

Cerium Titanate Nano dispersoids in Ni-base ODS Alloy

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1. Introduction

Oxide-dispersion-strengthened (ODS) nickel-base alloys have potential for use in rather demanding elevated-temperature environments, such as aircraft turbine engines, heat exchanger of nuclear reactor. For improved high temperature performance, several ODS alloys were developed which possess good elevated-temperature strength and over-temperature capacity plus excellent static oxidation resistance [1-3]. The high-temperature strength of ODS alloys is due to the presence of a uniform dispersion of fine, inert particles [4-6]. Ceria mixed oxides have been studied because of their application potential in the formation of nanoclusters. By first principle study, it was estimated that the formation energy of the Ce-O dimer with voids in the nickel base alloy is lower than other candidates. The result suggests that the dispersion of the Ceria mixed oxides can suppress the voiding or swelling behavior of nickel base alloy during neutron irradiation. Titanium is a fine oxide particle former, it is expected that the addition of ceria, titanium into nickel matrix during mechanical alloying and annealing process would result in the better performance with fine cerium titanates distributions. Different phases of ternary cerium titanates can be formed during annealing process, such as Ce_2TiO_5 , $Ce_2Ti_2O_7$, $Ce_2Ti_3O_9$, $CeTiO_4$, and $CeTi_2O_6$. In this study, the evolution mechanism of cerium titanate nano particles was investigated using in-situ TEM. Aduro Thermal E-chip provides a platform for precise temperature control, ultra-low drift, temperatures up to 1,200 °C. Nano-scale variations of cerium titanates were observed using in-situ technique, the phases were identified and their distribution were quantified.

2. Methods and Results

Chemical composition of specimen (Ni-base ODS powder) is shown in Table. 1. The specimen contains 1 wt% Ti, 0.87 wt% CeO_2 , as alloying elements. CeO_2 and Ti were added to form stable and fine oxide particles, respectively. Ti is known as a catalyst to form the finer oxide particles in Fe-base or Ni-base ODS alloys. Ni, Ti and CeO_2 are mixed as powders, and they were mechanically alloyed by using a high-energy miller (CM 20) at 240 rpm for 48 hours. The average diameters of mixed powders are shown in Table. 2, the purity of powders was almost 99.9 %.

Table. 1. Chemical composition of specimen.

	Mol. mass (g/mol)	density (g/cm ³)	wt [g]	wt.%	vol. [cm ³]	vol.%
Ni	58.56	8.9	900	98.13	101.1	97.065
Ti	47.867	4.54	9.15	1.00	2.0	1.935
CeO ₂	172.11	7.65	7.97	0.87	1.0	1.000

Table. 2. Average diameter of powders

	Purity	size
Ni	99.8%	45 μm (~325 mesh)
Ti	99.9%	45 μm (~325 mesh)
CeO ₂	99.9%	10-30 nm

In Fig. 1, insitu TEM holder and controller are shown. Aduro thermal chip can be attached to the conventional TEM holder, it shows extremely high thermal stability and low drift. Aduro can heat and quench at any rate up to 1000 °C per millisecond, capturing material changes. In Fig. 2, the internal structure of Aduro thermal E-chip is shown. TEM specimens are manufactured by focused ion beam (FIB) and picked by electrostatic attraction using glass tip. Afterwards, the specimens are dropped on to thermal chip.

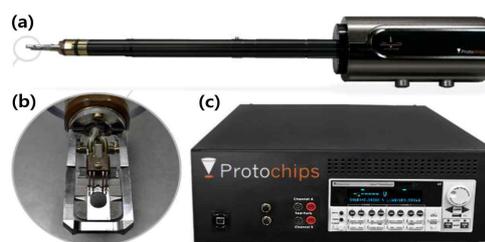


Fig. 1. Insitu TEM holder and controller. (a) TEM holder, (b) Thermal E-chip for heating TEM specimen, (c) Controller

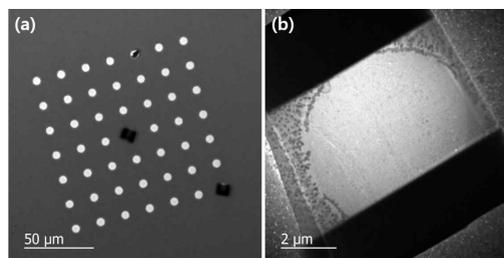


Fig. 2. Internal structure of Aduro thermal E-chip. (a) 49 holes on the thermal chip, the diameter of the holes are 5 μm. The two 15 μm X 8 μm sized TEM specimens are shown at the center and the outside of the chip. TEM specimens should be placed on the one of the holes. (b) The right positioning of the specimen, it was fabricated by focus ion beam. The thickness of specimen is controlled to be less than 100 nm.

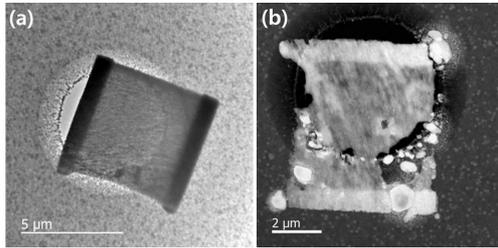


Fig. 3. Shape variation of specimens after annealing experiment. (a) before annealing, (b) after annealing at 1050 °C.

The specimen degradation during annealing is shown in Fig. 3. The heating elements are SiN layer on the chip surface, the heating is controlled by electrical resistance. Therefore, the specimen is degraded from the contact area around the hole. Heat uniformity across the specimen was acceptable; it was checked by observing degree of the microstructural variations. The specific figure of such variations is shown in Fig. 4. Recrystallization of grains started from 900 °C, the specimen was degraded after annealing at 1050 °C for 1 hour. The evolution of fine oxide particles after annealing is shown in Fig. 5. No oxide particles could be observed just after the mechanical alloying process (Fig. 5(a)), however, small circular oxide particles were observed (Fig. 5(b)). The nano oxide particles were identified by high resolution lattice image as shown in Fig. 6 and 7. The phase was $Ce_2Ti_3O_9$, which size is ~ 20 nm and evenly distributed.

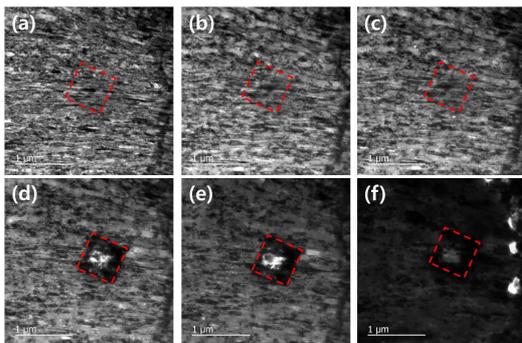


Fig. 4. Grain shape variations during heating. (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C, (f) 1050 °C

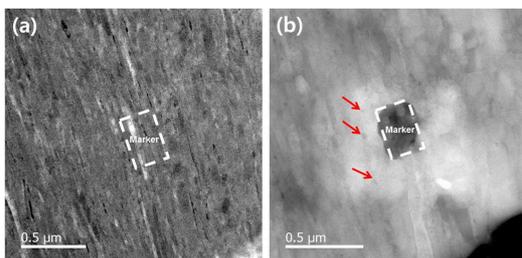


Fig. 5. Microstructure variation of mechanically alloyed Ni-ODS powder at the same area during annealing up to 1050 °C. (a) mechanically alloyed, (b) annealed at 1050 °C.

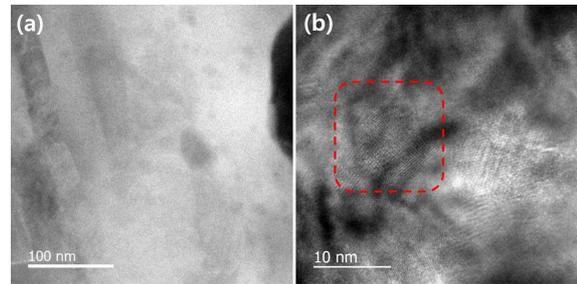


Fig. 6. (a) Evolution of fine oxide particles after annealing, (b) high resolution lattice image of nano-oxide particles.

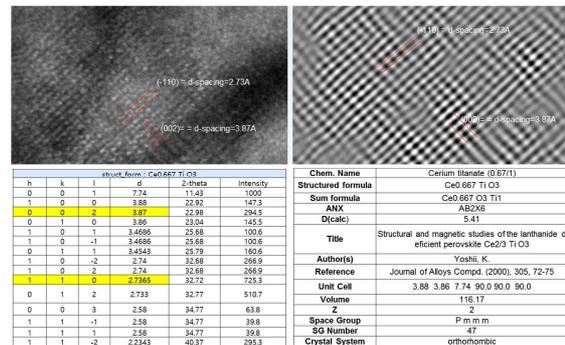


Fig. 7. (a) D-spacing index and phase identifications of the nano-oxide particle ($Ce_2Ti_3O_9$).

3. Conclusions

In this study, the evolution of cerium titanate nano particles was investigated using in-situ TEM. It was found that the $Ce_2Ti_3O_9$ phase was easily formed rather than remain as CeO_2 during annealing; Ti was effective to form the finer oxide particles. $Ce_2Ti_3O_9$ is expected to do the great roll as dispersoids in Ni-base alloy, contribute to achieve the better high temperature property, high swelling resistance during neutron radiation.

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