Effects of milling time on the microstructures of sintered Fe-16Cr-4Al-0.4Y_2O_3 ODS ferritic steel

E.A. Basuki,[1,*] F. Ramaputra,[1] N.A. Rabbani,[1] S. Ardiansyah,[1] A.M. Khan,[1] A. Korda,[1] F. Muhammad[1] and D.H. Prajitno[2]

[1] *Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Bandung Institute of Technology, Jl. Ganesha No 10, Bandung, 40132, Indonesia*
[2] *Nuclear Technology Center for Materials and Radiometry, National Atomic Agency of Indonesia, Jl. Taman Sari No 71, Bandung, 40132, Indonesia*

Oxide dispersion-strengthened (ODS) ferritic steels have high microstructural stability at high temperatures and provide high creep resistance as well as resistance to swelling due to neutron radiation in nuclear reactors. Mechanical alloying is normally used to manufacture the ODS alloys for nuclear reactor components. The parameters of this process influence strongly on the microstructures and properties of the materials. This paper discusses the effect of milling time on the microstructures of Fe-16Cr-4Al-0.4Y_2O_3 ODS ferritic steel. Planetary ball milling was used to prepare powder composites with milling times of 30, 60, 90 and 120 minutes. Sintering of composite green compacts was carried out at 800, 900, and 1000 °C. X-ray diffraction was used to characterize the phases formed in the ODS alloy. Analysis of microstructure, density and porosity of the sintered ODS ferritic steel was done using scanning electron microscopy and energy dispersive spectroscopy. It was found that milling for 60 minutes gave the lowest pore density in the sintered samples. A fully dissolved solid solution of α-Fe was found when the milling was carried out for at least 60 minutes.

Keywords: ferritic steels, oxide dispersion strengthening (ODS), planetary ball milling, sintering

1. Introduction

Nuclear reactors have been used to generate electricity by more than 30 countries.[1] One of the global requirements for such facilities is being able to work at high efficiency, in contrast to

* Corresponding author. E-mail: basuki@mining.itb.ac.id
[1] Zakine, C., Creep behaviour of ODS steels. *Materials Science and Engineering* **A219** (1996) 102–108.

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renewable energy. This needs operation of the reactors at high temperatures and pressures. Materials that can be used at higher temperatures are demanding. Ferritic martensitic steels containing 9-12 Cr are normally used in some 4th generation nuclear reactors.[2] These steels are heat-treated to obtain martensite after quenching from austenization, followed by tempering at around 760 °C to produce a final microstructure of tempered martensite and ferrite. Recently, oxide dispersion-strengthened (ODS) ferritic steels have been developed as material for the main wall of modern nuclear reactors of the 4th generation.[3] These materials have better properties compared with the conventional materials that are limited to temperatures of about 600 °C.[4] The strength of ODS ferritic steels is provided by the dispersion of ultrafine oxide particles in the ferrite α-Fe matrix,[5] which act as obstacles for dislocation movement along the slip planes of the crystal, through the strengthening mechanism of dispersion hardening.[6] Moreover, ODS ferritic steels have good thermal conductivity, swelling resistance due to neutron radiation, and creep resistance. At high temperatures, the oxide particles are very stable as they have ionic bonding that differ from that of the matrix, so that ODS materials do not have the coarsening problems that normally occur in non-ODS alloys.

Mechanical alloying has been used to prepare homogeneous mixtures of material components; i.e., metals and oxides known as composites, prior to the consolidation process known as sintering to obtain compact materials consisting of tiny oxides dispersed in the matrix. The properties of the sintered materials are strongly dependent on milling variables such as powder:ball ratio and time of milling, and sintering process variables. This paper reports the effects of milling time on the density and porosity of compacted and sintered Fe-16Cr-4Al-0.4Y_2O_3 ODS steel. The effect of sintering temperatures on the microstructures of ODS grains as well as the hardness was also considered in order to gain better understanding of Fe-16Cr-4Al-0.4Y_2O_3 ODS steel manufacturing.

2. Materials and methods

Samples were prepared for the alloy model Fe-16Cr-4Al-0.4Y_2O_3 by weighing pure Fe, Cr and Al_2O_3 powders (obtained from Sigma Aldrich) and mixing them in the compositions shown in Table 1. The average sizes of the powders were 150 μm, 74 μm and 70 nm, respectively. Based on binary phase diagrams of Fe–Cr, this model alloy of Fe-16Cr should give a single phase of α-Fe ferrite.

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[2] Murty, K.L. and Charit, I., Structural materials for Gen-IV nuclear reactors: Challenges and opportunities. *Journal of Nuclear Materials* **383** (2008) 189–195.

[3] Haijian, X. et al., Microstructural evolution in a new Fe-based ODS alloy processed by mechanical alloying. *Nuclear Materials and Energy* **7** (2016) 1–4.

[4] Lee, P.Y., Yang, J.L. and Lin, H.M., Amorphization behavior in mechanically alloyed Ni–Ta powders. *Journal of Materials Science* **33** (1998) 235–239.

[5] Klueh, R.L., Oxide dispersion strengthened steels: A comparison of some commercial and experimental alloys. *Journal of Nuclear Materials* **341** (2005) 103–114.

[6] Zhang, G. et al., The microstructure and mechanical properties of Al-containing 9Cr ODS ferritic alloy. *Journal of Alloys and Compounds* **648** (2015) 223–228.

Table 1. Powder mixtures prepared for different milling times.

Powder	Target composition (%)	Powder weight/g for different milling times/min			
		30	60	90	120
Fe	79.6	7.96	7.98	7.97	7.97
Cr	16	1.6	1.61	1.61	1.61
Al	4	0.4	0.40	0.41	0.41
Y_2O_3	0.4	0.04	0.04	0.04	0.04
Total	100	10	10.03	10.03	10.03

Using a planetary ball mill, shown in Fig.1, each sample and SS316 balls of 8 mm and 11 mm diameters, with a powder:ball ratio of 1:10, were filled into a cylindrical vial. After sealing and closing tightly, the vial was inserted into the planetary ball mill. Milling was carried out for 30, 60, 90 and 120 minutes at a rotation speed of 1290 rpm.

Figure 1. Vial, steel balls and planetary ball mill used in this study.

To remove the stored energy in the milled composite powders, each sample was annealed at 250 °C for 5 min in a tube furnace purged by high purity argon. Compaction was done in a compaction machine under 100 kg/cm^2 for each sample, resulting in tablets of about 11 mm diameter and 3 mm thick. Sintering of the sample tablets was carried out at 800, 900 and 1000 °C for 6 h in a tube furnace purged with high purity argon. Fig. 2 shows the raw materials of the samples and sample tablets resulting from cold compaction and sintering. Using a high-speed diamond saw, the sintered samples were cut into pieces for XRD and SEM analysis.

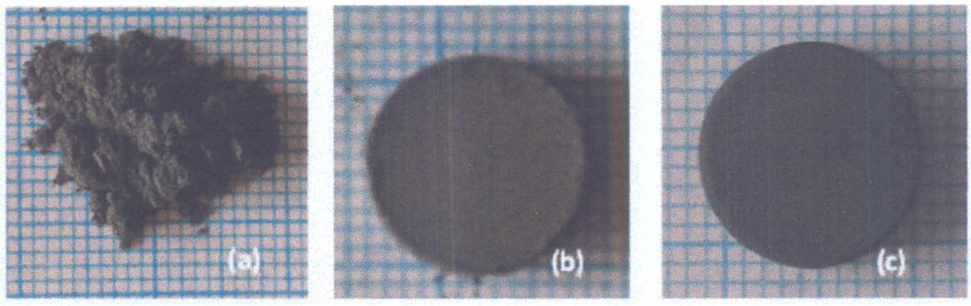

Figure 2. Samples of: (a) as-milled powders; (b) as cold-compacted; and (b) as-sintered.

3. Results and discussion

3.1 Milling and compaction of powders

Figs 3 and 4 show XRD diffraction patterns and X-ray mapping of Cr for the composite powders after milling for 30 and 90 min, respectively. The XRD patterns and X-ray mapping for both milling conditions established that a fully dissolved solid solution of α-Fe was obtained in the sample milled for 60 min. Some pure Cr powder, however, was still unalloyed in the sample milled for 30 min. Therefore, it is concluded from this experiment that to obtain a solid solution of ferrite using the mechanical alloying method requires milling for at least 60 min.

For a constant compaction force of 100 kg/cm^2, the density of the green pellet was, as expected, affected by the milling time. Fig. 5 shows the effect of milling time on the green density of the samples. Each value of these green densities was obtained as the average values of three different samples. The highest green density of 4.60 g/cm^3 was obtained in the sample milled for 60 min. The density of the green pellet was decreased for longer milling times and reached the lowest density (4.27 g/cm^3) at 120 min.

The green densities of the pellets are normally affected by the grain sizes of the milled powders. Gil has revealed that compared with coarse powder particles, fine particles are relatively more difficult to be compacted,[7] implying they would yield a low density. A longer milling time gave a finer milled powder, except for 60 min, where the density reached a maximum (Fig. 5). It is inferred that this is due to the welding process of plastically deformed metal particles of α-Fe that took place within about 60 min after milling was started. When the welding stage is reached, the number of coarse particles increases and this occurs after a relatively short milling time, when the metal particles still have the capability to plastically deform to enable a welding effect.[8] Milling for longer times produced smaller particles as the deformed α-Fe alloy particles have no plastic deformation capability and, consequently, the deformed powders experience fracturing when milling is continued. These results indicate that plastic deformation of metallic powders and cold welding among the deformed powders was very effective when milling for 60 min. Under this condition, the deformed particles still had the capability for plastic deformation during compaction of the samples and this reduced the interparticle voids. However, milling for longer times (i.e., 90 and 120 min) decreased the porosity of the samples. Excessive work-hardening and particle fracturing was responsible, and made the powders difficult to plastically deform during compaction as the particles had become very hard.[2, 4]

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[7] Gil, E. et al., Microstructural characterization of ODS ferritic steels at different processing stages. *Fusion Engineering and Design* **98–99** (2015) 1973–1977.

[8] Lee, J.H., Microstructure and strengthening mechanisms of oxide dispersion-strengthened ferritic alloy. *Journal of Applied Mechanics and Materials* **87** (2011) 243–248.

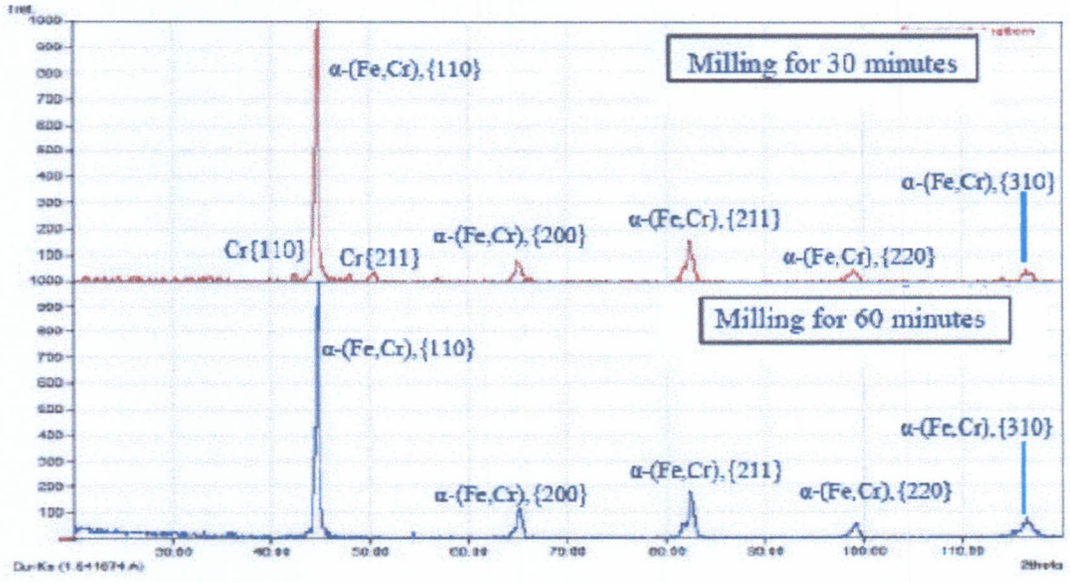
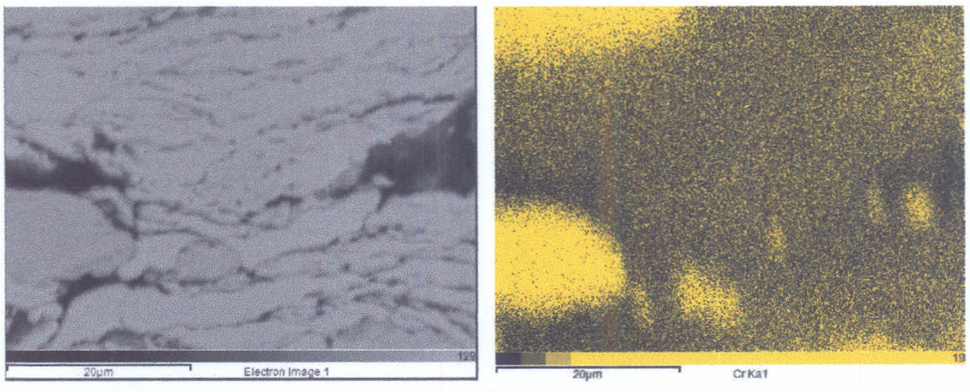
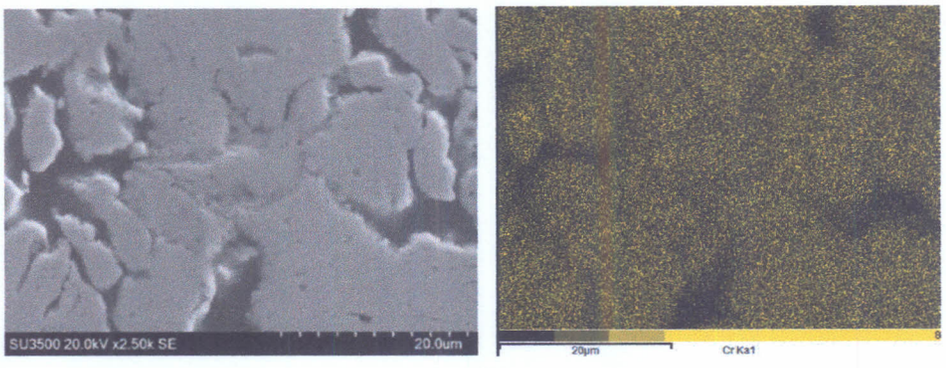


Figure 3. XRD patterns of composites after milling at different times.



(a)



(b)

Figure 4. X-ray mapping of Cr on samples after milling for: (a) 30 min; (b) 90 min.

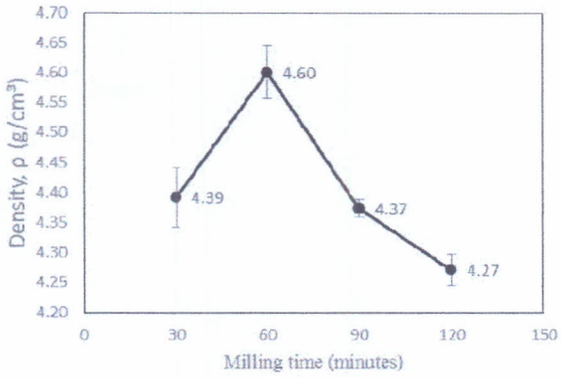


Figure 5. Relation between green density and milling times.

3.2 Sintering products

The experimental results show that after sintering of the green compacted samples the volume of the samples decreased. Sintering of the compacted green tablet samples at 800, 900 and 1000 °C changed the density of the ODS α-Fe sintered samples, as clearly seen in Fig. 6. The density change increased when the sintering temperature was increased, as the mobility or diffusion of the Fe and Cr atoms increased exponentially with temperature.[9, 10] Greater changes in density that gave highest density of sintered samples occur in sintering at 1000 °C. As shown in Fig. 7, the final density of the sintered samples increased with temperature. These densities are closely related to the pore content of the samples, as indicated in Fig. 8, showing that the pores of the sintered samples decreased with increasing sintering temperature.

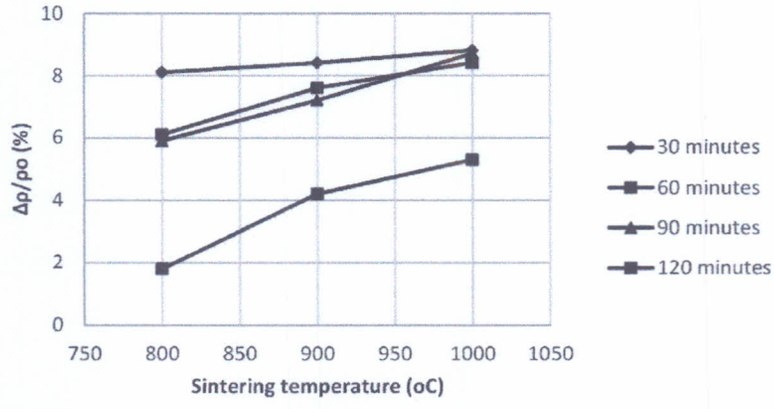


Figure 6. Effect of sintering temperatures on the dimensional changes of sintered samples with milling time.

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[9] Chen, C.L. and Dong, Y.M., Effect of mechanical alloying and consolidation process on microstructure and hardness of nanostructured Fe–Cr–Al ODS alloys. *Materials Science and Engineering* **A528** (2011) 8374–8380.

[10] London, A.J., Effect of Ti and Cr on dispersion, structure and composition of oxide nano-particles in model ODS alloys. *Acta Materialia* **97** (2015) 223–233.

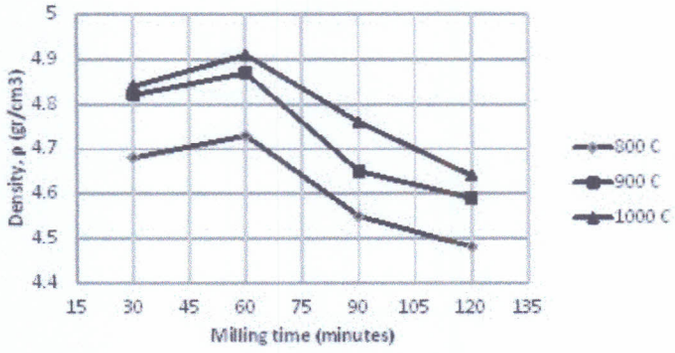

Figure 7. Effect of milling times on the final density of samples sintered at 800, 900 and 1000 °C.

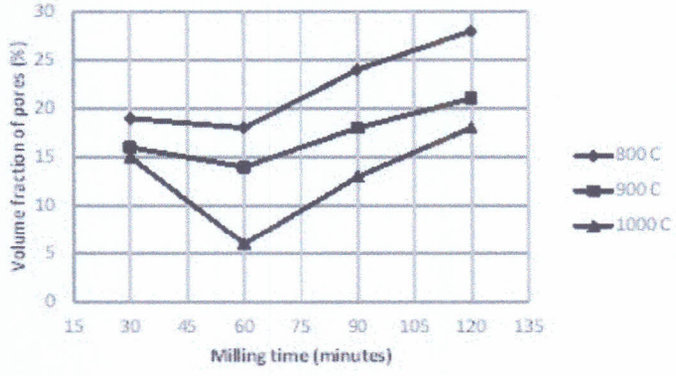

Figure 8. Effect of milling times on the volume fraction of pores in samples sintered at 800, 900 and 1000 °C.

Figure 8 also shows that especially with the sample milled for 60 min, the lowest observed porosity of about 6.1% was reached, due to intensive cold welding during milling and spare ductility for green compaction prior to sintering. Increasing porosity in the samples milled for longer times was caused by intensive fracturing of the powders during milling and loss of the capability for powder particles to cold weld and interlock. However, the pressure at 100 kg/cm^2 (about 9.8 MPa) used for cold compaction in this study was lower compared with that normally used by other researchers.[9,5] Therefore, high porosity was found in all samples milled for 120 min. As shown in Fig. 11, the powder particles in samples milled for 120 min were relatively rounded, even after cold compaction. This evidence indicated that repacking was poor for these samples and, consequently, this condition produced a minimum area for the particles to contact each other during sintering, causing a very slow sintering rate.

Sintered samples milled for 30 min showed elongated grains, as shown in Fig. 9. The size of the grains is relatively smaller and homogeneous in size compared with those milled for longer times; i.e., 60, 90 and 120 min. Few elongated grains are still found in samples milled for 60 and 90 min. However, the grains tended to be more equiaxial in the samples milled for longer times. Flattening of grains was observed in the samples milled for 30 min, but a welding mechanism was identified in the samples milled for longer times. Powder grains experience flattening

followed by welding, as also found in previous studies.[11] No flattened grains were found in samples milled for 120 min, as indicated in Fig. 11, in which the grains were globular and varied in size. The EDS analysis showed that the grains of α-Fe ferrite contained a dispersion of ultrafine Y_2O_3 particles as shown in Fig. 12 and corroborated by the spectra shown in Fig. 13. These particles were mostly observed in samples milled in 120 min and sintered at all temperatures. Tiny particles of Y_2O_3 are believed to be dispersed homogeneously throughout α-Fe ferrite grains of all samples, including samples milled for a relatively short time (30 min), when some chromium powders were still unalloyed.

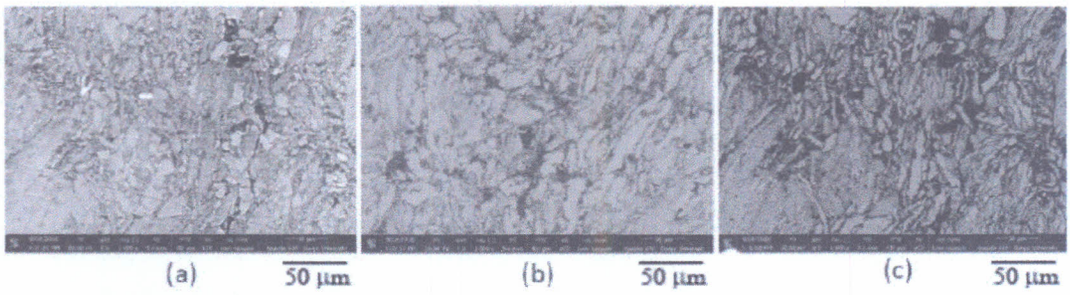

Figure 9. Microstructures of samples milled for 30 min and sintered at (a) 1000, (b) 900 and (c) 800 °C.

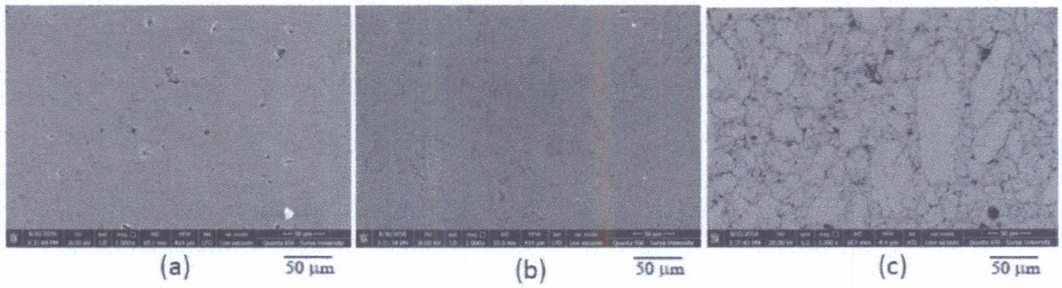

Figure 10. Microstructures of samples milled for 60 min and sintered at (a) 1000, (b) 900 and (c) 800 °C.

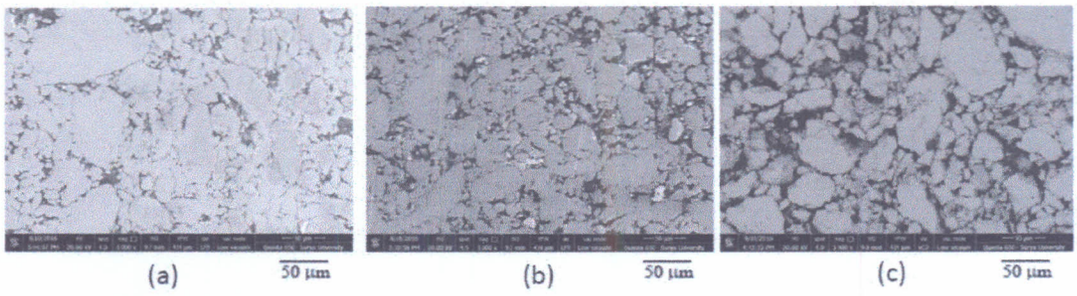

Figure 11. Microstructures of samples milled for 120 min and sintered at (a) 1000, (b) 900 and (c) 800 °C.

[11] Ding, H.L., Annealing effect on the microstructure and magnetic properties of 14%Cr-ODS ferritic steel. *Fusion Engineering and Design* **100** (2015) 371–377.

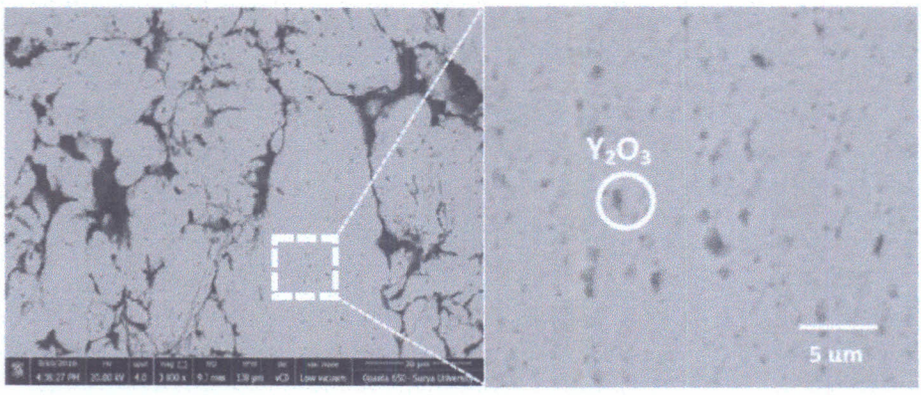

Figure 12. Dispersion of Y_2O_3 particles in ferrite grains of samples milled for 60 min and sintered at 800 °C.

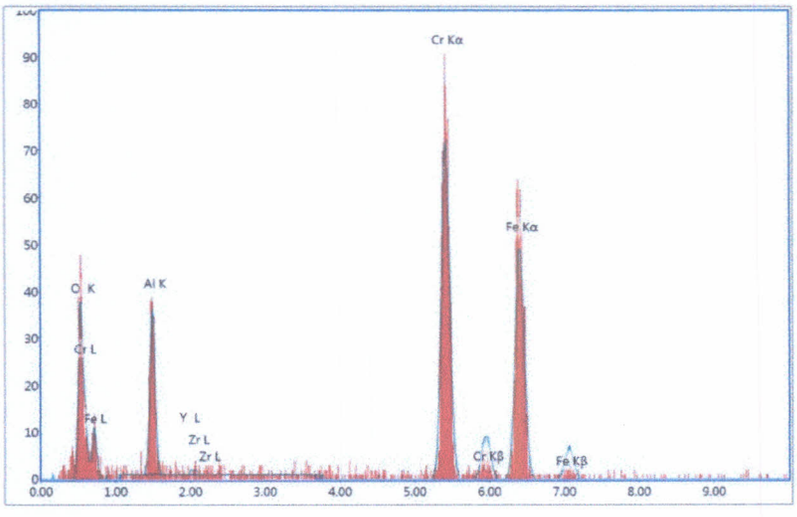

Figure 13. EDS spectra of samples milled for 30 min.

The experimental results confirmed that milling time affected the grain size of the sintered powders. After sintering, the grain size increased with increasing milling time, as shown in Fig. 14. This is predicted due to the higher facility of the atoms to diffuse through the defects resulting from deformation during milling. Moreover, sintering temperatures significantly influenced the rate of grain growth as the temperature activated atomic diffusion in the grains.

Even though the grains in sintered samples became larger with milling time, the hardness of the samples was higher in the samples milled for longer times at all temperatures, as shown in Fig. 15. It indicates that in addition to dispersion strengthening, which plays a significant role in mechanical alloying in powders milled for longer times, strain hardening produced in the milled powders still significantly contributes to the overall hardness of the samples sintered for 6 h.

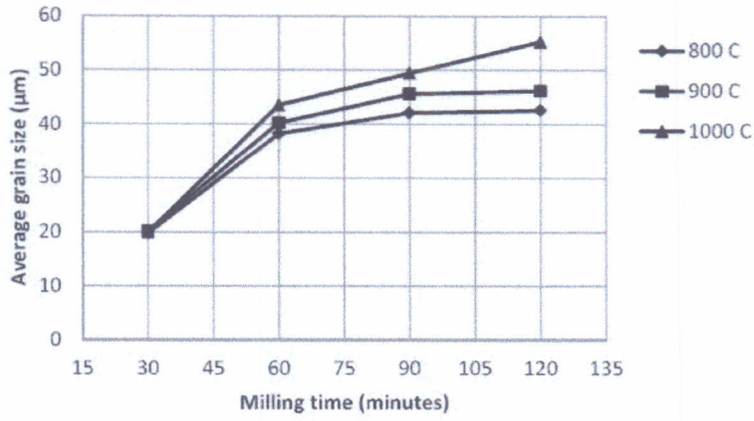

Figure 14. Average grain size for samples with different milling time and sintering temperatures.

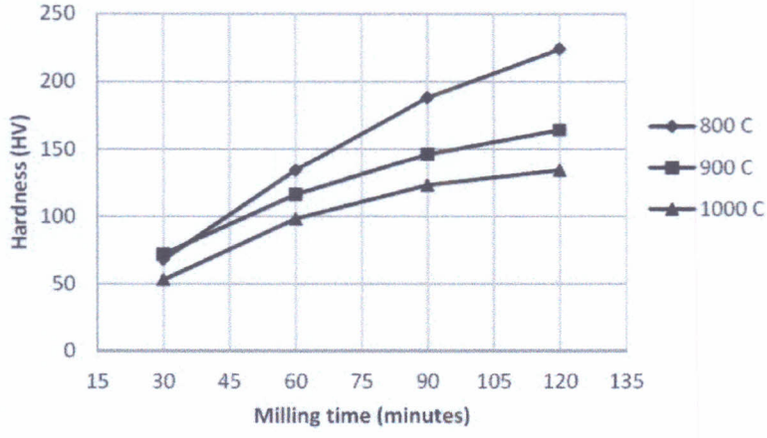

Figure 15. Hardness of samples milled for different times after sintering at different temperatures.

4. Conclusion

The effect of milling time on the microstructures of the Fe-16Cr-4Al-0.4Y_2O_3 ODS steel has been investigated. It was found that milling time strongly influenced the density and porosity of the ferritic ODS steel. Mechanical alloying was not fully obtained when milling was conducted for only 30 min, when pure Cr powder still existed in the composite milled powders. Milling for 60 min and longer provided an α-Fe ferrite solid solution in the matrix powders. The highest density of both green compacted and sintered samples was found in samples milled for 60 min, indicating that the milled powders still have a plastic deformation capability for cold compaction. The high density of dislocation in the deformed grains and high contact area among the compacted grains was responsible for this low pore density. Milling for longer times, however, produced a highly deformed powder that made powders lose their plastic deformation, reducing the contact area between powders for sintering and producing a high pore density in the sintered ODS steels.

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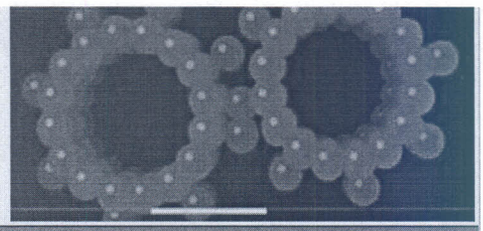

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