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Effects of Mn and Si additions on microstructural development in TiAl intermetallic compounds irradiated with He-ions

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Abstract

A Ti-47 at.% Al intermetallic alloy and three TiAl alloys containing ∼2.0 at.% Mn and/or ∼0.4 at.% Si were prepared by powder metallurgical processing. When the samples were irradiated with He-ions to 3 dpa at 773 K, formation of defect clusters and cavities in TiAl alloys were remarkably suppressed by the addition of Mn. In Mn-added TiAl, although no loops, which were observed in pure TiAl and Si-added samples, were formed, the defect clusters with large strain field were found. It was suggested that the defect clusters were formed by the migration of mixed dumbbell type Mn atom-interstitials. The addition of Si showed no beneficial effects on suppression of radiation damage in TiAl alloys.

1. Introduction

Use of TiAl intermetallic compounds for nuclear reactor materials has been considered because both Ti and Al are elements with small neutron-induced radioactivity, compared with conventional materials such as austenitic stainless steels [1]. The TiAl compounds are also expected to have a good potential for high radiation resistance owing to their ordered structures with strong intermetallic bonding [2–5]. One of the problems, which adversely affect their use as engineering materials, is their low ductility at low temperatures and lack of strength at elevated temperatures. In order to improve these properties, new microstructure control processings are developed [6–8]. The addition of third elements like Mn and Si is one useful method for improvement of mechanical properties. It was reported that the addition of Si increased the strength [9]. The addition of 1–3 at.% Mn improved the ductility of TiAl alloys, and their ductilization was attributed to the decrease of the deformation stress due to the increase of twinning deformation [10].

In this study, effects of Mn and Si on radiation damage were investigated for TiAl intermetallic compounds produced by powder metallurgical processing.

2. Experimental procedure

Materials used were four kinds of TiAl intermetallic alloys containing Mn and/or Si produced by powder metallurgical processing. Hereafter these four alloys are designated as TiAl, TiAl–Si, TiAl–Mn and TiAl–MnSi. Powders were prepared from cast mother alloys by a plasma rotating electrode process (PREP) [11]. Cylindrical compacts, 60 mm in diameter and 100 mm long, were made by HIP at 1423 K and 176 MPa for 10.8 ks. The compacts were forged isothermally with a strain rate of 3.8×10^{-4} /s at 1223 K in vacuum. Their chemical compositions are given in Table 1.

Disks, 3 mm in diameter and 0.25 mm thick, were made by wire cutting. The disks were electropolished into foils by a twin jet technique in a solution of 5% perchloric acid and 95% methyl alcohol at 268 K for TEM observation and He-ion irradiation. The 200 keV He-ion irradiation was carried out at 773 K up to 3×10^{21} ions/m^2 with a flux of 6×10^{17} ion/m^{2}s by using a Cockcroft ion accelerator. Although the damage peak

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Table 1
Chemical compositions of the materials used in this study (at.%)

Material	Al	Mn	Si	C	O	Ti
TiAl	46.9	<0.01	<0.01	0.75	0.31	Bal.
TiAl–Si	44.4	0.01	0.39	0.65	0.44	Bal.
TiAl–Mn	43.8	2.2	<0.01	0.61	0.48	Bal.
TiAl–MnSi	42.3	2.2	0.33	0.79	0.55	Bal.

and stopped-ion peak were 760 and 820 nm in depth [5], respectively, microstructure after the irradiation was observed at areas with about 200 nm thichness. The average damage in the area was estimated to be 3 dpa by the TRIM calculation [12], assuming a threshold displacement energy of 25 eV [3].

3. Results

All the samples contained a duplex structure of γ-TiAl and α_2-Ti_3Al with fine and equiaxial grains. Microstructures of the unirradiated samples are shown in Fig. 1. Mn-rich precipitates, about 300 nm in diameter, are mostly found on the grain boundaries in TiAl-Mn. Their typical composition is Ti-43 and Al-6 at.% Mn, which was determined by EDS analysis. A lot of small spherical Si-rich precipitates are observed in TiAl–Si and TiAl–MnSi. These precipitates are located in the matrix, and their sizes range from about 20 to 200 nm in diameter. Moreover, in TiAl–MnSi, the precipitates with a composition of Ti-18 at.% Al-3 at.% Mn-25 at.% Si are also found on grain boundaries.

Microstructures of radiation-produced defect clusters are compared with TiAl, TiAl–Si, TiAl–Mn and TiAl–MnSi (γ-grains) after irradiation to 3 dpa at 773 K in Fig. 2. The cluster density and average diameter are summarized in Fig. 3. Loops $5 \times 10^{21}/m^3$ in density and 25 nm in diameter are formed in TiAl. The loops are lying on {1 1 1} planes. In TiAl–Si, density of loops increases to $8 \times 10^{21}/m^3$, but their diameter decreases to 8 nm. Although no loops are formed, fairly large defect

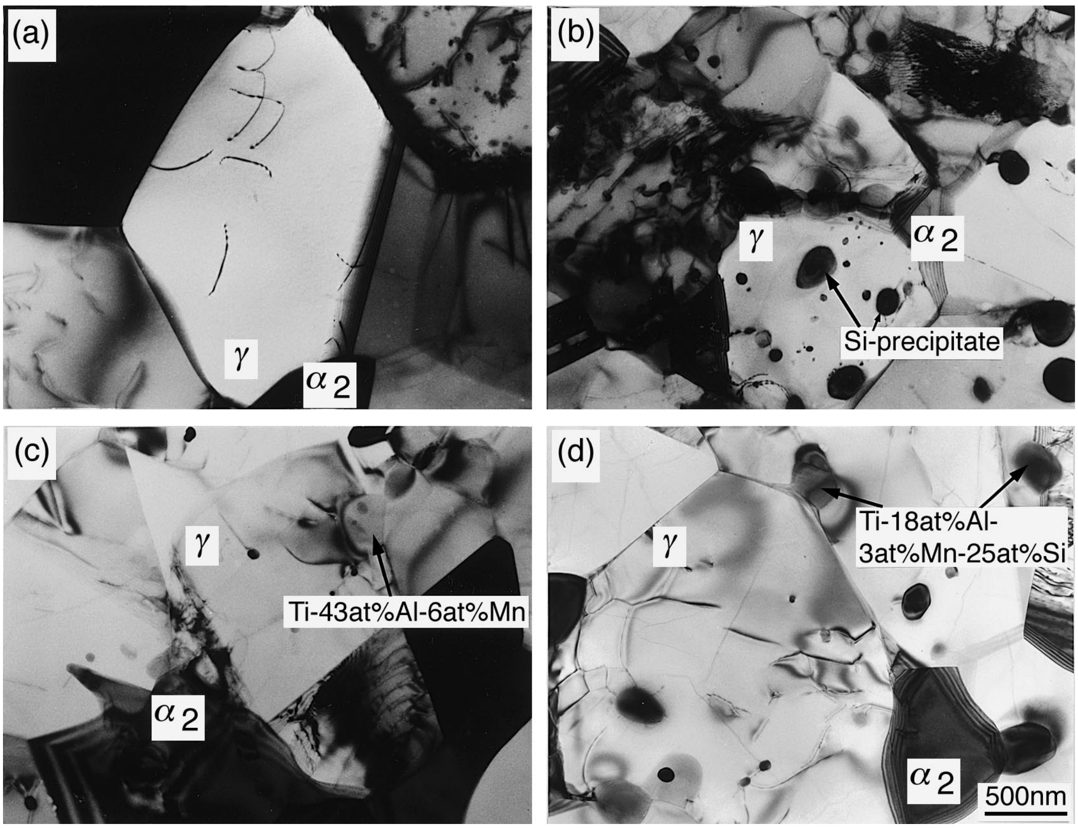

Fig. 1. Microstructures before irradiation in (a) TiAl, (b) TiAl–Si, (c) TiAl–Mn and (d) TiAl–MnSi.

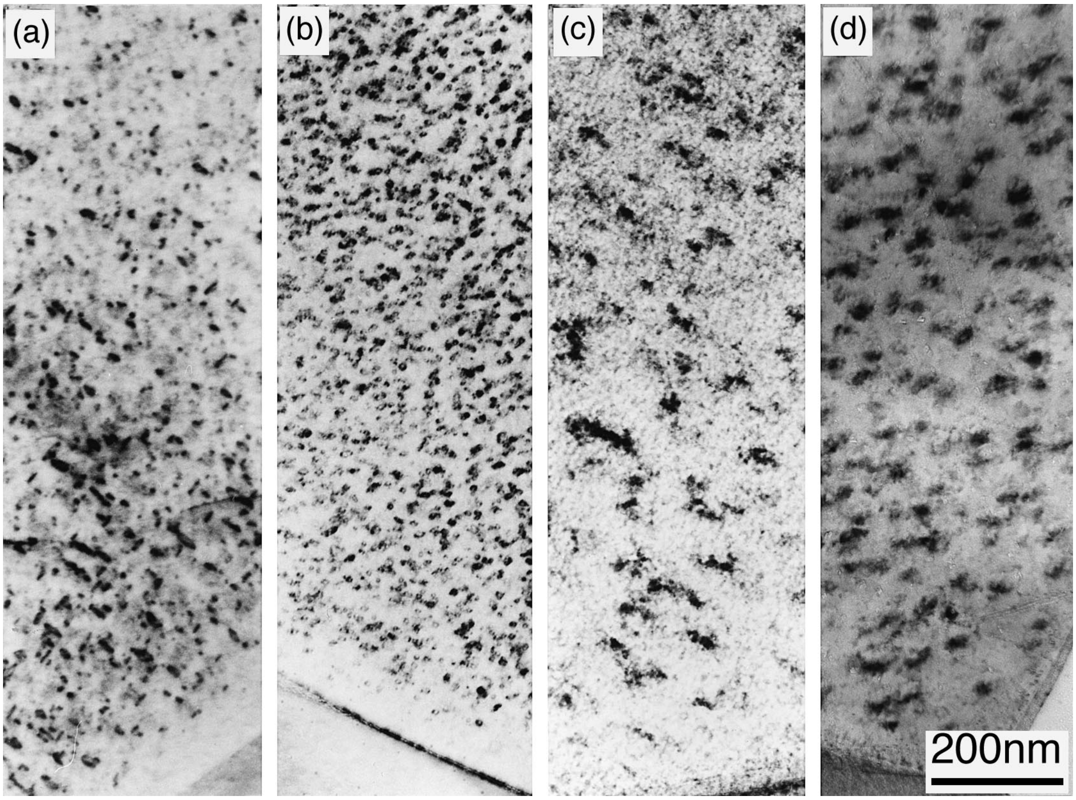

Fig. 2. Damage structures in (a) TiAl, (b) TiAl–Si, (c) TiAl–Mn and (d) TiAl–MnSi after the He-ion irradiation to 3 dpa at 773 K.

clusters of 80 nm in diameter, lying on (0 0 2) planes, are formed with a low density of $0.6 \times 10^{21}/m^3$ in TiAl–Mn. When EDS analysis was carried out in the irradiated TiAl–Mn using a FE-TEM with a 1 nm electron probe, Mn enrichment of about 1 at.% in the clusters was found. Similar clusters are also found in irradiated TiAl–MnSi, but the density of $2 \times 10^{21}/m^3$ is slightly higher than that in TiAl–Mn.

Table 2 gives cavity data and swelling calculated from the data for the samples irradiated to 3 dpa at 773 K. The cavity density in TiAl–Si, $1.0 \times 10^{22}/m^3$, is nearly the same as that in TiAl, but the cavity formation is completely suppressed in TiAl–Mn. In the sample containing both Mn and Si, cavities at a low density of $3 \times 10^{21}/m^3$ appear. This result suggests that cavity formation at 773 K is remarkably suppressed by the addition of Mn, and the Mn addition is beneficial to reduction of swelling in TiAl alloys.

In order to study the stability of defect clusters, some of the irradiated samples were annealed isochronally for 720 K at steps of 50 K. The changes of cluster density due to the isochronal annealing are shown in Fig. 4 for TiAl, TiAl–Si and TiAl–Mn. The loops produced in TiAl and TiAl–Si are annihilated above temperatures of 823 K, and annealed out up to 973 K. On the other hand, no defect clusters in TiAl–Mn are annihilated below 973 K. The clusters gradually disappear above 1023 K, but they are not completely annihilated even at 1073 K for 1.2 ks. The result suggests that the clusters in TiAl–Mn are more stable than those in TiAl and TiAl–Si. The microstructures after the annealing at each temperature are shown in Fig. 5, comparing in the same area of the sample. As irradiated, defect clusters and Mn-rich precipitates are observed in the matrix, and Mn-rich precipitates are also found on the grain boundary. While little structural change can be seen after the annealing at 973 K, new small precipitates (indicated by arrows in the figure), which also contain Mn, are formed on the grain boundary at 1023 K. The pre-existent Mn-rich precipitates, as well as the new ones, grow at that temperature.

4. Discussion

In the samples with added Mn, the damage structure was changed drastically: no loops appeared but defect clusters with a large strain field were formed during irradiation. According to EDS analysis, Mn was slightly

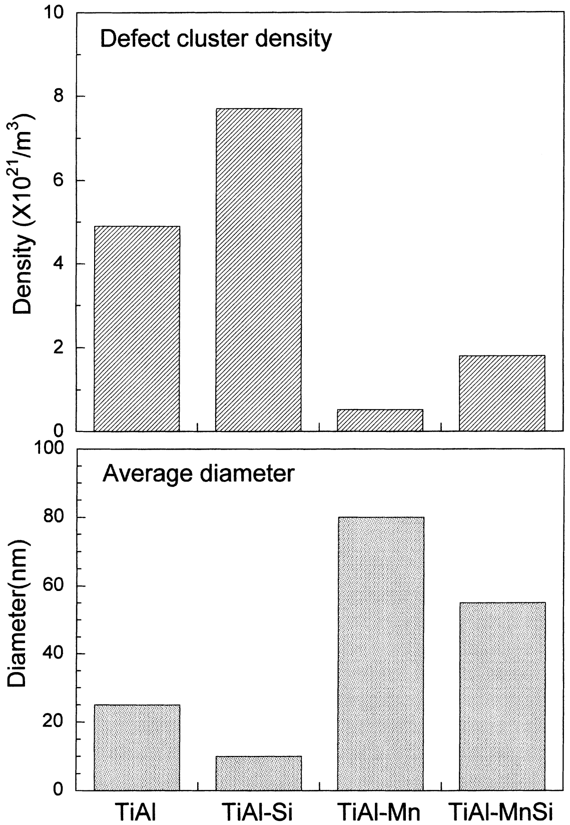

Fig. 3. Defect cluster density and average diameter in the samples irradiated to 3 dpa at 773 K.

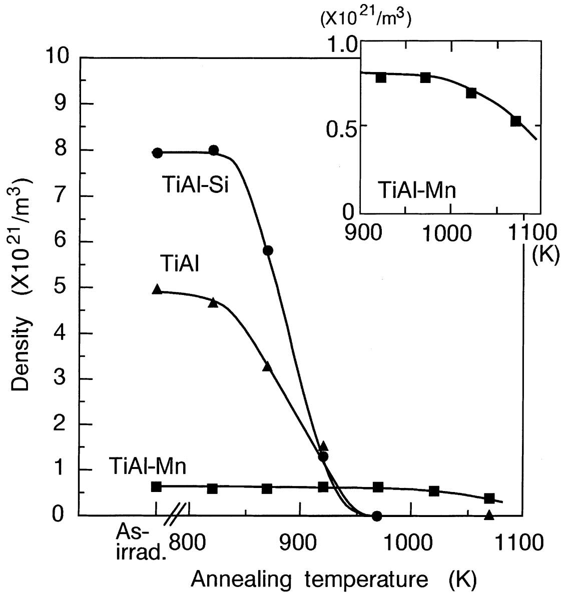

Fig. 4. Isochronal annealing curves of defect cluster density in TiAl, TiAl–Si and TiAl–Mn after the irradiation to 3 dpa at 773 K. (Annealed for 720 s at steps of 50 K.)

enriched in the clusters. Judging from the isochronal annealing experiment (Fig. 4), the clusters were more stable compared with the loops formed in TiAl and TiAl–Si. The temperature at which the clusters began to be annihilated was consistent with the temperature that new Mn-rich precipitates were formed and the Mn-rich precipitates existing before irradiation were enlarged (Fig. 5). From these results, it is concluded that the clusters are related to Mn atoms.

Mn atoms mainly replace Al atoms in the $L1_0$ ordered structure, according to X-ray diffraction analysis [13]. A Mn atom has a smaller atomic radius than Ti and Al atoms: in other words, it is an undersized atom in TiAl alloys. So, Mn atoms seem to form mixed dumbbell interstitials, as shown in Fig. 6(a). In order to keep the ordered structure, the mixed dumbbell interstitials migrate only on the (0 0 2) plane in four jump directions, because of the high antiphase boundary energy in the TiAl $L1_0$ structure [14]. Therefore, migration of the interstitials seems to result in Mn-rich interstitial clusters on the (0 0 2) plane, as demonstrated in Fig. 6(b).

On the other hand, although Si atoms also acted as nucleation sites of loops (Fig. 2), the addition of Si did not changed the radiation behavior of TiAl so much. This seems to be due to the small solubility of Si in TiAl, based on the observation that a large number of spherical Si-rich precipitates were found in unirradiated TiAl–Si (Fig. 1). These precipitates cause an increase in strength of TiAl alloys, but they have a small interaction with radiation-induced defects.

Table 2
Cavity data and swelling in the samples irradiated to 3 dpa at 773 K

Sample	Density (/m^3)	Average diameter (nm)	Swelling (%)
TiAl	9×10^{21}	3	0.013
TiAl–Si	1.0×10^{22}	3	0.014
TiAl–Mn	–	–	0
TiAl–MnSi	3×10^{21}	3	0.005

5. Summary

In order to clarify the effects of Mn and Si on radiation damage, TiAl intermetallic alloys containing Mn (about 2 at.%) and/or Si (about 0.4 at.%) were irradiated with He ions at 773 K up to 3 dpa, and the damage structure and annealing behavior of defect clusters were studied. The main results are summarized as follows:

1. The formations of defect clusters and cavities during irradiation in TiAl were remarkably suppressed by the addition of Mn.

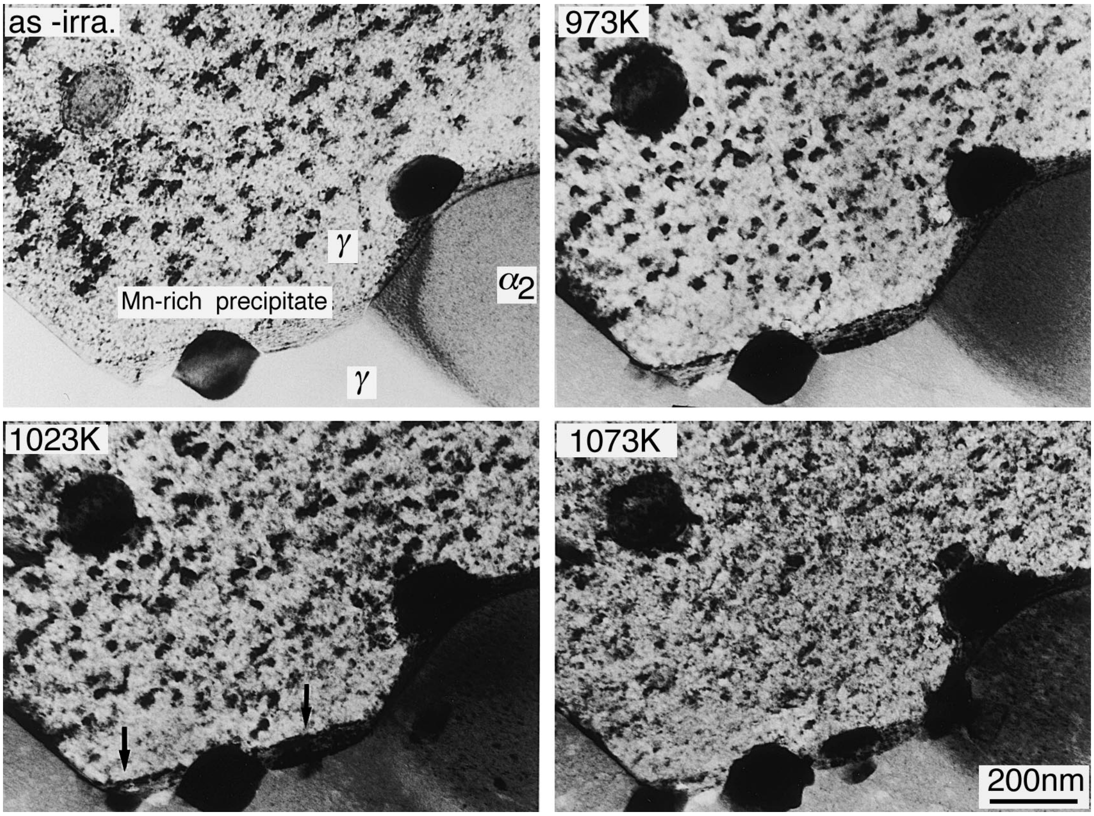

Fig. 5. The change of damage structure during isochronal annealing in TiAl–Mn. The annealing temperatures are indicated in the figure.

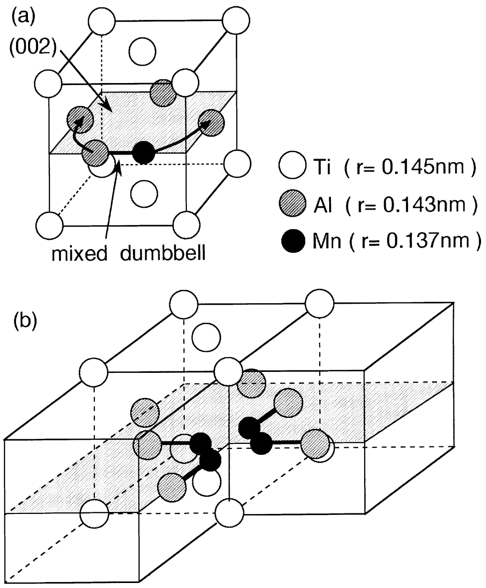

Fig. 6. Migration of a mixed dumbbell interstitial, (a), and an interstitial cluster related to Mn atoms, (b), in the $L1_0$ ordered structure of TiAl–Mn.

2. In Mn-added TiAl, the loops were not formed, but the defect clusters with a large strain field were formed, which were related to Mn atoms as conformed by EDS analysis and the isochronal annealing experiment.
3. The addition of Si showed no beneficial effects on suppression of radiation damage in TiAl alloys.

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