CLUSTER CARBURIZING

Progress Report

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Abstract

Tantalum alloys containing 27 at % Hf were vacuum carburized at 1900°K in flowing methane. The rate of carbon absorption, for methane pressure between 13 and 133 Pa, was determined from the rate of carbide formation. The rates determined by this technique were similar to those observed for the absorption of carbon in pure Ta. In a preliminary test of the cluster carburizing concept, a solutionized and quenched sample was simultaneously aged hardened and carburized at 1273°K for one hour. A hardened zone, 20 μ m deep, formed adjacent to the surface. The zone had a hardness of 800 KHN compared with 500 KHN for the age hardened and 300 for the solutionized alloy. These results can be applied to predicting suitable cluster carburizing conditions.

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1. 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 before¹⁻³. 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 phases present 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 objective⁴. Ta-27%Hf alloys were prepared and their age hardening behavior before cluster carburizing was characterized. In the second year, the rate of carbon absorption was considered. As a result of these experiments it is now possible to estimate appropriate conditions under which cluster carburizing can be performed.

The experiments on carbon absorption involved vacuum carburizing the alloys at various methane pressures below 133 Pa. The carburizing temperature was sufficiently high to produce massive carbides which could be viewed and measured by optical microscopy. The rate of carbide formation was taken as measure of the rate of carbon absorption. An additional experiment was performed to provide an initial test of the cluster carburizing concept.

II. EXPERIMENTAL PROCEDURE

1. Materials Preparation and Equipment

Arc melted Ta-27Hf alloys, described in a previous report⁴, were cut into (1 x 5 x 5)mm sections for the carburizing experiments. At the same time, notches were cut into the sides of the specimens with a .006" diamond saw. W3Re-W25Re thermocouple wires were later pressed into the notches before heat treatment. Attempts to maintain temperature by optical pyrometer proved unsatisfactory because the emissivity of the sample varied during carburizing. Therefore, thermocouples were adopted for temperature measurement and control.

All heat treatments were performed in the induction furnace described before⁴. In it a vacuum of 10^{-2} Pa could be maintained and the Ta-Hf alloys could be heated up to their melting point. The chamber tube was modified as shown in Figure 1, in order to accommodate the thermocouple wires and the addition of high purity argon or methane (CH_4). The methane was always used under flowing conditions; it was added at the top of the furnace tube and removed at the bottom by vacuum pumps and a cold trap. A micrometer valve controlled the methane input such that the pressure in the chamber, as measured by a McLeod Gauge, could be varied between 5 and 200 Pa.

2. Heat Treatments

Samples were wrapped in Ta foil, solutionized at 2100°K for a half hour, vacuum cooled to ambient temperature, polished with 10^{-6} m diamond abrasive, and then were reheated to 1900°K in flowing methane at pressures of from 13 to 133 Pa. After reaction times of 600-25,000 seconds, the samples were vacuum cooled and sectioned. These samples were carburized at a temperature which was above the solvus reported for the Ta-Hf system⁵. In an additional experiment a sample was quenched in woods

Figure 1: Chamber Tube Assembly of the Induction Furnace

metal after solutionizing and then was simultaneously aged hardened and carburized at 1273°K.

3. Sample Characterization

Half of each sample was mounted perpendicular to the carburized surface and the other half was mounted parallel to it. The samples were polished by standard techniques, but a special etch consisting of 5% NH_4F in concentrated HNO_3 was developed to increase the contrast between carbide and solid solution areas. The profile section was viewed by optical microscopy and on it the carbide penetration was measured as a function of time and methane pressure. Additional measurements on the volume of carbide as a function of depth from the surface are currently being made.

The phases present are being identified by x-ray analysis of the parallel surface and by observations of the carbide morphology. In this procedure the parallel surface is removed in stages by serial-sectioning and the disappearance of x-ray intensity peaks are related to morphological change.

III. RESULTS

The carbide morphology resulting from the 1900°K carburizing treatment as seen in profile is shown in Figure 2(a). The long thin platlets are nominally HfC while the phase coating the surface is nominally TaC . When viewing the polished surface under polarized light it is apparent that a non-cubic phase, presumably Ta_2C , is present between the TaC layer and the underlying Ta rich matrix as in Figure 2(b), however, it is not visible in the profile section, possibly because it is too thin.

From the shifts in the x-ray intensity peaks away from the stoichiometric positions, the composition of the various phases were determined on $\text{HfC} = \text{Hf}_{.89}\text{Ta}_{.11}\text{C}$, $\text{TaC} = \text{Ta}_{.95}\text{Hf}_{.05}\text{C}$, and $\text{Ta}_2\text{C} = (\text{Ta}_{.93}\text{Hf}_{.07})_2\text{C}$. These compositions are relatively unaffected by changes in time, temperature, methane pressure or position in the sample.

(a)

(b)

Figure 2: Views of a sample carburized at 1900°K for 4800 sec in flowing methane at a pressure of 133 Pa. (a) Profile view, 800X. (b) Surface view after light polishing, 600X

The carbide phases developed with time in the following sequence. First HfC platelets nucleate at the surface and grow into the matrix. While they are growing, additional HfC platelets initiate between the original plates and layers of TaC and Ta₂C form adjacent to the surface. The result is a very adherent TaC surface layer that is "keyed" to the alloys by the HfC platelets which are imbedded in it and extend into the matrix. As a result, the TaC layer never spalled off during hardening and could only be removed by polishing with diamond abrasive.

Measurements of the carbide penetration as a function of time and methane pressure are summarized in Figure 3. Preliminary results indicate that initially the penetration is proportional to time and then later becomes proportional to the square root of time. The rate in the linear region is roughly proportional to methane pressure while in the parabolic region it is apparently independent of pressure.

The sample which was simultaneously aged and carburized showed a distinct subscale, Figure 4(a), consisting of two regions. The hardness of the subscale, Figure 4(b), was 800 KHN compared with 300 KHN for the solutionized alloy and 500 KHN for the aged alloy.

IV. DISCUSSION OF THE RESULTS

The carbide morphology observed in the samples reacted at 1900°K can be rationalized in terms of layer growth in multicomponent systems and the phase diagram for the Ta-Hf-C system proposed by Rudy⁶. However, one must adjust the solvus temperature in the Ta-Hf system reported by Rudy to that reported by Carpenter *et al.*⁵, and consider that severe coring occurs during growth of the carbides. Without coring one would predict that a layer consisting of (Ta_{.73}Hf_{.27})C would form at the surface rather than the two separate MC carbides observed. The composition of the carbides deduced from shifts in x-ray intensity peaks are consistent with those

Figure 3: Penetration of the HfC platelets into the sample at 1900°K as a function of time and methane pressure.

(a)

(b)

Figure 4: Microstructure and hardness of the sample profile after simultaneous aging and carburizing at 1273°K for one hour. (a) Microstructure, 1000X (b) Hardness versus penetration curve.

predicted from Rudy's diagram.

Analysis of the kinetic data is still in progress, but should be completed in the current contract period. The important information that can be drawn from this data at present is that diffusion of Hf in Ta is much faster than Ta self-diffusion and that the rate of carbon absorption is very close to that measured by Hörz and Lindenmaier⁷ for pure Ta in methane. With this information in mind, it is possible to estimate suitable cluster carburizing conditions, and these are given in the next section.

An indication of the rapid diffusion of Hf in Ta is given by the growth rate of the HfC platelets. Assuming they grow by an edgewise mechanism and are controlled by the diffusion of Hf, theory⁸ would predict

$$D_{Hf}^{Ta} = v^{\max} \rho_c \quad (60).$$

According to our data, the velocity $v^{\max} = 3 \times 10^{-7}$ m/sec and the critical tip radius $\rho_c = 10^{-9}$ m which yields $D_{Hf}^{Ta} = 1.80 \times 10^{-14}$ m²/sec at 1900°K. If the pre-exponential factor for D_{Ta}^{Ta} and D_{Hf}^{Ta} are similar, about 10^{-5} m²/sec, then the activation energy for Hafnium diffusion is 327 KJ/mole compared with 409 KJ/mole for Ta self-diffusion and 160 KJ/mole for carbon diffusion in Ta. However, since the HfC growth rate is influenced by methane pressure, the process is not simply controlled by the diffusion of Hafnium and because of the various other approximations involved one must view the computed activation energy as an approximate value only.

Regarding the rate of carbon absorption, a comparison is made in Table 1 of the rate reported by Hörz and Lindenmaier⁷ for pure Ta and that deduced from the rate of carbide formation in the Ta-Hf alloy. When considering that the surface of the alloy is partially covered by carbides from the earliest times, these rates appear to be in reasonable agreement with one another.

Table I
Comparison of Carbon Absorption Rates

<u>Methane Pressure (Pa)</u>	<u>Carbon Absorption Rate (mg/cm²·sec)</u>	
	<u>in Pure Ta*</u>	<u>in Ta-27%Hf**</u>
133	37.2 x 10 ⁻⁴	6.5 x 10 ⁻⁴
65	18.6	6.2
33	9.3	4.5
13	3.0	3.0

* Measured by Hörz and Lindenmaier⁷ from the rate of resistivity changes.

** Measured in this study from the rate of carbide formation.

The results obtained in the alloy that was carburized during aging were encouraging. They show that a hard zone of significant size, on the order of twenty microns, can be formed in a one hour heat treatment at 1273°K. The importance of the results are twofold. First, it indicates the possibility of obtaining high strength by cluster carburizing, especially when controlling the microstructure more fully by a two-step aging plus carburizing treatment. Second, it suggests that the activation energy reported by Hörz and Lindenmaier⁷ is applicable to predicting reaction zone sizes as a function of temperature. For example, in one hour at 1900°K and 65Pa the reaction zone size was 65μm. The predicted size after one hour at 1273°K is

$$x = (65)e^{-(8.21) \left(\frac{1}{1273} - \frac{1}{1900} \right)} = \underline{7.7\mu m}$$

which is close to the observed size of 12μm for one of the subscale zones. In the next contract period the reactions in the two subscale zones will be investigated by electron microscopy in order that the kinetics of their formation can be more clearly understood.

V. PREDICTION OF CLUSTER-CARBURIZING CONDITIONS

With the above data in hand, it is now possible to recommend a series of experiments to fully test the cluster carburizing concept. Firstly, to obtain a range of microstructures, solutionized alloys will be heated to 1300°K for from $10^3 - 10^5$ sec to obtain both underaged and overaged samples. Then the alloys will be cooled to 1000°K where they will be carburized for times in a similar range. Based on the estimated diffusion coefficient given earlier, decreasing the temperature by 300°K should reduce the rms distance that a Hafnium atom can move by 100 times. However, it should still be possible to grow hardened layers which are .8μm to 80μm thick, based on the activation energy of Hörz and Lindenmaier⁷ and the size of the zone obtained at 1300°K.

It should be kept in mind, however, the many assumptions involved in making

these predictions. Changes in carbide stability could prevent the extrapolation of carbon absorption data and reduce the hardened layer growth rate. On the other hand, if the aged precipitates are not completely carburized the layer growth rate could be increased.

VI. REFERENCES

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VII. TIME DEVOTED BY THE PRINCIPAL INVESTIGATOR

By the end of the current period (May 31, 1975), the principal investigator, John E. Morral, will have spent, for each of two years, 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.