IMPROVING THE NOTCH-RUPTURE STRENGTH OF LOW-EXPANSION SUPERALLOYS

D. F. Smith, E. F. Clatworthy,
D. G. Tipton, and W. L. Mankins

Huntington Alloys, Inc.
Huntington, West Virginia

Age-hardenable iron-nickel-cobalt alloys that combine high strength with controlled thermal-expansion characteristics have attractive properties for various applications at temperatures to 650°C (1200°F). However, the alloys have had very poor notch-rupture strength unless stressed in the direction of retained warm work. Stress-rupture properties in air were further deteriorated by intergranular oxidation/stress-corrosion cracking. Through extensive research on the alloy system, those drawbacks have now been greatly reduced. A modified alloy shows much improved notch-rupture strength while retaining the desirable thermal-expansion characteristics. The improvement was brought about through lowered aluminum content, increased levels of columbium and titanium, and modified heat treatment.

INCOLOY* alloy 903 (38 Ni, 15 Co, 3 Cb, 1.4 Ti, 0.9 Al, bal. Fe) is an age-hardenable alloy with high strength, controlled low expansion coefficient, good thermal-fatigue resistance (1) and reduced sensitivity to high-pressure hydrogen embrittlement (2). Its properties make it attractive for gas-turbine components at temperatures up to 650°C (1200°F) where smooth- and notch-bar stress-rupture behavior becomes an additional property consideration.

Attaining good notch-rupture strength has long been a problem in the development of superalloys, particularly when processing or fabrication steps such as brazing expose the material to temperatures of 980°C (1800°F) or higher. Unfortunately, the development of low-expansion alloys for applications up to 650°C (1200°F) brought no relief in this area (3,4). Instead, apparently complicated by the lack of chromium, this problem is magnified by an environmental effect (2,5) as shown by the intergranular oxidation of the notch cross section, Fig. 1, that occurs during stress-rupture testing in air.

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Fig. 1. Intergranular oxidation in notch of INCOLOY alloy 903 rupture specimen.

To offset this environmental/rupture interaction in INCOLOY alloy 903, microstructure must be controlled by thermomechanical processing (TMP) (2,3). Hot-worked products must be finished with at least 40% reduction done at or below 870°C (1600°F) and the subsequent elongated grain structure must be retained by holding annealing temperature to 870°C (1600°F) or under. The stress-rupture properties of such a structure are directional (2) with 650°C (1200°F)/100 h notch strength in the transverse direction only about one-third that in the longitudinal direction (221 MPa vs. 690 MPa) (32 ksi vs. 100 ksi).

ALLOY DEVELOPMENT PROGRAM

The restricted process temperature and resulting directionality of properties severely limit the alloy's application. A development program was undertaken to reduce this notch-rupture/process-temperature sensitivity by modifications in composition or heat treatment. This program was done in three subsequent phases, each using a test method sensitive to the stress-assisted cracking mechanism:

- I. 650°C (1200°F) Notch-Rupture Studies
- II. 540°C (1000°F) Bent-Beam Testing
- III. 540°C (1000°F) Notch-Rupture Studies

Phase I - 650°C (1200°F) Notch Rupture Studies

Both heat treatment and compositional variables were evaluated using primarily combination-bar ($K_t = 3.6$) rupture tests run at 650°C (1200°F) at stresses ranging from 483 MPa (70 ksi) to 655 MPa (95 ksi). Test samples were thermomechanically processed bar, 14.3-mm (0.562-in.) square, in the annealed plus aged condition.

Heat Treatment. Improvements in sensitivity to process temperature were determined by evaluating various annealing temperatures and the corresponding

microstructures as outlined below:

<u>Anneal</u>	<u>Grain Structure</u>	<u>Notch-Rupture Rating</u>
845°C (1550°F)/1 h, WQ	Unrecrystallized	-
885°C (1625°F)/1 h, WQ	Partially Recryst.	C
925°C (1700°F)/1 h, WQ	Recryst. ($\leq$ ASTM #5)	B
1040°C (1900°F)/0.25 h, WQ	Recryst. ($>$ ASTM #5)	A

In the Phase I studies, the notch-rupture rating refers to the maximum annealing temperature with which 650°C (1200°F) notch life exceeded 23 h at a stress of 483 MPa (70 ksi) or greater. The highest rating, A, would provide the greatest latitude in process temperature during fabrication.

The aging treatment evaluated was primarily a double age of 720°C (1325°F)/8 h, furnace cool at 55°C (100°F)/h to 620°C (1150°F)/8 h, air cool. In a few cases, initial aging temperature ranged between 680°C (1250°F) and 760°C (1400°F) or three-step ages were included with intermediate aging temperature at 760°C to 790°C (1400°F to 1450°F) for times up to 8 h.

Compositional Modifications. About 110 laboratory-scale heats were tested, including single-element and factorial investigations of Al, Cb, Ti, Cr, Mn, Cu, Mo, B, C, V, Zr, Hf, Si, Ce, and La. Table 1 lists those factors found to reduce the process-temperature sensitivity of this alloy system. Included are comments about the effects these adjustments would have on other properties.

With the base composition, overaging heat treatments were only marginally effective as were higher titanium or columbium, increased boron (above .010%) and restricted aluminum (0.4% to 0.6%). The addition of up to 2% hafnium produced notch ductility with a 925°C (1700°F) anneal but not with a 1040°C (1900°F) anneal. As shown in Table 2, the most substantial improvements, i.e., good notch strength with a 1040°C (1900°F) anneal, were obtained by either the addition of about 2% or more chromium or by restricting aluminum to levels less than 0.4%. Chromium additions to this alloy system did result in altered thermal expansion behavior, specifically lowering the inflection temperature and increasing the expansion coefficient.

Table 1. Factors Reducing Sensitivity of Notch-Rupture Strength to Process Temperature

<u>Factor</u>	<u>Level</u>	<u>Rating</u>	<u>Comments</u>
Heat Treat	Overaging, Intermediate Age	C	Decreases strength.
Ti	Over 1.6%	C	Decreases ductility & weldability.
Cb	Over 4.0%	C	Decreases ductility.
B	Over 0.01%	C	Harms hot working & welding.
Al	0.4 to 0.6%	C	Slightly decreases strength.
Hf	1 to 2%	B	Costly. Scale-up problems.
Cr	Over 2%	A	Alters thermal expansion.
Al	Under 0.4%	A	Decreases strength.

Table 2. Effect of Aluminum and Chromium on Stress-Rupture Properties at 650°C (1200°F)

Al, %	Cr, %	Anneal ^a		Stress, ^b MPa		Life, h	Elong., %	RA, %
		°C	h	Initial	Final			
0.7	—	925	1	483	483	4.6	In Notch	
0.7	3.8	925	1	483	483	109.1	In Notch	
0.7	3.8	1040	0.25	586	827 ^c	1101.6	6	25
0.3	—	925	1	483	724	129.0	10	10
0.3	—	1040	0.25	552	690	101.3	4.5	5.5
0.08	—	925	1	483	552	64.4	14	45
0.08	—	1040	0.25	552	586	53.5	8	15

^aAll samples water quenched after anneal and aged 720°C/8 h, FC 55°C/h to 620°C/8 h, AC.

^bAfter 48 h, stress increased 35 MPa every 12 h except as noted.

^cAfter 100 h, stress increased 35 MPa every 12 h.

Lowering aluminum at the base titanium and columbium levels lowered room-temperature tensile and yield strengths and 650°C (1200°F) smooth-bar strength while increasing rupture ductility.

Phase II - SAGBO Testing at 540°C (1000°F)

Further investigation of the variables found effective in reducing notch-rupture sensitivity to process temperature was done with a two-point-loaded, bent-beam test. Fig. 2 shows the specimen and its mounting arrangement. Other researchers (6) found this test, known as SAGBO (stress-accelerated grain-boundary oxidation), effective in measuring the stress-cracking behavior of INCOLOY alloy 903 in air at 425°C to 650°C (800°F to 1200°F). The 540°C (1000°F) temperature was selected for Phase II and subsequent Phase III studies because it was shown to be more critical for this oxidation-cracking mechanism.

Fig. 2. Specimens in fixture for stress-accelerated grain-boundary oxidation (SAGBO) test.

Testing was done on 12.7-mm (0.500-in.) wide transverse specimens cut from 1.52-mm (0.060-in.) gage x 95.2-mm (3.75-in.) width cold-rolled strip. The ends of the specimens were chisel pointed to a length calculated from the ASTM G-39-73 formula for bent beams.

A factorial melt program was done to further demonstrate the effects of aluminum, chromium, and columbium on the oxidation-related cracking of this alloy. One melt having 3.8% chromium and 0.2% aluminum was also included in this analysis. Samples annealed at 1040°C (1900°F)/0.25 h, WQ, and given the 720°C (1325°F) double age were tested at 540°C (1000°F) and a pseudo stress of 1034 MPa (150 ksi).

The SAGBO results listed in Table 3 confirm findings from Phase I: decreased aluminum content improved stress-corrosion-cracking resistance. The melts with less than 0.1% aluminum showed a substantial gain in SAGBO life. Columbium seemed to show a slight positive effect on SAGBO life as it did in Phase I. The effect of chromium was more obscure but seemed to support the benefits found in Phase I at high aluminum and 3% columbium.

The regression equation developed from these data shows a strong negative aluminum effect, a more-complex chromium and aluminum/chromium interaction, and a slight positive columbium effect. For 540°C (1000°F)/1034 MPa (150 ksi) test conditions:

$$\begin{aligned} \text{SAGBO Life, } h = & -87.92 - 141.3 (\log \text{Al}) + 3.609 (1/\text{Cr}) \\ & - 3.428 \text{Al/Cr} + 32.54 (\text{Al} \times \text{Cr}) + 21.39 (\text{Cb}) \end{aligned}$$

A comparison of the effects of aluminum and chromium on notch strength at 650°C (1200°F) with those obtained from this 540°C (1000°F) SAGBO regression equation show an interesting parallel. In Fig. 3 the alloys indicated by darkened symbols had a notch life of less than 10 h at 650°C/483 MPa (1200°F/70 ksi) when annealed at 925°C (1700°F) or higher. Those represented by the open symbols would exceed 48-h notch life.

Table 3. SAGBO Results^a at 540°C (1000°F) and 1034 MPa (150 ksi) Pseudo Stress

Cb, %	Al, %	Cracking Time, h, at	
		0% Cr	1.8% Cr
3	<0.1	294	79.6
3	0.25	95 ^b	56.1
3	0.85	15 ^b	56.1
4	<0.1	227.8 ^b	205.2
4	0.25	129.3	75.0
4	0.85	78.5	56.1

^aAdditional sample containing 3.0% Cb, 0.2% Al, and 3.8% Cr cracked in 115 h.

^bCr of 0.19% to 0.33%.

Fig. 3. Effect of aluminum and chromium on notch-rupture strength at 650°C (1200°F).

Fig. 3 also includes isochronous 540°C (1000°F) SAGBO contours calculated from the regression equation above (at 3% columbium). This figure illustrates that lowering aluminum is the most effective way of improving resistance to stress-corrosion cracking and indicates that compositions having a 540°C (1000°F) SAGBO life greater than 75 h should have good 650°C (1200°F) notch strength.

Phase III - 540°C (1000°F) Notch-Rupture Studies

Since both the 540°C (1000°F) SAGBO and 650°C (1200°F) notch-rupture results were similar, particularly the improvements with lowered aluminum, alloy development was narrowed to optimize the 540°C (1000°F) notch strength in a chromium-free alloy having low aluminum and high columbium. A 14-kg (31-lb) melt with 0.02% aluminum and 4.3% columbium was processed to a flat 16-mm (0.62-in.) thick and 102-mm (4-in.) wide. Initial stress-rupture testing was done in the long transverse direction at 540°C (1000°F) and 690 MPa (100 ksi).

Effect of Annealing. Sensitivity to process temperature was measured by varying the annealing temperature from an unrecrystallizing anneal at 925°F (1700°F) (with this composition) to a grain-coarsening anneal at 1040°C (1900°F). All samples were given the 720°C (1325°F) double age.

Table 4 shows that the unrecrystallized, low-aluminum alloy would have a transverse notch strength at 540°C (1000°F) of over 690 MPa (100 ksi), compared with 310 MPa (45 ksi) for alloy 903. However, even with the low-aluminum alloy, recrystallizing anneals were extremely detrimental to notch strength.

Effects of Overaging. To improve the transverse 540°C (1000°F) notch strength of recrystallized material, the benefits of overaging were examined. Heat treatments included various double ages of 720 to 815°C (1325 to 1500°F), intermediate ages of 775 to 885°C (1425 to 1625°F), and furnace-cooling treatments (7). Also investigated were treatments of 815 to 870°C (1500 to 1600°F) applied before annealing.

Overaging did considerably boost the transverse notch strength of recrystallized material as shown by the two examples at the bottom of Table 4. The tradeoff of room-temperature tensile properties resulting from such overaging is illustrated in Table 5. Even with the 775°C (1425°F) overage, room-temperature strength exceeded that of, for example, INCONEL* alloy X-750.

Table 4. Effect of Annealing Temperature and Overaging on Transverse Rupture Properties at 540°C (1000°F)^a

Heat Treatment	Stress, b MPa		Life, h	Elong., %	RA, %
	Initial	Final			
925°C/1 h + Age ^c	690	931	120.0	In Notch	
955°C/1 h + Age ^c	690	690	13.6	In Notch	
980°C/1 h + Age ^c	690	690	12.6	In Notch	
1040°C/1 h + Age ^c	690	690	5.5	In Notch	
Overaged ^d	690	690	190.0	2	1
Overaged ^e	690	862	103.0	In Notch	
Overaged ^f	690	690	528.9	2	2.5

^aTests on 16-mm x 102-mm hot-rolled flat having 37 Ni, 14 Co, 4.4 Cb, 1.5 Ti, .02 Al, bal. Fe.

^bAfter 48 h, stress increased 35 MPa every 12 h.

^c720°C/8 h, FC 55°C/h to 620°C/8 h, AC.

^d845°C/4 h, AC; 980°C/1 h, FC 55°C/h to 595°C, AC, plus "c" above.

^e980°C/1 h, WQ; 775°C/8 h, FC 55°C/h to 620°C/8 h, AC.

^f845°C/4 h, AC, plus "e" above.

Table 5. Effect of Overaging on Room-Temperature Properties

Heat Treatment	Yield Strength (0.2% Offset), MPa	Tensile Strength, MPa	Elonga- tion, %	Area Reduct., %
980°C/1 h, + Age ^a	1103	1310	18	35
Overaged ^b	1000	1241	16	25
980°C/1 h, + Overaged ^c	862	1207	12	18

^a720°C/8 h, FC 55°C/h to 620°C/8 h, AC.

^b980°C/1 h, FC 55°C/h to 595°C, AC, plus "a" above.

^c775°C/8 h, FC 55°C/h to 620°C/8 h, AC.

Typical microstructures of overaged material are shown in Fig. 4. The structures in a, b, and c illustrate the effects of increasing hardener content. The amount of Ni_3Cb (δ) and Ni_3Ti (η) increases with hardener levels of the appropriate elements. Precipitate decoration occurs on present and prior structural features. The amount of gamma prime, $\text{Ni}_3(\text{Cb, Ti, Al})$, while not visible, is directly influenced by the precipitates that form on overaging.

Figure 4d shows the effects of a low-temperature aging treatment. The amount of the rod-morphology precipitate is decreased and the longer species (Ni_3Cb) predominates. The amount of hardener available for gamma prime precipitation is increased.

Regression Analysis. To further assess variables influencing the notch strength of recrystallized, overaged material at 540°C (1000°F), a linear regression analysis was conducted. The data base represented various hot-rolled and forged products from twelve laboratory-scale melts and one

Fig. 4. Microstructures (500X) of material with different hardener contents. (a) Low hardener content: 3.85% Cb, 1.38% Ti, 0.02% Al. (b) Medium hardener content: 5.0 Cb, 1.36 Ti, 0.01 Al. (c) High hardener content: 5.04 Cb, 1.68 Ti, 0.02 Al. (d) Same as (c) but with the 720°C (1325°F) aging treatment instead of the 775°C (1425°F) overaging treatment given (a), (b), and (c). Etchant: phosphoric electrolytic.

commercial melt. The aluminum, columbium, and titanium contents were not completely orthogonal, but reasonable compositional ranges were represented within the area of low aluminum and high columbium. Test data were from longitudinal or long transverse specimens depending on the product.

Annealing treatments were 955°C (1750°F)/1 h, WQ, 980°C (1800°F)/1 h, WQ, or 1040°C (1900°F)/0.25 h, WQ. A preannealing treatment of 845°C (1550°F)/4 h, AC was included in some cases. The overaging treatment was either the furnace cool or the 775°C (1425°F) double age shown in the examples in Table 4.

Table 6 shows the final regression equation selected based on the data fit. Given the nature of the notch-rupture test, particularly with an alloy in which fracture is related to outer fiber stress, the 71% correlation coefficient (r^2) is very good. All terms were significant at less than the 1% level except pretreatment (1% < α < 5%).

Even though restricted to a range below 0.15%, aluminum continued to show a negative effect on 540°C (1000°F) notch life. Columbium and titanium both showed a positive effect probably resulting from the increased intergranular precipitates previously discussed. A directionality effect still existed, but it was less than half an order of magnitude compared with two to three orders of magnitude difference in life for the unrecrystallized original alloy.

Heat treatment and grain structure effects showed that (a) the preanneal treatment had a slight positive effect, (b) the 775°C (1425°F) treatment (more-overaged condition) gave half an order of magnitude advantage over the furnace-cool treatment, and (c) finer grain structures increased notch life.

Table 6. Regression Equation^a for Notch-Rupture Life at 540°C (1000°F) and 690 MPa (100 ksi)

$$\begin{aligned} \text{Log Rupture Life, } h = & -6.127 \times \text{Al} + .502 \times \text{Cb} + 1.965 \times \text{Ti} \\ & + .515 \times \text{T.O.} + .205 \times \text{P.T.} + .465 \times \text{H.T.} \\ & + .259 \times \text{G.S.} - 5.800 \end{aligned}$$

Variable	Minimum	Maximum
Columbium	3.91%	5.54%
Titanium	1.11%	1.56%
Aluminum	0.01%	0.14%
Test Orientation (T.O.)	1 (Transverse)	2 (Long.)
Pretreatment (P.T.)	0 (None)	1 (845°C/4 h)
Heat Treatment (H.T.)	1 ^b	2 ^c
Grain Size (G.S.)	ASTM 4	ASTM 7

^a45 observations, correlation (r^2) = 0.71.

^bAnneal, FC 55°C/h to 595°C, AC; 720°C/8 h, FC 55°C/h to 620°C/8 h, AC.

^cAnneal, WQ; 775°C/8 h, FC 55°C/h to 620°C/8 h, AC.

SUMMARY

The notch-rupture strength of commercial age-hardenable low-expansion alloys is sensitive to test environment. Use of these alloys is restricted because of the thermomechanical processing and directionality required to develop good longitudinal notch strength. An alloy-development program has shown that:

1. Restricting aluminum content to levels below 0.2% improves the intergranular oxidation resistance and related notch-rupture strength.
2. With the low-aluminum alloy, both overaging and increasing columbium and titanium levels provide a further benefit to notch strength.

This work has resulted in a new commercial alloy, INCOLOY alloy 903A, that has greatly improved notch-rupture strength while retaining the low expansion coefficient of the original material.

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