C00-2354-1

CLUSTER CARBURIZING

Progress Report

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June 1, 1973 - May 31, 1974

**PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NO. AT(11-1)-2354**

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ABSTRACT

Tantalum alloys containing 27a% Hf and one a% (c + o) were age-hardened in a carbon free environment as a standard for comparison with cluster carburized alloys. After aging for one hour, the alloys showed two hardness peaks in the temperature range 393-1078°C; one at 600°C and the other at 960°C. From a solutionized hardness of 350 VHN, the hardness increased to 700 VHN at the low temperature peak and to 500 VHN at the high temperature peak. The strengthening mechanisms responsible for these peaks were not determined, but they will be the subject of future work.

A cellular reaction was observed to occur when annealing for one hour between 943°C and 1078°C. An equation was tentatively proposed which predicts the volume fraction of cellular precipitate as a function of time and temperature. With it carburizing times and temperatures can be selected for which the amount of cellular microconstituent formed will be small. The above information is relevant to the first objective proposed for the cluster carburizing work, that of characterizing the starting materials.

I. INTRODUCTION AND SCIENTIFIC SCOPE

Cluster carburizing is a technique for forming fine carbide dispersions in age hardened alloys. Suitable alloys contain a strong carbide former that concentrates in precipitate clusters during aging. When the alloy is subsequently carburized, at a temperature which limits further aging, the clusters transform into carbides and the carbides inherit the cluster morphology.

Alloys containing strong carbide formers have been carburized before^{1,3}. However, previous work has dealt with dilute alloys that were homogeneous, while the present work is concerned with concentrated alloys that age harden. This difference should result in more control over carbide shape, distribution, and volume fraction.

The objectives of this research are threefold; first, to characterize the properties of materials which can be cluster carburized; second, to characterize the rate of carbon absorption as a function of the precursor phase microstructure and the carburizing temperature; and third to describe the carbide formation and morphology.

Initial experiments, during the first year of work, were directed toward the first objective. Ta-Hf alloys were prepared and their age hardening behavior before cluster carburizing was characterized. The techniques involved and the results obtained are the subject of this technical report.

II. MATERIAL PREPARATION AND EXPERIMENTAL PROCEDURE

Tantalum alloys containing nominally 30 and 20 at% Hf were prepared both in our own laboratory and in the Pratt and Whitney Laboratories at Middletown, Connecticut. The starting materials for the alloys, purchased from Atomergic Chemical Co., were 5n Ta, and 4n Hf.

These alloys were melted in the modified Centorr Series 5 arc melter shown in Fig. 1. The way the equipment was prepared for melting was first, by flushing it with argon gas; second, by evacuating to 10^{-2} torr while flowing water at 100°C through the copper roof and floor of the furnace; and third, by back filling with argon gas to a pressure of .5 atmosphere. Before melting the sample, a Ta-Hf getter was heated in the chamber for five minutes. After melting, the sample was turned and the above procedure was repeated. Finally, the sample was turned and melted a third time to assure a homogeneous melt.

An important part of this work was to describe the age hardening behavior of these alloys before cluster carburizing, both for comparison with the carburized behavior and to determine the optimum carburizing temperature. For this purpose an arc melted button containing 27% Hf was cut into slabs that were 1 mm thick. The slabs were solutionized in a graphite furnace at 1665°C and quenched into woods metal. They were then cut into smaller pieces (2 mm squares), wrapped in Ta foil, encapsulated in quartz tubes, and aged for one hour at temperatures between 393° and 1078°C . After each treatment the hardness was measured and the microstructure was observed.

For the microstructural analysis, samples were etched in a 10% Hf- H_2O solution which exposed grain boundaries and, in samples aged above 921°C , a cellular microconstituent. The volume fraction of cellular product was measured using light microscopy by systematic point counting while the lamellar spacing of the cellular microconstituent was determined using scanning electron microscopy from the minimum spacing found in a random section.

In preparation for future work, an induction furnace was built that can solutionize samples at higher temperatures than was possible with the graphite

Figure 1. Arc Melting Assembly.

furnace. The induction furnace, depicted in Fig. 2, consists of 7 mm ID - 9 mm OD quartz tube that is wrapped with 5 turns of 1/8" copper tubing. As shown in Fig. 3, the induction coil is powered by 2.5 KW, 450 KHz Lepel induction generation, which is controlled by a thermal detector to maintain constant temperature, and the quartz tube is connected to vacuum and argon services.

In operating the furnace a gas purging procedure, like the one used in arc melting, is followed by heating a Ta-Hf getter to 1900°C for 10 minutes before heating the sample. Temperature measurements, made by optical pyrometer from outside the quartz tube, indicate that samples can be heated in this furnace to over 2000°C. The samples are manipulated by a magnet, as indicated in Fig. 2, and after solutionizing are dropped into a molten woods metal bath at 90°C.

III. RESULTS

1. Alloy Chemistry

In Table I a comparison can be made between our alloy and the one provided by Pratt and Whitney. In both cases the alloys contain about half an atomic percent carbon. This amount, while possibly important to mechanical properties of the starting materials, is only a small fraction of the amount of carbon that will be added by cluster carburizing and, therefore, it isn't considered significant. Also, it is typical for these alloy systems⁴.

Table I

Chemical Analysis of Ta-Hf alloys after Melting

Alloy	at% Hf	at% C	at% O
P. & W.	26.71	.505	.523
U.Conn.	18.54	.669	.569

Figure 2. Induction Furnace Assembly .

Figure 3. Detail- Induction Furnace Tube Assembly.

2. Age Hardening of Uncarburized Ta-Hf Alloys

The microhardness of solutionized, 27% Hf alloys was measured after aging for one hour at temperatures between 393 and 1078°C. The results are given in Fig. 4, where one can see that two hardness peaks were obtained: a low temperature peak reached a hardness of 700 VHN, which is double the initial hardness of about 350 VHN, while the high temperature peak reached 500 VHN.

A cellular microconstituent was observed in samples aged between 943 and 1078°C for one hour. It appeared to grow with uniform thickness out of special grain boundaries. Its volume fraction as a function of temperature is shown in Fig. 4 (the line drawn through the data points corresponds to the line drawn in Fig. 5 which will be discussed later). In samples aged below 1055°C, the lamellar spacing increased with distance from the grain boundary and couldn't be resolved near the boundary. Measurements of lamellar spacings have not been completed. This data will be plotted as reciprocal spacing versus temperature in order to obtain the solvus temperature for the cellular reaction.

IV. DISCUSSION OF RESULTS

Chemical analysis indicated that several percent hafnium were lost and about one percent $\epsilon + \delta$ was absorbed by the sample during melting. Further analysis is needed to determine what effect solutionizing and aging has on chemistry. These changes, if monitored, should not influence the cluster carburizing experiments significantly.

The two hardness peaks in Fig. 4 suggest that at least two types of hardening reactions occur in the 27% Hf alloy. One can speculate either that the low temperature peak is caused by the formation of Hf rich G.P. zones out of the β

Figure 4. Hardness observed after one hour of aging for solutionized Ta-27%Nb alloys. Also, volume fraction of cellular microconstituent as a function of temperature.

(bcc) matrix and the high temperature peak by the formation of Hf rich α (hcp) phase, as was observed in Nb-Hf alloys by Carpenter et al⁴, or that the low temperature peak is caused by local ordering of interstitials and that only the high temperature peak is caused by precipitation of a Hf rich phase. The latter speculation is supported by diffusion data reported for interstitial^{5,6} and substitutional⁷ atoms in Ta. The question of which reactions are responsible for hardening will be studied in future work by transmission electron microscopy.

In order to obtain a uniform structure during cluster carburizing the cellular reaction should be avoided, and therefore, it is desirable to know when it forms over a wide range of temperatures and aging times. Although our study of the cellular reaction is not yet complete, a tentative analysis of the data obtained will be given.

Equation (1), which follows, was used to extrapolate the data over temperatures and times not investigated:

$$V_v = k(\Delta T)^2 e^{-Q/kT} t \quad (1)$$

In it V_v is volume fraction of cellular microconstituent, t is time, R is gas constant, Q is activation energy, k is constant, T is temperature, and ΔT is undercooling below the cellular reaction solvus. The equation is based on a theoretical model for cellular reactions which nucleate and spread over grain boundaries in negligible time and then grow at a constant rate into the matrix grain, but it applies only when $V_v \ll 1$. Although it is not yet certain whether the assumptions of the model are all justified in this case, equation (1) fits the data obtained and provides a basis for predicting how the cellular reaction can be avoided.

By assuming that the solvus temperature is 1125°C, one obtains a straight line when plotting $\ln(V_v/(\Delta T)^2)$ versus $1/T$ as is shown in Fig. 5. V_v on this plot is the volume fraction of cellular microconstituent after one hour of aging at temperature T .

Figure 5. Experimental values of V_v plotted as $\ln(V_v/\Delta T^2)$ versus $1/T$. Error bars represent the standard deviation in V_v for systematic point counting measurements.

he slope of the line, equal to $-Q/R$, is $-41,320$, corresponding to an activation energy of $82,100$ cal/mol; and the intercept on the ordinate, equal to $\ln kt$, is 19.78 , corresponding to a k value of $3.88 \times 10^8/\text{hr}^\circ\text{K}^2$. With these values of k and Q , equation (1) can be used to predict the aging temperatures and times which will produce a given fraction transformed: these conditions are given in Figure 6 for the case of $V_v = .01$. Fig. 6 can be viewed as giving a first estimate for aging temperatures and times that will not produce excessive cellular microconstituent. For example, when following this diagram, one would not cluster carburize for more than 400 hours at 700°C .

V. CONCLUSIONS

In compliance with the original objectives of the "Cluster Carburizing" grant, the following conclusions were drawn from the first eight months work.

1. Uncarburized Ta-27% Hf alloys, containing one at % $\text{C} + \text{O}$ show two hardening peaks when they are aged for one hour in the temperature range 393 - 1078°C : a low temperature peak of 700 VHN at 600°C and a high temperature peak of 500 VHN at 960°C . These values provide a base line for comparison with cluster carburized materials.

2. A cellular reaction occurs in the Ta-27% Hf alloy. The kinetics of its formation can be described, based on presently available data, by the expression

$$V_v = 3.88 \times 10^8 (1398-T)^2 e^{-\frac{82,100}{RT}} t \quad (2)$$

Carburizing temperatures and time will be selected to avoid this reaction.

VI. REFERENCES

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Figure 6. Aging times and temperatures that will produce 1 % cellular microconstituent as predicted by equation (1).

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VII. TIME DEVOTED BY THE PRINCIPAL INVESTIGATOR

By the end of the current period (May 31, 1974), the principal investigator, John E. Morral, will have spent two summer months and 10% of the nine-month academic year on the "Cluster Carburizing" project. This averages to 24% time over the entire contract period.