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Letter to the Editors

A positron annihilation study of TiC precipitation in plastically deformed austenitic stainless steel

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1. Introduction

Among the radiation-induced degradations of the properties of reactor structural materials, void swelling and helium embrittlement are the two major effects which have received extensive attention over the years. It is now well established that these two problems can be reduced by introducing efficient traps for vacancies and helium such as dislocations and precipitate–matrix interfaces which can be altered by adjusting alloying elements and thermomechanical treatments [1,2]. Accordingly, titanium-modified austenitic stainless steel has become the primary candidate for structural applications, with extensive studies on this alloy in recent years covering different physical and mechanical properties (see Refs. [1–6] and references contained therein). Titanium-modified stainless steel type D-9 with Ti/C ratio of 6 is the material chosen to be used for the fuel clad and the hexagonal wrapper for fuel subassemblies of Prototype Fast Breeder Reactor in India [5]. Studies on D-9 alloys using microhardness measurements [5] showed that 17.5% cold work is the highest prior cold work level that gives minimum variation in hardness on ageing. This is important because, the production of cold-work-induced microstructures that are stable at service temperatures upto 973 K in reactor, is one of the important controlling factors for irradiation-induced void swelling [5]. However, the recent microhardness measurements and refined analysis in D-9 alloys concluded that 20% of cold working is the optimum level for the stability of this alloy [6]. Earlier reported TEM observations in Ti-modified stainless steels [3] also had shown that 20% cold work is the optimum level required for microstructural stability.

Positron annihilation spectroscopy is an established technique for studies on properties of vacancies and dislocations [7] as well as studies on early stages of solute atom clustering and precipitation [8]. Positron annihilation results showing significant refinement of helium bubble size and bubble concentration, upon titanium addition, have been reported in Ti-stabilised austenitic stainless steel [9]. In this letter, we report for the first time, positron lifetime studies on the defect recovery stages associated with TiC precipitation in cold-worked D-9 alloy. These results are compared with the positron lifetime measurements on a Ti-free model austenitic alloy.

2. Experimental

The chemical compositions of D-9 [10] and Ti-free model alloy used in the present study are listed in Table 1. The samples of both D-9 and Ti-free model alloy with dimensions 10 mm×10 mm×1 mm were subjected to solution annealing treatment at 1343 K/30 min followed by 1373 K/5 min [10]. These samples were cold rolled to 17.5 and 50% thickness reduction. Isochronal annealing treatments were done from 300 to 1273 K in steps of 50 K in a vacuum of 10^{-6} Torr. The annealing time for each temperature was fixed at 30 min. Positron lifetime measurements were carried out at room temperature after each isochronal annealing step using a spectrometer having a time resolution of 225 ps (FWHM). The measured positron lifetime spectra were analysed into different lifetime components and their intensities using the programmes RESOLUTION and POSITRONFIT [11].

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Table 1
Chemical compositions of D-9 and Ti-free model alloy used in the present study

Element	Composition (wt%) D-9	Ti-free model alloy
Ni	15.068	14.9
Cr	15.051	15.6
Mo	2.248	2.09
Mn	1.509	2.52
Si	0.505	–
Ti	0.315	–
C	0.05	0.03
(Ta+Nb)	0.02	–
Co	0.015	–
P	0.011	–
S	0.0025	–
B	0.001	–
N_2	66 wppm	–
Fe	Balance	Balance

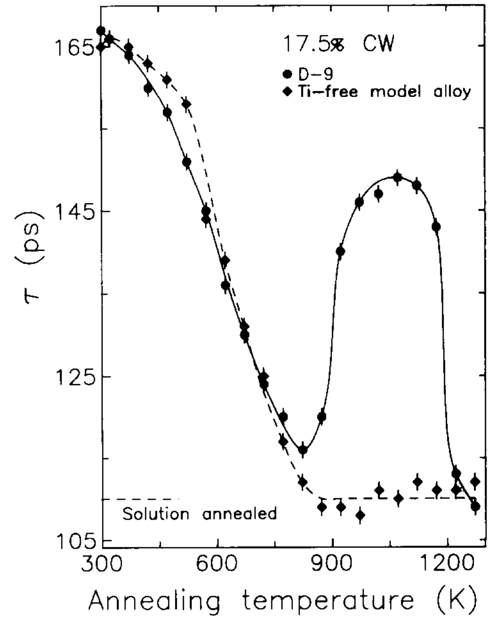

Fig. 1. Variation of positron lifetime with annealing temperature in 17.5% cold-worked D-9 (filled circles) and 17.5% cold-worked Ti-free model alloy (filled squares). Lines are drawn to guide the eye.

3. Results and discussion

Positron lifetime in the solution annealed state for both D-9 and Ti-free model alloy is 110 ± 1 ps. Upon cold working to 17.5% of thickness reduction, D-9 sample yielded a single lifetime of 167 ± 2 ps and Ti-free model alloy showed 165 ± 2 ps. These values correspond to complete trapping of positrons at cold-work-induced defects such as vacancies and dislocations. Fig. 1 shows the variation of positron lifetime as a function of annealing temperature for D-9 and Ti-free model alloy, which were cold rolled to 17.5% of thickness reduction prior to annealing sequence. Only a single lifetime component is observed throughout the annealing range. As seen from the Fig. 1, positron lifetime for the Ti-free model alloy decreases gradually up to 523 K followed by a sharp decrease above 523 K. Lifetime corresponding to the solution annealed state is reached by 873 K. Thereafter no detectable change is observed. On the other hand, in the case of D-9 alloy, lifetime shows a monotonic decrease up to 823 K. Beyond 823 K, a new feature develops in the variation of lifetime corresponding to D-9. As seen in Fig. 1, lifetime increases sharply in the temperature interval of 823 to 1073 K, followed by a sharp decrease above 1073 K for D-9. Lifetime corresponding to the solution annealed state is reached only at 1223 K.

The observed variations are understood as follows. The initial decrease in lifetime up to 823 K in both D-9 and Ti-free model alloy is explained as due to migration of vacancies to sinks such as cold-work-induced dislocations. This will lead to the restructuring and annihilation of dislocations. Similar defect recovery was reported in cold-worked SS 316 using Doppler broadening measurements [12]. Vehanen and coworkers reported microvoid formation in pure iron plastically deformed to 60% of thickness reduction [13], where microvoids have been observed to be stable up to 600 K. In contrast to pure iron [13], both D-9 and Ti-free model alloy do not show vacancy clustering leading to microvoid formation in the annealing interval of 300 to 823 K.

As shown in Fig. 1, the annealing feature exhibited above 823 K in D-9 is due to the effect of addition of titanium, since Ti-free model alloy does not show an equivalent feature. In the TEM studies reported earlier [2,3] the formation of TiC precipitates in cold-worked titanium-modified stainless steel has been observed in the temperature interval of 923 to 1073 K. These earlier studies also show that the process of precipitation of fine TiC particles is dislocation controlled. These TiC precipitates have a face centered cubic lattice structure with an extremely high mismatch in the austenitic matrix having a difference in lattice parameters ranging from 19 to 21%. Large strain arising from this lattice mismatch results in generation of misfit dislocations at the TiC–matrix interface [14]. These misfit dislocations are effective traps for positrons. Hence, the variation of positron lifetime in the temperature range of 823 to 1073 K in D-9 corresponds to positron trapping at the TiC precipitate-matrix interface region. The increase in lifetime indicates an increase in positron trapping rate arising from the increase in number density of TiC precipitates as well as an increase in number of misfit dislocations, since the interface area also increases. Such an increase reaches a maximum at 1073 K, suggesting that TiC precipitation is complete by this temperature. This observation is in accordance with TEM studies reported earlier [3].

Beyond 1073 K, the lifetime corresponding to D-9 de-

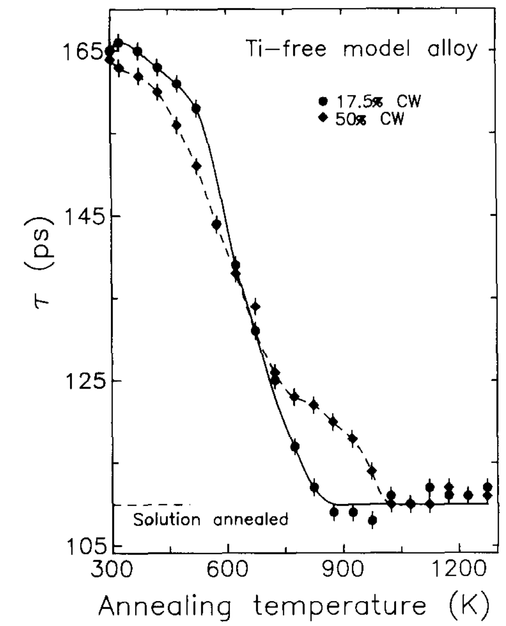

Fig. 2. Positron lifetime variation as a function of annealing temperature corresponding to 17.5% (filled circles) and 50% (filled squares) cold-worked Ti-free model alloy. Lines are drawn to guide the eye.

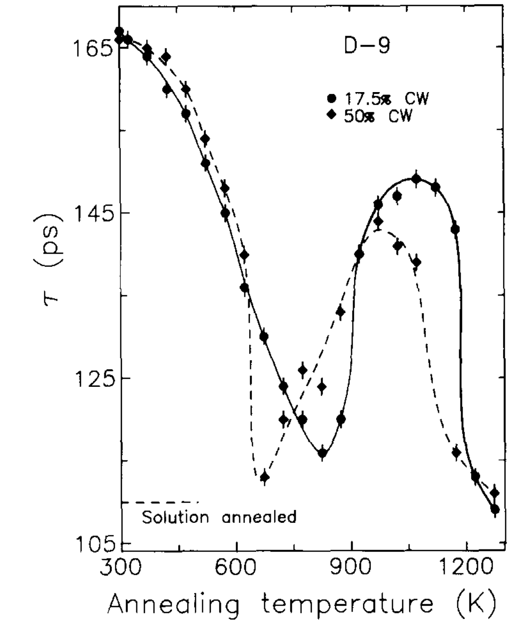

Fig. 3. Variation of positron lifetime parameter with annealing temperature for 17.5% (filled circles) and 50% (filled squares) cold-worked alloy D-9. Lines are drawn to guide the eye.

creases again and reaches that corresponding to the solution annealed state by 1223 K. This decrease in lifetime suggests that the number density of TiC precipitates is decreasing. It could also suggest that the density of misfit dislocations is reduced. Earlier reported studies have shown that fine TiC particles, formed in cold-worked Ti-modified stainless steel at temperatures less than 1073 K, disappear to form coarse TiC precipitates of larger size and smaller number density above the recrystallisation temperature [3]. Vasudevan et al. [15] have recently reported that the recrystallisation occurs at 1073 K for 20% cold-worked alloy D-9 based on microhardness and ultrasonic velocity measurements. Such a recrystallisation would also reduce the density of misfit dislocations. Hence, the present observations can be attributed to rapid coarsening of TiC precipitates at moving recrystallisation fronts. Also, there is a reduction in interfacial barrier between matrix and TiC precipitates due to the rearrangement of atomic structure at the recrystallisation front. This results in a discontinuous change of particle size and concentration as well as density of misfit dislocations from unrecrystallised to recrystallised grains. Thus, the present observation of decrease in lifetime above 1073 K is a clear indication of such a recrystallisation controlled TiC precipitate coarsening.

Effect of degree of cold work on defect recovery stages in Ti-free model alloy is shown in Fig. 2 as a variation in positron lifetime with annealing temperature for 17.5 and 50% cold-worked Ti-free model alloy respectively. As seen from Fig. 2, the defect recovery has shifted to lower temperatures up to 573 K with increasing degree of cold work. This is the normal behaviour expected for defect annealing in cold-worked materials [7]. However, recovery in 50% cold-worked Ti-free model alloy seems to be inhibited beyond 573 K, where lifetime exhibits a shoulder between 800 and 1000 K. Inhibition of defect recovery with increasing degree of cold work suggests that dislocations are pinned down possibly by precipitates, which might have been formed with higher degree of cold work. Indeed, accelerated precipitation of $M_{23}C_6$, which generally occurs as grain boundary precipitate, can also occur on dislocations in the matrix in highly cold-worked austenitic stainless steels [16].

Fig. 3 shows the effect of degree of cold work on defect recovery in D-9. As seen from the figure, defect annealing in 50% cold-worked D-9 is complete by 673 K as compared to 823 K for 17.5% cold-worked sample. Interestingly, the TiC precipitation is also seen to occur at lower temperatures in 50% cold-worked sample, as compared to that in 17.5% cold-worked sample. This shift in temperature for TiC precipitation can be understood as follows. Increased concentration of vacancies produced by higher degree of cold work would enhance solute atom diffusivity. In addition, high density of dislocations generated during cold working provides a large number of heterogeneous nucleation sites [3]. These two factors would lead to enhanced kinetics of TiC precipitation reaction which explains the observed shift in precipitation stage.

Beyond 873 K, the lifetime corresponding to 50% cold-worked D-9 again decreases after reaching a maximum (Fig. 3). This is to be compared with the temperature of 1073 K for the onset of similar stage in the case of 17.5% cold-worked D-9. This indicates that recrystallisation and the associated precipitate coarsening is shifted to lower temperatures with increasing degree of cold work. This is understandable, since a larger driving force is available in the form of higher stored energy for recrystallisation with increasing degree of cold work. Hence recrystallisation and the concomitant coarsening reaction will occur at lower temperatures. Such reasoning is supported by earlier studies reported using TEM [3] and microhardness [6].

4. Conclusions

Positron annihilation spectroscopy has been used in studying the TiC precipitation in Ti-modified austenitic stainless steel type D-9. Comparative study on a Ti-free model alloy has clearly identified the stages of formation of fine TiC particles and precipitate coarsening reaction leading to formation of larger sized TiC precipitates above the recrystallisation temperature. Increasing the degree of cold work has shifted the TiC precipitation as well as onset of recrystallisation and its associated precipitate coarsening to lower temperatures.

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