Proceedings of the Korean Nuclear Society Spring Meeting
Kwangju, Korea, May 1997

Formation of Particles in the Laser Melted Zone of Alloy 600

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Abstract

Studies on particles formed in the laser melted zone (LMZ) of sensitized Ni base Alloy 600 have been carried out using microscopic equipments. Most of them were identified as TiN type and MgS type particles were also found in the cell boundaries. All of the particles were located in the cellular solidification regions, but no particle was formed in the plane front solidification regions of the LMZ. Cr carbides which had formed during sensitization treatment were completely melted during laser surface melting and hardly re-precipitated during the matrix solidification.

1. Introduction

It is now well recognized that Ni base Alloy 600 which have been widely used for steam generator tubes in nuclear power plants are susceptible to localized corrosion such as intergranular corrosion (IGC) and/or intergranular stress corrosion cracking (IGSCC) in the primary and secondary cooling water of PWR in some environments. These failures are known to be caused by precipitation of Cr carbides and resultant creation of Cr depletion zones along the grain boundaries[1,2]. Therefore, Alloy 600 is now being replaced with Alloy 690 which is more resistant to IGC/IGSCC due to a higher Cr content than Alloy 600 is. However, up to now, the only remedy to the tubes failed during plant operation is sleeving or plugging, which is not efficient for the operating plants. Since the late 1980s, laser surface melting (LSM) has been being studied as an in-situ repairing technique for the degraded areas in steam generator tubes.[3]

As reported earlier, LSM of sensitized Alloy 600[4], and sensitized stainless steels[5,6] improves IGC and IGSCC resistance. It is caused mainly due to characteristically microstructural and compositional changes during solidification process of these Alloys, such as de-sensitization (or healing) of Cr depleted zones and Cr enrichment in the cell boundaries and grain boundaries in the laser melted zone (LMZ). The microstructure of the LMZ of Alloy 600 consists of fine cells (or, dendrites in a crystallographical sense) with narrow plane front solidification regions. The charactristic feagure in LSM of Alloy 600 was formation of TiN type particles along the cell boundaries with tangled dislocations around them. For more details on TiN type particles, see Reference 7. Fine particles with a large number density and associated dislocations might influence advantageously or disadvantageously the mechanical properties such as micro-hardness or creep. Therefore, it is necessary to look more closely into these particles and know the mechanism of their formation in the LMZ. In this paper, we presented experimental results on particles in the LMZ using a transmission electron microscope (TEM) equipped with EDS (energy dispersive X-ray spectroscope) and a scanning electron microscope (SEM).

2. Experimental Procedures

2.1 Materials and heat treatment : A plate, 1.6 mm in thickness, of commercially mill-annealed Ni · base Alloy 600 was used in this study and the chemical composition of this alloy is listed in Table 1. Before laser surface melting, the specimens sealed in a quartz tube were solution annealed at 1050 ℃ for 30 min. and subsquently water cooled, followed by sensitization treatment at 600 ℃ for 24 hours in a vacuum furnace.

2.2 Laser surface melting : Laser surface melting of the sensitized specimens was carried out using a 4 kW CO_2 CW laser. Before laser melting, the specimens were polished on a 600 grit SiC paper to increase the absorption of laser beam. During laser treatment, a continuous flow of Ar (30 l/min) was blown onto the surface around the laser beam to prevent the melted region from oxidation. In Table 2, the important laser parameters used in this study are summarized. To get an area large enough to make TEM specimens, the specimens were scanned by overlapping the treated tracks by about half of the beam size.

2.3 Specimen preparation for microscopy : TEM, JEOL 2000FX II equipped with a Oxford Link Energy Dispersive X-ray Analyser, was used to examine the particles of the laser surface melted specimens. Thin foils were prepared by thinning mechanically down to approximately 15 μm, followed by ion milling processs to get the final TEM specimens. SEM was also used to observe the shapes and the distribution of the particles in the LMZ clearly. The specimens for SEM were made by etching the polished samples with solution of 2% hydrochloric acid and 98% methanol for 2-3 sec at 6V.

3. Experimental Results and Discussion

Fig. 1 represents a schematic drawing of microstructural changes in the sensitized Alloy 600 by laser surface melting, which shows the typical solidified microstructure during welding. It consists of three different zones, a LMZ, a heat-affected zone (HAZ), and an unaffected bulk zone (matrix). Here we will restrict our discussions to the LMZ.

In our earlier papaer[7], we reported that 1) the microstruture of the LMZ was mainly cellular (or dendritic), growth direction of cells was always parallel to <100>, and the cell spacing was approximately 1.5 μm, 2) the crystal structure of the solidified regions was γ austenite like that of the bulk matrix, 3) Cr segregation occurred in the cell boundaries, 4) very tiny particles, whose size was measured to be up to approximately 150 nm, were shown along the cell boundaries with tangled dislocations around them, 5) the particles had fcc sturcture with lattice constant approximately 4.2 Å, and finally, 6) the major metallic element of the particles was Ti with minor metallic elements Cr and Nb, and with non-metallic element N (possibly C), which mean that the particles were titanium nitride type particles.

From further experiments, another type of particles, supposed to be magnesium sulfide type were also found. MgS has fcc structure (NaCl type) which is same as that of TiN, with lattice constant 5.1913 Å[8]. They were always found as being sticked with TiN with the exception of rare occations. Their size was measured to be up to approximately 50 nm, which is even smaller than TiN type particles. MgS is known to react with water and easily decompose. Therefore, the conventional carbon extraction replica method is not useful to detect its chemical composion since the use of water is common for unrolling a carbon extraction replica. Fig. 2(a) shows the sticked TiN and MgS particles in a thin foil specimen. Fig. 2(b) shows EDX spectra obtained from TiN, and Fig. 2(c) from MgS. Here, Cu peaks come from a Cu grid. The atomic percents of Mg and S (except Cr, Fe and Ni which come from the matrix) were nearly 50%:50%, which clearly means that the particle is a MgS type.

The particles were distributed uniformly (and especially along the cell boundaries) all-over the cellular solidification regions of the LMZ, as shown in Fig. 3. An approximate number density of particles is 10^{13} #/cm^3, which is very large. Moreover, there is no particle in the plane front solidification regions of the LMZ, as shown in Fig. 3. The plane front solidification regions are characterized as dislocation- and particle-free, which is quite different from the cellular solidification regions.

Cr carbides having formed along grain boundaries during sensitization treatment, were not observed in the LMZ, which means that all carbides were completely dissolved, and there might not be enough time for Cr carbides to precipate during rapid solidification.

4. Conclusion

From the microscopic study on the particle formation in the laser melted zone of Alloy 600, the following conclusions could be derived.

1. TiN and MgS type particles were formed during laser surface melting with a large number density.
2. The particles were distributed uniformly along the cell boundaries all-over the cellular solidification regions, but no particle was formed in the plane front solidification regions.
3. Cr carbides which had formed by heat treatment were completely melted during laser surface melting and hardly re-precipitated.

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Table 1. Chemical composition of Alloy 600 (wt%)

Ni	Cr	Fe	C	S	Mo	Co	Si	Mn	Al	Cu	Ti	Nb	Mg	N
Bal.	15.9	7.6	0.04	0.002	0.25	0.38	0.15	0.17	0.12	0.22	0.21	tr.	0.008	0.04

Table 2. Laser parameters used in the experiments

Real laser power	500 W	Beam diameter	1 mm
Beam scanning rate	200 cm/min.	Scanning mode	Multi overlapped

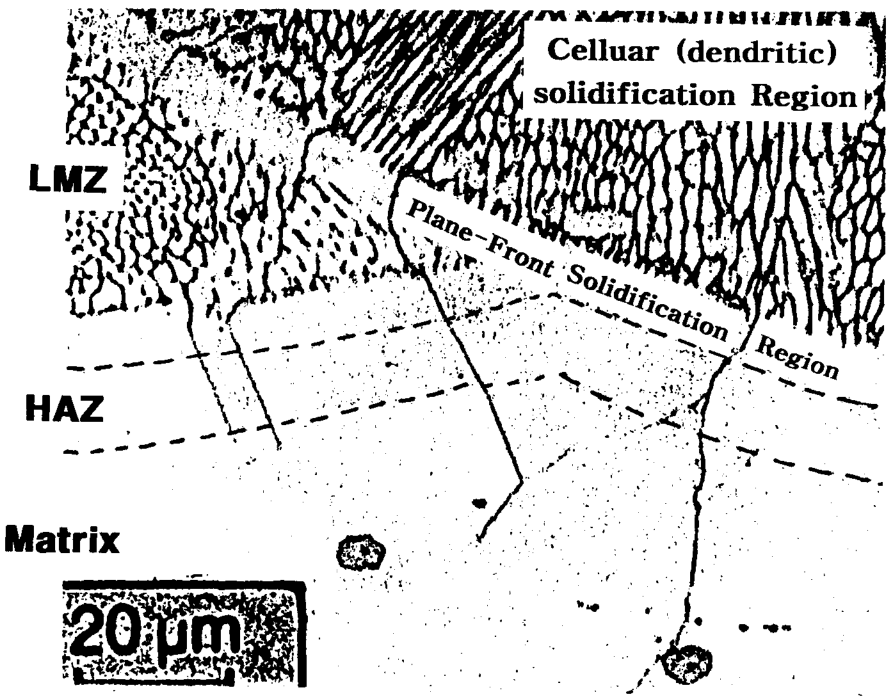
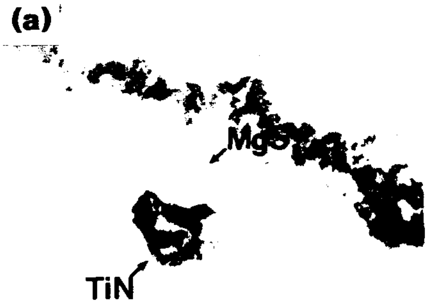


Fig. 1. Schematic drawing of laser surface melted Alloy 600



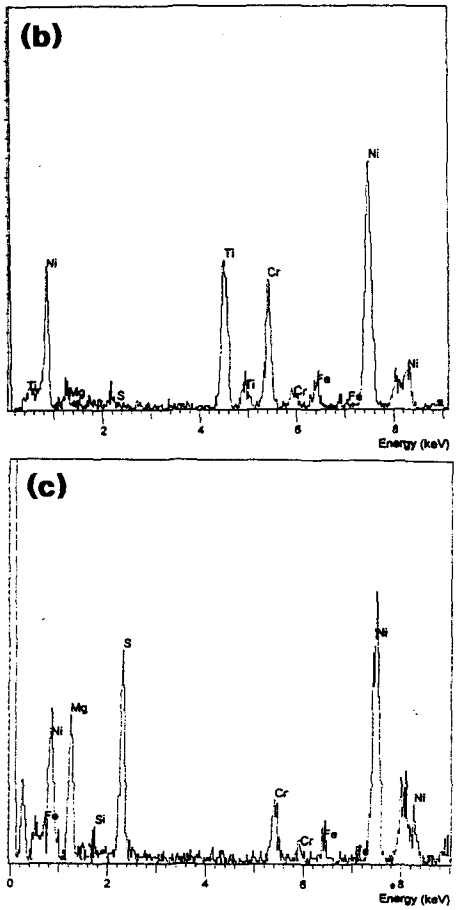


Fig. 2. (a) Bright-field image of sticked particles in the LMZ;
(b) EDX spectra from TiN in (a);
(c) EDX spectra from MgS in (a)

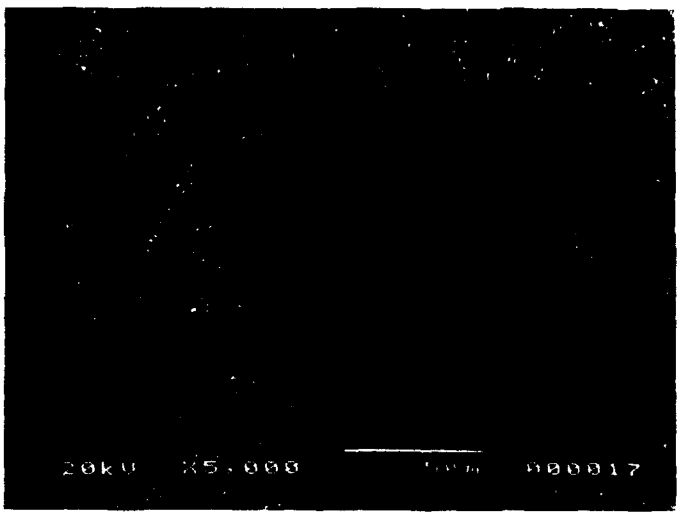


Fig. 3. SEM micrograph showing the distribution of particles in the LMZ