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Surface co-segregation of minor alloying elements in Ti-modified stainless steel studied by Auger electron spectroscopy

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Abstract

Surface segregation of alloying elements in Ti-modified stainless steel, D9, upon thermal annealing has been studied using Auger electron spectroscopy. Minor alloying elements viz., P, S, N and Ti were found to segregate to the surface between 670 and 970 K. The influences of pre-annealing thermo-mechanical treatments on the surface segregation behaviour of various elements are presented and their implications are discussed. Cold working was observed to increase the extent of surface segregation. Nitrogen and titanium were found to be co-segregating with carbon and maximum segregation was observed for the cold-worked sample. This observation correlates well with the known secondary TiC precipitation stage, occurring in the cold worked Ti-modified stainless steels.
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1. Introduction

Ti-modified 15Cr–15Ni–2.2Mo stainless steel, D9, is the candidate material for the structural applications in the fast reactor environment [1]. Optimum amount of minor alloying elements and proper thermo-mechanical treatments are known to improve and enhance the resistance to irradiation induced void swelling [1,2]. Among various precipitates formed in Ti-modified stainless steels, MC and M_2P are the most preferred ones due to the fact that they form in nanometer size and are distributed throughout the bulk [2]. MC precipitate formation is also known to take away carbon and suppress $M_{23}C_6$ precipitation at grain boundaries, which are detrimental by way of embrittlement and intergranular cracking [2]. Segregation of alloying elements to surface and grain boundaries is crucial in the usage of the Ti-stabilised stainless steel type D9 alloys for reactor applications, as these structural materials are subjected to prolonged exposure at elevated service temperature of about 823 K and also short time transients to higher temperatures in the reactor environment. Segregation studies are also important from the point of view of effects on weldments of Ti-modified steels, wherein preferential migration of alloying elements is known to cause hot cracking [3]. Auger Electron Spectroscopy

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has been extensively used to study the segregation behaviour of alloying elements in stainless steels [4,5]. In this paper, we report the influence of prior cold work and elevated temperature annealing on the surface segregation of alloying elements in Ti-modified austenitic stainless steel type D9 alloy using Auger electron spectroscopy (AES).

2. Experimental

The iron based D9 alloy is made with Ni (15.068 wt%), Cr (15.051 wt%), Mo (2.248 wt%), Mn (1.509 wt%), Si (0.505 wt%), Ti (0.315 wt%), C (0.05 wt%), Ta + Nb (0.02 wt%), Co (0.015 wt%), P (0.011 wt%), S (0.0025 wt%), B (0.001 wt%) and N (66 wt ppm). The sample history of the alloy is given elsewhere in a detailed study [1]. The samples were cut to a dimension of 8 mm × 8 mm × 0.5 mm and polished to have smooth surface. These samples were solution annealed at 1340 K for 30 min, subsequently held at 1470 K for 5 min and finally furnace cooled. The average grain size is 20 μm. One set of samples were cold rolled to 20% thickness reduction to study the effect of cold work induced segregation behaviour. Chemical composition of segregated elements were monitored using Auger electron spectroscopic measurements as a function of isochronal annealing temperature between 300 and 1000 K for both solution annealed and cold-worked samples. The annealing time at each temperature is 600 s. A cylindrical mirror analyser (CMA) from M/S Omicron, having energy resolution of 0.4% and operating under differential mode, was used for the analysis in an UHV surface analysis chamber. The primary electron beam energy is 3 keV and the beam diameter is 100 μm. The basic vacuum in the analysis chamber was 2.5×10^{-10} mbar. For compositional analysis, the prominent auger lines of Si (92 eV), P (120 eV), S (152 eV), Mo (186 eV), Ar (215 eV), C (272 eV), N (379 eV), Ti (418 eV), O (503 eV), Cr (529 eV), Fe (703 eV) and Ni (848 eV) were used [6]. Auger peak heights of various elements are normalised with respect to that of the Fe (703 eV) line in each spectrum to present relative trends as the annealing temperature is increased. As received samples were sputtered with 3 keV Ar$^+$ ions for 10 min after loading into the UHV chamber so as to remove the surface contamination. Carbon and oxygen were the dominating contaminants in the as received sample. Nearly constant carbon and oxygen levels were reached for the sputtering time of 10 min. Since annealing treatments were done in the same chamber without breaking vacuum, subsequent measurements were done without additional sputtering. In order to verify the surface segregation effects, samples were sputtered after the final annealing step at 973 K with 3 keV Ar$^+$ ions for 10 min.

3. Results and discussion

Fig. 1 compares raw differential Auger spectra for 20% cold-worked D9 alloy with a Ti/C ratio of 6 in: (a) as-received and sputtered condition, (b) after 973 K annealing and (c) sputtered with 3 keV Ar$^+$ ions for 10 min after final annealing. As seen from Fig. 1(a), the major constituents viz. Fe, Cr, Ni, and Mo are clearly seen along with Si, N and Ti. Carbon and Oxygen were found to be present in all the samples under most of the annealing conditions. After annealing at the final temperature of 973 K (Fig. 1(b)), sulphur, nitrogen and titanium are prominently seen along with phosphorous. Surface segregation of S, P, N and Ti is clearly confirmed by the disappearance of S and P along with drastic reduction of N and Ti, after sputtering as shown in Fig. 1(c). The silicon line is seen only after
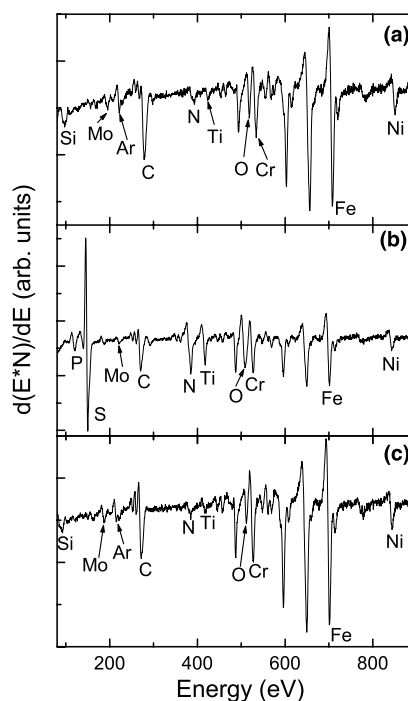

Fig. 1. Auger electron spectra of 20% cold-worked sample with Ti/C ratio of 6 after: (a) as-received and sputtered, (b) annealing at 973 K and (c) sputter cleaning after 973 K anneal.
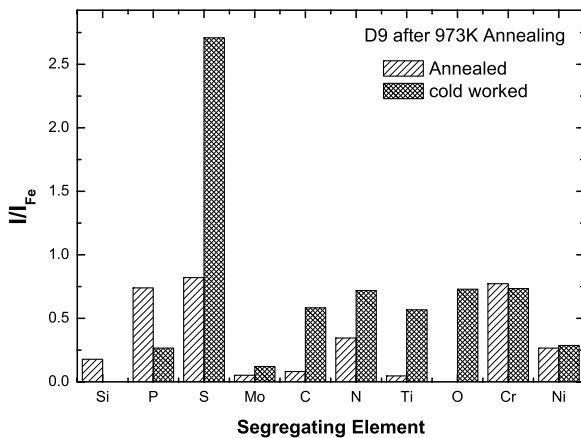
Fig. 2. Variation of normalised Auger peak heights for various elements for solution annealed and cold-worked D9 samples after annealing at 973 K.

Fig. 3. Variation of normalised peak heights of Ti, C and N as a function of annealing temperature in solution annealed and cold-worked samples.

sputtering. These observations are qualitatively similar for the solution annealed sample also.

Fig. 2 compares intensities of various segregated elements for solution annealed and cold-worked samples after final annealing at 973 K. Normalisation of individual elemental peak heights has been done with respect to the Fe (703 eV) peak height. As seen from Fig. 2, Sulphur is the most dominating surface segregating species along with Cr, P, N, Ni and Ti at 973 K, agreeing with previous segregation studies in steels [4,7]. However, the striking feature is the observation of high surface segregation of Ti along with C and N for cold-worked sample. It can be seen that the extent of surface segregation of these elements in the solution annealed sample is appreciably less. Detailed analysis of surface compositional variation of all the elements for various Ti/C ratio will be discussed elsewhere [8]. Here, we discuss the interesting surface segregation of Ti, C and N in annealed and cold-worked samples.

Fig. 3 shows the variation of normalised peak heights of Ti, C and N as a function of annealing temperature in annealed and cold-worked samples. As seen from Fig. 3(a), Ti segregation in solution annealed D9 almost remains constant, except for small peaking around 870 K. On the other hand, the cold-worked sample shows a sharp increase in Ti segregation above 800 K. Surface content of carbon is seen to decrease with increasing temperature for solution annealed D9, while it increases with annealing temperature above 800 K in the cold-worked sample, as shown in Fig. 3(b). Nitrogen segregation in annealed sample, as seen in
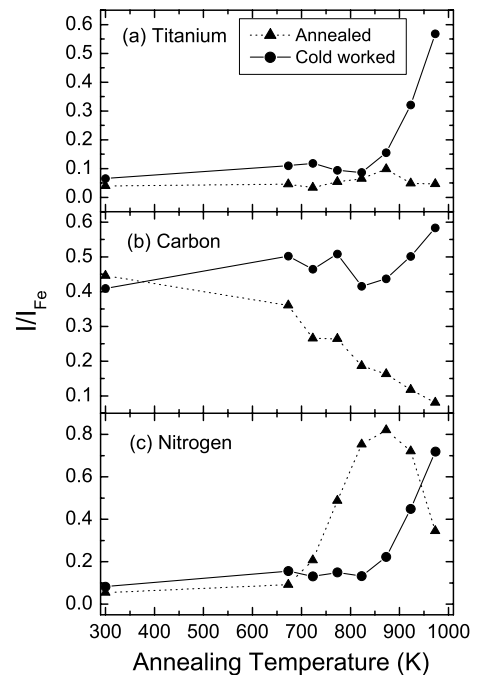
Fig. 3(c), shows a clear peak around 850 K and falls there after. On the other hand, the cold-worked sample shows a sharp increase beyond 800 K. Sulphur segregation increases above 850 K in both annealed and cold-worked samples [8]. This behaviour is consistent with the site competition between N and S. Sulphur, having higher segregation enthalpy, ultimately dominates over N segregation above 850 K in solution annealed sample [5].

The concomitant increase of Ti, C, and N segregation above 800 K in the cold-worked sample can be understood in light of the TiC(N) precipitation in these type of alloys. It is well established that nanometer size TiC(N) precipitation occurs above 800 K throughout the bulk in Ti-modified alloys [2]. Our positron annihilation studies on cold-worked D9 alloy with Ti/C ratio of 6 also revealed a sharp increase in positron trapping above 800 K, as shown in Fig. 4 [9]. The initial fall in positron lifetime at lower annealing temperatures for both D9 and Ti-free model alloy is due to annealing of cold work induced defects. As seen in Fig. 4, the sharp increase in lifetime above 800 K in D9 sample is due to positron trapping at the nano TiC(N) precipitate-matrix interface [9]. The concentration of these nano TiC(N) precipitates increases with increasing
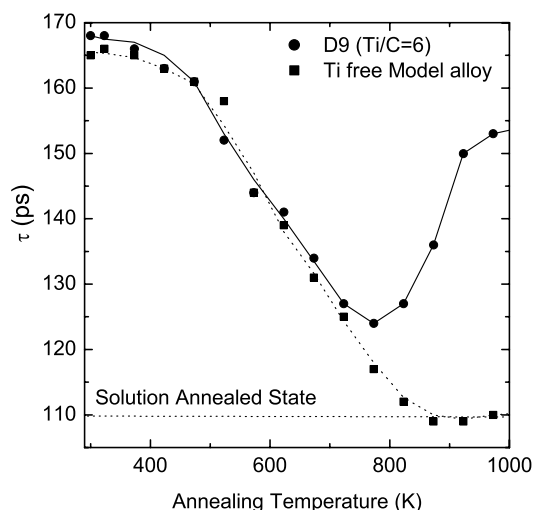
Fig. 4. Variation of positron lifetime as a function of annealing temperature in cold-worked D9 alloy with Ti/C = 6 and Ti-free model alloy [9]. The solution annealed state is marked by the horizontal line. Lines are guides to the eye.

annealing temperatures above 800 K. Such a TiC(N) precipitation is responsible for the present observation of enhanced Ti, C and N surface segregation in cold-worked D9 sample. However, positron lifetime measurements on solution annealed D9 sample did not show any signatures of nano TiC(N) precipitation, which is also in agreement with the present segregation behaviour in solution annealed sample. The controlling mechanism for TiC precipitation in Ti-modified steel was studied in detail using TEM by Kesternich [10]. It was clearly shown that the cold working is a must for TiC precipitation [10]. Diffusing dislocations and Ti-dislocation binding were known to control the nucleation of TiC precipitates at dislocations [10]. These nucleated TiC precipitates subsequently impede the dislocation movement, resulting in sluggish growth kinetics. Rapid growth of TiC precipitates was finally observed to occur along with the grain growth during recrystallisation at temperatures above 1100 K [10]. In light of above observations, the co-segregation of Ti, C and N in cold-worked samples is attributed to the complex

interplay between solute and dislocation binding as well as impeded diffusion and annihilation of dislocations at temperatures above 800 K.

4. Conclusions

The influence of prior cold work and exposure to elevated temperature on the surface segregation of alloying elements in D9 sample was investigated using AES. Prior cold work was found to influence the surface segregation behaviour of S, C, N, Ti and Cr. Sulphur was the dominant segregating species at high temperatures. Ti and N were found to co-segregate along with carbon upon cold working. This co-segregation was associated with the nano-scale TiC(N) precipitation in D9 alloy which agrees well with our earlier positron lifetime measurements.

References

[1] S. Venkadesan, A.K. Bhaduri, P. Rodriguez, K.A. Padmanabhan, J. Nucl. Mater. 186 (1992) 177.
[2] E.H. Lee, L.K. Mansur, J. Nucl. Mater. 278 (2000) 11.
[3] V. Shankar, T.P.S. Gill, A.L.E. Terrance, S.L. Mannan, S. Sundaresan, Metall. Trans. A 31A (2000) 3109.
[4] C.L. Briant, R.A. Mulford, Metall. Trans. A 13A (1982) 745.
[5] H.J. Grabke, ISIJ Int. 29 (1989) 529.
[6] L.E. Davis, N.C. Macdonald, P.W. Palmberg, G.E. Riach, R.E. Weber, Handbook of Auger Electron Spectroscopy, Physical Electronics Industries, Eden Prairie, 1976.
[7] M.M. Eisl, B.M. Reichl, H. Störi, Surf. Sci. 336 (1995) 377.
[8] P. Gopalan, R. Rajaraman, G. Amarendra, to be presented in Int. Conf. on Pressure Vessels and Piping, Chennai, February 2006.
[9] R. Rajaraman, P. Gopalan, B. Viswanathan, S. Venkadesan, J. Nucl. Mater. 217 (1994) 325.
[10] W. Kesternich, Philos. Mag. A 52 (1985) 533;
    W. Kesternich, Mater. Res. Soc. Symp. Proc. 62 (1986) 229;
    W. Kesternich, J. Nucl. Mater. 155–157 (1988) 1025.