Development of Low Thermal Expansion Superalloys

K. Sato and T. Ohno

Alloy 903 and Alloy 909 are well-known Fe-Co-Ni-Al-Ti-Nb alloys with controlled low thermal expansion, but they have some properties that can be improved. To improve stress-accelerated grain boundary oxidation embrittlement of Alloy 903 and instability of the γ′ phase of alloy 909, two new alloys with good stress-rupture ductility, high creep-rupture strength, high tensile strength at high temperature, and good controlled thermal expansion were developed. These property improvements were accomplished by the combination of optimizing the Fe-Co-Ni ratio of the matrix and stabilizing the γ′ phase with the addition of aluminum.

Keywords
coefficient of thermal expansion, Laves phases, stress rupture, superalloys

1. Introduction

FOR heat-resistant gas turbine components, superalloys with a controlled low thermal expansion coefficient can solve the high-temperature problems of thermal stress and clearance. Alloy 903 is a well-known Fe-Co-Ni-Al-Ti-Nb alloy with controlled low thermal expansion, but it is susceptible to stress-accelerated grain boundary oxidation embrittlement (SAGBO) above about 500 °C.[1,2] This phenomenon is related to notch bar stress-rupture embrittlement in air around 500 °C. Alloy 909, which solved the SAGBO problem of Alloy 903, was developed by eliminating aluminum, adding silicon, and strengthening achieved by additions of niobium and titanium.[3]

This improvement in strength in Alloy 909 is directly related to the presence of a nickel/niobium-rich Laves phase. It precipitates during hot working and solution treatment, refines the grain size, and modifies the grain boundary structure.[4,5] However, the lack of aluminum and excessive amount of niobium in Alloy 909 have negated the advantage of Alloy 903, namely a more stable γ′ phase at high temperature. If strain is introduced to the matrix of Alloy 909 between the annealing and aging treatments, this instability of the γ′ phase causes the precipitation of the ε″ phase, $(Ni,Co,Fe)_3(Ti,Nb)$, which decreases tensile strength.[6]

Considering the above characteristics of low thermal expansion superalloys, the authors tried to develop new alloys that would have a stable γ′ phase like Alloy 903 and a dispersion of small nickel/niobium-rich Laves precipitates like Alloy 909 to refine the grain size. Furthermore, an effort was made to produce superalloys with a lower coefficient of thermal expansion and higher elevated temperature tensile strength than either Alloy 903 or Alloy 909. For heat-resistant alloys, it is useful to decrease the thermal expansion for improved adherence of low thermal expansion ceramic coatings like zirconia, and it is also advantageous to increase tensile strength to prolong life.

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2. Experimental Procedures

The experimental alloys and conventional alloys were melted in a vacuum induction furnace and cast into 10-kg ingots. Table 1 gives the chemical compositions of these alloys. Heats 6-1 and 6-2 are of the same alloy. Heat 6-1 was used for basic experiments, and heat 6-2 was used for evaluation tests. The relationship between heat 7-1 and 7-2 is the same as the relationship between heat 6-1 and 6-2. Heats 9 and 10 are Alloy 903 and Alloy 909, respectively. They were melted according to the compositions given in Ref 6.

All alloys were homogenized at 1150 °C for 20 h and forged into 30-mm square bars. Specimens except Alloy 903 were heat treated as noted in Table 2. Alloy 903 was solution treated at 930 °C to retain a fine grain size because it does not contain a Laves phase. Aging treatments were conducted at standard conditions. The overaging treatment, which simulated an actual blazing treatment, was carried out to determine the stability of the γ′ phase.

Microstructures of these specimens were observed by optical microscopy and transmission electron microscopy (TEM). Tensile tests and creep-rupture tests were conducted in air using ASTM testing methods. Specimens were oriented in the longitudinal direction. A specimen with 6.35-mm diameter was used for tensile testing. A combination smooth/notched specimen with gage and notch diameters of 4.52 mm was used for creep-rupture testing. The coefficients of thermal expansion (CTE) were determined from 30 °C up to 800 °C by a differential thermal expansion testing method. Oxidation tests were carried out by using 7-mm diameter × 15-mm long specimens. After 100 h at 800 °C in air, the thickness of the internal and external oxidation layers was measured using optical microscopy techniques.

3. Development of a Lower Thermal Expansion Superalloy

3.1 *Alloy Design*

Heats 1 to 6 in Table 1 are the experimental alloys used for this study. Initially, an attempt was made to raise the Co/Ni ratio above those of Alloy 903 and Alloy 909 to decrease thermal ex-

Table 1 Chemical composition of material tested

Heat No.	C	Si	Ni	Co	Composition, wt% Cr	Al	Ti	Nb	Fe	B
1	0.03	<0.01	26.3	23.2	...	<0.01	1.56	4.72	Bal	0.004
2	0.03	0.02	29.4	19.6	...	<0.01	1.56	4.74	Bal	0.005
3	0.03	0.45	26.4	23.2	...	<0.01	1.53	4.71	Bal	0.004
4	0.03	0.49	29.3	19.6	...	<0.01	1.64	4.74	Bal	0.005
5	0.03	0.44	26.5	23.2	...	0.57	1.30	4.08	Bal	0.005
HRA929										
6-1	0.03	0.45	29.2	19.6	...	0.55	1.29	4.02	Bal	0.004
6-2	0.03	0.44	29.3	19.6	...	0.50	1.30	3.99	Bal	0.005
HRA929C										
7-1	0.04	0.31	29.5	22.5	2.03	0.54	1.30	4.07	Bal	0.004
7-2	0.03	0.33	29.4	22.8	1.99	0.53	1.17	4.17	Bal	0.005
8	0.04	0.31	33.4	18.2	1.51	0.55	1.29	4.07	Bal	0.004
Alloy 903										
9	0.03	<0.01	37.8	15.0	0.16	0.81	1.47	2.69	Bal	0.006
Alloy 909										
10	<0.01	0.43	38.2	13.2	0.03	0.06	1.42	4.71	Bal	0.007

Table 2 Heat treating schedule

Solution treatment

982 °C/1 h, AC ... All alloys except Alloy 903
930 °C/1 h, AC ... Alloy 903

Aging treatment

Standard............ 720 °C/8 h → 55 °C/h → 620 °C/8 h,AC
Overaging.......... 750 °C/1.5 h → 850 °C/0.5 h → 100 °C/h → 650 °C, AC

Table 3 Effect of nickel and cobalt on coefficient of thermal expansion

Heat No.	Ni + Co	Co/(Ni + Co)	CTE: 30 to 400 °C $\times 10^{-6}$/°C
1	49.5	0.47	5.99
2	49.0	0.40	5.73
3	49.6	0.47	6.65
4	48.9	0.40	6.31
5	49.7	0.47	6.16
6-1 (HRA929)...	48.8	0.40	5.79
9 (Alloy 903).....	52.8	0.28	7.44
10 (Alloy 909)...	51.4	0.26	7.69

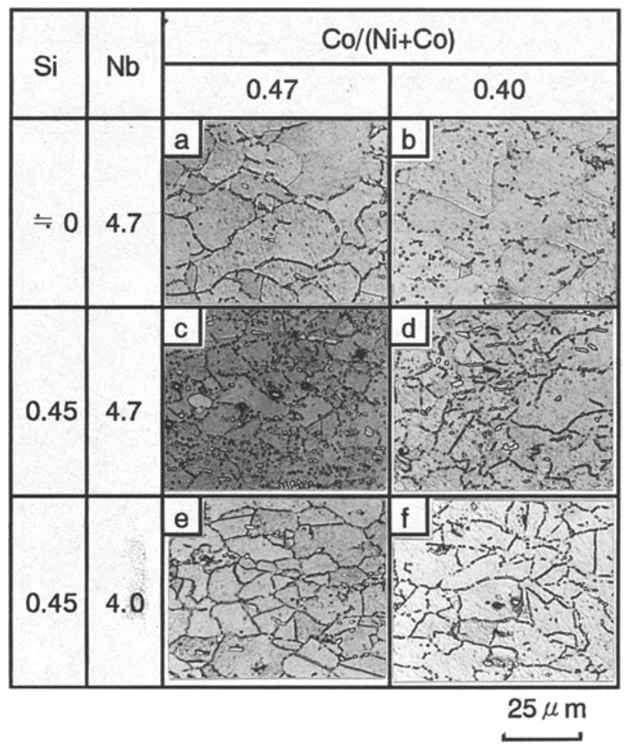

Fig. 1 Effect of alloying elements on microstructures of specimens. (a) Heat 1. (b) Heat 2. (c) Heat 3. (d) Heat 4. (e) Heat 5. (f) Heat 6-1 (HRA929).

pansion according to the relationship between Invar (36Ni-Fe) and Super Invar (31Ni-5Co-Fe). Additionally, increasing the Co/Ni ratio would be expected to increase the amount of Laves phase (helpful in preventing SAGBO embrittlement) because the solubility of niobium in the Co-Nb binary system is lower than in the Ni-Nb binary system. Heats 1, 3, and 5 contained about 26.4 wt% Ni and 23.2 wt% Co (Co/Ni = 0.88); heats 2, 4, and 6 contained about 29.3 wt% Ni and 19.6 wt% Co (Co/Ni = 0.67). By comparing these two groups, the effect of the difference in Co/Ni ratio was examined. Additions of aluminum, titanium, and niobium for the Co/Ni ratio mentioned above were then investigated to obtain stable γ' precipitates. Heats 1 to 4 had the same amount of titanium and niobium as Alloy 909. Heats 5 and 6 had the same amount of aluminum, titanium, and niobium. Aluminum content was higher, and titanium and niobium were lower than Alloy 909. The effects of aluminum, titanium, and niobium contents on stability of the γ' precipitation hardening phase and mechanical properties were investigated by comparing heats 1 to 4 with heats 5 to 6. The effect of silicon on precipitation of Laves phase was next investigated by comparing heats 1 and 2 with heats 3 and 4.

Table 4 Effect of alloying elements on stress-rupture properties(a) at 500 °C

Heat No.	Si	Al	Nb	Co/(Ni + Co)	Stress(b), MPa Initial	Final	Life, h	Elongation, %	Reduction of area, %
1	<0.01	<0.01	4.72	0.47	784	1078	318.6	10.8	27.8
2	0.02	<0.01	4.74	0.40	784	1029	290.1	Notch	...
3	0.45	<0.01	4.71	0.47	784	1029	261.1	10.6	19.7
4	0.49	<0.01	4.74	0.40	784	1078	322.8	10.3	9.9
5	0.44	0.57	4.08	0.47	784	1029	375.4	9.5	18.1
6-1 (HRA929)...	0.45	0.55	4.02	0.40	784	1078	323.5	11.7	21.7

(a) Specimens were aged by standard aging process. (b) After 200 h, stress was increased by 49 MPa every 8 to 16 h.

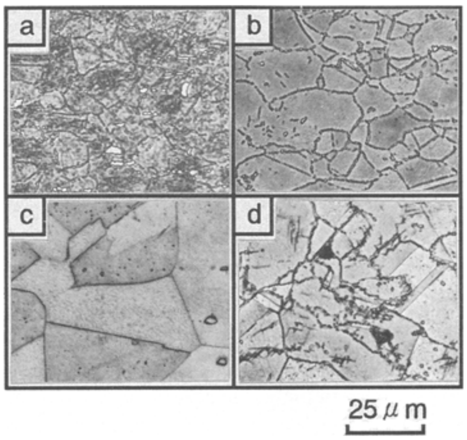

Fig. 2 Microstructures of overaged specimens. (a) Heat 4. (b) Heat 6-1 (HRA929). (c) Heat 9 (Alloy 903). (d) Heat 10 (Alloy 909).

3.2 *Results and Discussion*

Table 3 shows the effects of niobium and cobalt on the coefficient of thermal expansion (CTE) at temperatures from 30 to 400 °C for the experimental alloys, Alloy 903, and alloy 909 in the standard aged condition. The CTE for heats 1 to 6-1 were lower than those for Alloy 903 and Alloy 909 by about 1 $\times 10^{-6}$/°C. These results are attributed mainly to the increase of Co/(Co + Ni) ratio and partly to a lower amount of Ni + Co. The different Co/(Co + Ni) ratios of 0.40 and 0.47 for heats 1 to 6-1 did not significantly affect the CTE.

The effect of alloying elements on stress-rupture properties for heats 1 to 6-1 are shown in Table 4. All heats, except for heat 2, exhibited good creep-rupture strength and ductility. Only heat 2 failed at the notch location. Figure 1 shows their microstructures. The spherical particles of micrometer dimensions, shown at higher magnification in Fig. 4, were identified by TEM diffraction patterns as two- and four-layered hexagonal Laves phases, the same phase that is formed in Alloy 909.[4] By comparing heat 1 with 2, heat 3 with 4, and heat 5 with 6, the higher the Co/(Co + Ni) ratio, the more the Laves phase was precipitated. Heat 2, having a lower silicon content, and a lower Co/(Co + Ni) ratio, precipitated the least amount of Laves phase and had the largest grain size among the experimental heats. Therefore, it was found that addition of silicon and increasing the Co/(Co + Ni) ratio increased the amount of Laves phase precipitates, and the presence of Laves phase was beneficial for creep-rupture ductility and for obtaining a fine grain size. The high affinity of aluminum for oxygen was considered detrimental to rupture ductility and SAGBO embrittlement,[7] but aluminum additions in the cases of heats 5 and 6 did not affect rupture ductility. From these results, it appears that notch ductility is improved primarily by the existence of Laves phase and a fine grain size, and the affinity of aluminum for oxygen has little influence on rupture ductility if the Laves phase is present.

Table 5 Vickers hardness of overaged specimens

Heat No.	4	6-1 HRA929	9 Alloy 903	10 Alloy 909
Hardness, HV:	319	346	349	317

Comparing the Co/(Co + Ni) ratio of 0.40 with 0.47 with silicon held constant at 0.45%, there was little difference in rupture ductility and thermal expansion. The reason may be that increasing cobalt produces only an increase in the amount of Laves phase and does not change the matrix composition. Because cobalt is an expensive element and its production has been unreliable in the past, the high temperature γ' stability experiment was conducted on heats 4 and 6 (lower cobalt heats).

Stability of the γ' phase at high temperature was studied by overaging heat 4, heat 6, Alloy 903, and Alloy 909. Vickers hardness values and microstructures are shown in Table 5 and Fig. 2, respectively. A needle-, or platelet-, shaped phase was observed in heat 4 and Alloy 909. These two heats had hardness values that were lower than those of heat 6-1 and Alloy 903. The phase is supposed to be the ε phase, which has a *D*019 hexagonal Ni_3Sn-type structure and is optically similar to the δ phase in Alloy 718.[4] The phase appears to reduce the amount of γ' phase and results in lower hardness values. On the other hand, no strange phases except the Laves phase were observed in heat 6-1 and Alloy 903, and they had higher hardness values than heat 4 and Alloy 909. The reason may be due to the existence of aluminum, which stabilizes the γ' phase at high temperatures.

As a result of these experiments, it was found that heat 6 was an alloy with a lower coefficient of thermal expansion than Alloy 903 and Alloy 909. Heat 6 also exhibited good rupture properties and good γ' stability at high temperatures. Heat 6 was designated HRA929, and additional evaluation tests were conducted (see expanded mechanical properties evaluation section).

4. Development of a Higher Strength Low Expansion Superalloy

4.1 *Alloy Design*

HRA929 has some margin of thermal expansion when compared to Alloy 903 and Alloy 909. The addition of chromium is known to result in a marked increase in thermal expansion for Alloy 903,[7] but it is supposed to improve high-temperature tensile strength by solid solution strengthening of the γ matrix. Furthermore, it increases high-temperature oxidation resistance. Therefore, chromium was added to HRA929 to obtain high-temperature strength greater than Alloy 903 and Alloy 909 while maintaining an equivalent CTE.

The effect of chromium on mechanical properties and thermal expansion was studied by evaluating heats 7-1 and 8 in Table 1. Heat 7 had higher chromium and a higher Co/(Co + Ni) ratio than heat 8. Both have silicon levels that are less than HRA929 because of the expected improvement in SAGBO behavior from the addition of chromium.[7] Both have the same amount of aluminum, titanium, and niobium and should precipitate the γ' phase. Both were overaged to observe the stability of the γ' precipitates. Mechanical properties and thermal expansion were evaluated.

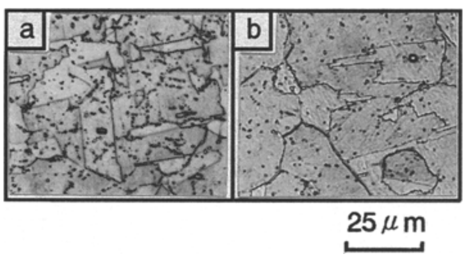

Fig. 3 Microstructures of overaged specimens. (a) Heat 7-1 (HRA929C). (b) Heat 8.

4.2 *Results and Discussion*

Table 6 gives Vickers hardness, rupture properties, and coefficients of thermal expansion for heats 7-1 and 8. These alloys had almost the same level of hardness and thermal expansion. The CTE were nearly the same as Alloy 903 and Alloy 909 given in Table 2, in spite of the chromium addition. Heat 7-1 exhibited good rupture strength and ductility. Heat 8 failed in the notch at a lower net section stress than heat 7-1. This result is due to the decrease in Laves phase and accompanying larger grain size for heat 8, as shown in Fig. 3. This figure also shows that the γ' precipitation hardening phase in these alloys is stable like HRA929, as shown in Fig. 2.

As a result of these experiments, it was found that heat 7 was an alloy with good high-temperature strength and ductility and a CTE similar to Alloy 903 and Alloy 909. Heat 7 was designated HRA929C, and additional evaluation tests were conducted, as discussed in the next section.

5. Expanded Mechanical Properties Evaluation of HRA929 and HRA929C

To characterize HRA929 and HRA929C, a major test program was conducted, which included Alloy 903 and Alloy 909.

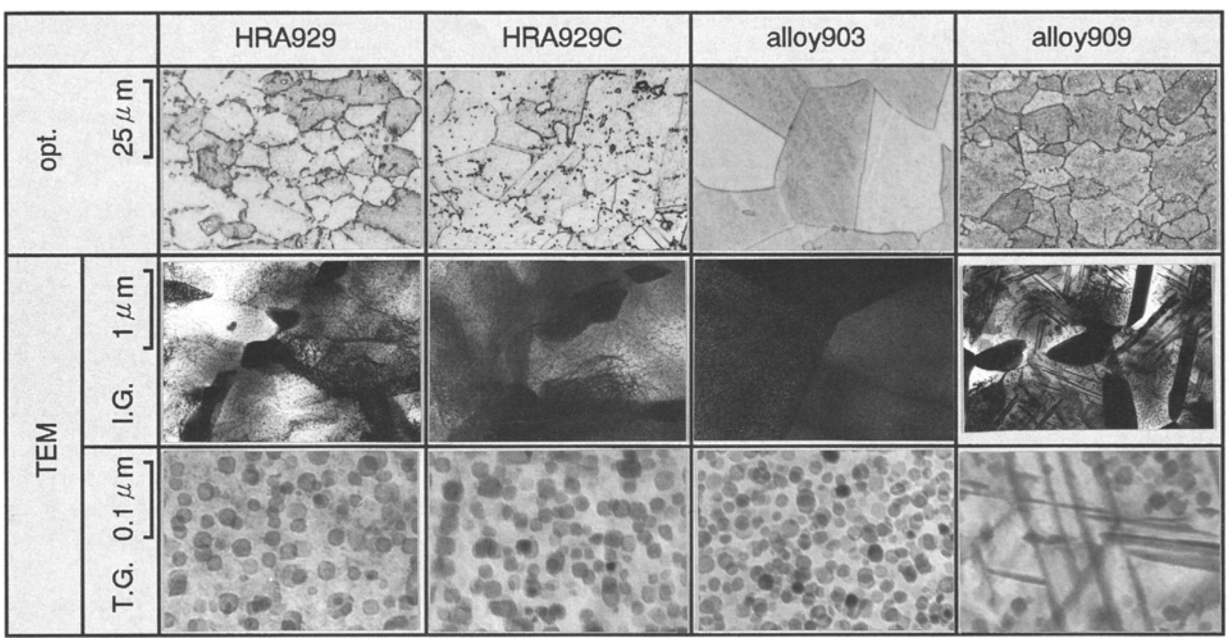

Fig. 4 Microstructures of experimental alloys, Alloy 903, and Alloy 909. IG, intergranular; TG, transgranular.

The program evaluated microstructure via TEM; thermal expansion up to 800 °C; tensile strength at room temperature, 500, and 650 °C; creep-rupture strength at 649 °C under constant stress; and stress-free oxidation at 800 °C. Chemical compositions of HRA929, HRA929C, Alloy 903, and Alloy 909 are given in Table 1 and are designated as heats 6-2, 7-2, 9, and 10, respectively. All of the specimens were given a standard aging heat treatment.

5.1 *Microstructure*

Figure 4 shows the microstructure of HRA929, HRA929C, Alloy 903, and Alloy 909. All alloys except Alloy 903 have a fine grain size attributed to the pinning of grain boundaries by the Laves phase. Spherical or cubic intergranular precipitates approximately 10 nm in diameter are γ' precipitates. HRA929, HRA929C, and Alloy 903 have significant amounts of γ'. Alloy 909 has less γ' and a platelet precipitate. This platelet phase is supposed to be the ε'' phase, a $(Ni,Co,Fe)_3(Nb,Ti)$ transition phase,[4] which is not effective for increasing tensile strength.[6] It is believed that the lack of aluminum and excess amount of niobium cause the reduction in the amount of γ' and the precipitation of the ε'' phase.

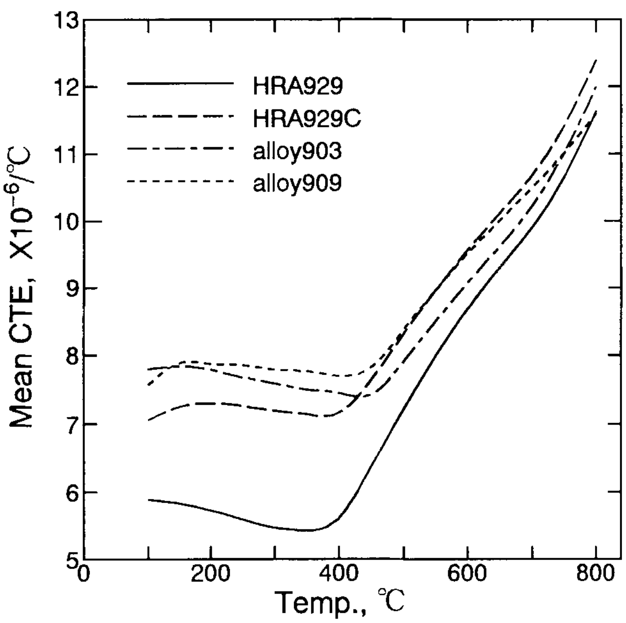

Fig. 5 Coefficients of thermal expansion of experimental alloys, Alloy 903, and Alloy 909.

5.2 *Thermal Expansion*

As shown in Fig. 5, the CTE of HRA929 is 25% lower than Alloy 903 and 909 for the temperature range 30 to 400 °C, whereas the CTE for HRA929C is almost the same as Alloys 903 and 909.

5.3 *Tensile Properties*

In Fig. 6, HRA929C exhibits the highest strength at 500 and 650 °C because of the chromium addition. Alloy HRA929 has a higher 0.2% yield strength than Alloys 903 and 909 at 500 and 650 °C. The tensile strength of Alloy 909 is lower than that reported in Ref 4, probably because an excess amount of ε'' phase was precipitated in this heat. HRA929 and HRA929C have adequate elongation values.

5.4 *Creep-Rupture Properties*

Figure 7 shows the creep-rupture properties at 649 °C and 510 MPa. Alloy 903 is evidently inferior to the other alloys in

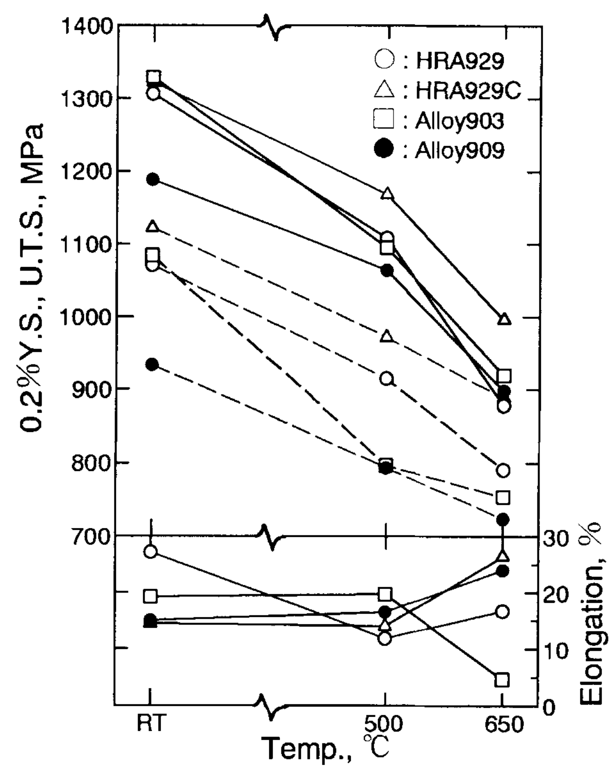

Fig. 6 Tensile properties of experimental alloys, Alloy 903, and Alloy 909.

Table 6 Effect of Cr and Co/Ni ratio on Vickers hardness, stress-rupture properties, and coefficient of thermal expansion(a)

Heat No.	Si	Cr	Co/(Ni + Co)	Hardness, HV	Stress(b), MPa Initial	Final	Life, h	Elongation, %	Reduction of area, %	CTE: 30 to 400 °C × 10^{-6}/°C
7-1 (HRA929C).....	0.31	2.03	0.43	352	784	1078	263.5	13.9	29.3	7.92
8	0.31	1.51	0.35	362	784	784	151.3	Notch	...	7.72

(a) Specimens were aged by overaging process. (b) After 200 h, stress was increased by 49 MPa every 8 to 16 h.

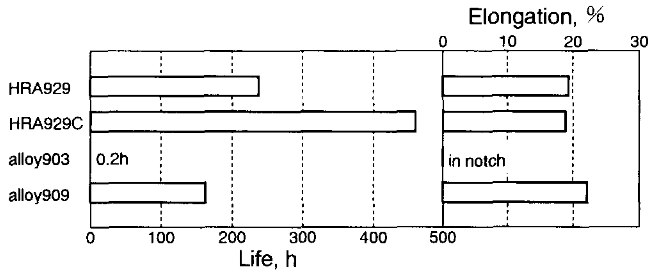

Fig. 7 Stress-rupture properties of experimental alloys, Alloy 903, and Alloy 909. Test conditions: 649 °C and 510 MPa.

rupture life and ductility, due to SAGBO embrittlement. The percent elongation for HRA929, HRA929C, and Alloy 909 is almost the same, but rupture lives for HRA929 and HRA929C are nearly one and a half times and three times longer, respectively, than Alloy 909. HRA929C exhibited the longest rupture life, probably due to the chromium addition.

5.5 *Oxidation Resistance*

The poor oxidation resistance of low thermal expansion superalloys has been a problem area for this type of alloy. Figure 8 shows the results of oxidation tests. HRA929C with 2 wt% Cr exhibited better oxidation resistance than Alloy 903 and Alloy 909, whereas HRA929 exhibited almost the same level of oxidation resistance as Alloy 903 and Alloy 909.

6. Summary

Two alloys, HRA929 and HRA929C, were developed, which when compared to Alloys 903 and 909 either achieved a lower thermal expansion coefficient while maintaining equivalent tensile strength, or increased tensile strength while maintaining an equivalent CTE. For HRA929, an increase in the Co/(Co + Ni) ratio produced a finer grain size (grain boundaries were pinned by Laves phase) and lower thermal expansion coefficient. The addition of aluminum did not affect rupture ductility, but improved the stability of the γ' phase. The combination of a high Co/(Co + Ni) ratio and a stable γ' phase produced a lower thermal expansion alloy compared to Alloy 903 and Alloy 909, while maintaining good rupture ductility. The composition (wt%) is 0.4Si-29Ni-19.5Co-0.55Al-1.25Ti-4Nb (bal Fe).

For HRA929C, a 2 wt% Cr addition and slight chemistry modification of HRA 929 produced an alloy with improved high-temperature tensile strength, rupture strength, and oxidation resistance, while maintaining almost the same level of thermal expansion as Alloy 903 and Alloy 909. The composition (wt%) of this alloy is 0.3Si-29.5Ni-22.5Co-2Cr-0.55Al-1.25Ti-4Nb (bal Fe).

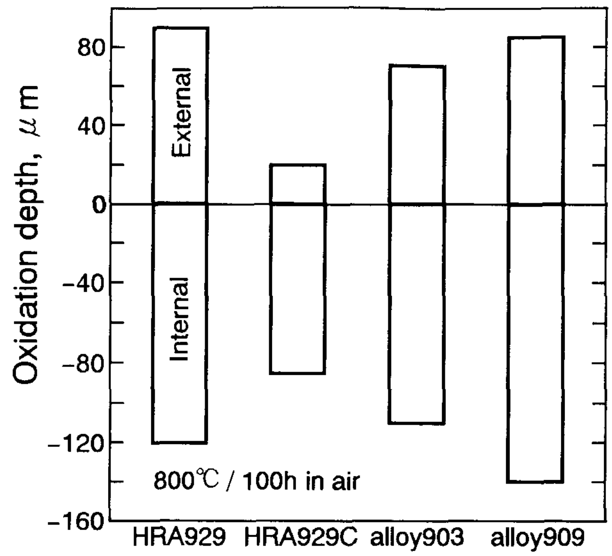

Fig. 8 Oxidation resistance of experimental alloys, Alloy 903, and Alloy 909.

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