THERMAL STABILITY OF SOLID SOLUTION STRENGTHENED HIGH PERFORMANCE ALLOYS

S. J. Matthews

Cabot Corporation, Technology Division, Kokomo, Indiana

ABSTRACT

Long term thermal stability of several solid solution strengthened alloys has been studied. HASTELLOY alloys X, C-4 and S and HAYNES alloys No. 625 and 188 were exposed to temperatures of 1200, 1400 and 1600°F for 1000, 4000 and 8000 hours. Microstructure and room temperature tensile and Charpy impact properties are given for these materials in both the annealed and aged condition. Except for those alloys which have very low carbon (less than .02%), all alloys show a significant degradation in room temperature ductility after a few thousand hours and then level off into a ductility plateau. The amount of ductility in this plateau depends on the isothermal aging temperature which dictates the phases capable of being precipitated in the particular alloy.

In addition to aging studies on plate, data were gathered for all weld metal samples. The reduced values of room temperature tensile ductility due to aging were invariably lower in segregated weld metal compared to more homogeneous wrought alloy product.

INTRODUCTION

Producers of high performance alloys traditionally supply wrought products in the mill annealed condition. Subsequent exposure of these materials to elevated temperatures will produce changes in both microstructure and original room temperature (R.T.) mechanical properties. Thermal stability can be defined as a material "property" characterizing these changes after long time exposure to elevated temperature.

In 1974, an on-going program was initiated to document the long-time thermal stability of several solid solution strengthened, high performance alloys, among them: HASTELLOY alloys S, C-4, C-276, B-2, B, X, HAYNES alloys No. 188 and 625, MULTIMET and HAYNES Developmental alloy No. 556. The aging temperatures of interest are 800, 1000, 1200, 1400 and 1600°F. Aging times of 16,000 hours are anticipated. The purpose of this paper is to report interim 1000 hour, 4000 hour and 8000 hour data on only a few pertinent alloys studied to date.

MATERIALS AND PROCEDURE

The chemical analyses of the materials referred to in this report are listed in Table 1. Only one heat of each alloy was tested.

With the exception of alloy No. 188 (in the form of 1/8-inch thick sheet), all other alloys were aged in the form of plate, 1/2-inch thick.

Weld metal samples of alloys C-4, S and X were prepared by manual gas tungsten arc welding. Large 5-inch long fillets were deposited into the quadrants of a cruciform structure and 1/2-inch diameter bars were subsequently electro-discharge machined from the weld fillet areas.

With the exception of a few tests, all aging experiments were conducted isothermally $(\pm 25\,^{\circ}\text{F})$ in static air, without the application of stress. After aging for the desired length of time (1000, 4000, 8000 hours), sufficient alloy was withdrawn from the aging furnaces, sectioned and machined into samples for R.T. tensile testing and Charpy impact testing. In addition to metallographic examination, some preliminary X-ray diffraction (of extracted residues) and electron diffraction (of thin foils) were performed. However, comprehensive structural work is being reserved for a future date.

Table 1: Heat Chemistries of Solid Solution Strengthened
High Performance Alloys

Element	HASTELLOY alloy S	HASTELLOY alloy C-4	HASTELLOY alloy X	HAYNES alloy No. 625	HAYNES alloy No. 188
Ni	67.35	65.74	47.13	60.49	21.82
Cr	14.36	15.06	21.09	20.67	21.36
Mo	14.34	15.99	8.75	9.05	0.40
Fe	0.82	0.72	18.82	3.49	1.61
Со	0.14	0.12	1.71	0.09	37.75
W	0.22	0.23	0.39	-	13.79
С	0.005	0.002	0.09	0.05	0.10
Si	0.37	0.04	0.45	0.38	0.39
0ther	0.01 La	0.38 Ti	-	3.62 Cb	0.04 La

Thastelloy, Haynes and Multimet are registered trademarks of Cabot Corp.

RESULTS

Thermal stability behavior of the five solid solution strengthened alloys listed in Table 1 are documented in Figures 1, 2, 3, 5 and 6. In addition to photomicrographs showing annealed and aged microstructures, each figure contains a plot of R.T. yield strength "ratio" versus aging temperature and plot of R.T. elongation "ratio" versus aging time (the "ratio" is the room temperature property after aging, divided by the same property in the original mill annealed condition). The tensile test data represent an average of three tests.

DISCUSSION

HASTELLOY alloy S

The thermal stability of alloy S is characterized by excellent retention of R.T. ductility after 8000 hours exposure in the temperature range 800 to $1600\,^\circ\text{F}$ (Fig. 1). The decreasing impact properties reported in Table 2, after exposure at 1200 and $1400\,^\circ\text{F}$, may be due to the precipitation of sparsely distributed second phases visible in Figure 1 (M₆C and M₃B₂ according to preliminary X-ray diffraction results). It was also found that alloy S will undergo an A₂B (Ni₂Cr,Mo) ordering reaction, but only upon exposures to lower temperatures (1000 to $1100\,^\circ\text{F}$). Ordering is accompanied by a marked increase in R.T. yield strength and only a mild reduction in ductility (i.e., $70\,^\circ$ of the original R.T. elongation is maintained even after 8000 hours exposure). The Charpy impact resistance of alloy S in the ordered condition ($1000\,^\circ\text{F}/8000$ hours) was 66 ft-1bs.

A limited number of aging experiments were conducted on alloy S in which tensile samples were given various amounts of prestrain (0.1 to 1.0%) and were aged with and without the application of stress (10,000 psi). Neither of these conditions markedly lowered the aged R.T. ductility of the alloy.

Table 2: Room Temperature Charpy Impact Energy (ft-1bs) of Plate Materials in Aged Condition (Data Are Averages of 4 Tests)

Aging Temp. <u>°F</u>	Aging Time Hours	HASTELLOY alloy S	HASTELLOY alloy C-4	HASTELLOY alloy X	HAYNES alloy No. 625
1200	1000	85	93	24	11
1200	4000	67	84	12	8
1200	8000	54	55	15	5
1400	1000	79	73	10	5
1400	4000	52	41	10	4
1400	8000	48	32	8	5
1600	1000	107	121	15	12
1600	4000	109	97	12	11
1600	8000	105	125	15	15
Mill Annealed		140	223+	95	81

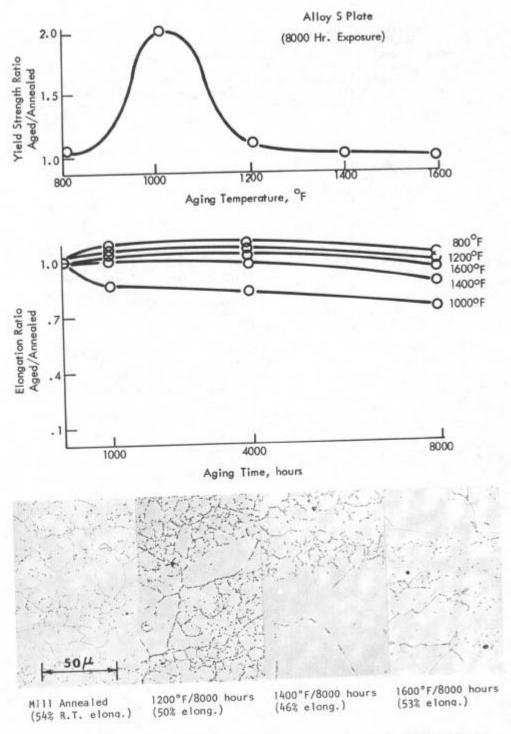


Figure 1: Yield strength ratio versus aging temperature, ductility versus aging time and microstructure of aged HASTELLOY alloy S plate

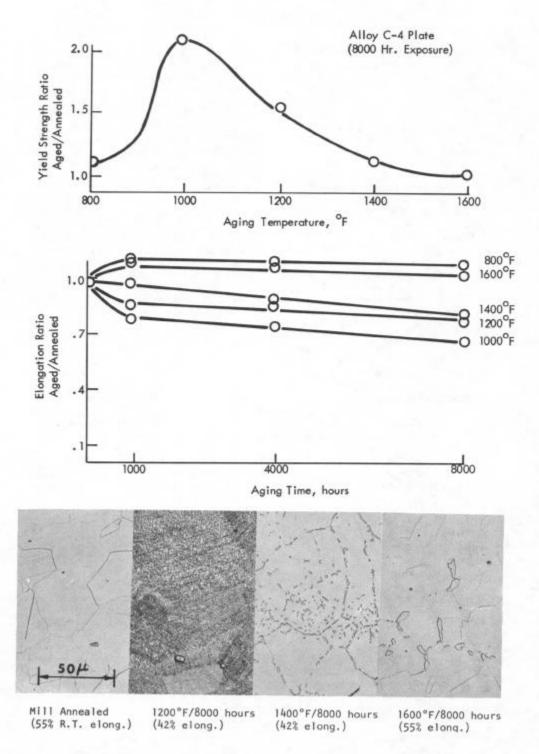


Figure 2: Yield strength ratio versus aging temperature, ductility versus aging time and microstructure of aged HASTELLOY alloy C-4 plate

HASTELLOY alloy C-4

The composition of alloy C-4 is similar to that of alloy S and exhibits similar thermal stability behavior, i.e., excellent ductility retention after long-time exposure at temperatures between 800 and 1600°F (Fig. 2). Likewise, alloy C-4 will undergo an A_2B ordering reaction upon aging at 1000°F and be accompanied by a R.T. yield strength maximum; but unlike alloy S, ordering also occurs upon exposure to 1200°F. This was verified by the appearance of superlattice spots associated with electron diffraction patterns of aged material. At 1200°F, the ordered "domain" size apparently has increased significantly producing a very distinct microstructural effect visible in the photomicrographs. Despite the "heavily aged" microstructural appearance, samples of alloy C-4 exposed to 1200°F for 8000 hours still retain over 70% of the original mill annealed ductility.

No carbides or borides were detected by preliminary X-ray diffraction of extracted residues. However, Mu phase was identified in specimens aged at 1400 and 1600°F. A semi-continuous network of Mu phase precipitation is also visible in the optical photomicrograph of the 1400°F sample. This precipitate apparently does not drastically lower tensile ductility, but does markedly reduce impact resistance (32 ft-lbs). Impact properties, however, were found to be considerably higher (125 ft-lbs) in samples aged at 1600°F, where the Mu phase is more agglomerated and more coarsely distributed throughout the microstructure.

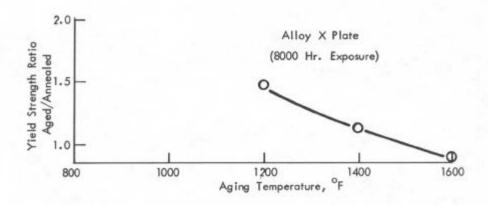
HASTELLOY alloy X

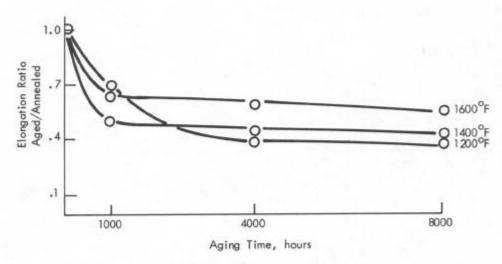
Precipitation of M₆C carbides, visible in Figure 3, appears to be a major factor controlling thermal stability behavior of alloy X. Any long-time exposure to intermediate temperatures ranging from 1200 to 1600°F will produce about a 50% decrease in R.T. ductility and even more distinct degradation in Charpy impact resistance (Table 2). Photomicrographs in Figure 3 also illustrate that carbide phases can be distributed differently throughout the microstructure depending upon isothermal aging temperature.

It is worthwhile to note that the ductility degradation due to aging at elevated temperature becomes apparent at temperatures less than the actual aging temperature and is maximized at room temperature. This relationship is illustrated in Figure 4, a plot of tensile ductility versus tensile test temperature for alloy X sheet material removed from actual engine hardware after 5600 hours service. Figure 4 also contains a plot of ductility versus temperature for mill annealed (unaged) alloy X. The two curves converge at 1300°F, the approximate operating temperature of the particular component that was destructively examined.

The decreased ductility in alloy X due to aging can also be completely restored to the original mill annealed value by a solution heat treatment. As an example, the R.T. percent elongation of samples machined from a gas turbine combustion can after 3200 hours of service was raised from 11% to 50% by solution annealing at 2150°F.

The ambient temperature nature associated with maximum ductility degradation and the ability to restore original properties by reannealing are believed to be applicable to long-time aging reactions in other solid solution strengthened alloys as well.





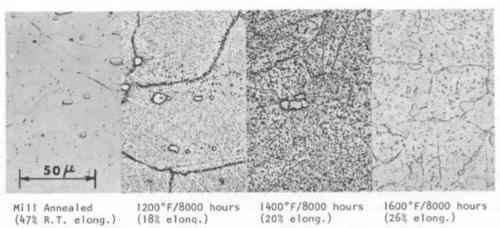


Figure 3: Yield strength ratio versus aging temperature, ductility versus aging time and microstructure of aged HASTELLOY alloy X plate

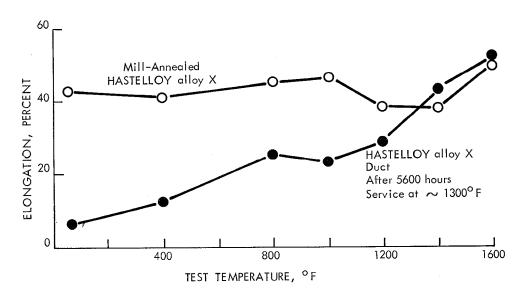


Figure 4: Influence of test temperature on ductility of HASTELLOY alloy X annealed and after elevated temperature service

HAYNES alloy No. 625

The most notable characteristic of alloy No. 625 thermal stability is the profuse precipitation of Ni₃Cb platelets upon exposure to 1400°F , accompanied by a marked decrease in R.T. ductility (Fig. 5). Less Ni₃Cb precipitation appears to form when alloy No. 625 is aged at 1600°F . When alloy No. 625 is aged at 1200°F , the Ni₃Cb phase is not detectable by X-ray diffraction of the extracted residues, nor are any platelets observed in the microstructure.

HAYNES alloy No. 188

The thermal stability behavior of alloy No. 188 is characterized by distinct degradation of R.T. ductility upon aging 4000 hours at 1400 and 1600°F. X-ray diffraction of phases extracted from samples aged 8000 hours at 1600°F reveal a $\text{Co}_2(\text{Ta},\text{Mo},\text{W})$ intermetallic phase (Laves). Laves phase precipitation, presumably, is responsible for the loss in ductility at both temperatures. The loss in R.T. ductility can be restored by reannealing. The R.T. elongation of the alloy No. 188 sample aged at 1400°F for 8000 hours (Fig. 6) was raised from 9% to 50% by annealing at 2050°F for 10 minutes.

Aging at temperatures less than 1400°F (1200°F) does not seem to be as harmful to alloy No. 188 (Fig. 6). The microstructure is characterized by grain boundary carbide precipitation (M $_{23}$ C6) and some intragranular precipitation at twin boundaries.

Properties of All Weld Metal Specimens vs. Wrought Plate Material

Table 3 documents the room temperature elongation of alloys C-4, S and X, in weld metal and wrought metal form, both in the as-received condition and after aging 8000 hours at 1200°F. As expected, the R.T. tensile ductility of weld metal was lower than its wrought counterpart. The reason for this difference is undoubtably attributed to the segregation of solutes associated with weld metal solidification. This condition seems to aggravate the ductility degradation due to aging.

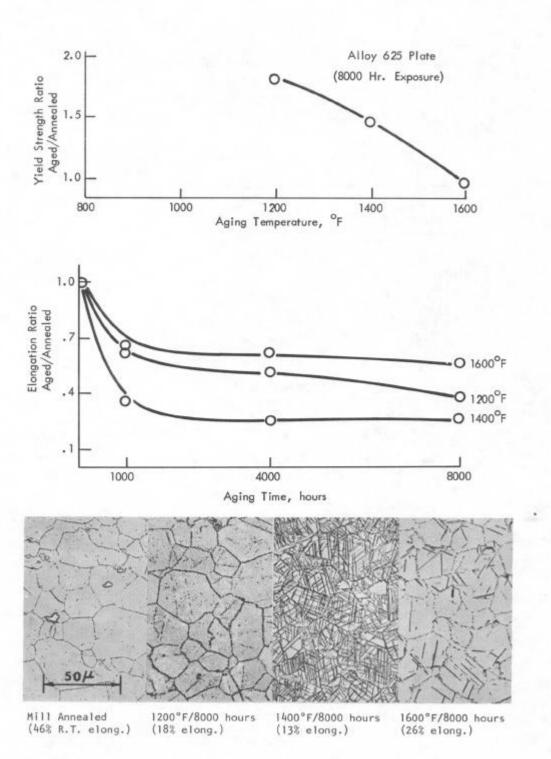


Figure 5: Yield strength ratio versus aging temperature, ductility versus aging time and microstructure of aged HAYNES alloy No. 625 plate

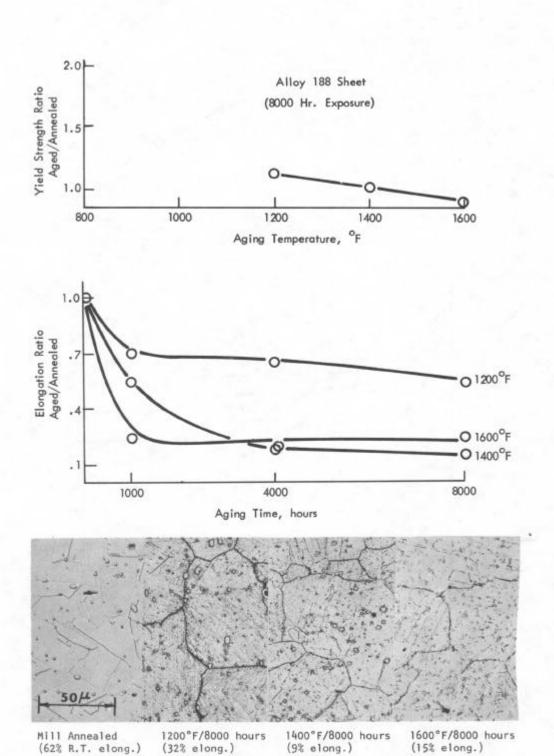


Figure 6: Yield strength ratio versus aging temperature, ductility versus aging time and microstructure of aged HAYNES alloy No. 188 sheet

Table 3: Room Temperature Tensile Elongation (%) of Wrought
Metal Versus Weld Metal

	Alloy Wrought	C-4 Weld	Alloy Wrought	S Weld	Alloy Wrought	X Weld
Annealed (or as welded)	54.5	48.7	53.8	47.8	47.2	20.0
Aged 1200°F/ 8000 hours	42.0	38.3	49.8	21.4	18.0	5.7

It is interesting to note that the aged weld metal ductility of the nickelbase alloys in Table 3 appears to be highly influenced by carbon and silicon levels of each alloy. Alloy X, for instance, contains the highest carbon (.09%) and silicon (0.45%) levels compared to the other two alloys and resulted in an aged weld metal ductility of only 5.7% elongation. Conversely, alloy C-4 has the lowest carbon and silicon levels (.002%) and .04%, respectively) and this resulted in an 8000-hour-1200% aged weld metal ductility of 38.3% elongation. Finally, alloy S, with a low carbon level (.005%), but with a moderate silicon content (.37%), had an aged weld metal room temperature elongation of 21.4%, a ductility level in between the values reported for alloys C-4 and X aged weld metal.

The excellent aged ductility of the alloy C-4 and S weld metal suggest application of these materials as dissimilar metal filler materials, especially in multipass superalloy welded joints previously hampered by aged embrittlement(1).

Empirical Relationships Between Mechanical Properties

The generation of several hundred tensile, Charpy impact and hardness tests thus far in the thermal stability program provided a unique opportunity to develop empirical relationships between mechanical properties. This was only possible because of the wide range of property values attributed to the aging characteristics. For instance, 86 average values of R.T. tensile ductility were correlated with the 86 values of Charpy impact energy measured for the corresponding aged specimen, using a computer curve fitting program. The following exponential relationship was developed:

$$C_V = e^{\frac{(\% RA + 11.94)}{14.37}}$$
 (Equation 1)

where C_{V} is the R.T. Charpy impact energy in ft-lbs and % RA is the percent reduction of area of a tensile sample measured at room temperature

In the same fashion, Equation 2 was obtained by computer correlation of hardness and yield strength data:

Y.S. =
$$2.6 e^{(.0547 \text{ HRA})}$$
 (Equation 2)

where Y.S. is the R.T. yield strength in ksi and HRA is the Rockwell A hardness value

Neither equation represents a perfect fit of the data. For instance, the index of correlation for Equation 2 was .87. Nevertheless, the development of empirical property relationships proved to be an interesting and perhaps useful by-product of the thermal stability studies.

CONCLUSTONS

This paper is an interim report intended to summarize only a small portion of the thermal stability data gathered to date. Specific conclusions regarding the thermal stability behavior of a given alloy would not be appropriate at this time, especially since it would be based upon the evaluation of only one heat of material.

From the information presented, however, there are some general trends that have become apparent. These trends can be summarized as follows:

- a. Nickel-chromium-molybdenum alloys containing very low carbon (less than .01%) and very low concentrations of iron, columbium and tungsten are characterized by excellent retention of room temperature tensile ductility, even after 8000 hour exposures in the temperature range 800 to 1600°F. An A_2B ordering reaction will occur upon aging at temperatures between 1000 to 1200°F, but this phenomenon does not appear to lower room temperature tensile ductility drastically.
- b. Solid solution strengthened high performance alloys which contain higher carbon levels (.05 to .1%) show a significant degradation in room temperature ductility after a few thousand hours of intermediate temperature exposure and then the ductility levels out into a "plateau". In general, when aging is conducted in the 1400 to 1600°F range, this plateau is reached within 1000 hours. When aging in the 1200 to 1400°F range, ductility degradation appears to level out after 4000 hours exposure. Between 4000 and 8000 hours, the R.T. ductility degradation remains relatively unchanged.
- c. The magnitude of the ductility "plateau" depends on the isothermal aging temperature, which dictates the phases and phase distribution characteristics associated with the microstructure of each alloy. Usually the phases responsible for ductility degradation are carbides; however, in some alloy systems, other phases such as Ni₃Cb or Co₂(Ta,Mo,W) are largely responsible for the reduced ductility. R.T. ductility degradation can usually be restored by reannealing.
- d. The amount of ductility degradation experienced by an alloy due to aging is invariably greater when the material is in weld metal form (segregated condition) rather than in the form of a wrought product (more homogeneous condition).

REFERENCES

(1) Ireland, D. R., "Age Embrittlement of Multipass Welded Superalloy Joints", Welding Journal Research Supplement, June, 1967.