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Microstructure of Laser Surface Melted Ni-Base Alloy 600 after Heat Treatment

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Abstract

A study of heat treatment effects on laser surface melted Ni-base alloy 600, especially on precipitation behavior and chemical composition changes on the grain boundary were conducted with microscopic equipments. Long-term aging treatment at 400 ℃ caused no considerable effects on the grain boundary properties. Cr-rich $M_{23}C_6$ *and* Cr_7C_3 *carbides were precipitated and the resultant Cr depletion below 12 wt pct on some high angle grain boundaries was occurred by heat treatment at 600 ℃ for 24 hours. These results can imply that the resistance of intergranular stress corrosion cracking of heat treated alloy 600 might not be changed considerably in comparion with the as-LSM one.*

1. Introduction

It was reported that laser surface melting (LSM) of sensitized alloy 600[1] prevented intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC), which are major failures of this alloy during operation of nuclear power plants. The main causes for improvement on localized corrosion properties come from the microstructural changes during LSM, such as complete melting of pre-existed Cr carbides, its resultant disappearance (or healing) of Cr depleted zones, and Cr enrichment in the cell boundaries according to solute segregation during matrix solidification[2]. It can be therefore expected that the laser treated area or the laser melted zone (LMZ) provides an effective barrier between the corrosive environment and the underlying sensitized substrate.

The next step to be studied is how the microstructure of LSM alloy 600 changes due to the real nuclear power plant operation. Since a nuclear power plant continually operates at high temperature, no considerable changes should be occurred in the microstructures and compositions even after long-term operation.

In the present paper, microstructural changes due to heat treatments of LSM alloy 600 were examined with a transmission electron microscope (TEM) equipped with an energy dispersive X-ray analyzer (EDX) and a scanning electron microscope (SEM).

2. Experimental Procedures

Since the present study is a part of a series of experiments on the microstructural changes of the Ni-base alloy 600 by LSM, many parts of experimental methods are identical to those given in Ref. 2. They include the chemical composition of specimens used, the important parameters for laser treatment, and the preparation methods and equipments for TEM specimens. The only differences are isothermal heat treatments of laser treated specimens, and their subsequent SEM and TEM observations.

Isothermal aging experiments were conducted after LSM at two temperatures which simulate various service conditions. The first of these was 400 ℃ for 235 days, which should simulate at some what shorter times microstructural changes that would occur at the normal reactor service temperature of 320 ℃ (hereafter, long-term aging treatment). The second is 600 ℃ for 24 hours, which is known as the most susceptible heat treatment condition to SCC for this alloy[2](hereafter, sensitization heat treatment).

The specimens for SEM observation were made by etching the polished samples with solution of 2% HCl and 98% methanol at 6 V for about 3-5 sec. As can be seen later, this etching condition shows clearly not only the compounds such as TiN and MgS type particles but also the grain boundary Cr carbides such as Cr-rich $M_{23}C_6$ and Cr_7C_3.

3. Experimental Results and Discussion

3.1 as-LSM alloy 600

The microstructure and its characteristics of alloy 600 due to LSM were given elsewhere[2,3], therefore, it will be briefly mentioned on the parts which are relevant to discussion on the heat treatment effects of laser treated alloy 600.

Fig. 1 is a SEM micrograph which shows the particle distribution in the LMZ.

In this figure it can be seen that tiny particles are distributed along the cell boundaries in the celluar solidification regions with a large number density. They were indentified as TiN type particles. Another type of particle, MgS, was also found as being stucked on TiN type. By the high power density of a laser beam, TiN inclusions pre-existing in the matrix before laser treatment had been dissolved and re-precipitated as new TiN type particles with different compositions. Additionally, no Cr-carbides on the grain boundaries are seen in the figure, which means that Cr-rich carbides such as $M_{23}C_6$ and Cr_7C_3 in the sensitized specimen had been completely melted/dissolved and did not re-precipitate during re-solidification due to the fast cooling in the LSM process[2].

3.2 Long-term aging treatment

Fig. 2 shows a microstructure of LSM alloy 600 after long-term aging treatment (400 ℃ for 235 days). From this figure, it can be cleary seen that the characteristics of TiN and MgS type particles, such as the distribution, number density, volume fraction, etc. were not changed after the aging treatment. Moreover, no Cr-carbides such as Cr-rich $M_{23}C_6$ and Cr_7C_3 were precipitated on the grain boundaries in the LMZ, and accordingly, Cr depletion along the grain boundaries did not occur, as confirmed by TEM observation. From these results, it can be expected that IGA/IGSCC resistance of the LSM alloy 600 after the aging treatment would be same as the as-LSM alloy 600.

3.3 Sensitization heat treatment

Fig. 3 is an SEM image of the LSM alloy 600 after sensitization heat treatment. First of all, the characteristics of high temperature compounds, TiN and MgS type particles, inside the grain boundaries were not changed, like Fig. 2, after the aging treatment. However, small and discrete precipitates are seen on some grain boundaries. From TEM observation, they were identified as Cr-rich $M_{23}C_6$ and Cr_7C_3.. Fig. 4 (a) is a TEM bright field image which shows grain boundary Cr-rich carbides. Cr-rich $M_{23}C_6$ has a bulky shape and it was found, as reported[4], to have a cube-cube orientation relationship, such as $\{100\}_\gamma//\{100\}_{M23C6}$, $<100>_\gamma//<100>_{M23C6}$, with one grain of the matix as shown in Fig. 4 (b). Another type of Cr-rich carbide, Cr_7C_3, has a long needle or plate shape as shown in Fig. 4 (a). And the characteristic of Cr_7C_3 was identified to have stacking faults in it[5] by the bright and the dark field images at high magnification. Fig. 4 (c) is a selected area diffraction pattern taken from Cr_7C_3, which shows some streaks due to stacking faults in Cr_7C_3.. However the size and the number of Cr-rich carbides precipitated on the grain boundaries were much smaller than those of the fully sensitized and not laser treated alloy 600, therefore, the Cr depletion around the grain boundary was not so severe. The minimum Cr concentration at the grain boundary was measured 12 wt%. It is higher than 10 wt% which is known as the critical value of IGA/IGSCC sensitization for alloy 600[6]. Moreover Cr-rich carbide precipitation was found to precipitate only at some high angle grain boundaries. These results can imply that the resistance of IGA/IGSCC of sensitization heat treated alloy 600 might not be changed considerably in comparion with the as-LSM one.

4. Conclusion

From the microscopic study on heat treatments of LSM alloy 600, the following conclusions could be derived.

1. The characteristics of high temperature compounds, TiN and MgS type particles, were not affected by long-term aging treatment (400℃ for 235 days) and sensitization heat treatment (600℃ for 24 hours).
2. Any other microstructural and compositional changes were not occurred by the long-term aging treatmennt.
3. Cr carbides such as Cr-rich $M_{23}C_6$ and Cr_7C_3 were precipitated at some high angle grain boundaries by the sensitization heat treatment, and the minimum Cr concentration was measured 12 wt%.
4. From the experimental results, it can be expected that resistance to IGA/IGSCC of the heat treated alloy 600 might not be changed considerably by these heat treatments in comparision with the as-LSM one.

Reference

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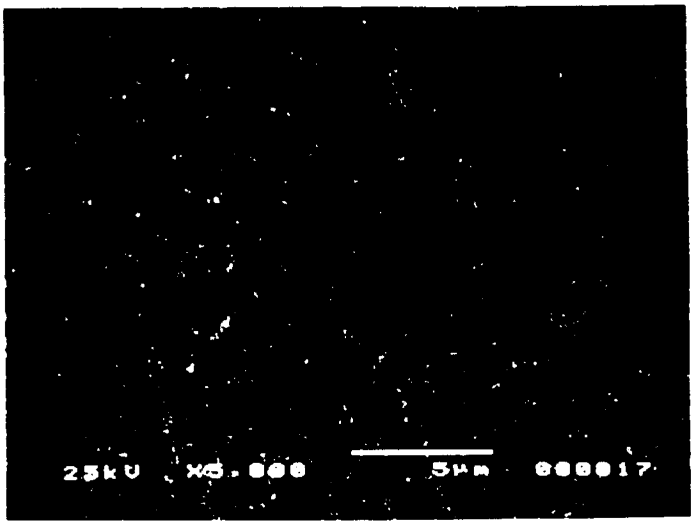

Fig. 1 SEM micrograph showing particle distribution in the LMZ of as-LSM Ni base alloy 600

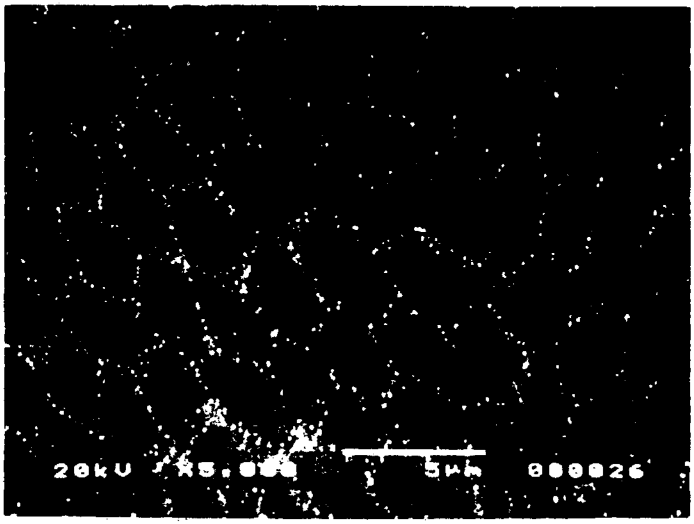

Fig. 2 SEM micrograph showing particle distribution in the LMZ of Ni base alloy 600 after long-term aging treatment (400℃ for 235 days)

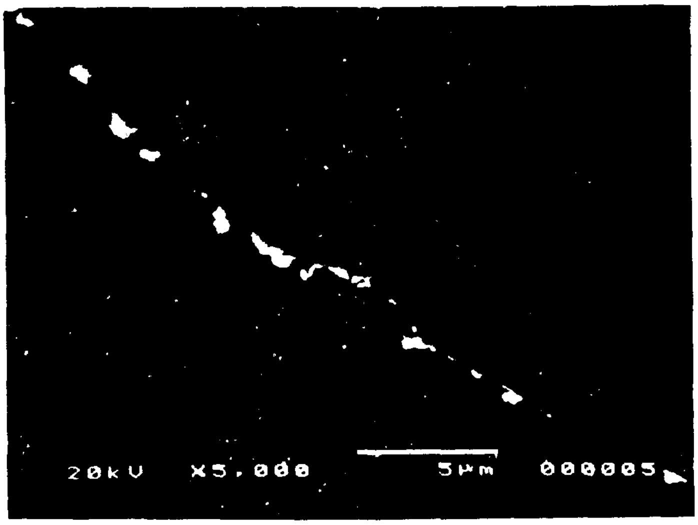

Fig. 3 SEM micrograph showing particle distribution in the LMZ of Ni base alloy 600 after sensitization heat treatment (600℃ for 24 hours)

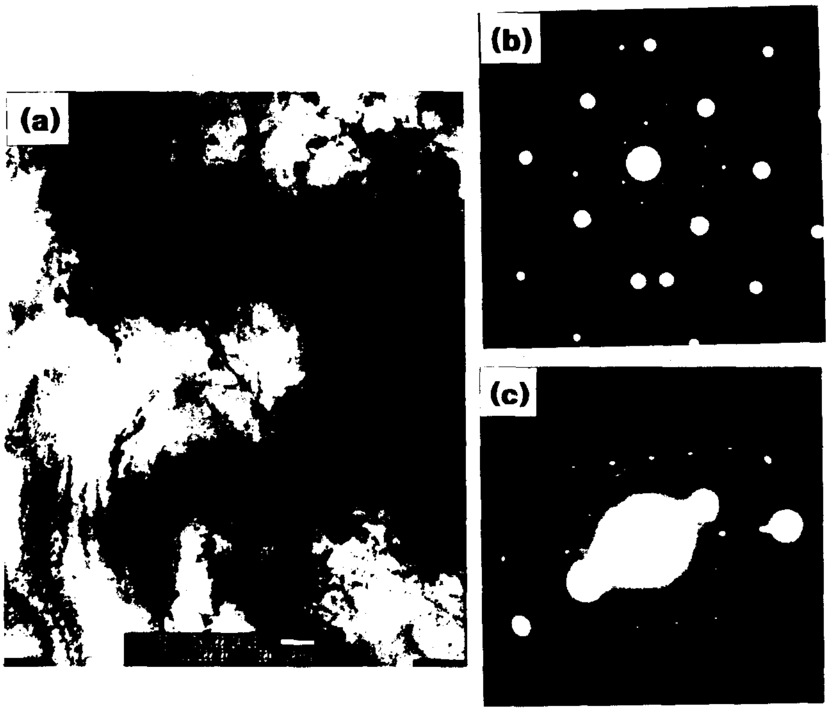

Fig. 4 (a) TEM bright field image showing grain boundary Cr-rich carbides,
(b) diffraction pattern taken from Cr-rich $M_{23}C_6$, and
(c) diffraction pattern taken from Cr_7C_3