III. THERMAL STABILITY OF REFRACTORY METAL ALLOYS*

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SUMMARY

The thermal stability of refractory metal alloys which showed promise for application in high temperature space power systems was determined. Only the very fabricable columbium and tantalum base alloys were evaluated. These included T-111, T-222, Ta-10W, FS-85, D-43, B-66, C-129Y, Cb-752, and SCb-291. These represent all of the commercial alloys prominent at the inception of the aging studies. T-111, T-222, and FS-85 eventually received the greatest emphasis because they demonstrated a superior balance of creep strength, weldability, and liquid metal corrosion resistance when evaluated in concurrent programs.

The purpose of this study was to screen the fabricable alloys for high temperature stability over long exposure times. This required that the effects on welds in particular be emphasized since welds represent severe metallurgical discontinuities whose behavior cannot be readily predicted. The alloys were thoroughly evaluated before and after aging to ascertain if degradation of mechanical properties occurred or if structural instability was otherwise noted. Bend testing for ductility changes as reflected in the bend transition temperature was emphasized as a screening technique. Considerable success was achieved using this procedure since changes in ultimate ductility and transition behavior reflect a wide spectrum of structural interactions. Tensile testing, hardness determinations, and extensive optical and electron metallography were also employed. Electron beam and gas tungsten arc welds were evaluated as well as base metal.

Instabilities were noted in all the alloys evaluated in this program. None of these were particularly detrimental in the normal application of these materials and, at most, would require only modest adjustment in hardware design. For the solid solution strengthened alloys Ta-10W and SCb-291 instabilities were confined

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to grain growth, whereas for the more advanced alloys responses were more complicated. The alloys with the highest creep strengths (T-111, T-222, and FS-85) demonstrated strikingly similar responses associated almost entirely with cored weld structure. These responses did not lend themselves to metallurgical analysis even under close scrutiny. D-43 displayed a classic overaging response ascribed to precipitation and subsequent coarsening of carbides while varying degrees of complexity in responses were displayed by the remaining alloy systems. In these latter systems responses were ascribed insofar as possible to previously identified mechanisms.

Fracture mode differed markedly for the tantalum based alloys as compared with the columbium based alloys. Even though bend test results indicated a weld aging response in T-111 and T-222, bend test fractures occurred through ductile grain boundary tearing and did not represent a design limitation. In contrast, columbium alloys displayed an abrupt change from ductile to brittle behavior at the transition. These results reflect the same general observation of the weldability evaluation of these materials; namely, based on fabricability the columbium alloys appear to have been alloyed to the maximum extent possible, whereas current tantalum alloys are conservatively alloyed.

INTRODUCTION

This paper summarizes results of thermal stability studies sponsored by NASA. In this program the structural effects of high temperature exposure were determined for promising refractory metal alloys. These alloys are uniquely suited for space power hardware applications because of excellent high temperature strength and compatibility with liquid alkali metal working fluids. However, they have not been extensively utilized because of their relatively high cost. Hence, this program provided the impetus for the detailed definition of the long time and high temperature performance of these materials.

The alloys evaluated were primarily those considered to be fabricable by welding. Hence, weld stability as well as base metal stability was emphasized. The thermal stability study was preceded by a weldability study in which the base line weld parameters were established for use throughout the thermal stability study. This assured a consistent basis for processing and comparing the stability of the various alloys.

The alloys were screened for thermal stability by exposures between 1500^o and 2400^o F and hold times up to 10 000 hours. Sputter ion pumped furnaces were used exclusively, providing an optimum furnace environment of less than 10⁻⁸ torr

total pressure. This assured that specimens would remain uncontaminated even after 10 000-hour exposures. Further, the potential load loss in event of furnace failure was nil since ion pumped systems are totally closed and do not lose vacuum with loss of power.

Bend testing (to determine the ductile-brittle transition temperature) was used extensively for screening since it provides an excellent indication of a wide variety of structural interactions. Over 3000 bend tests were required. Bend test screening was complemented by tensile testing to 2400° F for each alloy requiring over 600 tensile tests. Final analyses of instabilities were supported with optical and electron microscopy as required.

TECHNICAL PROGRAM

Alloys

The alloys evaluated in this program are listed in table III-1, which shows their nominal composition and general metallurgical classification. Specific processing parameters, as-received structure, and chemistry have been documented elsewhere (ref. 1). All these materials were procured in the recrystallized condition and to optimum processing schedules where these were identified by suppliers. Hence, insofar as possible, all alloys were normalized for long life testing.

Of the alloys evaluated, T-111, T-222, and FS-85 eventually received the greatest emphasis in this program. This resulted because they were identified in the earlier welding phase of this program and in companion creep and corrosion test evaluations as those alloys demonstrating optimum combinations of these characteristics. Hence, they demonstrated the greatest potential for advanced space power system applications.

AGING PARAMETERS

The aging matrix for this program was as follows:

Aging time, hr	Aging temperature, °F
100	1500
1 000	1800
5 000	2100
10 000	2400

All alloys were tested at all temperatures through 1000 hours of aging. The most promising alloys were carried through completely to 10 000 hours. T-111, T-222, and FS-85 were aged at all combinations; D-43 and B-66 received modest attention beyond 1000 hours; and all the other alloys were evaluated only through 1000 hours.

For each temperature-time combination each alloy was evaluated by determining bend transition temperatures of base metal, tungsten arc welds, and electron beam welds, all in both the longitudinal and transverse directions. In addition, room and elevated temperature tests were conducted in accordance with the test matrix shown in figure III-1. Optical and electron metallography, hardness traverses, and chemistry determinations were performed as required to analyze results and demonstrate adequacy of experimental techniques.

Specimen Preparation

Specimens were prepared for aging by pickling, welding, postweld annealing, blanking and machining, and repickling in sequence. Following final pickling specimens were handled only with clean cotton gloves prior to aging. Specimen groups were packaged by alloy and wrapped in tantalum foil for aging. All alloys were then aged together for any particular time-temperature combination. Welding parameters and postweld anneals were selected to provide maximum ductility as previously established (ref. 1). These are listed in table III-2. Since alloys were normalized to optimum starting ductility, we rationalized that they would be most sensitive to structural instability. Selection of a postweld anneal further satisfied a general requirement for corrosion resistance in refractory metal alloys. All specimens were produced from 0.035-inch sheet. Again, general details of specimen preparation, dimensions, and test procedures have been previously documented (refs. 1 and 2). Maintenance of optimum cleanliness was emphasized in every phase of processing.

Aging was accomplished in Varian ultrahigh vacuum sputter-ion pumped furnaces. These provided pressures from $\sim 10^{-11}$ to 10^{-8} torr for aging. Numerous

checks for contamination of specimens were performed, and all proved negative, as shown typically in table III-3. These furnaces have been fully characterized for this application (ref. 3). The high vacuum facility is shown in figure III-2.

RESULTS AND DISCUSSION

High Strength Alloys of Greatest Interest (T-111, T-222, FS-85)

These alloys are grouped for discussion because of both similarities in thermal stability results and excellent balance of creep strength, weldability, and liquid metal corrosion resistance. Behavior of FS-85 differed only in being typical of other columbium alloys in fracture mode. FS-85 displayed a classic transition from ductile-to-brittle behavior in bend testing. In contrast, T-111 and T-222 bend specimens responded to aging by displaying an increased temperature for ductile tearing primarily in the weld metal. This was based on the 1t bend test, which is essentially a 'go - no go' test for $33\frac{1}{3}$ percent outer fiber strain.

The behavior of T-111, T-222, and FS-85 following long time exposures at elevated temperatures was markedly similar. The ultimate tensile strength at room temperature and 1800° , 2100° , and 2400° F as a function of aging time is shown in figures III-3, III-4, and III-5 for T-111, T-222, and FS-85, respectively. The tensile strength of FS-85 shows no change within the range of conditions evaluated, while a modest decrease in the tensile strength of T-111 and T-222 is seen to result from the aging. The decrease is most significant for tests at 1800° F. This could be rationalized on the basis of strain aging, which is pronounced at this temperature for both T-111 and T-222. Aging at 1500° F had much less effect on the 1800° F tensile strength than aging at the higher temperatures.

Unlike the tensile test results, determinations of the bend ductile-brittle transition temperature indicated a significant aging response for T-111, T-222, and FS-85 (figs. III-6, III-7, and III-8). Several similarities are noted for the three alloys:

- (1) The magnitude of the response is greatest for gas tungsten arc welds and least for base metal specimens.
- (2) Ductility is not impaired by aging at 2400° F.
- (3) Aging at 1500° F caused no discernible effect in T-111 and T-222, but some response was noted for the lower melting, columbium-base FS-85.
- (4) Maximum response for these alloys was after aging at 1800° and 2100° F.

Subsequent to the aging study reported here, the aging response for T-111 received further scrutiny to more completely define its characteristics. It was deter-

mined that T-111 weld aging was not responsive to postweld annealing to 3000° F. Hence, an averaged structure was not achievable using any practical annealing temperature. This is shown in figure III-9. Further, the aging response as measured by the longitudinal tensile ductility of T-111 gas tungsten arc welds was not as severe as might be inferred from the bend test data. This is shown in figure III-10 for tensile tests run at 32° F. The welds all have good ductility but less than that required to pass the 1t bend test of this study, which produces $33\frac{1}{3}$ percent outer fiber strain. In this respect the bend test should always be viewed as a "go - no go" test for a given level of strain. Figures III-9 and III-10 show that no thermal solution to aging could be achieved in this alloy and also that based on tensile ductility no solution was required. However, the necessity to understand the observed aging response could not definitely be dismissed. Hence, a considerable effort was expended to identify the mechanism responsible for the observed aging response. It does not appear that the observed aging compromises the uses of T-111. This stems from the fact that all tantalum alloy fractures occurred by intergranular tearing exhibiting considerable ductility.

T-111 (Ta-8W-2Hf). - Responses of T-111 were evaluated in greatest detail both because of its general importance and because the similarity of responses indicated that only one alloy of this group required detailed analysis. Microstructures of the weld zone, heat affected zone (HAZ), and base metal of selected T-111 specimens are shown in figure III-11. Gas tungsten arc welds are shown since these represent the condition of maximum response.

The 1 hour 2400° F postweld anneal (fig. III-11(a)) has resulted in a weld zone relatively precipitate-free. In the HAZ the only evidence of precipitates is along the grain boundaries. The bend DBTT of this structure was below -320° F.

After aging for 10 000 hours at 1800° F the microstructure is altered from that of figure III-11(a) to that shown in figure III-11(b). Weld zone precipitates can be observed in the aged structure, mainly along the interdendritic boundaries of the original cored weld structure. This suggests that gradients in solute concentration associated with the cored structure provide the driving force for this precipitation. There is, in addition, a nearly continuous precipitate phase located at the grain boundaries of the fusion zone. Fine, dispersed precipitates are apparent in the HAZ, while the base metal appears to be quite clean except for the presence of coarse precipitates along the grain boundaries. The bend DBTT of this specimen was 125° F.

The effect of aging T-111 at 2100° F for 5000 hours can be seen in figure III-11(c). The amount of interdendritic precipitate has decreased while the amount of grain boundary precipitate in the fusion zone has remained relatively unchanged. Little change has occurred in the HAZ except that possibly a little more precipita-

tion has occurred. The base metal, shown at a magnification of 500, is similar to that shown in figure III-11(b). The bend DBTT is now -25°F .

After 10 000 hours at 2400°F , for which the bend DBTT was below -320°F , complete homogenization had occurred, and, except for isolated coarse precipitates at the grain boundaries, the structures were single phase. This structure could essentially be restored in specimens aged 10 000 hours at 1800°F by postaging anneals of 1 and 16 hours at 2400°F . The microstructures of weld, HAZ, and base metal following these anneals are shown in figure III-12. Comparison with figure III-11(b) indicates the postage anneals have effected a reduction in the amount of weld zone precipitates at both interdendritic and grain boundary areas and the nearly complete elimination of precipitates in the HAZ while having virtually no effect on the base metal. The postage annealed structure appears to be quite similar to the 1 hour 2400°F postweld annealed structure of figure III-11(a).

There appears to be a correlation between the bend transition temperature and the amount of interdendritic and grain boundary precipitates in the weld fusion zone. Since the transition temperature decreases with a decrease in the amount of precipitate, it seems likely that a cause-effect relation exists between them. Further evidence of such a relation, particularly in the case of the grain boundary precipitates, is the fact that weld fractures during bend testing were invariably intergranular. Hence, efforts were directed toward identification of the precipitates in order to obtain an understanding of the ductility impairment mechanism.

Bulk extraction residues were obtained from base metal and weld metal specimens of T-111 both before and after aging. Debye-Scherrer diffraction patterns of these residues indicated the presence of monoclinic HfO_2 , the FCC monocarbide $(\text{Hf}, \text{Ta})\text{C}$, and the dimetal carbide Ta_2C . The relative amounts of these phases did not vary significantly with specimen history. While these results are meaningful and useful, it must be recognized that there are a number of limitations of this technique. Some of these are

- (1) Some phases present may be attacked and dissolved by the bromine-methanol-tartaric acid solution used to dissolve the matrix.
- (2) If a dispersed phase is present in a very small quantity, it may be obscured by the background radiation.
- (3) No information is obtained regarding the size, shape, and distribution of the extracted particles.

To supplement the X-ray selected area electron diffraction was performed on standard fractograph replicas of T-111 specimens aged as follows:

Time, hr	Temperature, °F
5 000	1800
10 000	1800
1 000	2100
5 000	2100

The fractograph replicas were prepared from the surfaces of freshly fractured specimens which were fractured by bending in a vise at -320°F . Standard replicating procedures were used except that shadowing was not employed since the primary aim was to ascertain the existence of, and to identify if possible, any particles which might be associated with the fracture surface. Examination with the electron microscope revealed second phase particles had been successfully retained on the replicas. Despite the fact that high quality single crystal selected area electron patterns were obtained on a number of particles, efforts to identify them were not successful. A typical electron micrograph and an electron diffraction pattern are shown in figure III-13.

Additional extraction replicas were prepared from the fracture surfaces of GTA welds aged 1000 hours at 2100°F and 5000 hours at 1800°F . Platelet particles on these replicas were chemically analyzed at Advanced Metals Research Corporation using a focusing X-ray spectrometer attachment to a Philips EM-200 Electron Microscope. With this instrument the exciting electron beam can be focused to a diameter of about 1 micron on the surface of the specimen being analyzed. The chemical analysis of the excited area is afforded by analysis of the characteristic radiation of the specimen by the X-ray spectrometer. Tantalum was the only metallic element found in the platelets analyzed. This suggests the platelets are light element compounds of tantalum such as carbides, oxides, or nitrides.

To further characterize the weld zones and the effect of aging, electron microprobe techniques were employed to study microsegregation in GTA welds of T-111 in the as-welded plus 1 hour 2400°F postweld annealed condition and also in a similar weld aged 10 000 hours at 1800°F . The results of this work, also performed at Advanced Metals Research Corporation, are given in table III-4.

These measurements indicate the magnitude of the coring which exists in the weld structure after the 1 hour 2400°F postweld anneal is being affected very little by 10 000 hour aging at 1800°F , an observation not unexpected since the kinetics of W and Hf diffusion would be quite slow at that temperature.

The results presented above indicate a case can be made for the existence of two different phases in the fusion zone. The observed W and Hf segregation indi-

cates the interdendritic precipitates may be a heavy metal phase such as W_2Hf , whereas the grain boundary phase is more likely a light element compound of tantalum. Observations of a decreasing amount of precipitate at both regions with higher aging temperatures are consistent with enhanced diffusion kinetics. The fact that the fractures appear to be intergranular rather than interdendritic and the fact that some aging response is observed in uncured base metal suggest that, if two different phases are involved, the grain boundary phase may be more important with respect to the aging response.

Briefly reviewing the precipitate behavior, we find

(1) No evidence of the grain boundary precipitate is seen in the fusion zones of T-111 welds in either the as-welded or the as-welded and postweld annealed specimens. Modest interdendritic precipitation was noted (fig. III-11(a)).

(2) Aging at 1800° and 2100° F results in precipitation on fusion zone grain and dendrite boundaries (figs. III-11(b) and (c)).

(3) Short time annealing at 2400° F of welds aged at 1800° and 2100° F decreases the amount of both grain and dendrite boundary precipitate (fig. III-12).

The fact that the amount of precipitate observed after aging at 1800° and 2100° F is seen to decrease on subsequent exposure at 2400° F suggests a solvus temperature is being exceeded and the precipitate is going into solution.

Hypothesis for the T-111 aging response. - The 1800° to 2100° F reaction range suggests that the grain boundary precipitate is an interstitial compound behaving in a manner typified by Ta_2C . The interdendritic precipitate occurs simultaneously but in such large quantity and at a slower rate such that one is inclined to suspect this to be an intermetallic compound typified by W_2Hf . Neither was identified using the various experimental techniques of this program. However, the expected behavior of these two types of precipitates appears consistent with the observed aging response. The grain boundary precipitate exerts the most pronounced influence since the fractures were intergranular. The interdendritic precipitate probably has an indirect influence on the aging response. Its substructure-like arrangement could lead to strengthening within the weld grains. This would lead progressively to a greater differential between grain boundary and matrix strength forcing the grain boundaries to accommodate an increasingly larger share of the total strain with aging. This enhances the tendency for grain boundary failures, a failure mode already promoted in welds by their large grain size (and, hence, low total grain boundary area). This hypothesis is shown schematically in figure III-14.

The evidence suggesting that the grain boundary precipitate is an interstitial compound such as Ta_2C (ref. 4) is as follows:

- (1) Located preferentially at grain boundaries
- (2) Stable within the approximate aging temperature range

- (3) Unstable at or about 2400° F (may transform and go into solution at this temperature)
- (4) Primarily Ta-base (no W or Hf) as observed by X-ray spectrometry of the fracture surface compound

The evidence suggesting the presence of an intermetallic phase (such as W_2Hf) at the interdendritic boundaries is as follows:

- (1) The observed sluggishness in formation is typical of an intermetallic compound.
- (2) The large volume fraction of interdendritic precipitate seems to preclude the possibility it is an interstitial compound.
- (3) Solute redistribution to dendrite boundaries, as determined by electron beam microprobe analysis, results in W and Hf concentrations nearly stoichiometric with W_2Hf .

The compromising evidence for this hypothesis includes

- (1) Neither the grain boundary phase nor the interdendritic phase was positively identified. Ta_2C was detected by X-ray diffraction of bulk extraction residues but could not be definitely associated with the grain boundaries. Extraction of the intermetallic would be particularly difficult.

- (2) Phase relations for W_2Hf in the ternary system are not known.

Other possibilities which were considered but seem to be precluded by the experimental evidence include

- (1) That the grain boundary precipitate is the MC phase (or some analogous phase), since this phase invariably is Hf-rich, a possibility refuted by the results of the X-ray spectrometry. Also, MC exhibits no preference for grain boundary precipitation.
- (2) That the interdendritic phase is a complex Ta-Hf compound forming due to the $\beta' - \beta''$ miscibility gap known for this alloy system. For such a reaction to occur an enormous local concentration of Hf (>30 percent) would be required.
- (3) That either the interdendritic or the grain boundary phase is HfO_2 since this compound, both in the monoclinic and cubic forms, is easily and routinely extracted and its concentration determined using bulk diffraction techniques. The HfO_2 concentration did not vary with location or aging conditions.

T-222 (Ta-9.6W-2.4Hf-0.01C). - The aging response of this alloy as revealed by changes in the bend transition temperature was similar to that of T-111. The rationale developed and presented for T-111 extends quite well to T-222, requiring only minor modification.

Typical microstructures of T-222 welds aged at 1800°, 2100°, and 2400° F are shown in figure III-15. Comparison of figure III-15(a) with figure III-11(b) reveals that, after 10 000 hours at 1800° F, the aging reaction has resulted in a substantially

greater amount of both grain boundary and interdendritic precipitation in T-222 than occurred in T-111. This was not an isolated case but was true for most aging conditions. The greater amounts of precipitate formed by the 1800° and 2100° F aging coupled with the fact that the carbon level was apparently greater than the 2400° F solubility limit in the alloy resulted in residual precipitates being apparent in the structures aged 10 000 hours at 2400° F. The intragranular precipitates observed in the HAZ regions in figures III-15(a) and (b) appear to be those identified by Ammon and Harrod (ref. 4) as the Hf-rich monocarbide (Hf, Ta)C. After 10 000 hours at 2400° F this carbide appears to be undergoing coarsening.

Efforts at phase identification were much more limited for this alloy than for T-111. However, the similarity of aging response, microstructural features, and fracture behavior suggests that only modest revision of the hypothesis presented for T-111 would be required for T-222.

FS-85 (Cb-27Ta-10W-1Zr). - While the aging response of this columbium-base alloy was generally similar to that of T-111 and T-222, several important differences were noted in the bend test results. The fracture mode of this alloy was generally by brittle cleavage and not by ductile grain boundary tearing as was noted for T-111 and T-222. An apparent effect of this failure mode was that fractures in weld specimens were not arrested in the base metal. Further, this fracture mode probably accounts for the increased response of base metal and electron beam welds to aging as compared with T-111 and T-222. This fracture behavior is typical of columbium-base alloys, and does not in itself imply any difference with respect to the aging mechanism of this alloy. Finally, FS-85 responded to aging at a lower temperature than T-111 or T-222, perhaps partly because of its lower melting point.

Microstructures of FS-85 are shown in figure III-16 for several aging conditions. In figures III-16(b) and (c) the interdendritic precipitate is visible in the weld zone. For most aging conditions there appeared to be less grain boundary and interdendritic precipitation than was observed in comparably aged T-111 and T-222.

In FS-85, zirconium is the reactive metal addition which behaves in a manner analogous to that of hafnium in tantalum-base alloys. However, in FS-85 there is only about 1 atomic percent Zr, whereas the tantalum-base T-111 and T-222 alloys contain approximately 2.0 and 2.4 atomic percent Hf, respectively. One might reasonably expect then that the zirconium enrichment at interdendritic boundaries in FS-85 welds does not approach the hafnium enrichment in T-111 and T-222 welds. In addition, the carbon level of the FS-85 sheet used for this program was notably less (in terms of atomic ppm) than that of either tantalum-base alloy. Both of these conditions would tend to decrease, relative to T-111 and T-222, the amount of interdendritic and grain boundary precipitate in the fusion zones.

Note the hypothesis presented for T-111 can be extended quite well to FS-85 since W_2Zr and Cb_2C provide direct analogs to W_2Hf and Ta_2C . In view of the differences in the amount of precipitate between FS-85 and T-111, it may not be possible to ascribe the exact same rationale to their respective aging responses. Admittedly there are two possible explanations which could account for the similarity in behavior in spite of the microstructural differences:

(1) A very small volume of precipitate is required to control the observed aging response in that FS-85 fractured largely by brittle cleavage.

(2) The similarity may be strictly fortuitous. The response observed in the bend transition temperature may be reflecting the bulk or net change of a number of complex interacting factors.

Following $2400^{\circ}F$ aging, for which microstructures are not shown, considerable grain growth had occurred, weld zones could no longer be distinguished from HAZ and base metal, and very little evidence of precipitates remained. The fact that the bend DBTT was about -150° to $-175^{\circ}F$ for all types of test specimens after aging 10 000 hours at $2400^{\circ}F$ implies a ductility limit due to grain size has been realized.

Miscellaneous Other Solid Solution and Dispersion Strengthened Alloys

(B-66, D-43, Cb-752, C-129Y)

B-66 (Cb-5Mo-5V-1Zr). - Considerable grain growth and modest changes in mechanical properties marked the response of B-66 to long time, elevated temperature aging. Base metal, GTA welds and EB welds were aged for times to 10 000 hours and temperatures to $2400^{\circ}F$.

Almost without exception, the results of tensile tests and bend DBTT tests could be interpreted in terms of grain size of the test specimens. Most of the aging temperatures employed in this study are quite high for this alloy, and the large grain sizes noted in the postage microstructures are not unexpected. Changes in ultimate and yield tensile strengths at room temperature and 1800° , 2100° , and $2400^{\circ}F$ were quite modest because of the thermal exposures.

The only significant exception to the above rationale would appear to be the slight "peak" in the bend DBTT found for GTA welds after $1500^{\circ}F$ aging (fig. III-17). That this peak diminishes with increased aging time at $1500^{\circ}F$ suggests the possibility that a classic precipitation reaction is occurring. By 5000 hours the overaged condition has apparently been attained and no ductility loss is apparent from the bend test results. Program emphasis did not allow further definition of

this reaction, but the slight improvement in room temperature yield strength for specimens aged at 1500° F relative to the other aging temperatures lends credence to this suggestion. After 5000 hours of aging, ductility of base metal and EB welds normalized to that of GTA welds, an effect easily explained in terms of grain size.

Like other columbium alloys this alloy displayed a classic abrupt transition in bend testing from ductile-to-brittle behavior.

D-43 (Cb-10W-1Zr-0.1C). - This carbide-dispersion strengthened alloy provided the prime example of classic overaging and subsequent loss of strength of the alloys included in the aging study. This alloy has been the object of considerable metallurgical interest, primarily because of its aging reactions. As a result, extensive investigations of these reactions have led to a unique, for refractory metal alloys, and precise identification of the various reaction stages and products. The work of Ostermann and Bollenrath (ref. 5) is particularly outstanding in this respect.

The ultimate tensile strength as a function of aging time and temperature for base metal and GTA welds is shown in figure III-18 for tensile tests conducted at room temperature and 1800°, 2100°, and 2400° F. That only overaging behavior observed is believed due to an apparent optimum condition achieved in the as-received D-43 sheet using a 2400° F postweld anneal. The microstructure of the base metal, as viewed by light microscopy at a magnification of 1500, changed very little from that of the as-received sheet throughout aging treatments as long as 10 000 hours at 1800° F, being composed of a very fine (Cb, Zr)C precipitate dispersed throughout the grain interiors and a coarser columbium carbide, Cb₂C, present as intragranular platelets and a grain boundary precipitate.

The microstructure of the base metal following 10 000-hour aging at 1800° and 2100° F is shown in figure III-19 along with representative weld heat-affected-zone (HAZ) areas for each of these aging conditions. In the base metal both the fine (Cb, Zr)C precipitates and the Cb₂C precipitates have coarsened somewhat during the long-time aging at 2100° F relative to those resulting from aging at 1800° F or lower. The reaction in the HAZ regions is quite different from that occurring in the base metal. During welding, complete solutioning occurs in the HAZ and, because of the rapid cooling to temperatures below about 1000° F, rejection of carbon from solid solution results in the formation of metastable ϵ carbides. These carbides are unstable at higher temperatures and transform to the hexagonal Cb₂C and the cubic (Cb, Zr)C, the relative amounts of which depend on temperature of transformation. Hence, the carbides in the HAZ following 10 000-hour aging at 1800° F appear to be a mixture of ϵ carbide and Cb₂C, while after 10 000 hours at 2100° F they are a mixture of Cb₂C and cubic (Cb, Zr)C.

The precipitate-free zones adjacent to grain boundaries which are apparent in

figure III-19, particularly following the 2100° F aging treatment, are probably indicative of carbon and/or vacancy depletion of the matrix due to interstitial and/or vacancy diffusion to grain boundaries. While solute depletion of the matrix by diffusion of Zr (or W) could lead to the same type of structure, the relatively low aging temperature renders this much less likely.

The averaged condition implied by the tensile data of figure III-17 for a base metal specimen aged 10 000 hours at 2400° F is shown in figure III-20.

The bend DBTT data followed the trend established by the tensile data in that, for nearly every aging condition, the aging process increased the ductility (i. e., lowered the bend DBTT). Hardness traverses of aged specimens were of little value as indicators of the aging process. Bend transitions were generally abrupt changes from ductile to brittle behavior as characteristic of columbium base alloys.

From this screening study it would appear the instabilities in structure and mechanical properties of D-43 which result from aging warrant careful consideration for applications involving long times at temperatures above 1500° F.

Cb-752 (Cb-10W-2.5Zr). - The response of this alloy to 1000 hour exposures at temperatures from 1500° to 2400° F was somewhat random. Bend DBTT tests indicated slight, irregular changes with aging temperature. Fracture behavior was typical of columbium alloys. The general trend, however, was for an improvement in bend ductility for specimens aged at 2400° F. Results of tensile tests indicated that, except for room temperature ultimate and yield strength, aging time and temperature had very little effect. In figure III-21, the room temperature strength is shown to improve while the elevated temperature strength is relatively unaffected by the aging.

Cb-752 is reported to achieve optimum tensile strength through the use of a duplex annealing treatment during processing (ref. 6). This treatment consists of a 1-hour, 2800° F solution anneal followed by a final cold reduction (40 percent) and a 1-hour, 2400° F aging anneal. The final anneal is used to induce (Zr,Cb)C precipitation, which provides dispersed phase strengthening. The Cb-752 sheet evaluated in this aging study was produced by a previous processing schedule which did not incorporate an in-process solution anneal and used a 1-hour, 2200° F final anneal. Hence, the program Cb-752 was presumably not in the optimum condition with respect to mechanical strength. Comparing the data of figure III-21 with those of Bewley (ref. 6) indicates the following:

- (1) The unaged room temperature tensile strength found in this study is noticeably lower than that attained using the duplex annealing treatment.
- (2) Following the 100- and 1000-hour aging at elevated temperatures, the tensile strengths determined in this study (fig. III-21) are identical with those expected for similarly aged, duplex annealed sheet.

(3) Elevated temperature tensile strength of the program Cb-752 (base metal and GTA welds) is approximately equal to that indicated for duplex annealed sheet.

Similar observations apply to the respective yield strength data.

These results imply that, at least with respect to the factors affecting mechanical strength, very little difference exists between the Cb-752 evaluated in this program and that produced by duplex annealing. The only notable exception appears to be the inferior unaged room temperature strength of the sheet used for this evaluation. This is probably due to the lack of an in-process solution anneal and the use of a lower final annealing temperature for the program Cb-752. Both of these would detrimentally affect the amount and distribution of the strengthening precipitates and would therefore contribute to the observed deficiency in room temperature tensile strength.

C-129Y (Cb-10W-10Hf-0.1Y). - Thermal exposures to 1000 hours at 2400° F had no discernible effect on the tensile properties of this alloy, while data from bend DBTT tests indicated some minor, nongeneral responses to aging had occurred. In typical fashion, the greatest response was seen in gas tungsten arc welds. Fracture behavior was again typical of columbium alloys.

Metallographic examination of aged specimens indicated the grain refining effect of the yttria was effective in controlling grain size of the base metal. Conversely, loss of yttria during welding is implied by continuous grain growth, which occurs in the weld fusion zones as a function of the severity of thermal exposure.

Solid Solution Alloys (Ta-10W, SCb-291)

The solid solution alloys included in this study were SCb-291 (Cb-10W-10Ta) and Ta-10W. For moderate temperature applications these alloys can be expected to perform adequately for extended periods of time. For the purposes of this program, however, their inclusion is mainly to provide base-line data to permit discrimination between those effects due to solid solution strengthening and those due to dispersed phase strengthening in more complex alloys. Alternatively, since these alloys should be very stable, they also acted as "referee" alloys to double check the aging and handling procedures. Their stable responses to aging did in fact demonstrate the adequacy of the experimental procedures.

Ta-10W. - No instability in structure or tensile strength resulted from 1000-hour exposures at temperatures to 2400° F. Bend transition temperatures of base metal, GTA welds, and EB welds were -320° F for all aging conditions. Microstructures in every case were single phase. Weld structures, particularly GTA welds, were characterized by extremely large grains which resulted in rather low

tensile elongation during tensile testing. However, this behavior was in no way influenced by the aging but rather was a property of the weld structure.

SCb-291 (Cb-10W-10Ta). - This Cb-base alloy demonstrated excellent thermal stability for all aging-time - temperature conditions evaluated. Aging was not performed beyond 1000 hours. Tensile properties showed no significant changes due to the thermal exposures. Bend transition temperatures were generally unaffected by aging except for a slight lowering of bend ductility following the 1000 hour exposures at the highest aging temperatures. Fracture mode in bend testing was brittle cleavage so that bend transitions always occurred with a classic change from ductile to brittle behavior. Subsequent metallography indicated this to be the result of the considerable grain growth which occurs at the most severe thermal exposures. Microstructures were single phase in all cases. Grain growth appeared to be a continuous process as expected for a single-phase, solid-solution alloy.

In conclusion, SCb-291 offers excellent structural and mechanical property stability following long time elevated temperature exposures. Its usefulness, however, is limited by its relatively low high temperature strength.

CONCLUSIONS

1. The alloys evaluated displayed a wide range of responses to the thermal exposures employed in this program. In most cases, these responses were most easily understood in terms of the metallurgy of the respective alloy system.

2. The alloys generally displayed satisfactory stability, as would typically be required for engineering applications. However, several alloys are temperature limited with respect to thermal stability. D-43 displayed loss of strength with increasing aging time and temperature. This would have to be accommodated in setting design stresses for long time applications for temperatures above 2000° F. SCb-291 and B-66 were prone to loss of ductility with increasing grain size caused by high temperature aging. Hence, these alloys should be used only at the lower temperatures for long time applications. Likewise, Ta-10W displayed similar grain growth related instabilities. Otherwise the alloys investigated were generally acceptable for high temperature application from the standpoint of structural stability.

3. The magnitude of the aging response tended to be greatest for gas tungsten arc welds and least for base metal specimens.

4. An important difference in bend test fracture mode was noted for aged T-111 and T-222 bend specimens compared with columbium-base alloys. Even though shifts in transition behavior were noted, fractures were ductile intergranular

separations which did not propagate from the weld metal into the base metal. Columbium-base alloys tended to display unarrested cracking and a classic, abrupt transition from ductile to brittle cleavage behavior. Hence, the bend transition temperature represents a design limit for columbium alloys but not for the tantalum alloys.

5. T-111, T-222, and FS-85 displayed similar responses to aging. These were detected only in measurements of the bend transition temperature, not being observed in tensile tests at room temperature or elevated temperatures. The fact that no evidence of a response was seen in high temperature tensile tests demonstrated that the thermal stability is excellent from a design standpoint. Of these, FS-85 alone would be limited but only in an unusual situation requiring periodic cycling from the aging temperatures to below the bend transition temperature.

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TABLE III-1. - ALLOYS EVALUATED FOR THERMAL STABILITY

Alloy	Classification ^a	Nominal composition, wt %
T-111 T-222 FS-85	Highest creep strengths Gettered alloys ^b Solid solution + dispersion strengthened	Ta-8W-2Hf Ta-9.6W-2.4Hf-0.01C Cb-27Ta-10W-1Zr
Ta-10W SCb-291	Solid solution strengthened Ungettered alloys ^b	Ta-10W Cb-10W-10Ta
B-66 D-43 C-129Y Cb-752	Solid solution + dispersion strengthened Gettered alloys ^b	Cb-5Mo-5V-1Zr Cb-10W-1Zr-0.1C Cb-10W-10Hf + Y Cb-10W-2.5Zr

^aFor weldability ratings see ref. 1.^bReactive element addition, Zr or Hf, provides corrosion resistance in liquid alkali metals.

TABLE III-2. - OPTIMIZED WELD CONDITIONS FOR 0.035-INCH SHEET

Alloy (a)	Process	Parameters (b)	1-hr postweld anneal temperature, °F (c)	Weld width ratio, top/bottom, in.	BDBTT, °F ^d	
					Longitudinal bends	Transverse bends
Ta-10W	GTA	7.5-1/4-118	No anneal	0.190/0.180	<-320	<-320
	EB	15-1/2-4.5	No anneal	.049/0.034	<-320	<-320
T-111	GTA	15-3/8-115	2400	0.195/0.189	<-320	<-320
	EB	15-1/2-3.8	2400	.038/0.027	<-320	<-320
T-222	GTA	30-1/4-190	2400	0.180/0.159	<-320	<-320
	EB	15-1/2-3.8	2400	.039/0.026	<-320	<-320
B-66	GTA	15-3/8-86	No anneal	0.190/0.180	0	+75
	EB	25-3/16-3.2	1900	.036/0.024	-225	-175
C-129Y	GTA	30-3/8-110	2400	0.180/0.130	-200	-225
	EB	50-1/2-4.1	2200	.040/0.026	-250	-250
Cb-752	GTA	30-3/8-87	2200	0.129/0.090	-75	0
	EB	15-3/16-3.3	2400	.036/0.017	-200	-200
D-43	GTA	30-3/8-114	2400	0.159/0.143	+100	0
	EB	50-1/2-4.4	2400	.040/0.027	-225	^e -225
FS-85	GTA	15-3/8-90	2400	0.204/0.195	-175	-175
	EB	50-3/16-4.4	2200	.038/0.026	-200	-200
SCb-291	GTA	15-1/4-83	2200	0.160/0.150	-275	-275
	EB	50-1/2-4.4	No anneal	.038/0.027	<-320	-250

^aAs-received alloys were in the recrystallized condition.^bFor GTA welds: speed, in./min; clamp spacing, (in.)(A); for EB welds: speed, in./min; clamp spacing, (in.)(mA). (All EB welds with 60-cycle, 0.050-in. longitudinal deflection and 150-kV beam voltage.)^cPostweld anneal was selected for optimum ductility but is also assumed to achieve an averaged structure with respect to internal reactive metal-oxygen reactions, which enhances its compatibility with alkali metals.^dBend ductile-brittle transition temperature at 1t bend radius for all except FS-85 welds; transition temperature at 2t bend radius for FS-85 welds.^eProbable value (determined value <-125° F).

TABLE III-3. - IN-PROCESS INTERSTITIAL ANALYSES (wt. ppm)

Alloy	Element	Base metal as-received	As-welded GTA welds	500-hr age ^a		10 000-hr age ^a			
				1800° F	2400° F	1500° F	1800° F	2100° F	2400° F
T-111	C	48	34	36	44	30	80	53	45
	O	15	24	20	13	12	13	13	20
	N	18	26	24	24	24	27	23	21
T-222	C	100	125	79	150	150	150	140	140
	O	29	22	45	32	25	15	46	30
	N	10	16	66	8	9	8	8	7
FS-85	C	12	14	39	---	48	47	48	38
	O	98	73	75	---	51	96	70	75
	N	50	41	24	---	45	47	41	27

^aAged specimens in nearly all cases were base metal.

TABLE III-4. - RESULTS OF ELECTRON MICROPROBE STUDY OF MICROSEGREGATION IN T-111 GTA WELDS

Specimen condition	Weld region analyzed (a)	Concentration, wt %	
		W	Hf
As-welded plus 1-hr 2400° F postweld anneal	Near HAZ; IDB	7.9	3.1
	Near HAZ; IDI	9.6	1.7
As-welded plus 1-hr 2400° F postweld anneal	Weld center; IDB	7.5	3.5
	Weld center; IDI	9.8	1.3
As-welded plus 1-hr 2400° F and 10 000-hr 1800° F postweld anneals	Near HAZ; IDB	7.8	4.5
	Near HAZ; IDI	10.1	1.9
As-welded plus 1-hr 2400° F and 10 000-hr 1800° F postweld anneals	Weld center; IDB	8.6	2.9
	Weld center; IDI	9.6	1.9

^aIDB, at the interdendritic boundaries; IDI, at the interdendritic interiors.

Figure III-1. - Typical tensile test schedule for aged specimens.

Figure III-2. - Ultrahigh vacuum annealing furnaces.

Figure III-3. - Ultimate tensile strength of T-111 as function of aging parameters. Optimum weld parameters; all samples annealed 1 hour at 2400° F prior to aging and testing.

Figure III-4. - Ultimate tensile strength of T-222 as function of aging parameters. Optimum weld parameters; all samples annealed 1 hour at 2400° F prior to aging and testing.

Figure III-5. - Ultimate tensile strength of FS-85 as function of aging parameters. Optimum weld parameters; all samples annealed 1 hour at 2400° F prior to aging and testing.

Figure III-6. - Bend ductile-brittle transition temperature of T-111 as function of aging parameters.

Figure III-7. - Bend ductile-brittle transition temperature of T-222 as function of aging parameters.

Figure III-8. - Bend ductile-brittle transition temperature of FS-85 as function of aging parameters.

Figure III-9. - Effect of postweld annealing on aging in T-111 welds. Data points within dashed block for tests on T-111 heat used this program. Remaining points from additional heat of T-111. (Low heat input welds made at 15 in./min.; high heat input welds made at 6 in./min.)

Figure III-10. - T-111 longitudinal weld tensile ductility at 32°F after aging as indicated. Data for T-111 heat used this study except as noted. (Low heat input welds made at 15 in./min.; high heat input welds made at 6 in./min.)

(c) Welded plus postweld anneal of 1 hour at 2400° F; aged 5000 hours at 2100° F; bend DBTT, -25° F.

Figure III-11. - Typical microstructures of weld, HAZ, and base metal of T-111 GTA weld specimens as function of postweld thermal history.

Figure III-12. - Microstructures of T-111 after indicated postage anneals.

(a) Electron micrograph
(X10 000).

(b) Electron diffraction
single crystal point pattern.

Figure III-13. - Particle extracted from T-111 fracture surface.

WELD STRUCTURE PRIOR TO AGING

AFTER AGING AT 1800° to 2100°F

GRAIN BOUNDARY PRECIPITATE - BELIEVED TO BE AN INTERSTITIAL COMPOUND; BEHAVIOR TYPIFIED BY THAT OF Ta_2C .

INTERDENDRITIC PRECIPITATE - BELIEVED TO BE AN INTERMETALLIC COMPOUND SUCH AS W_2Hf ; LARGE VOLUME FRACTION, SLUGGISH REACTION; ALMOST EXACT STOICHIOMETRIC COMPOSITION OBSERVED.

AFTER SHORT TIME POST AGE ANNEALS
AT 2400°F

GRAIN BOUNDARY PRECIPITATE - SHOWN AFTER NEARLY COMPLETE DISSOLUTION; DISAPPEARS BEFORE THE INTERDENDRITIC PRECIPITATE.

INTERDENDRITIC PRECIPITATE - ALSO SHOWN PRIOR TO COMPLETE DISSOLUTION.

Figure III-14. - Schematic representation of response of T-111 weld structure to aging.

Figure III-15. - Typical microstructures of selected T-222 GTA weld specimens as function of postweld thermal history.

Figure III-16. - Typical microstructures of FS-85 GTA weld specimens as function of postweld thermal history.

Figure III-17. - Bend ductile-brittle transition temperature of B-66 as function of aging parameters.

Figure III-18. - Ultimate tensile strength of D-43 as function of aging parameters. Optimum weld parameters; all samples annealed 1 hour at 2400° F prior to aging and testing.

BASE METAL

HAZ

18 865

X1500

18 866

X1500

(a) Welded plus postweld anneal of 1 hour at 2400° F; aged 10 000 hours at 1800° F.

18 867

X1500

18 868

X1500

(b) Welded plus postweld anneal of 1 hour at 2400° F; aged 10 000 hours at 2100° F.

Figure III-19. - Microstructures of D-43 GTA weld specimens as function of post-weld thermal history.

18 869

X1500

Figure III-20. - D-43 base metal aged 10 000 hours at 2400° F.

Figure III-21. - Ultimate tensile strength of Cb-752 as function of aging parameters. Optimum weld parameters; all samples annealed 1 hour at 2200° F prior to aging and testing.