PNL-SA-9293

CONF-810831--22

RADIATION-INDUCED SEGREGATION IN CANDIDATE FUSION-REACTOR ALLOYS

MASTER

J. L. Brimhall
D. R. Baer
R. H. Jones

July 1981

Prepared for the U. S. Department of Energy
under contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, WA. 99352

DISCLAIMER

RADIATION-INDUCED SEGREGATION IN CANDIDATE FUSION-REACTOR ALLOYS

J. L. Brimhall, D. R. Baer and R. H. Jones

Pacific Northwest Laboratory,
Richland, Washington 99352

The effect of radiation on surface segregation of minor and impurity elements has been studied in four candidate fusion reactor alloys. Radiation induced surface segregation of phosphorus was found in both 316 type stainless steel and in Nimonic PE-16. Segregation and depletion of the other alloying elements in 316 stainless steel agreed with that reported by other investigators. Segregation of nitrogen in ferritic HT-9 was enhanced by radiation but no phosphorus segregation was detected. No significant radiation enhanced or induced segregation was observed in a Ti-6Al-4V alloy. The results indicate that radiation enhanced grain boundary segregation could contribute to the embrittlement of 316 SS and PE-16.

1. INTRODUCTION

The effect of radiation on impurity segregation in candidate fusion reactor alloys has been investigated because of the potential effect impurity elements such as sulfur, phosphorus, and nitrogen can have on mechanical properties. Impurity elements such as these can segregate to grain boundaries by a thermally activated, equilibrium process and any enhancement in this process or inducement beyond the equilibrium concentration could have deleterious effects on the creep-rupture, fatigue crack growth rate or ductile to brittle transition temperature of these materials. Radiation induced segregation of minor alloying elements has been studied theoretically and experimentally because of the effect minor alloying elements have on phase stability. Radiation induced or enhanced segregation of impurity elements has received relatively little attention even though equilibrium segregation of impurity elements is a well known and studied phenomenon. The study reported here evaluated the effect of heavy ion irradiation on the surface segregation of minor and impurity elements in 316 type stainless steel, Nimonic PE-16, ferritic HT-9 and Ti-6Al-4V. Auger Electron Spectroscopy (AES) was used to analyze for surface segregation. Surface segregation was used as a qualitative indication of grain boundary segregation for the purpose of indicating potential problems from irradiation induced segregation in first wall fusion reactor materials.

2. EXPERIMENTAL PROCEDURES

The 316 SS (HT X-15893), PE-16 (HT TC-1747) and HT-9 (General Atomics Co.) were obtained from the fusion materials stockpile while the Ti-6Al-4V was obtained from the National Titanium Corp. Chemical compositions of all alloys are given in Table 1. Thin slices of 316 SS and Ti-6Al-4V were cut from 12 mm bar stock whereas specimens of HT-9 and PE-16 were punched from rolled sheet to produce specimens in the form of TEM disks, 3 mm diameter and 0.3 mm thick. The surface to be bombarded was highly polished using standard metallographic techniques. After polishing, each alloy was heat treated as follows: i) 316 SS; 0.5 hr at 1325 K, furnace cool, 8 hr at 1075 K ii) PE-16; 4 hr at 1315 + 1 hr at 1175 K, furnace cool, 4 hr at 1025 K, furnace cool iii) HT-9; 0.5 hr at 1325 K, furnace cool, 2.5 hr 1025 K iv) Ti-6Al-4V; 2 hr at 1175 K, furnace cool. All specimens were electropolished after heat treatment to remove any thermally induced surface segregation.

All specimens were bombarded with 5 MeV Ni^{++} from the PNL Tandem Accelerator using a current density of 13 mamps/m^2. The displacement damage was calculated using the Manning-Mueller approach and the dose rate at the surface was

TABLE 1. Typical Chemical Analyses in Wt%

316 SS

Cr	Ni	Mo	Si	P	S	Fe
17.3	12.5	2.23	0.65	0.013 (0.030)[1]	0.017	bal

PE-16

Ni	Cr	Mo	Al	Ti	P	S	Fe
43.8	16.8	3.3	1.20	1.16	0.004	0.002	bal

HT-9

Cr	Mo	Si	P	S	N	Fe
11.3	0.52	0.38	0.004 (0.019)[1]	0.006	0.045	bal

Ti-6Al-4V

Al	V	Fe	O	N	C	Ti
6.35	4.0	0.14	0.19	0.19	0.008	bal

(1) Other reported analysis.

approximately 3 x 10^{-3} displacements per atom (dpa)/sec for all alloys. The temperatures ranged from 725 K to 875 K and the vacuum varied between 2 x 10^{-6} Pa to 1 x 10^{-5} Pa during the irradiation. Thermal control specimens were heated in the target apparatus for a time equal to the irradiation time.

After irradiation, the specimens were transferred in air to the AES chamber for analysis. A 5 keV electron beam with a current of approximately 1-3 ma was used to generate AES spectra. Sputter profiling was done using 5 keV Ar ions and the sputter rate was calibrated for SiO_2. All sputter depths refer to the SiO_2 standard. Up to six elements were monitored continually during the profile and full AES spectra were taken periodically. The profiles were continued until the AES signals approached the bulk values.

3. RESULTS

The most significant result in the 316 and PE-16 alloys was the strong effect of irradiation on phosphorus segregation. The sputter profiles of phosphorus and chromium in these alloys are plotted in Figures 1 through 3 with the data normalized so that the bulk chromium level is equal to one in each case. Sensitivity factors have not been taken into account in these figures. Some slight segregation is apparent in the 316 thermal control at 875 K but the maximum phosphorus concentration is generally an order of magnitude greater than the thermal control level. The maximum concentration in all cases is slightly below the surface.

For this initial survey, some of the major and minor alloying elements were also analyzed but are not shown for sake of clarity. As an indication of the effect of radiation on these other elements, the ratio of the maximum (or minimum) AES peak to peak amplitude of a particular element observed during sputter profiling to that of the bulk chromium level is given in Table IIa and IIb for 316 SS and PE-16. The trends in the data for 316 SS e.g., enhanced nickel and silicon surface segregation and depletion of molybdenum, generally agreed with that reported by Okamoto and Rehn.(2) However, thermally activated segregation was quite pronounced in some cases such as silicon at 875 K whereas Okamoto and Rehn reported very little or nonexistent thermal segregation. In the PE-16, phosphorus was the only element clearly affected by radiation, Figure 3. Aluminum and titanium show a small increase in segregation after irradiation.

Sulfur segregation is also of interest but showed ambiguous results in the 316 SS. Radiation induced segregation was demonstrated at 775 K but the results were just the opposite at 875 K with the thermal control showing more

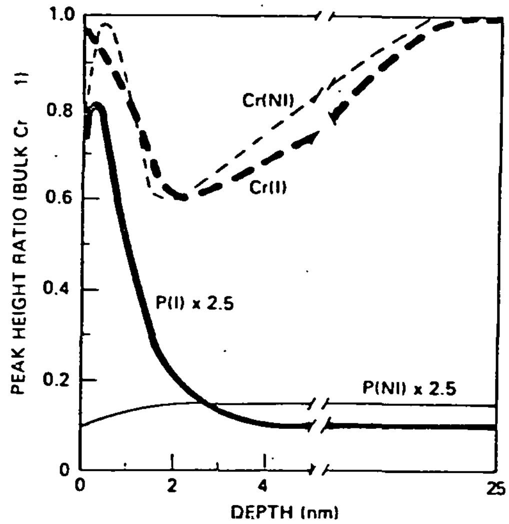

Figure 1 : AES depth profiles for P and Cr in 316 SS. Irradiated at 775 K (I). Thermal control at 775 (NI).

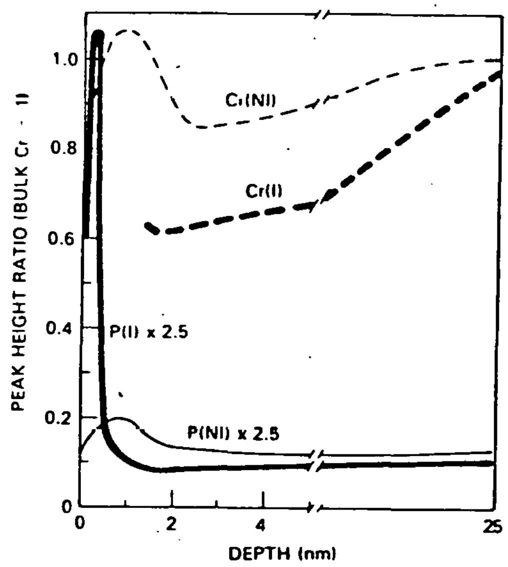

Figure 2 : AES depth profiles for P and Cr in 316 SS. Irradiated at 875 K (I). Thermal control at 875 (NI).

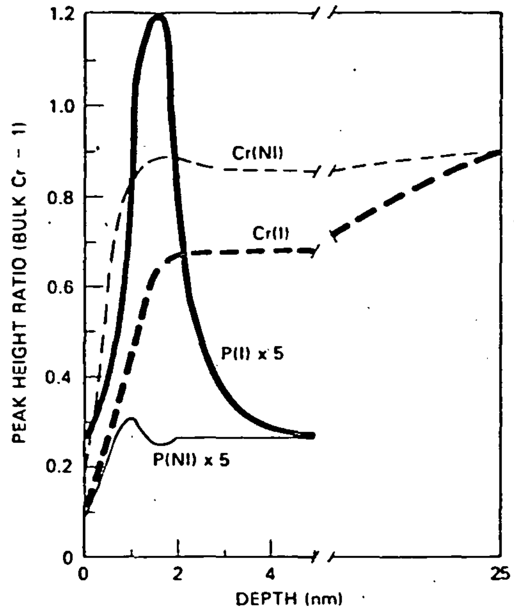

Figure 3 : AES depth profiles for P and Cr in PE-16. Irradiated at 775 K (I). Thermal control at 775 (NI).

segregation, Table II. In-situ annealing studies in the AES chamber indicated sulfur migrating to the surface at 875 K so thermal segregation should have been expected. It is not entirely clear, however, why sulfur segregation was not enhanced by irradiation at this temperature. There was no indication of sulfur segregation in the PE-16 alloy, either in the thermal control or irradiated specimens.

Radiation enhanced segregation of nitrogen was the only measurable effect of radiation in the HT-9 alloy, Figure 4 and 5. The data has again been normalized to a bulk chromium level of one. At 875 K, the effect of radiation is marginal. No phosphorus, sulfur or molybdenum segregation due to irradiation was observed. Depletion of iron at the surface was actually greater in the thermal control specimens, Table IIc. This surface depletion of iron was related to a greater oxide formation in the thermal control specimens. The slight sputtering from the high energy nickel ions during irradiation may retard oxide formation in the irradiated specimens and hence there is less apparent iron depletion at the surface.

There was no apparent effect of radiation on the segregation of elements in the Ti-6Al-4V alloy. Oxygen, carbon and sulfur were segregated to the same degree in both irradiated and

TABLE II. Maximum (or Minimum) Elemental Peak Height Ratios[1] Near the Surface

a. 316 STAINLESS STEEL

Condition	Element Si	S	P	Fe	Ni
775 K Irr	0.1	0.14	0.34	0.68	0.62
Unirr	0.025	0.07	0.035	0.78	0.52
875 K Irr	0.10	0.03	0.40	0.8	1.4
Unirr	0.14	0.22	0.06	0.48	0.52

b. PE-16

Condition	Element P	Al	Ti	Mo
775 K Irr	0.25	0.4	0.31	0.05
Unirr	0.06	0.32	0.21	0.057

c. HT-9

Condition	Element N	Fe
775 K Irr	0.6	1.3
Unirr	0.3	0.63
875 K Irr	0.9	0.86
Unirr	0.78	0.54

(1) Peak heights were normalized to the 529 eV Cr peak height for bulk Cr.

thermal control specimens. Vanadium and aluminum were slightly depleted to about the same degree in the irradiated and thermal controls. The AES analysis indicated significant oxide formation on the surface which greatly complicated the results.

4. DISCUSSION

The surface segregation of phosphorus in 316 SS and PE-16 under irradiation is consistent with reported results of grain boundary segregation of phosphorus in neutron irradiated 304 stainless steel.(3) In the latter work, however, long time, thermally annealed control specimens were not analyzed. Grain boundary segregation of both phosphorus and sulfur has also been reported in 304 stainless steel after creep deformation at 975 K for 1000 hours.(4) The question then remains whether the radiation enhances equilibrium phosphorus segregation or whether radiation will induce a nonequilibrium concentration. In the first case, radiation would increase the rate of embrittlement while in the second case it would also increase the degree of embrittlement by increasing the grain boundary impurity concentration beyond the equilibrium level.

A significant binding between solute elements and radiation produced defects, primarily interstitials, is invoked to explain the radiation induced solute segregation to sinks such

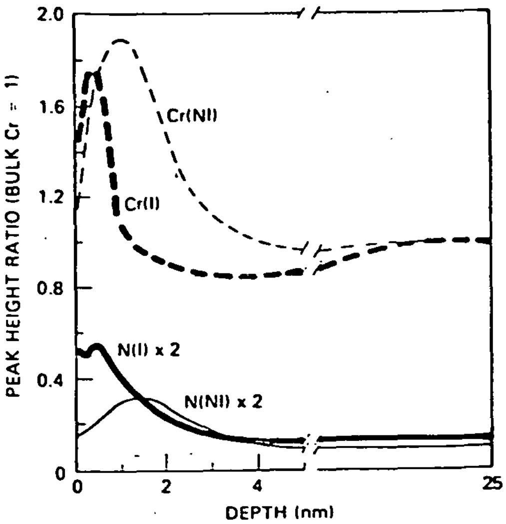

Figure 4 : AES depth profiles for N and Cr in HT-9. Irradiated at 775 K (I). Thermal control at 775 K (NI).

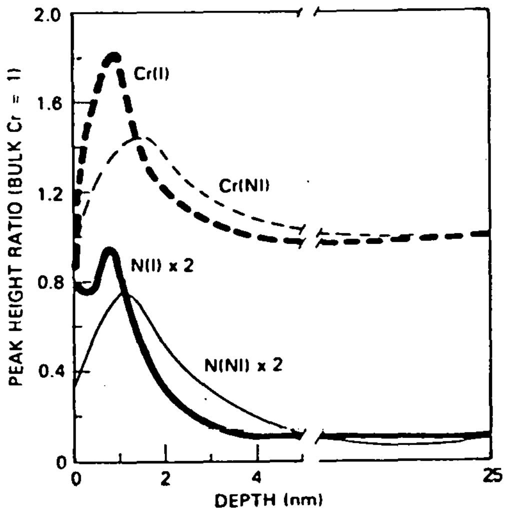

Figure 5 : AES depth profiles for N and Cr in HT-9. Irradiated at 875 K (I). Thermal control at 875 K (NI).

as free surfaces or grain boundaries.(5,6) The binding energies are not well known but in general, elements with atomic size less than the solvent tend to segregate to sinks and those of a larger atomic size tend to be depleted.(2) The atomic size of phosphorus in iron is not known but phosphorus does lower the lattice parameter of α iron which suggest a smaller atomic size, at least in bcc iron. The segregation observed in 316 SS and PE-16 is then consistent with a radiation induced phenomenon. A radiation enhanced diffusion process cannot be ruled out since at a slightly higher temperature, thermal segregation does occur (4) and in fact, a hint of segregation was noted in the 875 K thermal control specimen. Whatever the mechanism, it is apparent that phosphorus segregation could occur at grain boundaries during irradiation at lower temperatures than expected from thermal considerations. Long time annealing experiments and post-irradiation annealing experiments should provide insight as to whether the phenomenon is radiation enhanced or radiation induced.

The sulfur segregation results in 316 SS are not entirely clear at this time. Thermally induced surface segregation does occur at 875 K so radiation could enhance the segregation at a slightly lower temperature. The lack of any sulfur segregation in the PE-16 could be related to the low overall concentration compared to that in 316 SS. However, the phosphorus concentration is also low in the PE-16 yet significant phosphorus segregation was observed.

The absence of any phosphorus segregation in the HT-9 was surprising but may be related to the presence of other alloying elements. Grain boundary segregation of phosphorus in ferritic alloys is known to occur and has been widely studied because of the embrittling effect of phosphorus.(7-12) However, molybdenum has been found to counteract the embrittling effect of phosphorus by combining with the phosphorus in the grain interior. The optimum concentration of molybdenum is around 0.7 wt% which is close to the 0.52 wt% in the alloy used in the present investigation. At higher molybdenum concentrations or longer ageing times, the molybdenum precipitates as carbides thereby releasing the phosphorus to segregate to grain boundaries. However, the 1025 K aging treatment used in our study should also have precipitated the molybdenum as carbides, so it is not clear, in this case, that the molybdenum is retarding phosphorus segregation.

In general, the radiation induced or enhanced segregation of elements in ferritic HT-9 was less than in the austenitic alloys. An increase in nitrogen segregation in the irradiation specimens was the only significant phenomenon and the radiation effect was only marginal at 875 K. The trend is similar to the behavior of phosphorus in the austenitic alloys in that the effect of irradiation is greater at the lower temperature where purely thermally induced kinetics are slower. A radiation induced surface segregation is consistent with the small size of the nitrogen atoms. A strong Cr-N interaction at the free surface has also been reported which is also consistent with the results.(13) It is interesting that the rather broad profiles of the nitrogen concentration are inconsistent with a thermal equilibrium concentration profile even in the unirradiated case. The surface oxide film may be giving the apparent depletion effect at the surface and contributing to the broadening of the profiles.

Finally, the results on the Ti-Al-V alloy do not agree with some published results on an irradiated Ti-14% Al alloy in which segregation of aluminum to various interfaces was reported.(14) This contrasts with our results in which no strong radiation effect was observed and in fact a slight depletion of aluminum at the surface was observed. There is no apparent reason for the discrepancy except that the rather severe oxide formed on the titanium is complicating the analysis and refined experiments will have to be performed if reliable data are to be obtained.

5. CONCLUSIONS

The surface segregation of impurity type elements during irradiation was surveyed in four candidate fusion reactor alloys. Phosphorus was found to be significantly segregated in 316 type stainless steel and Nimonic PE-16 but not in ferritic HT-9. A smaller effect of radiation on nitrogen segregation was noted in HT-9. A suggestion of a radiation effect on sulfur segregation was noted in 316 stainless steel but not in PE-16 or HT-9. The results are consistent with a radiation induced non-equilibrium segregation but a radiation enhanced diffusion mechanism leading to the thermal equilibrium segregation can not be ruled out. The lack of phosphorus segregation in HT-9 may be related to the presence of molybdenum which combines with the phosphorus. The results suggest that radiation can enhance the rate of phosphorus segregation in 316 SS and PE-16 and therefore may enhance the embrittlement in these alloys. In HT-9 and Ti-6Al-4V, radiation enhanced segregation of embrittling impurities was not observed.

REFERENCES

[1] Proceedings of Workshop on Solute Segre- gation and Phase Stability During Irra- diation, J. Nucl. Mat. 83 (1979).

[2] Okamoto, P. R. and Rehn, L. E., ibid ref. 1, page 2.

[3] Clausing, R. E. and Bloom, E. E., Grain boundaries in engineering materials, in Walters, J. L., Westbrook, J. W. and Woodford, D. A. (eds.), (Claitors, Baton Rouge, 1975) p. 491.

[4] Park, J. Y., Danyluk, S. and Busch, D. E., presented at 5th Bolton Landing Conference, August 1978, Rep CONF 780834-3.

[5] Lam, N. Q., Okamoto P. R. and Johnson, R. A., J. Nucl. Mat. 78 (1978) 408.

[6] Marwick, A. D., Piller R. C. and Sivell, P. M., J. Nucl. Mat. 83 (1979) 35.

[7] McMahon, Jr., C. J., Cianelli, A. K. and Feng, H. C., Mat. Trans. 8A (1977) 1055.

[8] Yen, A. C., Graham, W. R. and Belton, G. R., Met. Trans. 9A, (1978) 31.

[9] Graham, W. R. and Yen, A. C., Met. Trans. 9A (1978) 1461.

[10] Yu, J. and McMahon, Jr., C. J., Met. Trans. 11A (1980) 277.

[11] Lemble, Ph., Pineau, A., Castagne, J. L., Doumoulin, Ph. and Guttmann, M., Met. Sci. 13 (1979) 496.

[12] Doumoulin, Ph., Guttmann, M., Foucault, M., Palmier, M., Wayman, M. and Biscondi, M., Met. Sci. (1980) 1.

[13] Doumoulin, Ph. and Guttmann, M., Mat. Sci. and Engr. 42 (1980) 49.

[14] Erck, R. A., Potter, D. I. and Wiedersich, H., J. Nucl. Mat. 80 (1979) 120.

ACKNOWLEDGMENTS

This work was supported by the Office of Magnetic Fusion Energy of the U.S. Department of Energy. The assistance of L. A. Charlot and H. E. Kissinger is gratefully acknowledged.