CLUSTER CARBURIZING

Progress Report
for Period June 1, 1977 - May 31, 1978

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February 1978

Prepared for
THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. AT(11-1)-2354

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ABSTRACT

When aging quenched Ta-27% Hf alloys at 685°C, excess thermal vacancies were found to condense into vacancy loops. The loops are responsible for the first age-hardening peak observed during heat treatment. In a study of binary alloys formed by two monocarbides, a miscibility gap was found in the NbC-HfC system with a critical temperature between 1100-1200°C, while homogeneous solutions were formed by TaC-HfC down to 1000°C. An investigation of solid phase carburizing of Ta-Hf and Nb-Hf alloys indicated that this technique results in a higher carbon activity, but slower kinetics than was obtained by gas carburizing. Work continues on improving this technique and on preparing cluster carburized specimens for study by transmission electron microscopy.

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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 before. 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 objective. Ta-27%Hf alloys were prepared and their age hardening behavior before cluster carburizing was studied. This activity was completed last year. In the second year, 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 year and lead to the discovery of a new limiting case in the field of subscale formation. The clue to this limiting case was found in the distribution of carbides in the carburized zone. 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.

The aging studies on Ta-Hf were completed in the fourth year and three different stages of age hardening were identified. The first stage involved the formation of vacancy loops, a finding not reported in the previous progress report but which is described below, while the second and third stages involved precipitation of transition and equilibrium phases. In addition a comparison was made at 1000°C between a Ta-Hf alloy which would cluster carburize at this temperature and a Nb-Hf alloy which would experience only conventional internal carburization. Although the initial hardness and heat treatments of the alloys were similar, the carburized hardness were significantly different, 1000 KHN for the aged Ta-Hf alloy and 700 KHN for the Nb-Hf alloy. Also, it was shown that the carburized hardness was related to the level of age hardening prior to carburizing, a finding which supports the view that cluster carburizing can lead to more control over carbide morphology and subsequently to the design of high strength materials.

In the current year a study of carbide miscibility was completed, the possibility of solid phase carburizing was investigated, and work began on a detailed TEM study of the cluster carburizing process in Ta-Hf alloys. A description of these activities are reported below.

II. Materials Characterization

A. Age Hardening Mechanisms

When aging Ta-27%Hf alloys at 685°C two age hardening peaks are observed. The second peak, appearing after 500 hours, is associated with the formation of an irregular precipitate structure while the first peak,
appearing after 100 minutes, corresponds to the formation of a loop or disk shaped structure. A similar disk structure was observed in a Nb-Hf alloy aged at 600°C for 1000 hours and was tentatively identified as Hf clusters. However, based on a diffusion coefficient reported earlier, the diffusion distance of a Hf atom is on the order of 2Å during aging to the first peak, making it unlikely that Hf clusters form in the Ta base alloy. By using a method described by Loretto and Smallman, in which the burgers vector is determined and then the loop is imaged with a positive and negative diffraction vector (i.e. ±g), it was found that the disks were vacancy loops with a burgers vector $\vec{b} = \frac{1}{2} <110>$. Therefore, we conclude that initial hardening is caused by quenched in thermal vacancies that condense into dislocation loops during the early stages of aging and then interfere with mobile dislocation motion during deformation.

B. Miscibility in Monocarbide Alloys

An x-ray diffraction study of Nb-Hf alloys carburized at 1000°C indicated the presence of two MC carbides in alloys containing more than 12%Hf. The lattice parameters of these two carbides, $\delta'$ and $\delta''$, are shown in figure 1. This observation prompted an investigation of miscibility gaps in TaC-HfC and NbC-HfC alloys in order to interpret the carburizing results.

First, a literature survey was made on the MC type carbides which form in all the group IVB and VB metal-carbon systems. It was found that how they react when combined as binary carbide alloys has been studied only above 1300°C. In this temperature range miscibility gaps have been found in TaC-VC, NbC-VC, TiC-HfC, and TiC-ZrC while other alloys including the ones of importance in this project show complete miscibility. Since no experimental evidence was available for the lower temperature
Figure 1: Lattice parameters of MC carbides formed in a series of Nb-Hf alloys after carburizing at 1000°C.
range of interest, for example at 1000°C, an attempt was made to estimate the miscibility temperature using strain energy calculations and approximate rules. These estimates predicted that immiscibility should occur around 370 to 930°C for TaC-HfC and 250 to 870°C for NbC-HfC.

Because estimated values of phase diagram features tend to be inaccurate, even by hundreds of degrees, an attempt was made to obtain evidence of immiscibility in arc melted binary carbides that were subsequently aged. Step scanning of the (200) x-ray diffraction peaks indicated the following changes. In the NbC-HfC alloy, the broad initial as-cast peak tended to sharpen and split into two individual peaks both after 43 days at 1000°C and after 50 days at 1100°C suggesting that phase separation was occurring, while aging at 1200°C for 32 days just served to sharpen the peak. From this evidence we conclude that there is a miscibility gap that peaks between 1100 and 1200°C and that this explains the formation of δ' and δ'' when Nb-Hf alloys are carburized. However, in the TaC-HfC system there was no tendency to form individual peaks after similar heat treatments and the initial peak just sharpened with aging. Therefore, the indication is that TaC-HfC alloys are homogeneous above 1000°C and that miscibility gaps, if present, occur at lower temperatures.

III. Carburizing Experiments

A. Solid Phase Carburizing

In order to obtain cluster carburized materials with the highest possible strength, it is necessary to age and carburize for several weeks at a time without contaminating the samples with other interstitials. Although we have been able to avoid contamination in gas-carburizing treatments which last for less than twelve hours, this equipment requires constant supervision and, therefore, is not practical for extended treatments.
In addition, treatments using pack-carburizing techniques were tried but proved unsuccessful. In the current contract period we have used a solid phase carburizing technique in which a steel alloy is pressed against the sample surface in order to act both as a source of carbon and as a shield against further interstitial contamination.

In preliminary experiments on Ta-Hf alloys using 4037 steel as the carburizing agent, it was found that an 8 µm carburized layer formed after two weeks at 850°C. Also, microprobe analysis showed that the sample was free of oxygen contamination. Comparing these results with those of gas carburizing points out a number of differences. First, the observed layer size was 7.5 times smaller than would have been expected for gas carburizing. Second the layers were harder, 2300 KHN vs 1300 KHN, indicating that the solid state technique was yielding an external carbide layer of TaC rather than the internally carburized zones obtained by gas carburizing. Similar results were obtained in later experiments using a high purity 1095 steel as the carburizing agent.

A Nb-Hf alloy was carburized with a 1.2% steel at 1000°C for nine days. The 30 µm carburized layer that formed contained two zones. The first was an externally carburized zone of 6' and 6" and the second was an internally carburized zone. Again the zone was smaller than expected from gas carburizing experiments.

The external carbides that result from solid phase carburizing suggest that the carbon activity is higher in this technique than in gas carburizing. The smaller carburized zone size, on the other hand, might occur because the layer growth is not strictly diffusion controlled. If this were the case, the external carbide could act to block the diffusion of carbon and thereby slow internal carburization.
Another possibility we have considered is that intermetallic compounds are forming between iron and the refractory metal elements. Although this could slow the diffusion of carbon out of the steel it would also lower the carbon activity at the refractory metal interface and possibly prevent the formation of external carbides. Currently we are putting a thin film of silver between the steel and refractory metal to both lower the carbon activity and prevent the formation of compounds. In this way we hope to prevent external carbide formation and increase the layer growth kinetics.

Once the solid phase carburizing technique has been improved, Ta-Hf alloys will be carburized over a temperature range of 685-850°C and for times of 1-10 weeks. This work should be completed by the end of the summer or before.

B. TEM Studies of Cluster Carburizing

Sheet samples of Ta-Hf alloys are being prepared for transmission electron microscopy studies by first carburizing and then electro-polishing. The methods used for this work are similar to those used in the age hardening studies. The only difficulty we anticipate having is selectively thinning the internally carburized layer for viewing in transmission. Once this technique has been perfected, it will be possible to follow the structural changes that take place during carburizing.
IV. REFERENCES

1. R. J. Murphy, N. H. Grant, ASM Trans. Quart. 60 (1967) 29.
V. TIME DEVOTED BY THE PRINCIPAL INVESTIGATOR

By the end of the current period (May 31, 1978), 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.