Processing and structure of a Nitrogen Alloyed Oxide Dispersion Strengthened Austenitic Stainless Steel by mechanical alloying

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Abstract. Pure metallic powders of Fe, Cr, Ni, W, Ti and nano-Y$_2$O$_3$ powders were mechanical alloyed by high energy mechanical milling under N$_2$ atmosphere to develop a nitrogen contained oxide dispersion strengthened austenitic steel powders. The compositions of the mixed powders are Fe-18Cr-8Ni-2W-1Ti-0.35Y$_2$O$_3$. The effects of milling time on nitrogen absorption were investigated. The nitrogen contents in the as-milled powders reached 0.31 wt% after milling for 60 hours and nearly 0.8 wt% after milling for 150 hours. The as-milled powders were then annealed under vacuum at 1173K and 1373 K to promote the formation of the resultant equilibrium phases. Fully austenitic structure was achieved after annealing at 1173K.

1. Introduction
Austenitic stainless steel is a kind of important structural materials for nuclear reactors due to their excellent overall mechanical properties, good corrosion and oxidation resistance compared with ferritic-martensitic steel. The disadvantages of austenitic steel are the low ultimate tensile strength, the inferior creep strength at high temperature and the irradiation induced swelling.

High nitrogen austenitic steels are promising due to their superior mechanical and corrosion properties. An austenitic stainless steel is considered as high-nitrogen steel if it contains nitrogen higher than 0.4 wt % [1]. The nitrogen element in the austenitic steel is benefit for stabilization of austenite phase, improving tensile strengths and corrosion resistance [2,3].

Oxide dispersion strengthened (ODS) ferritic steels fabricated through powder metallurgical route have been studied extensively in the field of nuclear energy during the past two decades. It is demonstrated that ODS ferritic steels are the only materials presenting jointly two important properties (a) high dimensional stability under irradiation, i.e. high resistance to swelling and irradiation creep, and (b) a potential high temperature strength resulting from the homogeneous dispersion of nanometric oxide particles [4]. Oxide dispersion particles are much more stable than carbide at high temperature. These dispersed oxide particles in steel matrix could prevent the movement of dislocations effectively, and thus improve its creep resistance and performances at high temperature. It can be expected that ODS austenitic steels will also show the above mentioned advantages. Especially, if combining the advantages of high-nitrogen austenitic steel with those of ODS austenitic steel, this new modified austenitic steel will show promising for further improvement. However, most of the
published literature on Fe-based ODS alloys concerns ferritic or ferritic/martensitic alloys. There has very little attentions on ODS austenitic steels [5, 6] and almost no research works on nitrogen-alloyed ODS austenitic steel.

In this work, pure powders of Fe, Cr, Ni, W, Ti, and nano-Y₂O₃ powders were processed by high energy mechanical milling under N₂ atmosphere to develop a nitrogen contained ODS austenitic steel.

2. Experimental procedure

The starting materials are pure metallic powders of Fe, Cr, Ni, W, Ti and nano-Y₂O₃ with a purity of 99.9 %. The particle size of all metallic powders are less than 74 μm, while the average particle size of nano-Y₂O₃ is 30 nm. The composition of the mixed powders are designed as Fe-18Cr-8Ni-2W-1Ti-0.35Y₂O₃, with weight ratio. The mechanical alloying (MA) process of the above mentioned powders was performed at room temperature under a high purity (99.99 %) nitrogen atmosphere by using a planetary high-energy ball mill. The nitrogen pressure during MA processing was controlled at one atmosphere by using a pressure appliance. The ball-to-powder weight ratio was 10:1. The rotating speed is fixed at 380 rpm. The milling time are 30, 60, 90, 120 and 150 hours respectively. The nitrogen contents in as-milled powders at different milling time were measured by CHN/O/S elemental analyzer (CE-440, produced by EXETER ANALYTICAL, INC.).

Heat treatment of the mechanically alloyed powders at 1173 K and 1373 K respectively for 5 hours was carried out after sealing the powder in quartz tubes under vacuum (10⁻⁴ Torr). X-ray diffraction (Type: D/MAX-RB) was used for phase identification for both as-milled powders and annealed samples. The micro-structure and the composition distribution of as-milled powders were examined by using Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS). The size distribution of the as-milled powders was measured by laser diffraction method.

3. Results and discussions

3.1 Effects of milling time on nitrogen absorption

Figure 1 shows the nitrogen content (wt %) in the powder mixtures as a function of milling time. It should be noticed that the curve exhibits three stages during processing, which correspond to three absorption rate related to the structure and morphology of the powder particles. During the first 30 hours of milling, the nitrogen content shows a very slow absorbability. Then, in the second stage, nitrogen absorbs rather quickly with the content increasing up to 0.55 wt % after 90 hours of milling. In the third stage, the nitrogen content continues to increase with a slightly slower slope than the second stage, with almost 0.8 wt % after milling for 150 hours.

During the milling process, the ball-to-ball, ball-to-powder, ball-to-wall collided and grinded strongly and frequently, which resulted in the application of compression and shear forces to the powders and induced the rising of the local temperature. The compressed and sheared powders were flattened, fractured and welded during MA processing, thus a large amounts of defects and dislocations in the crystal structures were expected due to the severe plastic deformation. The repeated deformation and the collisions induced local temperatures rising prompt the dynamic energy of the nitrogen atoms which cause the diffusion of nitrogen atoms along the defects and dislocations more easily. The kinetics of nitrogen infusion in the powder mixture should be controlled by the total surface area exposed to the nitrogen gas environment [7]. Figure 2 shows the size and geometry evolution of the powder grains with milling time of 30, 60, 90 and 120 hours. Figure 3 shows the apparent particle size of powders after milling at different time. The size of milled powders decreased obviously when milling time was less than 90 hours, but the size increased after milling for 120 hours. From figure 2 and figure 3, it can be seen that at the first stage of mechanical alloying (milling time less than 30 hours), the powders were deformed but not fractured obviously; the powder sizes were still rather large, which indicates the specific surface area of milling powders is still rather small. This could be an explanation for the very low nitrogen absorption at first 30 hours of milling. When further
increasing the milling time to 90 hours, the accumulated energy in the as-milled powders reached at a very high point, which results in the strong fractures of milling powders and increasing the specific surface area significantly. Thus the nitrogen absorption rate increases obviously during this stage. It is interested to find that when increasing the milling time to 120 hours, the powders became coarse severely. Actually, most of the powders adhered to the vial’s wall. This explained why the nitrogen absorption rate will be decreased at this stage, as shown in figure 1.

![Figure 1. Nitrogen content as a function of milling time](image1)

![Figure 2. SEM micrographs of the powders milled for (a) 30h, (b) 60h, (c) 90h, and (d) 120h](image2)
Figure 4 shows the XRD patterns of powders milled for 30 h, 60 h, 90 h and 120 h respectively. It should be noticed that the peaks corresponding to the initial mixed powders tend to broaden or disappear with the prolongation of milling time. The reasons for this phenomenon should be (1) high density of defects and dislocations were generated during milling, (2) the infinite solid solution was formed between Cr and Fe because of the subtle atomic radius of these two metal elements, (3) the size of as-milled powders become smaller due to the fractures during milling, (4) the lattice instant and plane distance were enlarged as the alloying elements (including Y$_2$O$_3$ and Ti) diffused into the Fe matrix [8-11].

![Figure 3](image3.png)

**Figure 3.** The powder size evolution of as-milled powders as a function of milling time

![Figure 4](image4.png)

**Figure 4.** XRD patterns of initial and as-milled powders (30h, 60h, 90h, and 120h)
3.2 Annealed structure
As-milled powders with different milling time were encapsulated in quartz capsule under vacuum circumstance and annealed at 1173K and 1373K for 5 hours to promote the formation of massive equilibrium austenitic phase. The phases of annealed powders were analysed qualitatively by XRD, as shown in figure 5. The equilibrium phase of as-milled powders after annealing were austenite and no other phases appeared (figure 5 (a)).

![XRD of N2 alloyed ODS austentic steel powders after annealing at 1173K (a) and 1373K (b)](image)

**Figure 5.** XRD of N2 alloyed ODS austentic steel powders after annealing at 1173K (a) and 1373K (b)

The results of annealing indicated that fully austenitic structure could be obtained by mechanical alloying. The outcome of desired structure could be explained by isothermal section of the equilibrium for Fe-Cr-Ni system. At both annealing temperature, no nitride and carbide were found. However, at temperature of 1373 K, FeNi solid solution phase appeared. But only for powders milling for 90 hours, this phase appeared apparently.

4. Conclusion
The nitrogen alloyed ODS authentic steel powders with composition of Fe-18Cr-8Ni-2W-1Ti-0.35Y2O3–xN were prepared by mechanical alloying successfully. The alloying compositions of Y2O3 and Ti diffused into the Fe matrix after milling for 30 hours.

The amount of nitrogen introdourced into the structure increased with the milling time. The absorption of nitrogen content during milling time showed three apparent stages. At the first stage of 30 hours of milling, the amount of nitrogen increased very slowly, and then saw a much quicker growth in the following time of milling (30 to 90 hours). From 90 hours to 120 hours of milling, the absorption rate slowed down a little.

Fully austenite was achieved after annealing the as-milled powders at 1173K. FeNi solid solution formed when annealing at 1373K.

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