High-temperature oxidation behavior of nano-structured ferritic oxide dispersion-strengthened alloys☆

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ABSTRACT

The effect of yttrium and nanoclusters on the high-temperature oxidation behavior of Fe–14Cr–3W–0.4Ti nano-structured ferritic oxide dispersion-strengthened alloys was investigated. For comparison purposes, conventional stainless steels with the same chemical composition were studied as well. Long-term oxidation tests were conducted at 800 °C for up to 2000 h in atmospheric air. The mass-gain versus time curves were obtained and the microstructure and chemical elements distribution in different regions of the specimens after oxidation were then analyzed by SEM/EDS and XRD. The experimental results showed that an addition of yttrium to Fe–14Cr–3W–0.4Ti alloy sufficiently reduced the oxidation rate. However, ODS processing to precipitate nanoclusters is a more effective means of improving high-temperature oxidation rather than a simple yttrium addition.

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1. Introduction

Over the last decade, numerous works on advanced oxide dispersion-strengthened (ODS) alloys have been conducted, as ODS alloys can overcome several drawbacks of conventional ferritic/martensitic steels, of which utilization is limited to operations with a maximum operating temperature of 550 °C due to the inferior creep strength of these materials [1–4]. Advanced ODS alloys contain a very high number density of nano-sized oxide clusters (NCs) with a mean diameter of 3–10 nm. NCs are known to have a NaCl-type Y–Ti–O structure [5] which provides excellent high-temperature stability. Thus, the initially very fine microstructures can be maintained even at very high temperatures that exceed 800 °C. As a result, advanced ODS alloys are quite different from conventional ODS alloys which contain only coarse oxide particles with much smaller number densities. Therefore, advanced ODS alloys are emerging as strong candidate materials for high temperature applications such as SOFC interconnect plates, gas turbine components, next generation nuclear power systems, and

so on. However, to satisfy the material performance required at high temperatures, it is necessary for ODS alloys to have suitable high-temperature oxidation resistance levels for long-term service times. Although it is known that advanced ODS alloys exhibit good oxidation resistance, the detailed mechanism behind this is not well understood thus far. Kaito et al. [6] showed that 9Cr and 12Cr ODS alloys exhibit greatly improved oxidation resistance compared to SUS430 and 11Cr stainless steel. They also suggested that the oxidation resistance is higher in a fine-grained structure than in a coarse-grained structure. Regarding the alloying effect, Lee et al. showed that an addition of 4 wt.% Al can effectively increase the corrosion resistance of 16Cr ODS alloy because the continuous alumina scale suppresses the outward iron diffusion [7]. It is also well known that small additions (<1%) of oxygen reactive elements such as cerium, yttrium, or yttria improve the oxidation resistance in general alloys at high temperatures [8,9]. In contrast, Ul-Hamid [10] suggested that 0.7 wt.% of Y_2O_3 in Fe–Cr–Al ODS alloy gives rise to a high degree of porosity within the scale, resulting in a relatively high-scale growth rate.

In summary, it is thought that advanced ODS alloys have superior oxidation resistance compared with conventional stainless steels. However, the origin of the improvement is not yet clear. Most research compared the oxidation behavior of various alloys systems with different chemical compositions; thus, their analyses may contain an alloying effect, which can improve or deteriorate the oxidation properties. Also, the mechanical alloying process used in the production of all ODS alloys can have a significant

Table 1
The production routes of programmed alloys.

Alloys	Yttrium addition	Processing method
V1	–	VAR melting
V2	0.3 wt.% of Y	VAR melting
K1	0.3 wt.% of Y_2O_3	Mechanical alloying at R.T.
K4	0.3 wt.% of Y_2O_3	Mechanical alloying at −150 °C.

effect. Nonetheless, there remains great curiosity as to whether the improved oxidation resistance of ODS alloy is due to the nature of the powder metallurgy, the presence of NaCl type Y–Ti–O NCs, or the segregation of yttrium itself at the grain boundaries.

The present work is undertaken to investigate the aforementioned questions using four different alloys with the same chemical compositions. Two of them were ODS alloys produced by a powder metallurgy route while the others were similar to conventional stainless steels manufactured by vacuum arc remelting. From this approach, the effect of the processing route, chemical composition, and the presence of NCs were studied.

2. Experimental details

2.1. Materials preparation

Four different program alloys with a nominal composition of Fe–14Cr–3W–0.4Ti–0.05Mn (wt.%) were prepared under various processing conditions, as summarized in Table 1 with material designations. Except for the V1 alloy, ~0.3 wt.% of yttrium or yttria was added to the materials.

The cast alloy, designated as sample V1, was cast into 80 mm × 80 mm × 200 mm ingots by vacuum arc remelting without an addition of yttrium, while V2 contained 0.3 wt.% yttrium for a comparison. The other two alloys, designated as samples K1 and K4, were prepared by the powder metallurgy route with the same chemical compositions except for the Y_2O_3. The pre-alloyed powders prepared by the gas atomization process were mixed with

0.3 wt.% Y_2O_3 powder with a particle size of 30–50 nm. The mixture of the two powders was then put into a milling chamber. Mechanical alloying (MA) was performed in a high-purity Ar (99.999 wt.%) atmosphere for 40 hours at room temperature and at −150 °C for samples K1 and K4. To lower the temperature, liquid nitrogen was flowed around the outside of the chamber. The milling temperature was monitored using a thermocouple inserted into the wall of the milling chamber. After milling, the Ar pressure level was checked to ensure that the seal was intact. The ball-to-powder weight ratio was 25, and AISI 52–100 hardened steel was used for the milling container and grinding media. The mechanically alloyed powders were filled into a mild steel can which was evacuated to a vacuum of ~1 Pa at a temperature of 400 °C and then sealed and consolidated by HIP at 1100 °C for 4 h. The consolidated samples were hot rolled at 1150 °C to a thickness reduction of 50% and subsequently annealed at 1100 °C.

2.2. Oxidation tests and characterization

For the high-temperature oxidation process, specimens with a surface area of 10 mm × 15 mm × 5 mm were made of each sample material. The oxidation test specimens were polished to a 0.3 mm finish. Prior to the oxidation step, the specimens were ultrasonically cleaned in acetone and methanol, dried, and then put into individual annealed alumina crucibles with lids. The specimens were exposed at 800 °C in atmospheric air for 50 100, 200, 500, 1000, and 2000 h. At these intervals, the specimens were taken out of the furnace and cooled to room temperature for mass measurements. The total mass of a specimen together with the crucible was recorded. The oxidation behavior was evaluated by the mass-gain of the samples. Accordingly, if oxide scales spalled from the surface during oxidation, their masses were counted together with that of the sample.

After oxidation, the specimens were examined using a Rigaku International Corporation D/Max-2500VL/PC to determine their X-ray diffraction pattern. In order to observe the structure of
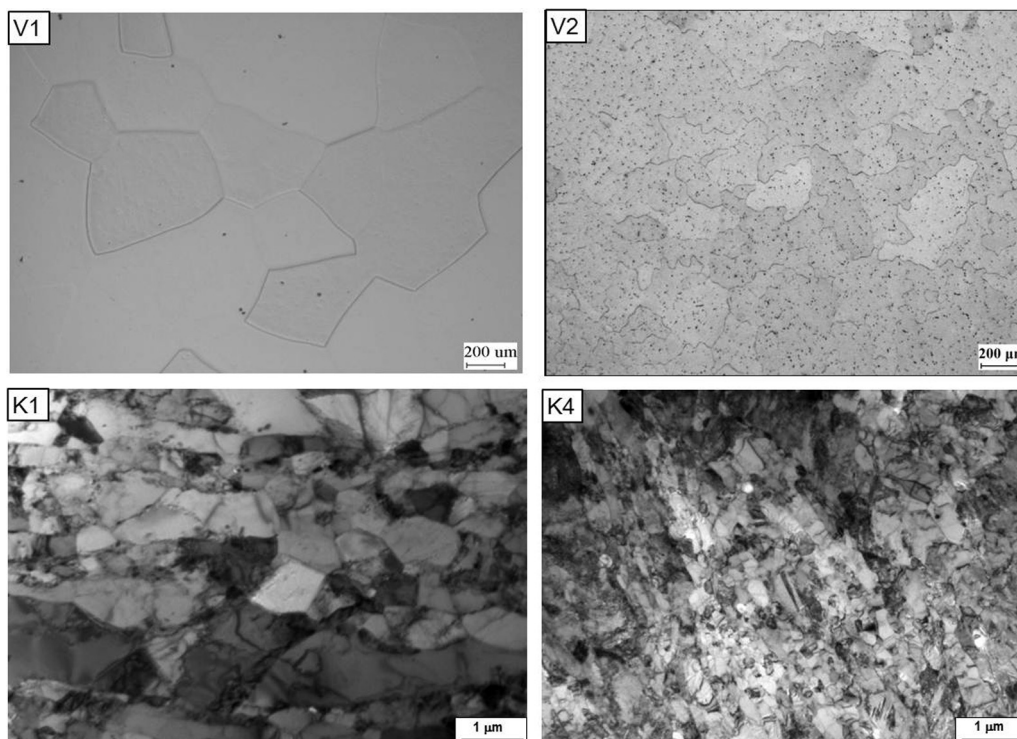
Fig. 1. As-received microstructures of V1, V2, K1, and K4 specimens.