

Characterization of Nano-sized ODS Clusters in Mechanically Alloyed NiAl-(Y,Ti,O) Alloys

Yong Deog Kim^{a*}, Yong Bae Kim^a, Hyon-Jee L. Voigt^b, Brian Wirth^b
^aKHNP-CRI, 70 Yuseongdaero 1312beon-gil, Yuseong-gu, Daejeon 305-343, Korea
^bUTK, Knoxville, Tennessee, USA

1. Introduction

This study focuses on characterizing and modeling advanced oxide dispersion strengthened (ODS) NiAl intermetallics with improved high temperature creep strength driven by incorporating a high number density ($\sim 10^{24} \text{ m}^{-3}$) of very thermally stable Y-Ti-O nano-clusters, akin to those recently observed to improve creep strength and radiation resistance in nano-structured ferritic alloys [1-6]. Advanced ODS NiAl alloys have been produced by mechanical alloying of pre-alloyed Ni-50at%Al with Y_2O_3 and Ti elemental powders. The milled powders were subsequently consolidated by spark plasma sintering, with the objective of producing very high number densities of nano-sized Y-Ti-O precipitates, along with fine grain size. The motivation of the study was; what structure and composition do the nm-scale features/precipitate clusters have and what processing variables control their formation. To answer these questions, advanced experimental characterization techniques, combined with atomic modeling, were used to investigate the material microstructure and strength following processing. In particular, the size, number density and composition of nano-clusters were assessed.

2. Experimental and Characterization Methods

2.1 Mechanical alloying

In this study, ODS NiAl raw matrix materials were prepared from prealloyed, gas-atomized Ni-50at% Al powders supplied by Crucible Industries LLC. Y_2O_3 and Ti particles were added as dispersoid elements. All three powders have the same particle size of -325 mesh and purity of 99.99%. NiAl, Y_2O_3 , and Ti powders respectively. Mechanical alloying was performed for these three compositions with 100Cr6 steel ball media under Ar gas sealed environment. The milling speed was set to 1200 rpm (linear speed of 11 m/sec) and the milling times to investigate an optimum powder alloying condition were 2, 5, 10, and 15 hrs respectively.

The high energy milling machine, Simoloyer-CM01 was used.

2.2 Spark Plasma Sintering (SPS)

The SPS process [7] is a combination of conventional electric-current sintering and hot-pressing based on high temperature plasma instantly generated in the gaps between powders by electrical discharge current. In this study, SPS method was utilized to consolidate the ODS

NiAl alloys with improved high temperature strength. Densification behavior, micro-structure and mechanical properties of the consolidated alloy specimens will be discussed in this presentation.

2.3 Atomic modeling

An ab-initio calculation on various Ni-Al-Y-Ti-O alloys to derive inter-atomic bond energy was performed by VASP code. All bond energies fit with Rose's universal equation of state. For the Lattice Monte Carlo (LMC) simulation, several things are assumed; rigid BCC lattice with tetrahedral interstitial sites for oxygen, vacancies omitted neglecting kinetic effects, the lattice parameters of nano-clusters with 1.0, 1.1 and 1.2 times of that of the NiAl. Figure 1 shows a schematic diagram interacting between atomic modeling and experimental characterization.

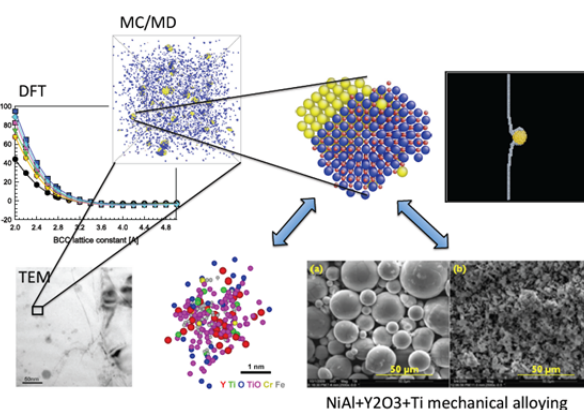


Figure 1. Schematic diagram of the work between atomic modeling and experimental

3. Characterization Results

Various experimental characterization techniques, scanning electron microscopy, X-ray diffraction (XRD), energy dispersive spectroscopy, transmission electron microscopy, atom probe tomography along with atomic simulation were used to investigate the material microstructure. As well, Vickers microhardness measurement was used to assess the basic mechanical property of the alloys. The microstructural characterization results of as-milled and as-consolidated NiAl alloys to assess the optimal milling time are discussed. Besides, the effort has gone into rationalizing the relationship between the strength and the microstructure of the ODS NiAl alloys.

3.1 X-ray diffractometry

Figure 2 illustrates the evolution of XRD before and after 10 hour milling for NiAl alloy powder blends. Bragg diffraction peaks of NiAl, Y_2O_3 and Ti are clearly visible for the initial powder mixtures but the peaks of alloying elements, Y_2O_3 and Ti, cannot be revealed for the powders after 10 hour ball milling. It is considered that 10 hour of milling time led to the disappearance of the XRD peak for Y_2O_3 and Ti caused by dissolution into the NiAl matrix. Grain size, strain, and dislocation densities estimated as a function of milling time will be discussed in the presentation.

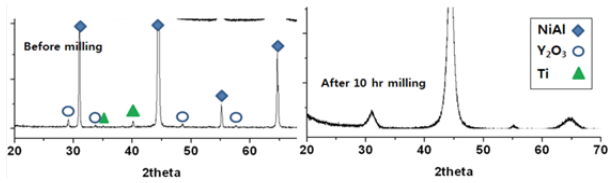


Figure 2. XRD patterns of the mechanically alloyed powders as a function of milling time (a) NiAl (b) NiAl-1wt% Y_2O_3 (c) NiAl-1wt% Y_2O_3 -1wt%Ti

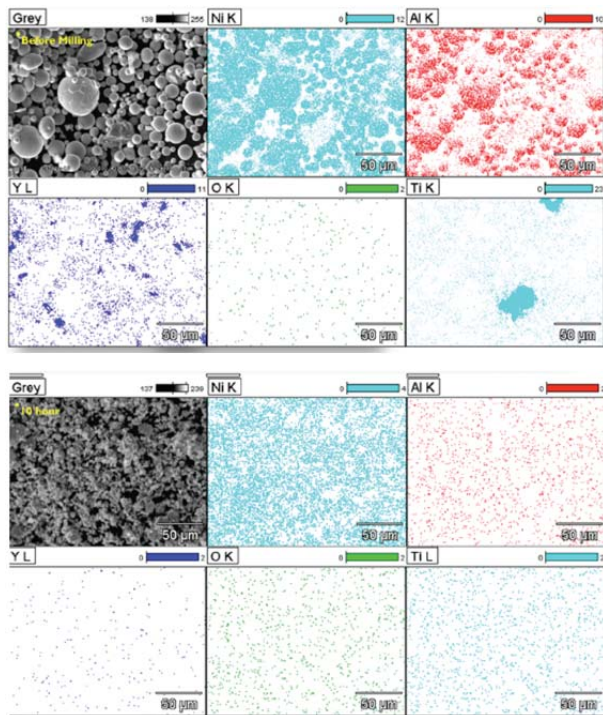


Figure 3. SEM micrographs of NiAl-1wt.% Y_2O_3 -1wt.%Ti powder as a function of milling time; (a) before milling (b) 10 hr ball milling

3.2 Scanning electron microscopy (SEM)

Figure 3 shows typical SEM micrographs of the NiAl-1wt% Y_2O_3 -1wt%Ti composition powders before and after the ball milling using a Hitachi S-4300 SEM machine with 20kV accelerating voltage. Figure 3(a) shows the micrographs of elemental mixture powders before the ball milling. The powders are spherical shape and have various sizes of 5 – 40 μm . After 10 hr ball

milling (Figure 3(b)), the powders are uniformly refined and have a flake shape less than 10 μm .

3.3 Consolidated specimen characterization

Vickers microhardness measurement was performed to characterize the basic mechanical properties of the ODS NiAl alloy materials. Figure 4 shows the microhardness results of the SPSeD NiAl alloys as a function of the milling time. The results can be summarized as follows: The addition of Y_2O_3 results in smaller increases in microhardness than for additions of both Y_2O_3 and Ti. The microhardness increased with increasing milling time up to 5 hrs and then saturated. The main microstructural contributions to this microhardness, or strength, of these alloys are believed to be grain refinement and particle strengthening. A quantitative relation between the microstructure and microhardness will be discussed in the presentation.

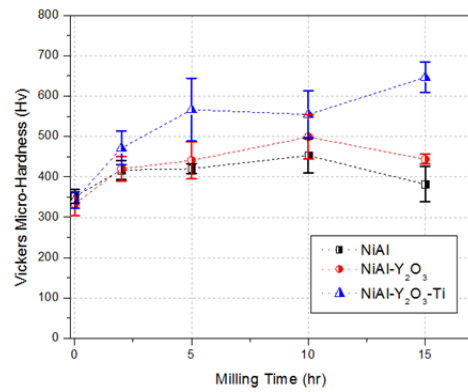


Figure 4. Vickers microhardness test results of the consolidated NiAl specimens as a function of milling time

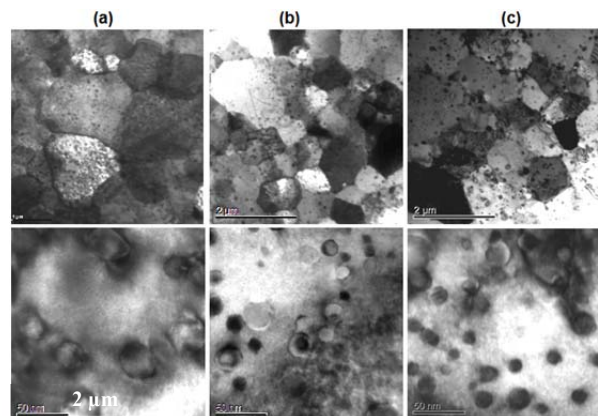


Figure 5. TEM micrographs of the as-consolidated NiAl alloys, (a) NiAl (b) NiAl-1wt% Y_2O_3 (c) NiAl-1wt% Y_2O_3 -1wt%Ti

3.4 Transmission electron microscopy (TEM)

TEM analysis of the as-consolidated NiAl alloys after ball milling for 10 hr was conducted to investigate the microstructure of the ODS NiAl alloys. Figure 5(a)-

(c) shows the TEM microstructure evolution of the 10 hr milled and SPS consolidated NiAl alloys. The grain size and precipitate number density, measured by TEM, are summarized in Table 1. The grain size has a multimodal distribution with both fine (< 200 nm) and coarser (> 1 μm) grain regions. The average grain size of the NiAl alloys including either Y₂O₃ or both Y₂O₃ and Ti is smaller than that of the pure NiAl alloy. The tempting conclusion is that the grain growth during the consolidation was definitely controlled by the addition of Y₂O₃ and Ti. The NiAl-1wt%Y₂O₃ and NiAl-1wt%Y₂O₃-1wt%Ti alloys have very similar grain size distribution. Aluminum oxide particles with sizes around 40 nm were observed in the pure NiAl alloy (Figure 5(a)). Precipitates of 10 to 20 nm size were distributed in both the NiAl-1wt%Y₂O₃ and NiAl-1wt%Y₂O₃-1wt%Ti alloys (Figure 5(b) and (c)). The particle number densities of each alloy were 0.3x10²²/m³, 0.8x10²²/m³, and 1.4x10²²/m³ for NiAl, NiAl-1wt%Y₂O₃, and NiAl-1wt%Y₂O₃-Ti respectively. Despite the high levels of strain introduced by the mechanical alloying, this TEM investigation of the consolidated NiAl alloys rarely found dislocations.

Table 1. Summary of the characteristics measured in the NiAl alloys

Alloy	NiAl	NiAl-Y ₂ O ₃	NiAl-Y ₂ O ₃ -Ti
Grain size (μm)	1.04±0.19	0.67±0.12	0.68±0.11
Precipitate N (10 ²² m ⁻³)	0.3	0.8	1.4
Precipitate size (nm)	30±7.5	15±6.6	14±6.1
Microhardness(kg/mm ²)	450±42	501±54	550±58

3.5 Atom probe tomography

Atom Probe Tomography (APT) was performed in collaboration with Mike Miller at ORNL. Figure 6 shows a 3-dimensional APT map for the as-consolidated NiAl-1wt%Y₂O₃-1wt%Ti alloy. Such atom maps can provide information on the overall solute distribution as well as the size and composition of fine scale precipitates. As shown in Figure 6, the Ni, Al and Fe elements were homogeneously distributed. There was indication of Y-Ti-O clustering along with some heterogeneous distributions of Y, Ti, and O. Additional APT studies are needed. However, limitations of the time available on the ORNL instruments and challenges of specimen preparation for the LEAP instrument precluded more extensive APT study.

3.6 Lattice Monte Carlo simulation

Figure 7 shows the Lattice Monte Carlo simulation result for NiAl-Y-Ti-O alloy. The number of LMC steps was 2 million and temperature was 1523K. It was indicated that larger than 10% lattice strain was required to form coherent nano-clusters. Ti and O show

a strong special correlation in nano-clusters in LMC and Neither Al or Ni were in the precipitate core.

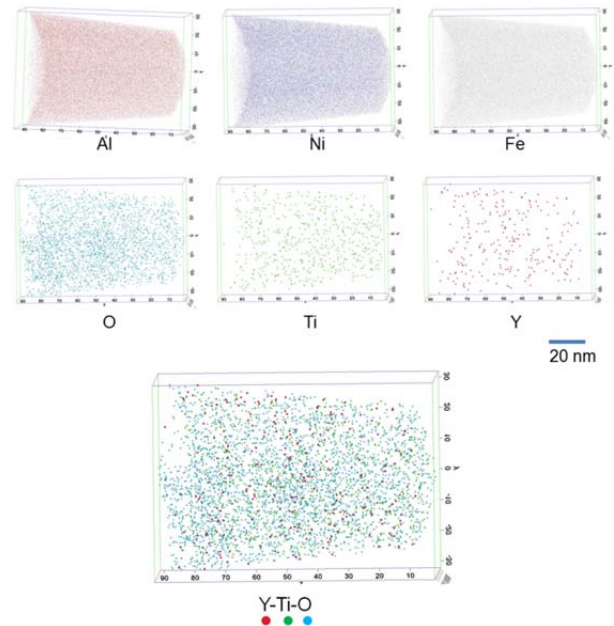


Figure 6. Atom probe tomography images of Al, Ni, Fe, Y, Ti, and O that were observed in the as-consolidated NiAl-1wt%Y₂O₃-1wt%Ti alloy

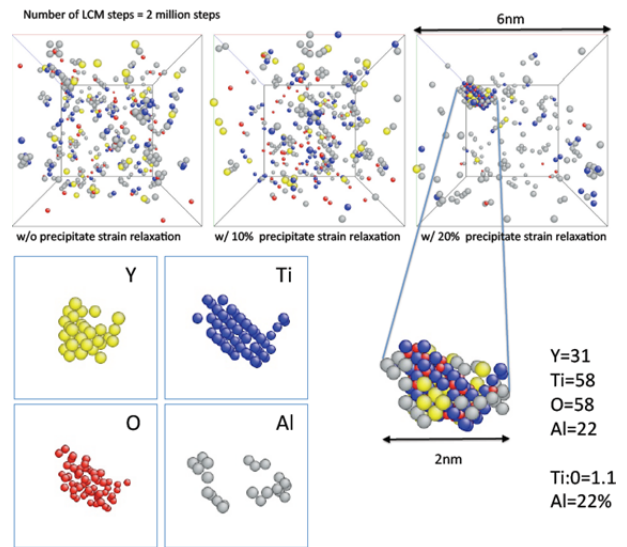


Figure 7. Lattice Monte Carlo simulation result for NiAl-1wt%Y₂O₃-1wt%Ti alloy

4. Conclusions

For ODS NiAl alloys, the key observations can be summarized as followings:

1. There was a clear indication that milling for 5-15 hrs was sufficient to produce good mixing during the mechanical alloying process, as determined by XRD, SEM, and EDS results.

2. Powder consolidation was carried out by spark plasma sintering. Fully dense NiAl alloy materials were produced by SPS.
3. A distribution of 10-20 nm precipitates was found in NiAl-Y₂O₃ and NiAl-Y₂O₃-Ti alloys, and those precipitates were identified as Y-Al-O (garnet) particles in the NiAl-Y₂O₃, while both garnet (Y₂Al₄O₇) and Y₂Al₉Ti₂O₆ phase particles were found at the NiAl-Y₂O₃-Ti alloy.
4. The Al composition of a particle increases as the particle size increases, and Y was dominantly found at the particles size of less than 50 nm while Ti was found at the relatively larger particles with size larger than 100 nm. The Al incorporation believed detrimental to the formation of nanoscale Y-Ti-O precipitates.
5. The effect of Hall-Petch grain size and dispersion strengthening mechanisms in ODS NiAl alloys will be semi-quantatively assessed.
6. The LMC simulations indicate that larger than 10% lattice strain required to form coherent nano-clusters.

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