MASTER

CLUSTER CARBURIZING

Final Report

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ABSTRACT

Three major accomplishments of the "cluster carburizing" program were first, showing that the hardness of aged and carburized materials could be controlled via the aged structure; second, developing a new and analytical theory of subscale formation; and third, characterizing the properties of Ta-Hf alloys with respect to precipitation kinetics and morphology, diffusion kinetics, age hardening, and subscale formation. The first of these verified the "cluster carburizing" concept, which has potential use in the development of high strength materials. The second has applications in the fields of hot corrosion, oxidation, and high temperature coatings. The third provided necessary background for this study and provided a further understanding of the behavior of refractory metals. Details about the above are contained in this final report as well as comments on the Ta-Hf, TaC-HfC and NbC-HfC phase diagrams, a comparison of hardening in the Nb-Hf and Ta-Hf system, and a discussion of possible future work.

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I. INTRODUCTION

Cluster carburizing is a technique for forming fine carbide dispersions in age-hardened alloys. Suitable alloys contain strong carbide formers which concentrate in precipitate clusters during aging. When the alloys are subsequently carburized, the clusters transform into carbides, thereby inheriting the cluster morphology.

The objectives of the "Cluster Carburizing" research program were threefold: first, to characterize the alloys that were to be carburized; second, to characterize the carburizing process; and third, to describe the resulting material properties. The progress made in pursuit of these objectives and the questions left unanswered are summarized in the report below.

II. CHARACTERIZING THE STARTING MATERIALS

A. Materials Studied.

Two alloy systems were studied; the Ta-Hf and the Nb-Hf. They were chosen because hafnium, the strongest carbide former of the three elements, concentrates in precipitates during aging. In addition, the TaC-HfC and NbC-HfC systems were studied for additional background information.

B. Precipitation in Ta-Hf Alloys.

The precipitate morphology and the precipitation kinetics were followed by optical and transmission electron microscopy (TEM) as a function of both temperature and time during aging of a Ta-27% Hf alloy. It was found that both continuous and discontinuous precipitation occurred. From a detailed characterization of the two reactions it was possible to design cluster carburizing treatments that would both avoid discontinuous precipitation and prevent overaging of the hafnium rich precipitates before they transformed to carbides.

With regard to the precipitation studies, it was observed that the sequence of events during isothermal aging was somewhat different than that reported for Nb-Hf, a system similar to Ta-Hf, which had previously been well characterized. The first event observed was the formation of a dispersion of "loops" which coarsened with time. Later, a dense structure of precipitates and dislocation was observed and, finally, the equilibrium phase appeared.

C. The Ta-Hf Phase Diagram.

It was observed that the β/α solvus in the Ta-Hf phase diagram shifted from 27%Hf to 7%Hf as the soluble carbon concentration increased. The shift was comparable with differences noted between reported phase diagrams in the literature. An attempt was made to simulate the effect of impurities on the Ta-Hf phase diagram with a computerized calculation based on a sub-regular solution model. The current conclusion on this work is that insufficient thermodynamic data is available to make reliable predictions.

D. The TaC-HfC and NbC-HfC Phase Diagrams.

Initial carburizing work performed early in the contract period suggested that the pseudo-binary TaC-HfC and NbC-HfC systems were not completely miscible as had been reported in the literature. Indeed elastic interaction models predict that these systems should be immiscible below 1000°C. At present we have experimental evidence that the NbC-HfC system has a miscibility gap which peaks between 1000-1100°C. Long term heat treatments are still being conducted on these systems in order to obtain more accurate data.

E. Diffusion of Hf in Ta.

The diffusivity of Hf in Ta has been deduced from age hardening kinetic studies and has been confirmed by the discontinuous precipitation kinetics. It is the following:

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

when compared with the self diffusivity of Ta ($D_{\text{Ta}}^{\text{Ta}} = .124 \exp(-98,700/RT)$), the above value indicates that Hf atoms move with anomalous speed through the Ta matrix, confirming previous qualitative observations by other workers.

III. CARBURIZING

A. Single-Phase Carburizing.

For ease in describing the carburizing process as a function of time, temperature, and methane pressure, the Ta-Hf alloys were carburized first at elevated temperatures, above the β/α solvus. These results were extrapolated to lower temperatures in order to predict the optimum conditions for cluster carburizing below the solvus temperature.

In high temperature work it was possible to distinguish three stages of carburizing. In the first stage, islands of HfC were formed on the free surface; in the second stage, HfC plates grew into the interior like Widmanstätten plates; and in the third stage, Ta_2C formed at the surface and the HfC plates developed a volume fraction profile which decreased with distance from the surface. With time the profiles extended deeper into the alloy, but the amount near the surface remained constant. The above observations were not consistent with previous theories of subscale formation, therefore, an extension of the theory was required.

B. Extention of Subscale Formation Theory.

Except for several specialized treatments, previous theories of subscale formation assumed a low solubility product between the alloy solute and the reacting gas species. In our alloys, the solubility product was not low and, for this reason, our observations did not conform with the classical theories. In attempting to explain our observations, we were first able to show that there are two limiting cases of subscale formation: one, when nearly all the alloy solute is tied up in subscale precipitates (i.e., corresponding to the classical treatment); and the other, when a vanishingly small amount of solute is reacted in the subscale zone (i.e., corresponding to our newly proposed limit). In addition, we showed that under certain conditions one could treat analytically the continuum of cases between limits. Currently, one member of our group is finishing work which further generalizes the theoretical work. He is also obtaining experimental evidence for comparison with the new theory. Applications of this theory are expected in the fields of hot corrosion, oxidation and high temperature coatings.

C. Cluster Carburizing.

Aged alloys were carburized both by gas carburizing and by a solid-state diffusion technique. In the latter method, the aged alloys were joined to Fe-C alloys to form diffusion couples. The advantages of the solid-state method were less contamination and the possibility of longer reaction times; however, the disadvantage found, that of lower-reaction kinetics, precluded extensive use of this technique.

The gas carburized alloys contained subscales that were featureless under light microscopy and varied from 7-20 μm in width. The kinetics of subscale growth were studied over a range of temperatures and were consistent with the elevated temperature results.

One objective of the "Cluster Carburizing" program was to study how the aged precipitates influenced the carbide morphology. The hardness data, discussed in the next section, showed conclusively that the two structures were related. However, further TEM work is needed to distinguish between the possible mechanisms responsible for the relationship.

IV. MECHANICAL PROPERTIES

A. Age Hardening of Ta-Hf Alloys.

Three hardness peaks were observed during age hardening studies. They corresponded to the following sequence of events:

$\beta \rightarrow \beta + \text{"loops"} \rightarrow \beta + \alpha'$ (fine dispersion of α' in a dense array of dislocations) $\rightarrow \beta + \alpha$ (rod-shaped, equilibrium precipitates)

The structure of $\beta + \alpha'$ gave the greatest microhardness of the three structures and formed in a few weeks at 685°C or a few hours at 1000°C.

B. Aged Hardness vs. Cluster Carburized Hardness.

It was generally observed that the hardness of carburized alloys was proportional to the prior hardness developed by aging. Thus, alloys that were aged to peak hardness would yield harder subscales after carburizing than would under or overaged alloys. We conclude that when trying to create high strength materials with the cluster carburizing method, the first step is to optimize prior age hardening (i.e., obtain the highest hardness possible in feasible times).

C. Comparison of Ta-Hf and Nb-Hf Alloys.

In the solutionized and quenched condition, the hardness of the Ta-Hf and Nb-Hf alloys were similar. However, the Ta-Hf alloys were harder both in the aged condition and in the cluster carburized condition. A simple explanation for this observation, based on the phase diagram, is that more Hf precipitates in Ta-Hf alloys than in Nb-Hf alloys of similar composition.

The carburized hardness could be greater for two reasons: because more carbide forms and because the hardness which develops from cluster carburizing is greater than that from single-phase carburizing.

V. SUMMARY OF THE MOST SIGNIFICANT RESULTS

The major accomplishments of the cluster carburizing program can be summarized as follows:

1. It was shown that the hardness of aged and carburized materials can be controlled via the aged structure, thereby confirming the cluster carburizing hypothesis.
2. A new and analytical subscale formation theory was developed which considers finite solubility products between the solute and the reacting gas.
3. The properties of Ta-Hf alloys were characterized with respect to the following:
 - a. precipitation kinetics and morphology
 - b. diffusion kinetics
 - c. age hardening
 - d. subscale formation due to carburizing above and below the α/β solvus.

VI. PUBLICATIONS

A. Journal Articles

1. G. R. LaFlamme and J. E. Morral; Limiting Cases of Subscale Formation, Acta Met., 26 (1978) 1791.
2. E. V. Ohriner and J. E. Morral; Precipitate Distribution in Subscales, Scripta Met., 13 (1979) 7.

B. M.S. Theses

1. G. R. LaFlamme, The Internal Carburization Kinetics of Ta-27%Hf at 1627°C, M.S. Thesis, University of Connecticut, 1975.
2. T. B. Cameron, Structure and Morphology of Internally Carburized Ta-27%Hf, M.S. Thesis, University of Connecticut, 1975.
3. E. V. Ohriner, Internal Carburization of Nb-Hf Alloys, M.S. Thesis, University of Connecticut, 1977.
4. V. Talwar, "Cluster Carburizing of a Ta-27%Hf Alloy", M.S. Thesis, University of Connecticut, 1979.
5. S. Pati, "An Investigation of the Psuedo-Binaries TaC-HfC and NbC-HfC", M.S. Thesis, University of Connecticut, 1979.
6. L. Tuyen, Discontinuous Precipitation and Solid-State Carburizing of Ta-Hf Alloys, M.S. Thesis in preparation (final draft accepted).

C. Ph.D. Theses

1. S-T. Chang, "Age Hardening Behavior of Ta-Hf Alloys", Ph.D. Thesis, University of Connecticut, 1977.
2. E. V. Ohriner, "Theory of Subscale Formation With a Finite Solubility Product and Its Application to the Internal Carburization of Ta-Hf and Nb-Hf Alloys", Ph.D. Thesis in preparation (expected to finish in 1979).

D. Journal Articles in Preparation

1. T. B. Cameron, G. R. LaFlamme and J. E. Morral, Internal Carburizing of Ta-Hf Alloys at 1900°K.
2. S-T. Chang and J. E. Morral, Precipitation and Age Hardening of Ta-Hf Alloys.
3. S. Pati and J. E. Morral, Miscibility in the TaC-HfC and NbC-HfC Pseudo-Binary Phase Diagrams.
4. L. Tuyen and J. E. Morral, Discontinuous Precipitation in Ta-Hf Alloys.
5. V. Talwar and J. E. Morral, Cluster Carburizing.