Effect of Trace Impurities in Ni-Base Single Crystal Superalloys on High-temperature Properties and Impurity Removal by CaO for Recycle of Superalloys

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Abstract

In determining the specifications for the production or recycling process of Ni-base single crystal superalloys, it is important to clarify the allowable trace impurity concentration. In this study, the effects of Pb and Sb on high-temperature strength and oxidation resistance of 6th generation superalloy TMS-238 were summarized. It was found that both Sb and Pb do not have a large effect on creep rupture life, but they degrade oxidation resistance. The removal of impurities by CaO was tested and its mechanism was examined. It was found that Ca forms a compound with impurities within the alloy and prevents the segregation of impurities at the oxide film/substrate interface. The effect of CaO was also confirmed in an experiment in which impurity S was removed from 1st generation Ni-base superalloy TMS-1700 in a 3-ton commercial melting furnace. Similar results were obtained for this alloy, where it was also found that CaS had formed inside the alloy, thus improving the oxidation resistance of TMS-1700.

Introduction

In the practical use of Ni-base superalloys, especially in superalloy recycling technology, it is important to control the content of trace impurities. Establishing recycling technology for Ni-base superalloys will lead to securing stable resources for high-price rare-materials, and reducing alloy prices, which will ultimately contribute to the practical application of high-performance alloys and improved efficiency of gas turbines. In polycrystalline superalloys, it has been suggested that the presence of low-melting point metal impurities at grain boundaries, which tend to be difficult to remove during casting process, adversely affects the mechanical strength [1-5]. However, since there are no grain boundaries in single crystal alloys, we believe that this is not the case, and have investigated the effects of impurities on the mechanical strength and oxidation resistance of Ni-base single crystal superalloys in our previous research. [6, 7]. Regarding the impurity S, its effects on mechanical strength and oxidation resistance have been clarified, and it was found that the S content greatly affects creep strength and oxidation resistance. Therefore, in this study, the effects of Pb and Sb, which are low melting point metals and difficult to remove, on creep strength and oxidation resistance are summarized. In addition, the removal of impurities by CaO is tested and its mechanism is examined.

Experimental Procedure

Small amounts of Pb and Sb were added to the 6th generation Ni-base single crystal superalloy TMS-238, and the single-crystal samples used for our experiments were vacuum-induction melted and fabricated using a standard directional solidification casting furnace. Al_2O_3 crucible and CaO crucible were used for melting. Materials were supplied as 10 mm in diameter cylindrical bars with orientations within 10 degrees of the [001] orientation. Then samples were solution heat treated and aged so that no residual eutectics and no visible TCP phases should exist in the microstructures. Those with orientations within 5 degrees of the [001] orientations were subjected to creep rupture test, and the others were subjected to oxidation tests.

Tensile creep-rupture tests were conducted on heat-treated samples; specimens were machined into creep specimens of 4 mm in diameter and 22 mm in gauge length (JIS Z-2271), and tested along the [001] direction to rupture under the following conditions: 800 °C/735 MPa, 900 °C/392 MPa, 1000 °C/245 MPa and 1100 °C/137 MPa. Specimens for oxidation tests were machined to 9 mm in diameter and 5 mm in thickness, and the surfaces were finished with 600-grade SiC paper polishing followed by cleaning with acetone. High-temperature cyclic oxidation tests were conducted at 1100 °C in air for 1 h per cycle. The change in weight of each specimen was measured at the end of each cycle.

Results and Discussion

Table 1 shows the nominal composition of TMS-238 and the analytical composition of each alloy after casting. The chemical compositions of the alloying elements were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) after heat treatment. Glow Discharge Mass Spectrometry (GD-MS) was also used for trace element analysis. Each alloy had similar S concentrations of 2-3 ppm. TMS-238 melted in a CaO crucible suppresses the segregation of S at the oxide/substrate interface [8] even if the S concentration is the same, so this alloy is named as TMS-238 sulfur-disabled (SD) in this paper. Alloy-1Pb, Alloy-30Pb and Alloy-24PbSD contain 0.9 ppm, 31 ppm and 24 ppm of Pb, respectively. Alloys containing Sb are named Alloy-1Sb, 4Sb, 8Sb, 9SbSD.

Table 1: Compositions of alloys.

Alloy	Crucible	Composition										
		wt.%, Ni bal.									ppm	
		Co	Cr	Mo	W	Al	Ta	Hf	Re	Ru	Sb	Pb
TMS-238 Nominal		6.5	4.6	1.1	4	5.9	7.6	0.1	6.4	5	-	-
TMS-238	Al_2O_3	6.33	4.42	1.1	3.99	5.83	7.74	0.1	6.44	5.01	0.16	< 0.1
TMS-238SD	CaO	6.27	4.43	1.18	3.82	5.63	7.48	0.10	6.39	5.01	-	-
Alloy-1Pb	Al_2O_3	6.4	4.55	1.12	4.07	5.99	7.85	0.1	6.64	5.08	-	0.9
Alloy-30Pb	Al_2O_3	6.39	4.62	1.12	3.96	5.84	7.6	0.09	6.45	4.98	-	31
Alloy-24PbSD	CaO	6.63	4.69	1.09	4.08	5.87	7.64	0.097	6.55	5.03	0.27	24
Alloy-1Sb	Al_2O_3	6.3	4.0	1.1	3.9	5.8	7.6	0.1	6.4	4.9	1.1	-
Alloy-4Sb	Al_2O_3	6.3	4.1	1.1	3.9	5.8	7.6	0.1	6.7	4.9	3.8	-
Alloy-8Sb	Al_2O_3	6.5	4.5	1.1	4.1	6.1	7.9	0.1	6.4	5	8.1	<0.1
Alloy-9SbSD	CaO	6.5	4.5	1.1	4.1	6.1	7.9	0.12	6.4	5	9.5	<0.1

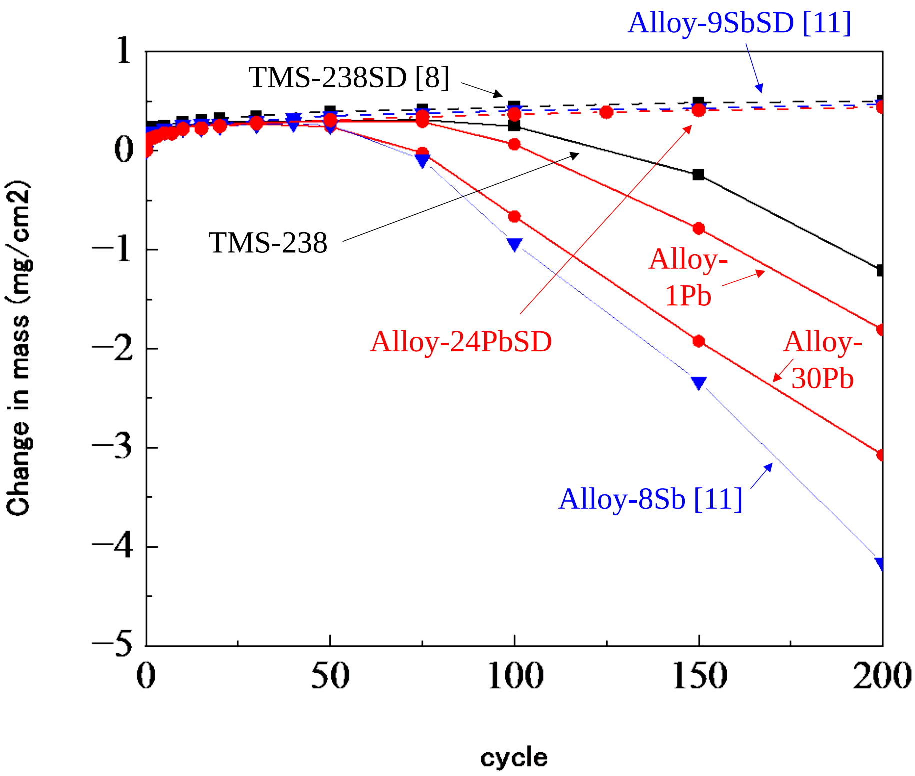
*Each cast alloy had similar concentration of S of 2-3 ppm.

Since Alloy-24PbSD and Alloy-9SbSD melted in a CaO crucible were expected to suppress S segregation at the interface, it is possible to evaluate the effect of Pb and Sb alone without the effect of S. On the other hand, Alloy-1Pb, 30Pb and Alloy-1Sb, 4Sb, 8Sb contain the effects of both S and Pb / Sb.

Figure 1 shows the creep test results at 900°C/392 MPa. The alloys with Pb added and the alloys with Sb added other than Alloy-9SbSD show almost the same creep curve and rupture life as TMS-238. This tendency was the same in creep tests under other conditions. Therefore, it was confirmed that the addition of a small amount of Pb and Sb do not greatly affect the creep properties, as shown in previous research [9, 10]. Alloy-9SbSD has longer creep rupture life than TMS-238. It was found that 9 ppm Sb had no effect on the creep strength, and melting by the CaO crucible eliminated the effect of S on creep strength.

Figure 2 shows the cyclic oxidation test results at 1100°C in air. TMS-238SD, Alloy-24PbSD and Alloy-9SbSD had less weight loss than TMS-238 and showed the best oxidation resistance. This is because melting by the CaO crucible reduced the amount of S that segregates at the oxide film interface even though the S content was the same. For Alloy-1Pb, Alloy-30Pb, and Alloy-8Sb, the effects of both 2ppm S and added Pb and Sb must be considered. In both alloys, addition of impurities caused weight reduction due to spallation of the oxide scale, and oxidation resistance was degraded. The higher the amount of Pb added, the lower the oxidation resistance of the alloys had become. In addition, even if the amount of Sb added was smaller than that of Pb, the amount of weight loss was larger, therefore it can be said that the effect of Sb on oxidation resistance was larger than that of Pb. The improvement of oxidation resistance in Alloy-24PbSD and Alloy-9SbDS revealed that melting by CaO crucible is also effective for impurity Pb and Sb.

Takata et al. found that Sb segregates at the oxide interface [9], and Maezawa et al. suggested that the formation of inclusions containing Ca and Sb suppresses the segregation of Sb at the interface [11]. Since the mechanism for improving the oxidation resistance of alloys containing Pb impurities was not yet clear, we attempted to observe the microstructure of as-cast Alloy-24PbSD in this study. Figure 3 illustrates Scanning Electron Microscope Energy Dispersive X-ray Spectrometry (SEM-EDS) observation images of Pb-containing inclusions found at sub-grain boundaries for as-cast Alloy-24PbSD. Analysis revealed that the inclusions contained Pb, Ca, and O. Therefore, it was confirmed that oxidation resistance of Alloy-24PbSD was improved by reacting Pb and Ca in the alloy to form Pb and Ca oxides, which suppresses the migration of Pb to the surface and prevents the reduction of the oxide film adhesion. In this paper, the validity of the mechanism presented in previous studies was confirmed by the results shown in Fig. 2 and 3, which indicates that melting by CaO crucible had indeed improved the oxidation resistance of the alloys.



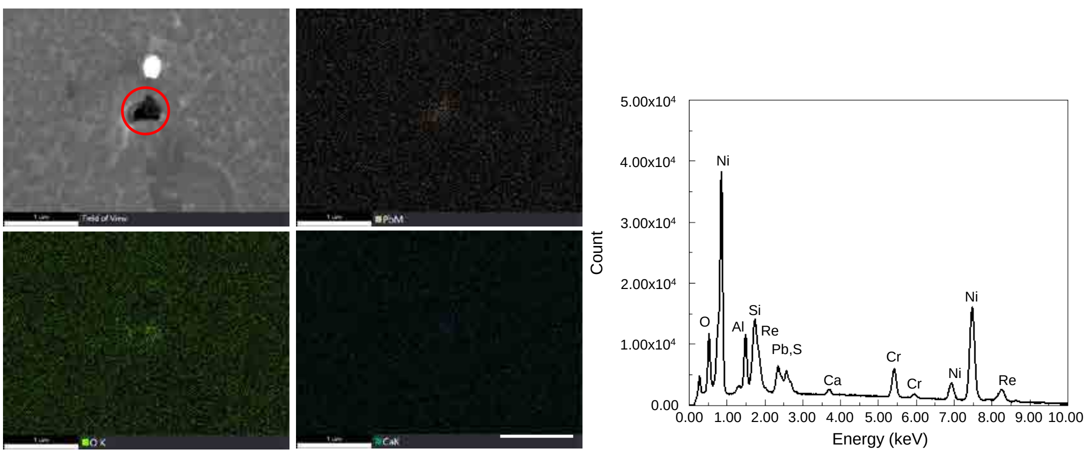


Fig. 3 SEM-EDS observations of the inclusion in as-cast Alloy-24PbSD.

The mechanism of removal and suppression of segregation of Pb and Sb by CaO is similar to that of S reported by Tabata et al. [8]. The authors also confirmed that the addition of CaO particles can reduce the S content even in a 3-ton melt in a commercial melting furnace [12]. This previous study revealed that the S concentration decreased with melting time and reacted with CaO to remove S. However, as described in Tabata's paper [8], if residual S reacts with Ca to form inclusions, the improvement of oxidation resistance can be expected.

Figure 4 shows the oxidation properties of TMS-1700, TMS-1700SD which was melted in a CaO crucible, and recycle-simulated TMS-1700 [12]. Nominal composition of TMS-1700 is shown in Table 2. The ingot of recycle-simulated TMS-1700 was cast using a 3-ton commercial melting furnace with intentional S addition and CaO particles for desulfurization, and the single-crystal test bars were cast from the ingot. Even though the S concentrations in these samples were similar at 2-3 ppm, recycled-simulated TMS-1700 and TMS-1700DS showed similar mass changes and improved oxidation

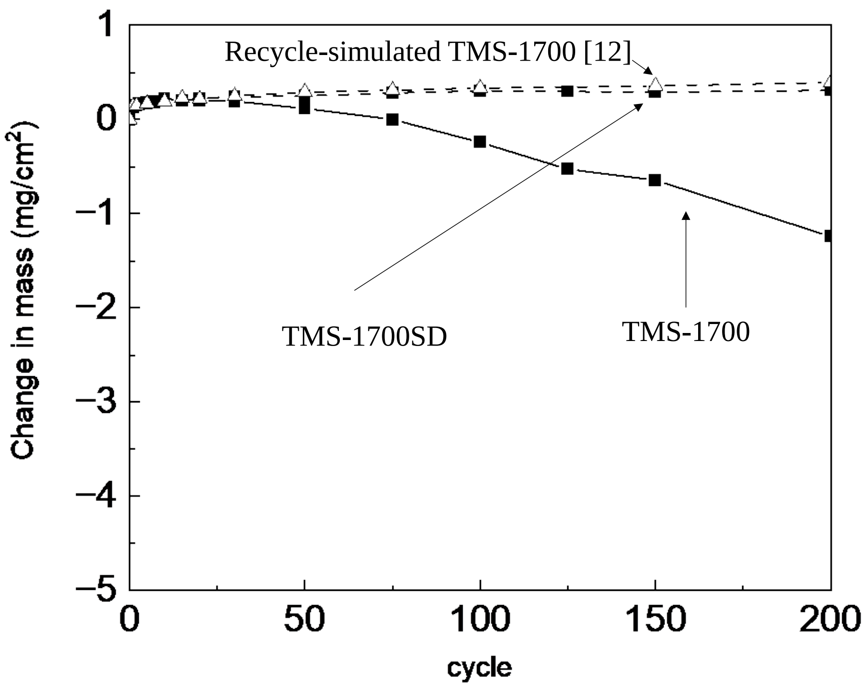


Fig. 4 Cyclic oxidation properties of TMS-1700, TMS-1700SD and recycle-simulated TMS-1700 at 1100℃.

Table 2 Nominal composition of TMS-1700.

Alloy	Composition wt.%, Ni bal.							
	Co	Cr	Mo	W	Al	Ta	Hf	Si
TMS-1700	0	9.0	0.6	7.6	5.4	10.0	0.1	0.04

resistance than TMS-1700. This indicates that the effect of improving oxidation resistance by dissolving in a CaO crucible and by adding CaO particles is equivalent.

To confirm the mechanism of improving oxidation resistance by adding CaO particles, we also observed the microstructure at the sub-grain boundaries of TMS-1700, which was cast as a single crystal using a 3-ton ingot smelted by adding CaO particles. As a result, as shown in Figure 5, inclusions consisting of Ca, S, Al, and O were found. Therefore, even in the melting of large-capacity ingots in commercial melting furnaces, the addition of CaO particles not only removes S, but also suppresses S segregation at the oxide film interface through the reaction between Ca and residual S and improves the oxidation resistance.

This study revealed that effect of CaO to disable trace impurities and improve oxidation resistance is effective not only for S but also for low melting point metals Pb and Sb. This effect can be expected for other impurities such as Bi, Sn or other trace elements that are difficult to remove. Further

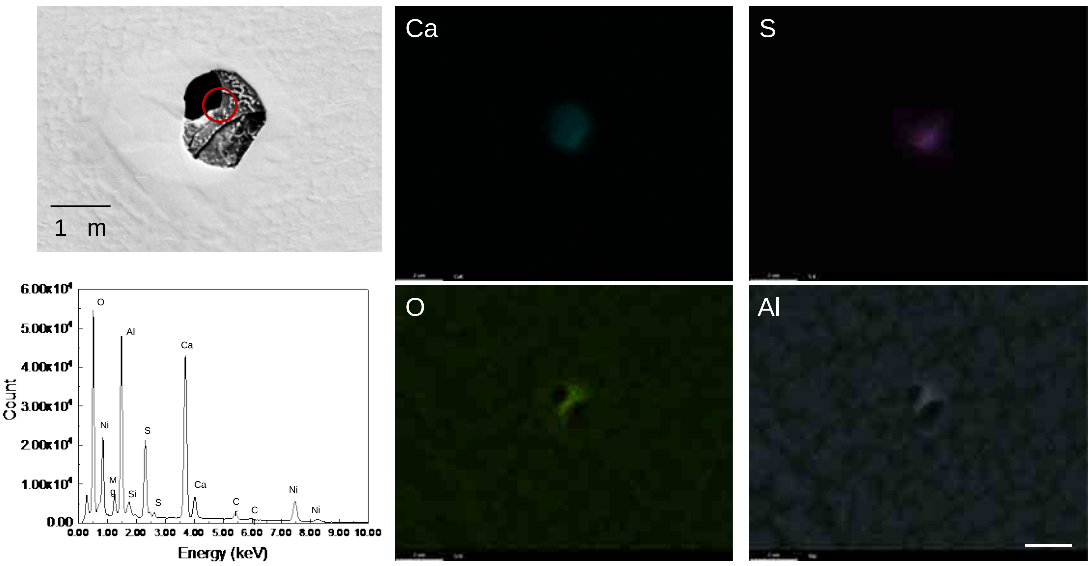


Fig.5 SEM-EDS observations of the inclusion in 3-ton melted TMS-1700.

investigation will be necessary for this method to contribute to the recycling industry of Ni-base superalloys.

Conclusions

The effects of trace impurities, such as Pb and Sb, on creep strength and oxidation resistance were clarified as follows.

1. Addition of small amounts of Pb and Sb did not affect the creep properties.
2. It was found that the addition of Pb and Sb lowers the oxidation resistance, and the larger the amount added, the larger the effect was on the alloys.
3. The oxidation resistance of the Pb and Sb-added alloys were improved by melting with CaO

crucible. This is because both S and Pb or Sb form inclusions through the reaction with CaO, which suppresses segregation at the oxide film/substrate interface and prevents deterioration of the adhesion of the oxide film.

4. The effect of CaO on removing S and suppressing interfacial segregation was also confirmed in large-capacity melting in a commercial melting furnace. This technology can also be expected for other trace impurities, and will be crucial for the development of recycling technology for Ni-base superalloys in the future.

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