comprising, joining of boiler tubes to the header is critical. percent $(wt. %), 23.5$ to $25.5%$ Cr, 15.0 to $22.0%$ Co, 1.1 to

alloys meeting requirements for both high strength at In an alloy of the present disclosure, the alloy comprises elevated temperatures and corrosion resistance under severe 30 at least one of the following: Cr content is 24.0 to 25.3%; Co environmental conditions. This quest for increasing perfor-
content is 18.0 to 21.0%; Al content environmental conditions. This quest for increasing perfor-
mance is far from over as designers and engineers seek to
content is 1.1 to 1.6%; Nb content is 1.0 to 2.1%; Mo content mance is far from over as designers and engineers seek to content is 1.1 to 1.6%; Nb content is 1.0 to 2.1%; Mo content is 0.25 to 0.8%; Fe content is 0.25 increase productivity and efficiency, lower operating costs is 0.08 to 0.8%; Mn content is 0.1 to 0.8%; Fe content is 0.25 and extend service lives. All too often, researchers termi-
to 2.8%; Ta content is 0.05 to less tha nated their efforts when the target combination of properties 35 is 0.05 to less than 0.3%.
was achieved, thereby leaving the optimization of the alloy In numerous alloys of the present disclosure, the alloy range open for example, in coal-fired, ultra-supercritical boiler materials in critical need of advanced alloys to maintain progress. This service requires ever-increasing strength at increasingly 40 is 0.2 to 0.6%; Mn content is 0.2 to 0.6%; Fe content is 0.5 higher temperatures, as operating conditions become more to 2.5%; Ta content is 0.1 to 0.3%; and higher temperatures, as operating conditions become more to 2.5%; Ta content is 0.1 to 0.3%; and W content is 0.1 to demanding and service lives are required to be trouble-free less than 0.3%. over the life of the equipment. Coal-fired ultra-supercritical At least one of the alloys of the present disclosure boiler designers must develop the materials meeting their possesses essentially fissure-free weldability. advanced requirements as they improve efficiency by raising 45 In another form of the present disclosure, a high tempera-

Today's boilers with efficiencies around 45% typically operate up to 290 bar steam pressure and 580° C. steam temperature. Designers are setting their sights on 50% Mn, up to 0.24% Si, 0.25 to 2.8% Fe, 0.05 to less than 0.3% efficiency or better by raising the steam conditions as high $\frac{50}{6}$ Ta, 0.05 to less than 0.3% W, 0 efficiency or better by raising the steam conditions as high 50 Ta, 0.05 to less than 0.3% W, 0.01 to 0.06% C, 0.05 to 0.25% as 325 bar/760° C. To meet this requirement in the boiler Zr , 0.001 to 0.004% B, 0.001 to 0. as 325 bar/760° C. To meet this requirement in the boiler Zr , 0.001 to 0.004% B, 0.001 to 0.04% rare earth metallies, the 100,000 hour stress rupture life must exceed a balance of Ni plus trace impurities is provided. 100 MPa at temperatures as high as 760° C. Additionally, In other alloys of the present disclosure: the Cr content is raising steam temperature has made steam corrosion more 24.2 to 25.2%, the Co content is 19.0 to 20.5%, troublesome placing a further requirement on any new alloy. 55 This requirement is less than 2 nm of metal loss in 200,000 This requirement is less than 2 mm of metal loss in 200,000 content is 1.0 to 2.0%, and the Mo content is 0.2 to 0.6%; hours for steam oxidation in the temperature range of 700° and the Mn content is 0.2 to 0.6%, the hours for steam oxidation in the temperature range of 700° and the Mn content is 0.2 to 0.6%, the Fe content is 0.5 to C. to 800° C. For service as a header alloy, the material must 2.5%, the Ta content is 0.1 to 0.3 be fabricable as thick-walled pipe (i.e., up to 80 mm wall to less than 0.3%;
thickness) and be fissure-free weldable into complex headers 60 In yet another form of the present disclosure, a high using conventional metal working and welding equipment. temperature, high strength Ni—Co—Cr alloy comprising, in This places a major constraint on the fabricability and weight %, 24.2 to 25.2% Cr, 19.0 to 20.5% Co, 1.2 to 1.6% welding characteristics acceptable in manufacture and field Al, 1.1 to 1.5% Ti, 1.0 to 2.0% Nb, 0.2 to 0.6% welding characteristics acceptable in manufacture and field Al, 1.1 to 1.5% Ti, 1.0 to 2.0% Nb, 0.2 to 0.6% Mo, 0.2 to installation. Such characteristics run counter to the need for 0.6% Mn, up to 0.24% Si, 0.5 to 2.5% Fe,

To meet the strength and temperature requirements of 0.2% Zr, 0.001 to 0.003% B, 0.001 to 0.03% rare earth future ultra-supercritical boiler materials, designers must metal, and a balance of Ni plus trace impurities is pro

 $\mathbf{2}$

ULTRA SUPERCRITICAL BOILER HEADER exclude the usual ferritic, solid solution austenitic and ALLOY AND METHOD OF PREPARATION age-hardenable alloys heretofore employed for this service. These materials commonly lack one or more of the require-CROSS-REFERENCE TO RELATED ments of adequate strength, temperature capability and sta-
A ppt ICATIONS APPLICATIONS ⁵ bility or steam corrosion resistance. For example, the typical age-hardenable alloy must be alloyed with insufficient chromium for oxidation resistance in order to maximize the This application is a continuation application of U.S. mium for oxidation resistance in order to maximize the tent application Ser. No. 12/420.251 filed on Apr. 8, 2009, age-hardening potential of the alloy, thereby develo but, if added in excess, can result in embrittling sigma or alpha-chromium formation. Since 538° C. to 816° C. is a very active range for carbide precipitation and embrittling FIELD very active range for carbide precipitation and embrittling
grain boundary film formation, alloy stability is compro-
header pipe in boiler applications and, more particularly, to
a high temperature strength and adeq

2.0% Al, 1.0 to 1.8% Ti, 0.95 to 2.2% Nb, less than 1.0% BACKGROUND 25 Mo, less than 1.0% Mn, up to 0.24% Si, less than 3.0% Fe,
less than 0.3% Ta, less than 0.3% W, 0.005 to 0.08% C, 0.01
Over the years, metallurgists engaged in material devel-
to 0.3% Zr, 0.0008 to 0.006% B, u Over the years, metallurgists engaged in material devel-
operator the utility industry have continually developed metals, and a balance of Ni plus trace impurities is provided.

to 2.8%; Ta content is 0.05 to less than 0.3% ; and W content

comprises one of the following: Cr content is 24.2 to 25.2% ; Co content is 19.0 to 20.5% ; Al content is 1.2 to 1.6% ; Ti content is 1.1 to 1.5; Nb content is 1.0 to 2.0%; Mo content

steam pressure and temperature.
Today's boilers with efficiencies around 45% typically $\%$, 24.0 to 25.3% Cr, 18.0 to 21.0% Co, 1.2 to 1.8% Al, 1.1 to 1.6% Ti, 1.0 to 2.1% Nb, 0.08 to 0.8% Mo, 0.1 to 0.8% Mn, up to 0.24% Si, 0.25 to 2.8% Fe, 0.05 to less than 0.3%

> 24.2 to 25.2%, the Co content is 19.0 to 20.5%, and the Al content is 1.2 to 1.6%; the Ti content is 1.1 to 1.5, the Nb 2.5%, the Ta content is 0.1 to 0.3%, and the W content is 0.1 to less than 0.3% ;

installation. Such characteristics run counter to the need for 0.6% Mn, up to 0.24% Si, 0.5 to 2.5% Fe, 0.1 to less than superior strength in boiler tube service. $65\,0.3\%$ Ta, 0.1 to less than 0.3% W, 0.02 to 0.05% perior strength in boiler tube service. $65 \quad 0.3\%$ Ta, 0.1 to less than 0.3% W, 0.02 to 0.05% C, 0.05 to To meet the strength and temperature requirements of 0.2% Zr, 0.001 to 0.003% B, 0.001 to 0.03% rare earth metal, and a balance of Ni plus trace impurities is provided.

associated with each element employed in this disclosure.

percentage as a function of aluminum and titanium in a temperatures. The function of these minor elements is to material comprising 24.5 wt. % Cr. 20 wt. % Co. 1 wt. % Nb. enhance scale adhesion, density and resistance to material comprising 24.5 wt. % Cr, 20 wt. % Co, 1 wt. % Nb, enhance scale adhesion, density and resistance to decompo-
1 wt. % Fe, 0.03 wt. % C and the balance Ni at 760° C, in 10 sition. The minimum level of Cr is chosen 1 wt. % Fe, 0.03 wt. % C and the balance Ni at 760° C. in 10 accordance with the present disclosure;

percentage as a function of aluminum and titanium in a ated α -chromia formation but did not change the nature of material comprising 24.5 wt. % Cr. 20 wt. % Co. 1.5 wt. % che scale. The maximum Cr level for this alloy material comprising 24.5 wt. % Cr, 20 wt. % Co, 1.5 wt. % the scale. The maximum Cr level for this alloy range was Nb, 1 wt. % Fe, 0.03 wt. % C and the balance Ni at 760 $^{\circ}$ C. 15 determined by alloy phase stability and Nb, 1 wt. % Fe, 0.03 wt. % C and the balance Ni at 760° C. 15 determined by alloy phase stability and workability in accordance with the present disclosure; and maximum level of Cr was found to be about 25.5%.

percentage as a function of aluminum and titanium in a because it contributes to hot hardness and strength retention material comprising 24.5 wt. % Cr, 20 wt. % Co, 2 wt. % Nb, at the upper regions of the intended s material comprising 24.5 wt. % Cr, 20 wt. % Co, 2 wt. % Nb, at the upper regions of the intended service temperature 1 wt. % Fe, 0.03 wt. % C and the balance Ni at 760° C, in 20 (538° C, -816° C,) and contributes in a sig 1 wt. % Fe, 0.03 wt. % C and the balance Ni at 760° C. in 20 (538° C.-816° C.) and contributes in a significant way to the accordance with the present disclosure. high temperature corrosion resistance of the alloy range.

specified. In accordance with the present disclosure, the deoxidation but also reacts with Ni in conjunction with Ti alloy broadly contains 23.5 to 25.5% Cr, 15-22% Co, 1.1 to and Nb to form the high temperature phase, gam 2.0% Al, 1.0 to 1.8% Ti, 0.95 to 2.2% Nb, less than 1.0% (Ni₃Al, Ti, Nb). The Al content is restricted to the range of Mo, less than 1.0% Mn, less than 0.3% Si, less than 3% Fe, 30 1.1 to 2.0%. The minimum total of A Mo, less than 1.0% Mn, less than 0.3% Si, less than 3% Fe, 30 less than 0.3% Ta, less than 0.3% W, 0.005 to 0.08% C, 0.01 less than 0.3% Ta, less than 0.3% W, 0.005 to 0.08% C, 0.01 to at least 14% hardener phase is shown in FIGS. 1 through to 0.3% Zr, 0.0008 to 0.006% B, up to 0.05% rare earth 3 for 1% Nb, 1.5% Nb and 2.0% Nb, respectively to 0.3% Zr, 0.0008 to 0.006% B, up to 0.05% rare earth 3 for 1% Nb, 1.5% Nb and 2.0% Nb, respectively at a service metals, 0.005% to 0.025% Mg plus optional Ca, balance Ni temperature of 760° C. 14% hardener phase is co metals, 0.005% to 0.025% Mg plus optional Ca, balance Ni temperature of 760° C. 14% hardener phase is considered including trace additions and impurities. The strength and the minimum required for strength at 760° C. The c stability are assured at 760° C. when the Al/Ti ratio is 35 sitions in accordance with the present disclosure (i.e., alloys constrained to between 0.95% and 1.25%. Further, the sum A through F) are depicted on FIGS. constrained to between 0.95% and 1.25%. Further, the sum A through F) are depicted on FIGS. 1 through 3 in association of Al+Ti is constrained to between 2.25% and 3.0%. The tion with the closest Nb content. The strength upper limits for Nb and Si are defined by the relationship: (% $Nb+0.95$)+3.32(% Si) \leq 3.16.

The above combination of elements possesses all the 40 critical attributes required of the header in an ultra - super - Al in conjunction with the other hardener elements markedly by alloying with a narrow range of Cr (23.5-25.5%) without ability of the alloy range.
destroying phase stability resulting from embrittling phases with higher amounts of Al. by concurrently limiting certain elements to very narrow 45 Titanium (Ti) in the alloy range 1.0-1.8% is an essential ranges (e.g., less than 1% Mo, less than 0.08% C, less than strengthening element as stated above and sh ranges (e.g., less than 1% Mo, less than 0.08% C, less than
3.0% Fe, less than 0.3% Si and the total Ta plus W content
1 through 3. Strength and stability is assured at 760° C. when
less than 0.6%). Less than 23.5% steam oxidation resistance and greater than 25.5% Cr pro-
durcher the sum of Al+Ti is constrained to between 2.25 and
duces embrittling phases even with the alloy restrictions 50 3.0. Titanium also serves to act as grain s duces embrittling phases even with the alloy restrictions 50 3.0. Titanium also serves to act as grain size stabilizer in defined above. Too often, striving for maximum corrosion conjunction with Nb by forming a small amou resistance results in alloys lacking the required high tem-
perature strength. This has been solved in the alloy of the limited to less than 1.0 volume percent in order to preserve perature strength. This has been solved in the alloy of the limited to less than 1.0 volume percent in order to preserve present disclosure by balancing the weight percent of pre-
hot and cold workability of the alloy. Tit present disclosure by balancing the weight percent of pre-
cipitation of the alloy. Titanium in amounts
cipitation hardening elements to a narrow range where the 55 in excess of 1.8% can be prone to internal oxidation lead cipitation hardening elements to a narrow range where the 55 in excess of 1.8% can be prone to internal oxidation leading
resulting volume percent of hardening phase is between to reduced matrix ductility and lead to forma resulting volume percent of hardening phase is between to reduced matrix ductility and lead to formation of unde-
about 14 and 20% within the Ni—Co—Cr matrix. The sirable eta phase formation. strength and stability are assured at 760° C. when the Al/Ti Niobium (Nb) in the alloy within a range of 0.95-2.2% is ratio is constrained to between 0.95% and 1.25%. Further, also an essential strengthening and grain size ratio is constrained to between 0.95% and 1.25%. Further, also an essential strengthening and grain size control ele-
the sum of Al+Ti is constrained to between 2.25% and 3.0%. 60 ment. The Nb content must allow for at lea the sum of Al+Ti is constrained to between 2.25% and 3.0%. 60 ment. The Nb content must allow for at least 14% gamma
Excessive amounts of the hardener elements not only reduce phase formation at 760° C. when Al and Ti are phase stability, lower ductility and toughness but also render
pipe manufacturability extremely difficult if not impossible. between gamma prime and the matrix and accelerates the pipe manufacturability extremely difficult if not impossible. between gamma prime and the matrix and accelerates the The selection of each elemental alloying range can be gamma prime growth rate. Conversely, Nb above 2.2% rationalized in terms of the function each element is 65 expected to perform within the compositional range of this

A better appreciation of the alloying difficulties is pre-
Sented by defining below the benefits and impediments
of the present disclosure because it assures development of
associated with each element employed in this dis oxidation resistance vital for the intended application . In DRAWINGS $\frac{5}{5}$ conjunction with the minor elements Zr (up to 0.3%), Mg (up to 0.025%) and Si (up to 0.3%), the protective nature of the scale is even more enhanced and made effective to higher FIG. 1 is an isopleth showing gamma prime weight the scale is even more enhanced and made effective to higher recentage as a function of aluminum and titanium in a temperatures. The function of these minor elements is to α -chromia formation at 538° and above. This level of Cr was found to be about 23.5%. Slightly higher Cr levels acceler-FIG. 2 is an isopleth showing gamma prime weight found to be about 23.5%. Slightly higher Cr levels acceler-
reentage as a function of aluminum and titanium in a ated α -chromia formation but did not change the nature of

FIG. 3 is an isopleth showing gamma prime weight Cobalt (Co) is an essential matrix-forming element recentage as a function of aluminum and titanium in a because it contributes to hot hardness and strength retention Beta However, because of cost, it is preferred to maintain the DETAILED DESCRIPTION level of Co below 40% of that of the Ni content Thus the level of Co below 40% of that of the Ni content Thus the beneficial range of the Co content becomes 15.0 to 22.0%.

The chemical compositions set forth throughout this 25 Aluminum (Al) is an essential element in the alloy range specification are in weight percentages unless otherwise of the present disclosure because it not only contrib tion with the closest Nb content. The strength and stability is assured at 760° C. when the Al/Ti ratio is constrained to between 0.95 and 1.25. Further the sum of Al+Ti is constrained to between 2.25 and 3.0. Larger amounts than 2.0% reduces ductility, stability and toughness and reduces workability of the alloy range. Internal oxidation can increase

gamma prime growth rate. Conversely, Nb above 2.2% increases the propensity for unwanted eta phase formation expected to perform within the compositional range of this and increases the fissuring tendency. Niobium along with patent application. This rationale is defined below. titanium can react with carbon to form primary carbid titanium can react with carbon to form primary carbides

which act as grain size stabilizers during hot working. An
excessive amount of Nb can reduce the protective nature of
protective scale and hence is to be avoided. It is a further
disclosure. These carbides also contribute limits. Nb and Si are inversely related in this regard. Higher Boron (B) in amounts between 0.0008 to 0.006% is
Nb levels require lower Si levels and vice-versa. In general effective in contributing to high temperature str Nb levels require lower Si levels and vice-versa. In general, effective in contributing to high temperature strength and the following formula defines an upper limit for Nb in stress rupture ductility. Base plates of alloy the following formula defines an upper limit for Nb in relation to that of Si content:

$$
(\% Nb+0.96)+3.32(\% Si)\leq 3.16
$$
 (1)

strengthening of the matrix but must be considered an Magnesium (Mg) and optionally calcium (Ca) in total element to be restricted to less than 1.0% due to its apparent amount between 0.005 and 0.025% are both an effective element to be restricted to less than 1.0% due to its apparent amount between 0.005 and 0.025% are both an effective deleterious effect on steam oxidation resistance and TCP desulfurizer of the alloy and a contributor to s

protective scale integrity. Consequently, this element is up to 0.05% to promote hot workability and scale adhesion.
maintained below 1.0%. Manganese, above this level, However, their presence is not mandatory as is that

 $\frac{\text{sin}}{\text{cos} \cdot \text{cos} \cdot \text{$ ing action that the silica layer contributes to inhibiting elements that make up the alloy of the disclosure ingress of the steam molecules or ions within the header and a presently preferred nominal composition. the egress of cations of the alloy. Excessive amounts of Si
can contribute to loss of ductility, toughness and workability.
Si because it widens the liquidus to solidus range of the
persiantial of the Compositional Range compositional range of the alloy of the present disclosure and contributes in a significant way to the formation of fissuring during welding, hence its content must be severely limited to 0.3% for optimum results. Si acts in conjunction 40 with Nb in this regard as defined in equation (1) above. The maximum in fissure-free weldability is best achieved provided the Si level is less than 0.05%. However, the use of alloy scrap and typical commercial feed stocks suggests that a range of 0.05 to 0.3% Si is satisfactory for essentially $_{45}$ fissure-free weldability.

Iron (Fe) additions to the alloys of the present disclosure
lower the high temperature corrosion resistance by reducing the integrity of the α -chromia by forming the spinel, FeCr_2O_4 . Consequently, it is preferred that the level of Fe be 50 maintained at less than 3.0%. Fe can also contribute to formation of undesirable TCP phases such as sigma phase. Where virgin metal feed stock is specified in the charge make-up, a maximum limit of 0.4% Fe is desirable for best steam oxidation resistance. However, the use of alloy scrap and typical commercial feed stocks suggests that a range of 0.25 to 3.0% Fe is satisfactory for both steam oxidation resistance and essentially fissure-free weldability.

Zirconium (Zr) in amounts between 0.01 to 0.3% is 60 effective in contributing to high temperature strength and EXAMPLES stress rupture ductility. Larger amounts lead to grain boundary liquation and markedly reduced hot workability. Zircoary liquation and markedly reduced hot workability. Zirco-

Examples are set forth below. Examples of compositions

nium in the above compositional range also aids scale

of Table II and current commercial and experimental

aid grain size control in conjunction with Ti and Nb since the

6

III, set forth hereinafter, demonstrate this point showing that $\frac{1}{10}$ boron in alloy I (0.009% B) that is outside the limits of this patent application is subject to gross fissuring (counts as Tantalum (Ta) and Tungsten (W) also form primary
carbides which can function similarly to that of Nb and Ti.
However, their negative effect on TCP phase stability limits
the presence of each to less than 0.3%. the presence of each to less than 0.3% .

were manual Gas Tungsten Arc Welded (GTAW) with filler

Molybdenum (Mb) can contribute to solid solution $_{15}$ metal of composition K in Table III.

phase formation when added to a greater extent to the alloys
 $\frac{1}{20}$ and lower product yield. Trace amounts of lanthanum (La), Manganese (Mn), while an effective desulfurizer during yttrium (Y) or Misch metal may be present in the alloys of melting, is overall a detrimental element in that it reduces the present disclosure as impurities or deliber the present disclosure as impurities or deliberate additions

	Designation of the Compositional Ranges for the Broad, Intermediate and Narrow Limits for Ultra Supercritical Boiler Header Pipe of the Present Disclosure					
	Element	Broad Weight %	Intermediate Weight %	Narrow Weight %		
	Сr	23.5-25.5	$24.0 - 25.3$	24.2-25.2		
	Co	15.0-22.0	18.0-21	19-20.5		
	Al	$1.1 - 2.0$	$1.2 - 1.8$	$1.2 - 1.6$		
	Ti	$1.0 - 1.8$	$1.1 - 1.6$	$1.1 - 1.5$		
	Nb	$0.95 - 2.2$	$1.0 - 2.1$	$1.0 - 2.0$		
	Mo	$0 - 1.0$	$0.08 - 0.8$	$0.2 - 0.6$		
	Mn	$0 - 1.0$	$0.1 - 0.8$	$0.2 - 0.6$		
	Si	$0 - 0.3$	$0.05 - 0.3$	$0.1 - 0.3$		
	Fe	$0 - 3.0$	$0.25 - 2.8$	$0.5 - 2.5$		
	Ta	$0 - 0.3$	$0.05 - 0.3$	$0.1 - 0.3$		
	W	$0 - 0.3$	$0.05 - 0.3$	$0.1 - 0.3$		
	C	$0.005 - 0.08$	$0.01 - 0.06$	$0.02 - 0.05$		
	Zr	$0.01 - 0.3$	0.05-0.25	$0.05 - 0.2$		
	B	0.0008-0.006	$0.001 - 0.004$	$0.001 - 0.003$		
	Rare Earth	$0 - 0.05$	$0.001 - 0.04$	$0.001 - 0.03$		
	Mg	0.005-0.025	$0.005 - 0.02$	0.005-0.015		
	Ni	45.0-58.0	45.0-56.0	45.0-55.0		
	Al/Ti	0.95-1.25	$1.0 - 1.20$	$1.0 - 1.15$		
	$Al + Ti$	$2.25 - 3.0$	2.30-2.90	2.40-2.80		
	Nb + Si	$<$ 3.16	<3.0	< 2.8		

hesion under thermally cyclic conditions.
Carbon (C) should be maintained between 0.005-0.08% to vying for consideration in boiler fabrication are listed in vying for consideration in boiler fabrication are listed in Table III. $\overline{7}$

* K is a commercial filler metal of NIMONIC alloy 263 , m = maximum

Alloy Preparation and Mechanical Testing gas metal arc welding (manual p-GMAW) was used to
Alloys A through F in Table III and alloys H, I and J in demonstrate defect-free weldability. The welding param-
Table III were vac and vacuum arc remelted. Alloy K is filler metal from a commercial heat of NIMONIC alloy 263. The ingots were homogenized at 1204° C. for 16 hours and subsequently hot worked to 15 mm bar at 1177° C. with reheats as required to maintain the bar temperature at least at 1050° C. The final 35 anneal was for times up to two hours at 1150° C. and water quenched. Standard tensile and stress rupture specimens were machined from both annealed and annealed plus aged bar (aged at 800° C. for 8 hours and air cooled). Annealed and aged room temperature tensile strength plus high tem- 40 perature tensile properties are presented in Table IV below.

Tensile Properties of Alloy B As-Annealed (1121° C/60 Minutes/Water Quenched) and As-Annealed Plus Aged (800° C./4 Hours/Air Cooled)							
		Ultimate					
	Yield	Tensile		Reduction of			
Temperature	Strength	Strength	Elongation	Area			
$(^{\circ}$ C.)	(MPa)	(MPa)	(%)	(%)			
As-Annealed Plus Aged (800° C./4 Hours/Air Cooled)							
74	743	1151	34.4	37.5			
750	618	743	6.8	9.3			

tion of a coal-fired ultra-supercritical boiler, performs the the full breadth of the appended claims and any and all function of concentrating steam from all the boiler tubes and equivalents thereof. sending the steam through transfer piping to the turbine. It 60 What is claimed is:
is usually a 5.0 to 8.0 cm thick extruded pipe (20-36 cm 1. A Ni—Co—Cr alloy, the alloy comprising in weight %: is usually a 5.0 to 8.0 cm thick extruded pipe (20-36 cm outer diameter) and is unique in the large number of welded tubes joined to the header pipe. The strength requirements 1.8% Ti, 0.95 to 2.2% Nb, 0.08 to 0.8% Mo, less than 1.0% are discussed hereinabove. The header pipe welded joints Mn, 0.05 up to 0.24% Si, less than 3.0% Fe, less are discussed hereinabove. The header pipe welded joints Mn, 0.05 up to 0.24% Si, less than 3.0% Fe, less than 0.3% must meet pressure code requirements (ASME Section IX). 65 Ta, less than 0.3% W, 0.005 to 0.08% C, 0.01 to The fact that the welded joints of this alloy range can be 0.0008 to 0.006% B, up to 0.05% rare earth metals, balance satisfactorily made is demonstrated below. Manual pulsed Ni plus trace impurities. satisfactorily made is demonstrated below. Manual pulsed

Manual Pulsed GMAW Parameters used in the Present Disclosure				
Parameters	Value			
Amperage Voltage Shielding Gas Wire Speed Travel Speed	$130 + - 5$ $27.0 + 6.75$ 75/25 Argon/Helium @35 cfh \sim 250 IPM/0.045" wire \sim 10.0 IPM			

1.6 cm sections of alloys B through E were welded using manual p-GMAW employing alloy G from Table III as the TABLE IV filler metal and the welding parameters of Table V. Prior to welding the alloys were aged and then re-aged after welding. 45 The welded joints were metallographically examined using
up to five views. The base metals of these joints were deemed essentially defect free and meeting the qualifications of ASME Section IX. The manual p-GMAW is a high heat input, rapid deposition welding technique. These results are
50 deemed extremely significant.

While specific embodiments of the disclosure have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings Establishing the Welding Characteristics of the Alloys of the 55 of the disclosure. The presently preferred embodiments Present Disclosure . The present Disclosure . esent Disclosure
Boiler header pipe, located outside the combustion sec-
limiting as to the scope of the disclosure which is to be given

23.5 to 25.5% Cr, 15.0 to 22.0% Co, 1.1 to 2.0% Al, 1.0 to 1.8% Ti, 0.95 to 2.2% Nb, 0.08 to 0.8% Mo, less than 1.0%

2. The alloy of claim 1, wherein the alloy comprises at 11. The alloy of claim 1, wherein the Ta content is 0.1 to least one of the following:

3. The alloy of claim 1, wherein the Cr content is 24.2 to $\begin{array}{c} \text{to } 25.2\% \\ \text{is } 1.2 \text{ to } 1.6\% \end{array}$

5. The alloy of claim 1, wherein the Al content is 1.2 to 1.6% .

6. The alloy of claim 1, wherein the Ti content is 1.1 to $_{20}$ 1.5.

7. The alloy of claim 1, wherein the Nb content is 1.0 to 2.0% .

9. The alloy of claim 1, wherein the Mn content is 0.2 to 25 0.6%.

10. The alloy of claim 1, wherein the Fe content is 0.5 to 2.5% .

Cr content is 24.0 to 25.3%;

Co content is 18.0 to 21.0%;

Less than 0.3%.

Less than 0.3%.

Al content is 1.2 to 1.8%;
 $\frac{5}{24.0 \text{ to } 25.3\% \text{ Cr}}$ 18.0 to 21.0% Co, 1.2 to 1.8% Al, 1.1
 $\frac{1}{24.0 \text{ to } 25.3\% \text{ Cr}}$ 18.0 to 21.0% Co, 1.2 to 1.8% Al, 1.1 %: 24.0 to 25.3% Cr, 18.0 to 21.0% Co, 1.2 to 1.8% Al, 1.1 Nb content is 1.0 to 2.1%;

Nb content is 1.0 to 2.1%;

Mn, up to 0.24% Si, 0.25 to 2.8% Fe, 0.05 to less than 0.3%

Mn, up to 0.24% Si, 0.25 to 2.8% Fe, 0.05 to less than 0.3% Mn, up to 0.24% Si, 0.25 to 2.8% Fe, 0.05 to less than 0.3%
Mo content is 0.08 to 0.8%;
Mn content is 0.1 to 0.8%;
Mn content is 0.1 to 0.8%;

Mn content is 0.1 to 0.07%,
Fe content is 0.25 to 2.8%;
 $10\,Zr$, 0.001 to 0.04% B, 0.001 to 0.04% rare earth metals,

Fe content is 0.25 to 2.8%, $\frac{1}{2}$ had balance Ni plus trace impurities.
The content is 0.05 to less than 0.3% and the alloy of claim 13, when W content is 0.05 to less than 0.3%. **14**. The alloy of claim 13, wherein the Cr content is 24.2 to 25.2% , the Co content is 19.0 to 20.5% , and the Al content

25.2%.

4. The alloy of claim 1, wherein the Co content is 19.0 to $\frac{15}{15}$. The alloy of claim 13, wherein the Ti content is 1.1 to 4. The alloy of claim 1, wherein the Mo content is 1.1 to 20.5%.

20.5% The allow of claim 1, wherein the Al content is 1.2 to $\frac{1.5}{100}$, the Nb content is 1.0 to 2.0%, and the Mo content is 0.2

16. The alloy of claim 13, wherein the Mn content is 0.2 to 0.6% , the Fe content is 0.5 to 2.5% , the Ta content is 0.1

to 0.3%, and the W content is 0.1 to less than 0.3%.
17. A Ni—Co—Cr alloy, the alloy comprising in weight %: 24.2 to 25.2% Cr, 19.0 to 20.5% Co, 1.2 to 1.6% Al, 1.1 **8.** The alloy of claim 1, wherein the Mo content is 0.2 to 1.5% Ti, 1.0 to 2.0% Nb, 0.2 to 0.6% Mo, 0.2 to 0.6% Mn, 0.6%.

up to 0.24% Si, 0.5 to 2.5% Fe, 0.1 to less than 0.3% Ta, 0.1 . up to 0.24% Si, 0.5 to 2.5% Fe, 0.1 to less than 0.3% Ta, 0.1 to less than 0.3% W, 0.02 to 0.05% C, 0.05 to 0.2% Zr, 0.001 to 0.003% B, 0.001 to 0.03% rare earth metals, balance Ni plus trace impurities.