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USE OF ANOMALOUS SMALL ANGLE X-RAY SCATTERING

TO INVESTIGATE MICROSTRUCTURAL FEATURES IN COMPLEX ALLOYS

Technical Progress Report

for period 1 August 1989 - 1 August 1990

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TECHNICAL PROGRESS REPORT FOR THE PERIOD

1 AUGUST 1989 TO 1 AUGUST 1990

The research thrust of this grant has been directed into two areas. The principal effort has been spent in an investigation of the use of anomalous small angle X-ray scattering (ASAXS) to observe changes in the microstructure of a relatively complex alloy produced by high temperature deformation or aging. A second effort involves a study of the high temperature behavior of several ferritic steels. In particular, we are investigating the precursors and earliest stages of fatigue crack initiation, especially how initiation is affected by hold times and by environment.

1. Anomalous Small Angle X-ray Scattering

Anomalous small angle X-ray scattering (ASAXS) offers the possibility of separating out the scattering caused by a particular scattering entity from the total scattering in a complex material containing a number of scattering systems. Thus it would be possible to follow the influence of various forms of high temperature service (simple aging, creep, cyclic stresses) on the different carbides or other precipitates in an alloy. With the use of a synchrotron for the source of radiation a monochromatic beam of X-rays is obtained that can be tuned over a wide range. The phenomenon of anomalous scattering then is used to separate out the contributions to the total scattering from the various scattering species.

We have been studying carbides in two ferritic steel alloys. The first is Fe9Cr1Mo modified by the addition of small amounts of the strong carbide formers, V and Nb. This alloy, which has been studied at ORNL and in the course of this grant, is used in power-generating equipment. The second alloy is AF1410 (primarily Fe14Co10Ni), an ultra high-strength, high toughness

steel used in carrier-based aircraft arresting hooks and in the space shuttle. It has been under intensive investigation, both theoretical and experimental, by a number of scientists in an integrated effort headed by Professor G. Olson at Northwestern. Thus extensive data bases are available for both materials.

To carry out the ASAXS measurements we have constructed, working in cooperation with Dr. G. Long of NIST, a superb small-angle X-ray scattering camera. The experiments have been performed on the NIST beam line at NSLS, Brookhaven National Laboratory.

INTRODUCTION

For the alloy Fe₉Cr₁Mo+V,Nb to be considered for long-term use, its microstructure must be stable at operating temperatures. Sikka et al. [1] have reported that precipitation of fine (V,Nb)C and Cr₂₃C₆ carbides contributes significantly to the hardness of this alloy. For tempering temperatures above about 525°C, they observed a monotonic decrease in hardness with increasing tempering temperature. The exact size of these carbides was not reported but were suggested to be of submicrometer diameter.

Alloy AF1410 achieves its desirable mechanical properties of high hardness, high toughness, and increased resistance to stress-corrosion cracking by an exacting heat treatment designed to promote a fine dispersion of coherent (Cr,Mo)₂C precipitates of 5-8 nm diameter while avoiding their conversion to the submicrometer size MC equilibrium carbides.

At the initiation of this research project, almost all existing SAXS (and for neutrons, SANS) cameras were capable of resolving only those scatterers whose dimensions are less than 100 nm. Using such cameras, one of the early workers on this project [2] discovered that for Fe₉Cr₁Mo+V,Nb, the number of carbides drops significantly between the aging temperatures of

538 and 704°C. Kim was unable to determine if this change was caused by a decrease in the population of (V,Nb)C or of Cr_{23}C_6 . In addition, the SANS cameras he used were not capable of resolving features larger than some tens of nanometers. It is for these two reasons that we have designed and built a double crystal diffractometer (DCD) for use with synchrotron radiation. Transmission electron microscopy reveals that we should find scatterers in this alloy that are larger than 100 nm.

The wave length of synchrotron radiation can be tuned without incurring drastic losses in X-ray flux. This fact enables us to take advantage of the phenomenon of anomalous dispersion (AD). AD is the drop in the X-ray scattering factor of an element that occurs when the incident radiation is close to that required to stimulate characteristic X-ray emission in atoms of that element. These "resonance" wave lengths are well separated for the transition metals. In an experiment the scattering from features in which chromium is concentrated, for example, may be changed by changing the wave length near the chromium resonance wave length (i.e., absorption edge). Scattering from non Cr-bearing particles is not significantly affected by these small alterations in the X-ray energy. In the case of $\text{Fe}_9\text{Cr}_1\text{Mo}+\text{V,Nb}$, the scattering from Cr_{23}C_6 can be changed while the scattering from (V,Nb)C remains virtually constant. (The effect of the changing energy on the scattering length density of the matrix is small, since it contains only 9% Cr.) Thus AD can be used with SAXS in a technique called anomalous small-angle X-ray scattering (ASAXS), to identify the contribution of Cr_{23}C_6 to the SAXS intensity, even when (V,Nb)C is present.

DCD CAMERA

The DCD camera and its capabilities were described quite extensively in last year's Progress Report. Attached to this

Progress Report are the manuscripts, "High Resolution Small Angle X-Ray Scattering Camera for Anomalous Scattering" and "Silicon Photodiode Detector for Small-Angle X-ray Scattering". Both have been accepted for publication by the Journal of Applied Crystallography. In addition, P. Jemian, the graduate student who worked on this project, is co-author on a number of papers and presentations describing research on other material systems in which the DCD camera was used and in which he participated in the measurements. (They were taken during periods of beam time shared with us.)

SMALL ANGLE SCATTERING RESULTS

Enclosed is the manuscript of a paper about to be submitted to Acta Metallurgica on the results of the ASAXS study of chromium carbides in the modified Fe₉Cr₁Mo steel. (The major results of the ASAXS work are contained in this paper. A number of related, more specialized papers [describing the DCD; the method of analyzing the ASAXS data; details of the maximum entropy analysis; etc.] have or are being written.) By working with photons near the chromium K absorption edge, it was possible to isolate the scattering from the Cr₂₃C₆ carbides from the total scattering (see Figure 2 of the MS). A straight subtraction of one curve in Figure 2 from another to obtain the scattering just due to the chromium carbides would lead to excessively noisy results. To get around the problem, size distributions (Fig. 3) calculated from each scattering curve using a maximum entropy method were combined with a scattering contrast gradient analysis to isolate the volume-fraction size distribution of the chromium carbides. Dr. Jemian devised this contrast gradient analysis technique. It appears to be an extremely useful method for analyzing quantitatively ASAXS data. Such data require special treatment since the changes in scattering with photon wave length are small. See the attached MS for details of the method.

The behavior of the chromium carbides was studied as a function of aging temperature. The ASAXS measurements show that the mean diameter of the chromium carbides is a minimum after aging at 538°C. In support of these ASAXS results is the fact that this aging temperature produces a maximum in the hardness of the steel. Over the range of aging temperatures investigated, the ratio of the largest mean diameter (704°) to the smallest (538°C) is 1.6 while the volume fraction of the chromium carbides varies by a factor of about 2.5.

In AF1410 and similar ultrahigh-strength steels, control of carbide precipitation in the recovery resistant Fe-Ni-Co martensitic matrix is of primary concern in developing the best overall microstructure. Of particular interest is the conversion during aging of the carbide phases. After the quench from the solution treatment temperature the main carbide phase is composed of fine particles. Most of these are transformed to a micrometer-scale M_3C structure by some 15 minutes of aging at 510°C. Over the next few hours of aging, the dominant process is the conversion of M_3C to a fine dispersion of M_2C carbides, which nucleate and coarsen with increasing time at temperature. It is the M_2C carbides that are responsible for the excellent strength properties of the steel. Due to the very different scale ranges of the M_3C (micrometer scale) and M_2C (nanometer scale) carbides, it has not been possible to study comprehensively the small angle scattering from both carbide phases in the same experiment. DCD SAXS has been used to study the changes in the M_3C population accompanying the nucleation and growth of the M_2C carbides, while SANS has been used for observing the much finer M_2C . Extensive TEM studies were carried out by Dr. D. Gavillet, a visiting scholar working on this grant, to furnish needed information for the scattering analysis and to verify the conclusions. The SANS and TEM results on the M_2C precipitation are contained in the enclosed MS by Allen, Gavillet and Weertman.

2. Influence of Environment and Cycle Pattern on Surface Fatigue Damage

INTRODUCTION

The goal of this work is to understand the influence of environment and hold pattern on the high temperature fatigue behavior of chromium ferritic steels. We observed [2] that Fe9Cr1Mo+V,Nb follows the hold time behavior exhibited by Fe2.25Cr1Mo [3-7] for strain controlled fatigue at high temperatures: a compressive hold in the fatigue cycle is more damaging and results in a shorter fatigue life than a tensile hold if the test is conducted in air. In vacuum, the reverse is true, with the tensile hold pattern being more damaging.

It has been suggested [3] that it is the oxide scale formed during high temperature tests that causes the compressive hold to be more damaging than the tensile hold. Past researchers have observed that as a result of the quick compression thrust that follows a tension hold, the oxide scale spalls off the specimen surface. On the other hand, if a quick tension thrust follows a hold in compression, the oxide does not spall off, but rather develops a rumpled texture with ridges perpendicular to the tensile axis. These ridges facilitate the early nucleation of fatigue cracks [3,4,6]. In light of the apparent importance of the oxide scale in causing fatigue damage, we are performing a series of fatigue tests which attempt to elucidate the role of the oxide in high temperature fatigue of chromium ferritic steels.

MECHANICAL TESTING

In this past year, our research has focused on Fe2.25Cr1Mo. In order to vary the oxide scale thickness during high temperature hold time fatigue tests, experiments are being

conducted in 10^{-6} Torr vacuum, in 10^{-3} vacuum, in air with a prompt start of the testing, and in air with a preheat period of 16 hours. Thin oxide scales form in vacuum, while the preheat period allows a thicker oxide scale to form before the test begins.

Tests are being conducted on hourglass-shaped specimens of Fe2.25Cr1Mo with 1.0% total axial strain range and 2 minute hold periods at 500°C and 600°C. The fatigue wave forms used are symmetric about zero strain, with a 2 minute hold period either in compression or tension followed by a quick strain excursion in the opposite strain sense. The effects of hold time and preheating on fatigue life at 500°C are illustrated in Figure 1. Differences in lifetimes were not so noticeable at 600°C. Preheating to develop an oxide scale was found also to affect the relaxation stress somewhat, as seen in Figure 2. Some tests were stopped at different fractions of lifetime in order to observe surface morphology development.

The oxide layer's role in fatigue damage must depend, at least in part, on its strain state and its ceramic nature. During a symmetric tension hold test, the scale grows primarily during the hold period, and the oxide is therefore at a relatively unstrained state while the bulk of the specimen endures the tension strain hold. When the specimen undergoes the compressive part of the fatigue cycle, the oxide may feel double the compressive stress experienced by the specimen. (Theoretically, the oxide could experience a compressive strain equal to the total strain range.) A ceramic oxide is most likely to crack perpendicular to a tensile stress. Hence when an oxidized sample is compressed longitudinally, the oxide feels a circumferential tensile stress and therefore may crack parallel rather than perpendicular to the specimen stress axis.

Conversely, during a symmetric compressive hold test, the oxide formed is at approximately zero strain when the specimen is in compression. During the quick tensile portion of the cycle, the oxide experiences a tensile strain double that of the specimen and cracks perpendicular to the stress axis. The cracks in the oxide initiate cracks in the underlying metal [6].

The preceding explanation assumes that (1) the oxide that grows during a hold is in a state of zero strain; and (2) the nature of the interface between metal and oxide is such that the state of strain in the metal is of little importance in the cracking behavior of the oxide. Both of these assumptions are open to question and need to be examined. For example, tests are under way to examine fatigue behavior when the hold period occurs at zero strain. The total strain range is kept the same. (See Figure 4.) The stress behavior appears to differ little from the case of a symmetric strain test, but the relationship between the state of strain in oxide and metal differs in the two cases.

ANALYTICAL WORK

A variety of analytical methods are being used, but to date the most fruitful results have been examination by SEM of the specimen surfaces. The surfaces of specimens fatigued with a compressive hold time always have cracks running perpendicular to the stress axis. We have observed evidence that a crack in the oxide layer leads to a crack in the metal, as in the SEM micrograph in Figure 3 where one can see ridges in outer layers continuing on to inner surfaces. Specimens fatigued with a tensile hold period look like chipping paint. The textures progress throughout the specimens' lifetime, as seen in Figure 5 for the compressive hold case. Comparing the texture resulting from a tension hold case, Figure 6, with the compressive hold case in Figure 5(c), shows how damaging the compressive hold is to the specimen surface.

The effects of preheating on specimen surfaces are illustrated in Figure 7. These micrographs show the similarities to the prompt start cases (Figures 5 and 6), but it is also apparent that the preheat condition results in oxide scale layers that are thicker and less broken up. This could explain why preheat tests exhibit shorter lifetimes even though the stress is the same. A less crumbled oxide would allow propagation of oxide surface cracks into the metal more easily.

The micrographs in Fig. 8 show surfaces resulting from hold-at-zero, tension-spike tests. They resemble the compressive hold test results seen in Fig. 5.

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PLANS FOR THE BALANCE OF THE GRANT YEAR

The test matrix of Fe2.25Cr1Mo at 1.0% total strain and at 500° and 600°C will be completed. Low vacuum (10^{-3} Torr) tests to failure and to specified fractions of life will be conducted. A start will be made on carrying out a fatigue test matrix on the higher chromium steel, Fe9Cr1Mo+V,Nb, that is similar to that for the Fe2.25Cr1Mo. SEM studies of fatigued surfaces will continue. Long range plans include cross-sectioning of the oxide/metal interface and its study by TEM, HREM, and AEM.

STATEMENT OF EFFORT

The Principal Investigator is devoting 15% of her effort during the academic year to this project. During the summer 25% of her time is being devoted to it. Former graduate student Pete Jemian, who did the ASAXS work, received his PhD early in the summer. He currently is writing up the rest of his research for publication. Rena Hecht, who is working on the damage initiation project, now is a fourth year PhD student. She has taken her PhD qualifying exam and been admitted to candidacy.

We have been very fortunate to work with Dr. Gabrielle Long from NIST on the design and construction of the DCD and on the scattering measurements. She is enthused about continuing the collaboration.

PUBLICATIONS IN PAST YEAR

"High Resolution Small Angle X-ray Scattering Camera for Anomalous Scattering", G. G. Long, P. R. Jemian, J. R. Weertman, D. R. Black, H. E. Burdette, and R. Spal, Journal of Applied Crystallography, in press.

"Silicon Photodiode Detector for Small-Angle X-ray Scattering", P. R. Jemian and G. G. Long, Journal of Applied Crystallography, in press.

"Characterization of Modified Fe₉Cr₁Mo Steel by Anomalous Small-Angle X-ray Scattering", P. R. Jemian, J. R. Weertman, G. G. Long and R. D. Spal, ready to be submitted to Acta Metallurgica as soon as cleared by NIST internal review procedures.

ORAL PRESENTATIONS IN PAST YEAR

"Isolation of the Chromium Carbide Distribution in Modified Fe₉Cr₁Mo Steel by Anomalous Small-Angle X-ray Scattering", P. R. Jemian, J. R. Weertman and G. G. Long, Fall 1990 TMS Meeting, Detroit, MI.

"Characterization of Steels by Anomalous Small-Angle X-ray Scattering", P. R. Jemian, Auburn University, Auburn, Alabama, 15 May 1990.

"Microstructural Characterization by SANS and ASAXS", J. R. Weertman, Johns Hopkins University, Baltimore, MD, 7 March 1990.

ADDITIONAL PUBLICATIONS IN PAST YEAR

Besides the papers and presentation cited above which deal directly with the research supported by this grant, P. Jemian was a co-author on several papers which involve the use of the DCD.

He participated in the scattering measurements since they were performed during the same period of beam time as our measurements.

"The Effect of Photodeposited Iron Oxide and Tin Oxide on the Consolidation of Porous Vycor Glass", E. A. Mendoza, E. Wolkow, H. D. Gafney, D. Sunil, M. Rafailovich, J. Sokolov, G. G. Long, and P. R. Jemian, in press, Applied Physics Letters.

"Small Angle Neutron Scattering and Small Angle X-ray Scattering from Bulk Microporous Silica", G. G. Long, S. Krueger, D. R. Black, J. P. Cline, P. R. Jemian and R. A. Gerhardt, Mat. Res. Soc. Symp. Proc. Vol. 166, 1990.

"Small Angle Scattering Determination of the Microstructure of Porous Silica Precursor Bodies", G. G. Long, S. Krueger, P. R. Jemian, D. R. Black, H. E. Burdette and J. P. Cline, in press, Journal Applied Crystallography.

Fig. 1 Fatigue lives of Fe2.25Cr1Mo hold time fatigue tests conducted at 500° C with $\Delta\epsilon_t = 1.0\%$. (N_f is actual fracture unless otherwise indicated.)

Samples: 2.25Cr-18 and 2.25Cr-21 Compression Hold Tests
 $T = 500\text{ C}$ -- Tot. Strain = 1.0 percent -- Air

Fig. 2 Stress vs. number of cycles for compressive hold fatigue tests conducted at 500 C in air with $\Delta\epsilon_t = 1.0\%$, one with a preheat period of 16 hours and another with a prompt start.

Fig. 3 Micrograph of surface of specimen fatigued at 500° C with $\Delta\epsilon_f = 1.0\%$ and a compressive hold of 2 minutes. One can see cracks on fragments of surface layers continuing on underlying material. Magnification 150X.

Fig. 4 Wave forms, strain vs. time, used in fatigue tests; shown here with $\Delta\epsilon_t = 1.0\%$ and a strain rate of $4 \times 10^{-3}/\text{sec}$.

(a)

(b)

(c)

Fig. 5 Surfaces of specimens fatigued with a compressive hold at 500°C and $\Delta\epsilon_t = 1.0\%$
 (a) after 500 cycles, magnification 300X, (b) after 900 cycles, magnification 300X,
 (c) after failure at 1600 cycles, magnification 150X, showing progression of surface
 damage.

Fig. 6 Surface of Fe_{2.25}Cr₁Mo specimen fatigued with 2 minute tension hold at 500° C with $\Delta\epsilon_f = 1.0\%$ after failure at 1775 cycles.

(a)

(b)

Fig. 7 Comparison of surface textures resulting from fatigue tests with a 16 hour preheat at 500° C. (a) Compressive hold, and (b) tensile hold. Magnification 100X.

(a)

(b)

Fig. 8 Surface textures on specimens fatigued with hold at zero, tension spike waveforms at 500° C with $\Delta\epsilon_t = 1.0\%$. (a) Specimen was fatigued to 625 cycles, and (b) specimen after failure at 1100 cycles.

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