CLUSTER CARBURIZING

MASTER

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ABSTRACT

The aging behavior of quenched Ta-27% Hf alloys was investigated over the temperature range 685-1000°C. A diffusion coefficient of $D_{Hf}^{Ta} = .048 \exp (-81,200/RT)$ was estimated from the aging kinetics. Two age hardening peaks were observed during isothermal treatments. Electron microscopy showed that at 685°C, the first peak was associated with the formation of a disk or loop structure while the second one was associated with α precipitation. When the aged material is carburized a subscale forms with a hardness that is proportional to the aged hardness. For example, subscales with a hardness of 1300 KHN form from an aged material of 650 KHN. When unaged Nb-27% Hf alloys are carburized, a subscale forms with a significantly lower hardness. A study of subscales in Nb alloys containing 4-37% Hf provided information on the Nb-Hf-C phase diagram at 1000°C. Preliminary evidence suggests that there is a miscibility gap in the pseudo binary NbC-HfC.

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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 results in more control over carbide shape, distribution, and volume fraction.

The objectives of this research are threefold; first, to characterize the initial properties of materials which can be cluster carburized; second, to characterize the carbide formation itself; and third to describe 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 studied. This activity has continued through the current year. In the second year⁵, the rate of carbon absorption during high temperature carburizing treatments was investigated and a preliminary cluster carburizing experiment was performed.

The high temperature carburizing work was completed in the third year⁶ and lead to the discovery of a new limiting case in the field of subscale formation^{7,8}. The clue to this limiting case was found in the distribution of carbides in the carburized zone^{9,10}. In addition the

affects of interstitials on the phase diagram and aging kinetics of Ta-Hf alloys were studied as were the formation kinetics and mechanical properties of cluster carburized zones.

In the current year, kinetic studies of cluster carburizing in both Ta-Hf and Nb-Hf alloys were performed. These systems react differently from one another, with respect to both the kinetics and material properties obtained. In addition, work on characterizing the aging process in Ta-Hf alloys indicates that a number of hardening processes are important during low temperature aging. These experiments coupled with a computer simulation of subscale formation have lead to a number of interesting results which are described more fully below.

II. Materials Characterization

A. Ta-Hf Alloys.

The age hardening behavior of Ta-Hf alloys has been studied throughout the cluster carburizing program. We found, as have others¹¹, that the properties of these alloys can be changed significantly by a few hundred ppm of interstitials and that the alloys are readily contaminated during processing. In addition they are difficult to study by electron microscopy. Although these problems tended to prolong this part of the program, we expect to finish it during the current contract period. In the following is a summary of the aging work.

As reported before⁴, a plot of hardness versus aging temperature for alloys quenched from 1850°C and aged for one hour shows two peaks, one at about 650°C and the other at 1000°C. Figure 1 shows that the high temperature peak does not shift appreciably with small composition changes while the low temperature peak does. In both cases the effect on peak hardness is small.

Figure 1 Hardness of Ta-Hf Alloys after Aging for One Hour at the Indicated Aging Temperatures

Electron microscopy of alloys aged at the lower peak temperature revealed a structure of disks or loops, while those aged at the higher temperature showed a precipitation.

Alloys held isothermally at the lower peak temperature exhibited two age hardening peaks, Figure 2. During the period when the first hardening peak occurred, the dispersion of disks or loops, Figure 3(a) was seen to coarsen and the diffraction pattern of this material remained unchanged, indicating only β was present. Satellite spots were observed around some of the β peaks, which disappeared on aging. A similar structure was reported in Nb-Hf aged at 600°C for 1000 hrs and was tentatively identified as Hf clusters¹¹. However, the diffusion of Hf in Ta is small at these temperatures (based on a diffusion coefficient we report later in this section) and it predicts that such a coarse structure of Hf precipitates could not form in the aging time. We are currently analyzing, through electron microscopy, the nature of this structure and we are trying also to understand the hardening mechanism responsible for the first peak.

The second peak that occurs during low temperature aging is associated with the formation of an irregular precipitate or a "cotton" structure, Figure 3(b). This peak, developing after 20 days, has a hardness of 750 KHN, which is the highest value obtained for Ta-27% Hf alloys in this study. Diffraction patterns of the cotton structure indicates that both α and β are present.

Alloys aged isothermally at the higher peak temperatures of 1000°C show two hardness peaks, Figure 2. The first peak corresponds to the formation of small precipitates while the second one corresponds to the formation of well-defined rods. The crystallography of these precipitates are still being analyzed, but our preliminary results indicate that the rods are similar to

Figure 2 Age Hardening as a Function of Time for Two Aging Temperatures

(a) 35,000X

(b) 58,000X

Figure 3 Peak Hardness Structures of Ta-27%Hf Alloys Aged at 685°C,
(a) After Aging for 1.2×10^4 Sec. (b) After Aging for 6×10^6 Sec.

those found in Nb-Hf alloys¹¹ which follows the prediction made by Carpenter, Liu and Mardon¹¹. If they are correct, the rods are incoherent precipitates with the lattice relationships $\{0001\}_{\alpha} // \{110\}_{\beta}$ and $\{11\bar{2}0\}_{\alpha} // \{111\}_{\beta}$ between the α and β phases.

One further property of Ta-Hf alloys has been measured in this study. The diffusion coefficient of Hf in Ta has been determined by analyzing the aging kinetics of α precipitates and the loss of Hafnium near the surface of alloys anneal at 1000°C. The value obtained is

$$D_{\text{Hf}}^{\text{Ta}} = .048 \exp (-81,200/RT).$$

The activation energy of 81.2 Kcal/mole is near the value of 82.1 Kcal/mole that we estimated from discontinuous precipitation kinetics in a previous program report⁵. It is interesting to note that even though Hafnium is a larger atom than Ta by 6%, its activation energy for diffusion is about 30% less than the activation energy for self-diffusion of Ta. That Hf is especially mobile in Ta and Nb systems has been observed before by others working with these systems¹¹.

B. Nb-Hf alloys.

The precipitate reactions that occur during isothermal aging of Nb-Hf alloys have been studied in detail by Carpenter, Liu and Mardon¹¹ and we have not duplicated their work. With regard to age hardening, Birla and Hoch¹² studied 15 and 33 at % Hf-Ta alloys that contained up to 1.5%C, while Williams and Briggs¹³ studied up to 6.6% Hf-Ta alloys containing up to 3.7 at %C. They found that aging produces little hardening and in some cases aging actually softens the material, presumably because of a loss in solid solution strengthening. Our solutionized and quenched samples were observed to soften by ~25 KHN when aged above the α/β solvus at 1000°C. We also characterized how the lattice

parameter of β in Nb alloys varies with Hf content, from pure Nb up to 37% Hf¹⁶.

III. Carburizing Experiments

A. Cluster Carburizing of Ta-Hf alloys.

In a previous report⁶, the results of simultaneously aging and carburizing were discussed. These were that an internally carburized zone forms, that its width varies with the square root of time, and that its activation energy for growth is essentially that for the diffusion of carbon in Ta. Since then we have obtained more detailed hardness profiles across the carburized zones and we have investigated the role of oxygen contamination in our samples.

Electron microprobe analysis for carbon and oxygen on samples carburized at 900°C for twelve hours revealed that significant amounts of oxygen were diffusing into the material. As shown in Figure 4, the oxygen content varies continuously from an elevated level at the surface to the background level at 30 μm into the sample. The carbon concentration, however, remains relatively constant until at 20 μm , the location of the zone interface, it drops abruptly to a lower value. Comparing this behavior with the hardness profile for the 900°C sample, Figure 5, one can conclude that the high hardness of the zone is caused primarily by carbides. However, the slight increase in hardness of the matrix in front of the zone is likely due to oxygen. The increased oxygen increases the volume fraction of α , as was reported by Carpenter, et al.¹¹, and this apparently increases the hardness. That the amount of α increases directly in front of the zone has been confirmed by x-ray diffraction intensity measurements¹⁴.

Figure 5 shows also that the hardness is not constant across the carburized zone. Instead, it varies in a way which tends to support the concepts

Figure 4 Electronmicroprobe Data for Carbon and Oxygen Profiles for a Sample Carburized at 900°C for 12 Hours.

Figure 5 Microhardness Profile of Ta-27%W Specimens Carburized at a Methane Pressure of 67 Pa while being Simultaneously Agehardened.

of cluster carburizing that were mentioned previously. For example, one can see in Figure 5 that the hardness of the carburized zone adjacent to the zone-matrix interface is proportional to the matrix hardness (i.e., the matrix hardness values of 470, 500 and 650 correspond to zone hardnesses of 1050, 1140 and 1300 KHN). This suggests that the structure of the aged matrix is influencing the structure of the carburized zones.

Further evidence of the relationship between the matrix and zone structures is given by the hardness profiles across the zones. In the 850°C and 900°C samples which were age hardened during carburizing, the hardness of the zone increased as it grew. However, in the 1000°C sample, which was overaged after twelve hours, the hardness profile goes through a peak, indicating that the hardness of the growing carburized zone followed the hardness of the matrix as it went from the underaged to the overaged condition.

The above observations can be contrasted with the classical prediction of subscale formation theory¹⁵, in which the precipitate size increases linearly with distance from the surface and, therefore, the hardness should gradually drop across the subscale zone. If one assumes that, in Figure 5, the alloy is initially homogeneous, then the hardness near the surface is the maximum that could be achieved by classical internal carburization. Since the hardness of the zone under classical conditions would decrease with distance, one can see that aging first, leads to an extra increment of hardening which is greater than 100 KHN.

B. Internal Carburizing of Nb-Hf Alloys

Although there are numerous similarities between the Nb-Hf and Ta-Hf systems, we were unable to cluster carburize them. At temperatures below the β/α solvus, the subscales that formed in the time available for heat treatment were too small to study. Even above the solvus, at 1000°C, in

which case classical subscale formation was expected, the zones formed in Nb-Hf were 3 times smaller than those formed in Ta-Hf. The slower kinetics of the Nb-Hf subscales must result from a smaller diffusion coefficient and/or solubility of carbon in Nb than in Ta. However, the scatter in published data of these properties made it impossible to predict this slower kinetics beforehand.

A study of subscale formation in Nb-Hf was performed in the current contract period. Although these alloys did not cluster carburize, they did offer an opportunity to compare cluster carburized with internally carburized material in a similar system. It also provided new information on the Nb-Hf-C phase diagram.

The width of the internally carburized zones were found to be proportional to the square root of time. The kinetics of zone formation was independent of acetylene pressure over the range of 6 Pa to 1000 Pa. Attempts to carburize in high purity methane (99.999%) were unsuccessful because of excessive internal oxidation.

A series of Nb alloys in the range of 4 to 37 at% Hf were carburized at 1000°C. In these experiments the rate constant for subscale formation did not appear to follow the classical behavior. For this reason additional theoretical work, described in section D, was performed. In addition, the results suggested that a stable miscibility gap might exist in the pseudo-binary NbC-HfC. A phase diagram consistent with our experimental observations is given in Figure 6. On this diagram the Hf concentrations are quantitative while the carbon concentrations are only sketched in qualitatively.

C. Pack Carburizing

Attempts to pack carburize Ta-27% Hf alloys were unsuccessful. Samples were packed in graphite, TaC, and Ta₂C powders with both oxygen (e.g., at 10⁻⁸ torr) and hydrogen used as carrier gases. In all cases either severe inter-

Figure 6: Possible isothermal section of the Nb-Hf-C ternary system at 1000° C. The alloy compositions investigated are indicated in at.% Hf.

granular embrittlement occurred, thereby making it impossible to study the subscale, or else internal oxidation dominated the structure.

D. Theory of Subscale Formation

In a previous study, two limiting cases of subscale formation were reported, both of which could be described by analytical solutions^{6,7,8}. The Nb-Hf alloys were found to be intermediate to these cases and required a numerical solution. A computer program was written to obtain this solution¹⁵ and the results of this effort are given in Figure 7. In these results the volume fraction of carbide is a function of the following two parameters.

1. $K/N_B^0 N_C^S$
2. $X(2D_C t N_C^S / \sqrt{N_B^0})^{-1/2}$

In the first, K is the solubility product, N_B^0 is the initial solute concentration, and N_C^S is the concentration of carbon at the surface. In one limiting case, when the first parameter is zero, the amount of carbide is a step function. In the other limiting case, when it is one, the amount of carbide is an error function. One can see in Figure 7 that even when the first parameter has the middle value of .5, it closely approximates the error function solution.

The second parameter indicates that the subscale zone width is proportional to both the square root of time and to $(N_B^0)^{-1/2}$ as predicted by classical theory. This second parameter is not thought to be a fundamental quantity, but it describes the results obtained over the limited range of N_B^0 and N_C^S considered here. Attempts to further generalize this solution are still in progress.

IV. Mechanical Properties

Typical hardnesses measured for the Ta-Hf and Nb-Hf system are summarized in Figure 8. There one can see the general trend that increasing the Hf con-

Figure 7: Carbide distribution in internally carburized low concentration alloys, where $N_c^s \ll N_B^0$, for several values of $K/N_B^0 N_c^s$. It is assumed that the matrix solid solution is initially saturated with carbon.

Figure 8: Hardness of Ta-Hf and Nb-Hf alloys before and after carburizing. All carburizing and aging treatments were at 1000° C for 6 hours.

tent increases both the single phase hardness and the carburized hardness in Nb alloys. Presumably a similar trend exists for Ta-Hf alloys.

Comparing the hardness of 27% Hf alloys after carburization, it is apparent that the Ta alloy, which was aged during carburizing, is harder than the Nb alloy, which was not. Part of the difference in hardness can be explained because Ta itself is harder than Nb, as evidenced by the single phase hardness of these alloys and because about 20% more carbide forms in the Ta than in the Nb system. However part of the difference is related to the influence of the aged precipitates on the carburized structure in the Ta-Hf material, according the hardness profiles in Figure 5.

The value of 1200 KHN for Ta-27% Hf in Figure 8 does not correspond to the maximum value obtained. The material that was carburized at 900°C reached 1300 KHN. Furthermore if one were to plot the aged hardness versus the carburized hardness and extend that relationship to the aged hardness of 750 KHN obtained in 2×10^6 sec at 685°C, one would predict that the hardness above 1400 KHN could be reached. In other words the full potential of this method has not yet been tested.

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VI. TIME DEVOTED BY THE PRINCIPAL INVESTIGATOR

By the end of the current period (May 31, 1977), the principal investigator, John E. Morral, will have spent one and a half summer months and 10% of the nine-month academic year on the "Cluster Carburizing" program. This averages to 21% time over the current contract period.