Morphology of Internal Scale Formed in Waspaloy by High-temperature Sulfidation

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Ni-Cr based alloys form an internal scale in the alloy interior by selective sulfidation of elements having a large affinity for sulfur together with an external scale formation on the alloy surface by high-temperature sulfidation. To examine directly the 3-dimensional morphology of the internal scale, authors have developed a metal matrix dissolution technique[1,2] for the sulfidized Ni-Cr based superalloys without dissolving the metallic sulfide phases constituting the scale by using an organic solvent system solution.

Test specimens of Waspaloy (Ni-19.5Cr-13.5Co-4.3Mo-3.0Ti-1.3Al) were sulfidized in molten Na_2SO_4 for up to 720ks at 1273 to 1473K. After sulfidation procedure, the specimens were mounted in a cold-setting resin, sectioned, and then ground and polished metallographically. The scale microstructure of sulfidized specimens sectioned was observed with an optical microscope and an electron probe microanalyzer (EPMA). Figure 1 shows a typical cross section of Waspaloy sulfidized at 1473K for 54ks, showing the formation of internal scale which consists of intergranular and intragranular scales. Corrosion products were identified by X-ray analyses. The internal scale was composed of Ti_2S, Cr_2S_3, Cr_5S_6, Cr_2O_3 and gamma matrix while the external scale was composed of Cr_2O_3.

In order to observe the 3-dimensional structure of the internal scale in sulfidized superalloys, a modified organic solvent system dissolution technique was applied. The organic solvent system used in this study is a solution of 3.2%bromine (Br_2) + 16.1%cetylpyridinium bromide ($[C_5H_5N(CH_2)_{14}CH_3]Br$) + 80.7%acetonitrile ($CH_3CN$). The dissolution procedure is shown in Fig. 2. The dissolution reactions are considered to proceed as follows:

$$Br_2 + [CP]^+Br^- \rightarrow [CP]^+ + Br_3^- \quad (1)$$

$$M + Br_3^- \rightarrow MBr_2 + Br^- \quad (2)$$

$$MBr_2 + 2[CP]^+Br^- \rightarrow 2[CP]^+ + [MBr_4]^{2-}, \quad (3)$$

where $[CP]^+$ and M mean cetylpyridinium ions and metallic elements in the matrix of the alloy, respectively. The $[CP]^+_2\,[MBr_4]^{2-}$ dissolves well in acetonitrile.

The alloy matrix of the test pieces was dissolved in the organic solvent system solution leaving sulfide and oxide phases of the scales in the solution. The three-dimensional morphology of intergranular and intragranular corrosion products was observed with a scanning electron microscope (SEM).

Fig.3 shows the SEM image of the 3-dimensional internal scale extracted from Waspaloy sulfidized at 1373K for 720ks. The dissolution was interrupted before it was completed. A part of the alloy matrix remains. The observation was carried out in an outward direction from the interior to the external scale of the alloy. It is obvious that intergranular (arrow) and intragranular (star) scales are formed along grain boundaries and in the grain interior of the alloy, respectively. The latter showed to be discrete and the former to be connected weakly in each other. The compositional analyses were also performed.

In conclusion, the organic solvent system dissolution technique is useful to examine the 3-dimensional morphology and the composition of the scales formed in the interior of Ni-Cr based superalloy such as Waspaloy.

References

(1) K.Kusabiraki, Y.Nakao and S.Saji, Mater. Trans. JIM, 62(1998), 1151-1156.
(2) K.Kusabiraki and Y.Nakao, Mater. at High Temperatures, 18(s)(2001), 63-66.

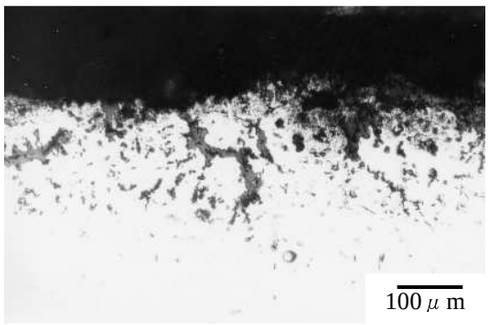

Fig.1 Cross section of Waspaloy sulfidized at 1473k for 54ks in molten Na_2SO_4.

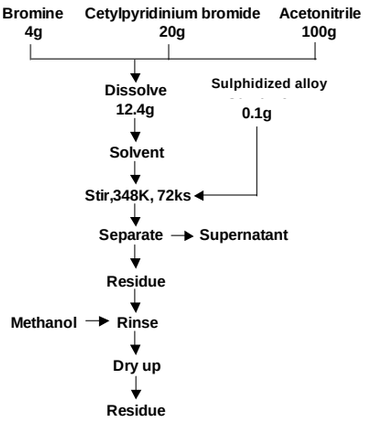

Fig.2 Organic solvent system dissolution procedure of sulfidized Ni-Cr based superalloys.

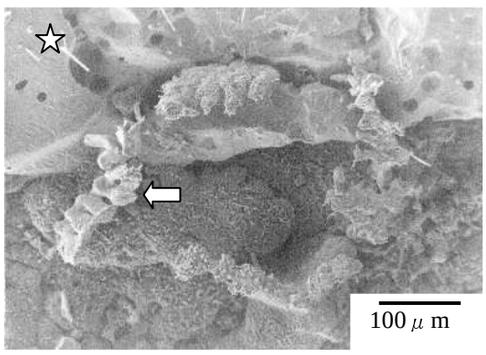

Fig.3 SEM image of the internal scale obtained from Waspaloy sulfidized at 1373K for 720ks in molten Na_2SO_4.