CLUSTER CARBURIZING

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ABSTRACT

The Ta-Hf phase diagram was found to be sensitive to carbon content, even at levels low enough to prevent carbide formation. The β/α solvus at 1200°C went from 27%Hf to 7%Hf as the soluble carbon concentration increased. This effect was seen in aged and carburized samples. Just below the carbide containing subscale the dissolved C concentration was greater than in the bulk sample and correspondingly the amount of α phase there was greater. The hardness of the subscales were related to the hardness of the aged, but uncarburized, material. For example, a material aged to 610 KHN produced a subscale of 1180 KHN, while one aged to 480 KHN produced a subscale of 660 KHN. The subscale had a uniform hardness across its width and grew parabolically with time. The activation energy for growth was 148kJ/mole, a value near that for C diffusion in Ta. Carburizing experiments at elevated temperatures, above the β/α solvus, were completed and two limiting cases of subscale formation were identified. In one limit the amount of compound is constant across the subscale and in the other limit it varies linearly with composition across the subscale.

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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 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, morphology and the resulting material properties.

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 year⁵, the rate of carbon absorption, during high temperature carburizing treatments, was studied and a preliminary cluster carburizing experiment was performed.

The high temperature carburizing work was completed in the current year and lead to a new discovery in the field of subscale formation. In addition, samples were carburized at lower temperatures, in the two phase $\alpha + \beta$ range. These experiments coupled with an investigation of the Ta-Hf-C phase diagram lead to a number of interesting results which are described in more detail below.

II. MATERIALS CHARACTERIZATION

In 1975, Krug, Oden and Romans⁶ published another version of the Ta-Hf phase diagram that differed in a significant manner from the one previously reported by

Carpenter, Liu and Mardon⁷ (see Figure 1). It was proposed that the reason for the difference lay in the interstitial content of the alloys studied in the two investigations. In order to understand more fully how interstitials in our alloys would influence our cluster carburizing experiments we did further work on characterizing the uncarburized alloys.

By annealing Ta-27%Hf alloys for various times and temperatures, we found, as is shown in Figure 1, that the phases present after 50-100 minutes correspond to Krug et al.'s diagram, while after several hours they correspond to Carpenter et al.'s diagram. Since Krug's diagram could not be a metastable variation of Carpenter's, we conclude that the changes are caused by the absorption of impurities during annealing.

More quantitative information on the effect of interstitials was obtained by heating a sample at 1200°C for 10 minutes in a poor vacuum of 130 Pa created by a mechanical pump. The structure and properties of this sample near the surface are given in Figure 2. By x-ray analysis of the serial sectioned sample, it was found that Ta₂C and HfC were present in the first 15 µm, but that the hardness gradient that extended to nearly 60 µm below the surface, was associated with a gradient in the amount of α phase present.

According to a preliminary investigation performed on a Cameca MBX microprobe, it was found that the increased hardness and α content could be associated with a higher level of carbon near the surface. A scan for oxygen, shown in Figure 2, indicated that it was present also, but that its penetration was limited to about 20 µm. This result suggests that carbon diffuses more rapidly than oxygen at 1200°C in this alloy by a factor of about three.

We expect to get quantitative estimates of the carbon concentration profile in this sample before the end of the current contract period by using the Cameca MBX unit and this will allow us to trace out the α + β portion of the Ta-Hf-C phase diagram. According to our measurements, we know already that the solubility limit for Hafnium in β at 1200°C can be shifted to about 7% by carbon additions. Since carbon is known to be a strong α stabilizer⁸ such an effect is not surprising.

Figure 1: Comparison of the Ta-Hf diagram of Krug et al.⁶ and Carpenter et al.,⁷ and data from this investigation. By picking up carbon from the environment in a poor vacuum, the β/α solvus was found to vary over the range indicated.

Figure 2: Structure and properties of a Ta-Hf alloy after heating at 1200°C for 10 minutes in a vacuum of 130 Pa. The phases present were measured by x-rays and the relative oxygen content by a Cameca MBX microprobe.

The influence that increased carbon content has on age hardening is shown in Figure 3. The upper curve shows the age hardening response of alloys solutionized in a graphite furnace, while the lower curve is for alloys solutionized in a glass-tube induction furnace. Figure 3 suggested that a higher initial carbon concentration results in higher hardness values and, for isochronal tests, a peak hardness at lower temperatures.

III. CLUSTER CARBURIZING

A. Carburizing Ta-Hf Alloys.

A series of experiments were performed in which samples were simultaneously aged and carburized between 850 and 1005°C. After solutionizing Ta-27%Hf alloys and carburizing them for six hours in flowing methane at a pressure of 65 Pa as described before⁵, they were sectioned in order to observe the microstructure of the subscale and to measure the hardness profile across it.

The carburized surface was free of the blocky Hafnium carbides that formed on the surface during carburizing at higher temperatures⁵. The profile view showed a fine, carbide dispersion with a feathery appearance (a picture of this structure is given in reference 5), unlike the massive carbides that form at 1673°C⁵. Both observations are explainable in terms of a reduced Hafnium mobility at lower treatment temperatures.

The most interesting results were found in the hardness profiles measured on the sectioned samples, Figure 4. There one can see distinct zones. The first one, adjacent to the surface and along which the hardness is relatively constant, corresponds to the visible subscale zone. The constant hardness implies a similar structure across the zone which, according to x-ray analysis of the carburized surface, is a mixture of Ta rich β (BCC structure) and Hf rich δ (HfC structure).

The hardness drops sharply below the subscale and then decreases gradually until the bulk value in the center of the sample is reached. Although we have not yet measured the structure below the subscale, based on the Ta-Hf-C phase diagram work, we presume it is a mixture of β and α (Hf rich HCP), with the amount of α increasing

Figure 3: The effect of carbon content on hardness after one hour of aging. Before aging, materials for the upper curve were solutionized in a graphite furnace, while those for the lower curve were solutionized in a glass-tube induction furnace.

Figure 4: Hardness profile of specimens carburized for 6 hrs at a methane pressure of 500×10^{-3} mm.Hg.

toward the surface as the carbon concentration increases. By the end of the current contract period we will have completed serial sectioning experiments in order to study the structure in more detail.

The age hardening behavior of these samples in the bulk is seen to pass through a maximum at about 900°C, as indicated in Figure 4. It is important to note that this trend is followed both just beneath the subscale and in the subscale itself. This suggests that the age hardened structure influences the carburized one. The highest hardness obtained in the subscale was 1180 KHN, but we suspect that higher hardnesses are obtainable by aging at one temperature and then carburizing at a lower one.

The relationship between the microstructure before and after carburizing could not be studied in detail because of difficulties encountered when trying to examine these alloys by electron microscopy. Although we plan to view our foils in a one MV microscope (our facility has a 200 kV instrument which allowed only a dim view of the precipitate structure) we expect to do most of our microscopy on Nb-Hf alloys which are easier to study.

Kinetic studies, Figure 5, indicated that the subscale thickness, x , could be described as a function of time, t , and temperature, T , according to the equation

$$x^2(\mu\text{m}^2) = 4.10t(\text{sec}) \exp(-148 (\text{kJ}\cdot\text{mole}^{-1})/RT) \quad (1)$$

The activation energy for the process is nearly that of the diffusion of carbon in pure tantalum⁹, 161 kJ·mole⁻¹. Further work intended to verify this relation should be completed in the current contract period. It's expected that equation (1) will be helpful in designing two step heat treatments in which alloys are aged to peak hardness at one temperature and then carburized at a lower temperature to restrict further aging.

B. Carburizing Nb-Hf Alloys.

Alloys in the Nb-Hf system have been prepared for cluster carburizing using techniques similar to those reported for Ta-Hf⁵. We expect to have kinetic data on this system, for simultaneous carburizing and aging, before the end of the current con-

Figure 5: Kinetic data and activation energy of subscale formation during simultaneous aging and carburizing.

tract year. Later work, possibly beginning this year, will involve studying the microstructural changes that occur during carburizing. Unlike the Ta-Hf system, the aging behavior of these alloys have been studied before by electron microscopy⁷.

IV. HIGH TEMPERATURE CARBURIZING

A high temperature carburizing investigation was completed in the middle of the current contract period. The work is described in two University of Connecticut masters theses^{10,11} and in two articles being prepared for publication^{12,13}. The major results and conclusions contained in these articles are abstracted in what follows.

A. Limiting Cases of Subscale Formation.

The treatment of subscale formation which is most often referred to in the literature is by Wagner¹⁴. It considers the limiting case when the solubility of the compound that forms in the subscale is near zero (i.e. when the solubility product for the compound formation approaches zero). In this case, as is shown in Figure 6(a), the amount of compound across the subscale zone is constant. All new compound is formed at the subscale-matrix interface, the rate of formation being controlled by the diffusion of solute to that interface.

In our high temperature carburizing experiments we noticed a strong deviation from the behavior predicted by Wagner. The amount of carbide forming in our samples varied nearly linearly with distance across the zone as shown in Figure 8. In attempting to understand this behavior, we discovered another limiting case for subscale formation¹³, which can be treated in a manner analogous to that used by Wagner. The limits for both treatments can be stated as follows: if b_0 is the initial concentration of a binary A + B alloy, c_s is the concentration at the sample surface of a third element which forms a BC compound, and K is the solubility product for the formation of that compound out of solid solution, then $K/c_s b_0 \rightarrow 0$ is the condition required for Wagner's Limit and $K/c_s b_0 \rightarrow 1$ is the condition required for ours. How our limit leads to a variable compound content with distance across the subscale is shown graphically in figure 7(b), where as the concentration varies from c_i to c_s the lever arm for the amount of BC is seen to vary from zero to a maximum value.

Figure 6: For the limiting case of a low solubility product; (a) a plot of moles of BC compound and soluble C across the subscale and (b) the average concentration across the subscale on an isothermal section of an A-B-C ternary phase diagram.

$$\text{Limit } \frac{K}{c_s b_o} \rightarrow 1$$

Figure 7: For the limiting case of a relatively high solubility product; (a) a plot of moles of BC compound and soluble C across the subscale and (b) the average concentration across the subscale on an isothermal section of an A-B-C ternary phase diagram.

Although more general treatments have been given for subscale formation, for example by Kirkaldy¹⁵, and solutions for special condition have been given¹⁶, they have not focussed on the two extremes mentioned above, which lead to simple solutions to the diffusion equation. In our analysis the distribution and amount of compound forming can be expressed as a function of time, both for when significant solute diffuses out ahead of the subscale interface and for when it does not (e.g. when the matrix is already saturated with solute, $c_i = c_0$). Also, the concentration profiles for soluble and insoluble B and C are obtained.

B. Internal Carburizing of a Ta-27%Hf Alloy.

The experimental procedure and many of the conclusions drawn from this work were described in a previous report⁵. In the current contract period the subscale zone formed during carburizing at 1673°C was further characterized by measuring the volume of carbide as a function of distance below the sample surface. It was by observing the nearly linear variation of carbide volume with distance shown in Figure 8, that lead us to the theoretical subscale formation work.

The structure of the subscale was investigated by x-ray analysis of serial sectioned samples. The ternary Ta-Hf-C phase diagram predicts that a region containing Ta_2C should exist in the subscale between that containing TaC on the surface and the region containing HfC in the interior. Although the Ta_2C could not be identified on the microstructure as a unique feature, its presence was detected by x-ray analysis, Figure 9.

It appears, as we reported before⁵, that the initial stages of subscale formation depend on methane pressure while at later times, once a continuous scale of TaC forms on the surface, it is independent of methane pressure. However, as can be seen in Figure 10, there is a great deal of scatter in the data obtained. We have not yet checked samples that were cluster carburized for short times to determine if this early transient occurs at lower temperatures, but we intend to investigate this possibility before the end of the current contract period.

Figure 8: Variation of carbide volume with depth, in a Ta-27% Hf alloy carburized in flowing methane at 1900°K.

Figure 9: X-ray intensities as a function of distance with a Ta-27% Hf alloy after carburizing at 1900°K in flowing methane.

Figure 10: Thickness of the subscale in a Ta-27% Hf alloy carburized at 1900°K as a function of time and methane pressure.

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VI. TIME DEVOTED BY THE PRINCIPAL INVESTIGATOR

By the end of the current period (May 31, 1976), the principal investigator, John E. Morral, will have spent two summer months and 10% of the nine-month academic year on the "Cluster Carburizing" program. This averages to 24% time over the current contract period.