

## NANOSTRUCTURED OXIDE DISPERSED STRENGTHENED STEELS: PREPARATION AND INVESTIGATION

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### **Abstract**

*This paper summarizes recent results for preparation, structural and mechanical investigation of oxide dispersed strengthened steel (ODS). Two commercial steel powders, austenitic 17Cr12Ni2.5Mo2.3Si0.1C and martensitic Fe16Cr2Ni0.2C powders have been used as starting materials. Nanosized yttria dispersed martensitic and austenitic sintered steel samples have been realized through powder metallurgical methods. An efficient dispersion of nano-oxides in ODS steels was achieved by employing high efficiency attrition milling. A combined wet and dry milling process of fine ceramic and steel particles has been proposed. Spark Plasma Sintering (SPS) was applied to realize nanostructured steel compacts. Grains with 100 nm mean size have been observed by SEM in sintered austenitic ODS. In comparison, the sintered martensitic dry milled and martensitic dry and combined milled ODS microstructure consisted of grain sizes with 100-300 nm in each case.*

**Keywords:** *oxide dispersed strengthened steel, attrition milling, spark plasma sintering, scanning electron microscopy, X-ray diffraction, mechanical properties*

### **INTRODUCTION**

Oxide-dispersion strengthened steels (ODS) have attracted attention for advanced nuclear applications such as fast and fusion reactors. Many countries such as Japan [1], Europe [2], and the United States [3] have developed and investigated this material for nuclear fission and fusion applications. The production of ODS involves many processes, such as mechanical alloying, degassing, canning, hot extrusion, and heat treatments. Powder metallurgy processes are applied to finely disperse these small oxide particles in the matrix, because oxide particles aggregate together and coarsen during conventional casting processes [4]. Nanostructured ferritic ODS alloys are ideal candidates for high temperature applications such as high temperature heat exchangers or nuclear power plants [5–9].

This paper presents recent results for the preparation, structural and mechanical investigation of oxide dispersed strengthened steel (ODS). Nano-yttria dispersed martensitic and austenitic steel compacts with nanostructure have been realized by the powder metallurgical method. An efficient dispersion of nano-oxides in ODS steels was achieved by employing high efficiency attrition milling. A combined wet and dry milling process of fine ceramic and steel particles is proposed to achieve the efficient oxide

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dispersion. Spark Plasma Sintering (SPS), a novel sintering method, is applied to realize nanostructured steel compacts.

## EXPERIMENTAL

### Starting material

Commercial austenitic „Metco 41C” (Fe17Cr12Ni2.5Mo2.3Si0.1C, AISI Type 316 stainless steel, water atomized, particle size:  $-106+45\ \mu\text{m}$ ) and martensitic „Metco 42C” (Fe16Cr2Ni0.2C, AISI Type 431 stainless steel, water atomized,  $-106+45\ \mu\text{m}$ ) powders were used for sample preparation (Table 1). Ytria with mean particle size 700 nm (grade C) has been purchased from Starck GmbH.

### Milling process

An efficient dispersion of nano-oxides in ODS steels was achieved by employing a high efficiency attritor milling. A combined wet milling in ethanol and dry milling process of fine ceramic particles is proposed by the aid of the mechano-chemical processes assured by attrition milling. A high efficiency attritor mill (Union Process, type 01-HD/HDDM) equipped with a stainless steel setup (tank, agitator, grinding media with 3 mm in diameter) working at 600 rpm for 5 hours was employed.

### Sintering process

For bulk processing, Spark Plasma Sintering (SPS) was used. This technique has a high potential to process „bulk” nanomaterials with good interparticle bonding [10-13]. The external field application is capable of inducing rapid densification and reasonable control of grain growth during the sintering of steels when starting with nanocrystalline powders. The main difference between SPS and hot isostatic pressing (HIP) is the simultaneous application of a pulsed current for SPS, which generates electrical discharges [13,14]. SPS has been applied with success to a wide range of metals, ceramics (oxides, nitrides, carbides) and composites [13]. By using this new sintering method, densification of samples without a considerable grain growth process can be achieved within few minutes. A set of composites were sintered by the help of spark plasma sintering, with the system capacity 10 V and 20,000 A from Sojitz Japan, Dr. Sinter-SPS-7.40MK-VII. The sintering was performed in vacuum, 50 MPa mechanical pressure, temperature 1210-1220 K and 5 minute dwelling time were applied. Circular samples of 50 mm in diameter and 5 mm in thickness have been produced. These samples have been cut by diamond wheels to bars with rectangular geometry (4x5x30 mm in dimension).

### Experimental methods

Morphology and microstructure of the powder and the fracture surface of sintered steels were studied by scanning electron microscope (Zeiss-SMT LEO 1540 XB and Jeol JSM-25-SIII). Phase analyses were performed on an X-ray diffractometer (Bruker AXS D8) with  $\text{CuK}\alpha$  radiation.

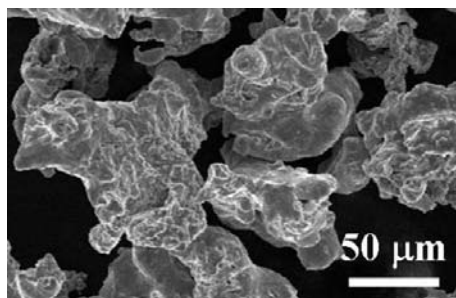
Hardness was determined using a Leitz Miniload2 microscope and micro- Vickers hardness tester by applying two loads 5 and 10 N for 10 seconds. Three point bending strength was determined on an Instron 1112 tensile/loading machine equipped with a data acquisition system. The fractured samples obtained after bending tests were passed on to electron microscopy investigations.

## RESULTS

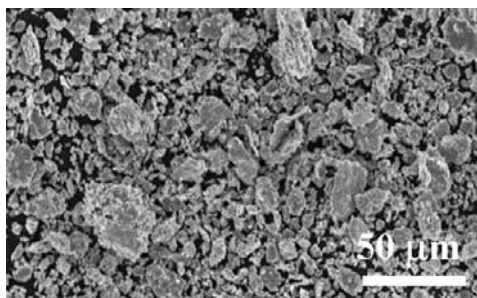
### Structural characterization

#### *Austenitic ODS steel*

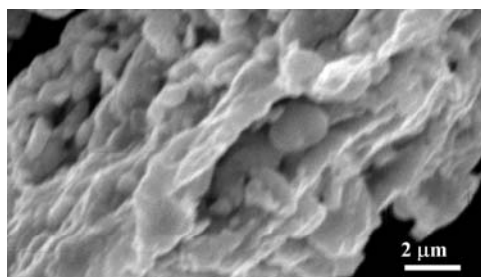
SEM investigations of the starting austenitic powder and milled powder with a 1%  $Y_2O_3$  addition are shown in Fig.1. The average grain size of the starting powder is about 100  $\mu m$  (Fig.1a). The structure of powders is considerably changed after this intensive milling as shown in Fig.1b. The metal grain size of austenitic ODS powder is around 2  $\mu m$  on average. However, these grains are stacked to 5 and 20  $\mu m$  aggregates (Fig.1c). Globular and lamellar shaped grains may be also observed. SEM images of austenitic ODS samples prepared by SPS are presented in Fig.1d. From this investigation is shown the homogenous fracture surface of a sintered “bulk” sample and steel grains with 100 nm mean size may be found.



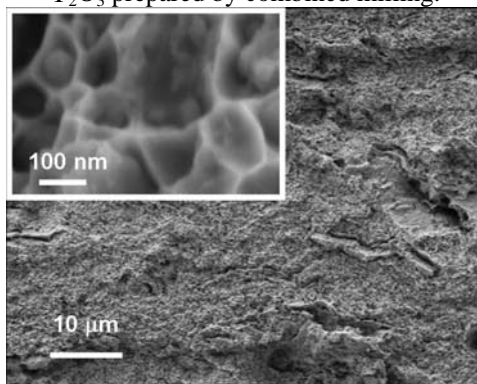
a) SEM image of starting austenitic powder.



b) SEM image of austenitic powder with 1%  $Y_2O_3$  prepared by combined milling.



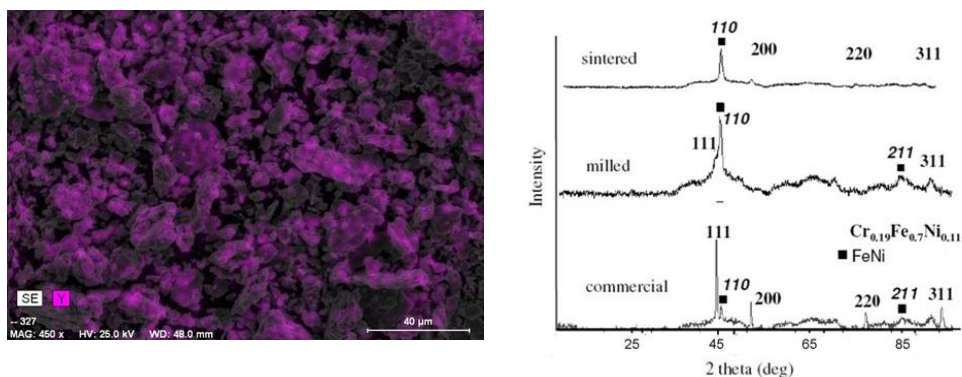
c) SEM image of austenitic powder with 1%  $Y_2O_3$  prepared by combined milling (high magnitude).



d) SEM image of austenitic milled powder with 1%  $Y_2O_3$  after SPS process (inside – high resolution image of sintered nano-structure)

Fig.1. SEM images of austenitic powders.

An addition of 1 wt.% yttria to the starting powder has the aim of achieving improvements in mechanical properties at a high temperature (higher than 775 K). The elemental mappings of dispersed  $Y_2O_3$  concentration in austenitic powder made with the help of energy dispersive spectroscopy are presented in Fig.2a. It was shown that the steel grains are covered homogeneously by yttria nanoparticles.



a) EDS map of  $Y_2O_3$  concentration in austenitic powder after high efficiency milling.

b) XRD measurement of austenitic powders before and after milling.

Fig.2. Structural investigation of austenitic ODS powders.

Phase analyses performed by X-ray measurements are shown in Fig.2b. The main lines of austenite cubic  $Cr_{0.19}Fe_{0.7}Ni_{0.11}$  phase (JCPDFWIN 33-0397) and cubic FeNi (JCPDFWIN 03-1209) have been assigned.

In the case of commercial austenitic powder, where the mean grain size was 100 microns, the  $CrFeNi$  phase is dominant ( $2\theta = 43.55^\circ$ ,  $50.75^\circ$  and  $74.6^\circ$ ). However, the FeNi phase is also present in the powder structure. This is demonstrated by EDS measurements, but the cubic FeNi phase main lines are present on XRD ( $2\theta = 44.5^\circ$ ,  $64.2^\circ$  and  $82.1^\circ$ ). The XRD analyses show the structural changes of powder during milling and the following sintering steps (Fig.2b). The dominant  $CrFeNi$  phase in commercial powder can hardly be observed after milling, but the FeNi main lines became stronger.

### Martensitic ODS steel

The SEM study of martensitic powders is shown in Fig.3. The martensitic ODS powder grain size (Fig.3b) is considerably lowered compared to the initial grain size of the starting powder (Fig.3a). The average grain size is 1-2 microns, but the same sticking tendency is revealed as in the case of austenitic ODS powder. Because of this, the mean secondary grain size can reach 5-10 microns with non-regular morphology, as is shown in Fig.3c. Fracture surfaces of martensitic sintered ODS samples are presented in Fig.3d. The “bulk” ODS steel with a homogenous surface consists of steel grains of 100-300 nm in size.

The most interesting is the distribution of yttria in martensitic powder after an intensive milling process. The EDS mapping shows that the steel grains are covered homogeneously by yttria nanoparticles (Fig.4a).

In the starting martensitic powder the cubic FeCr phase ( $2\theta = 44.7^\circ$ ,  $65.4^\circ$  and  $82.3^\circ$ ) (JCPDFWIN 34-0396) is dominant (Fig.4b). Minor  $CrFeNi$  phase (JCPDFWIN 33-0397) is also present. The average grain size is decreasing without phase change during milling. With the correlation of SEM investigations, the broadening of the FeCr peaks may be related to a decrease of grain size during sintering. The location, dispersion and evolution of yttria in steel matrix is of particular interest in ODS research [14]. In this case, the lines of  $Y_2O_3$  (JCPDFWIN 82-2415) expected at  $2\theta = 29.15^\circ$ ,  $33.79^\circ$ ,  $48.53^\circ$  and  $57.62^\circ$  could not be observed on the XRD spectra.



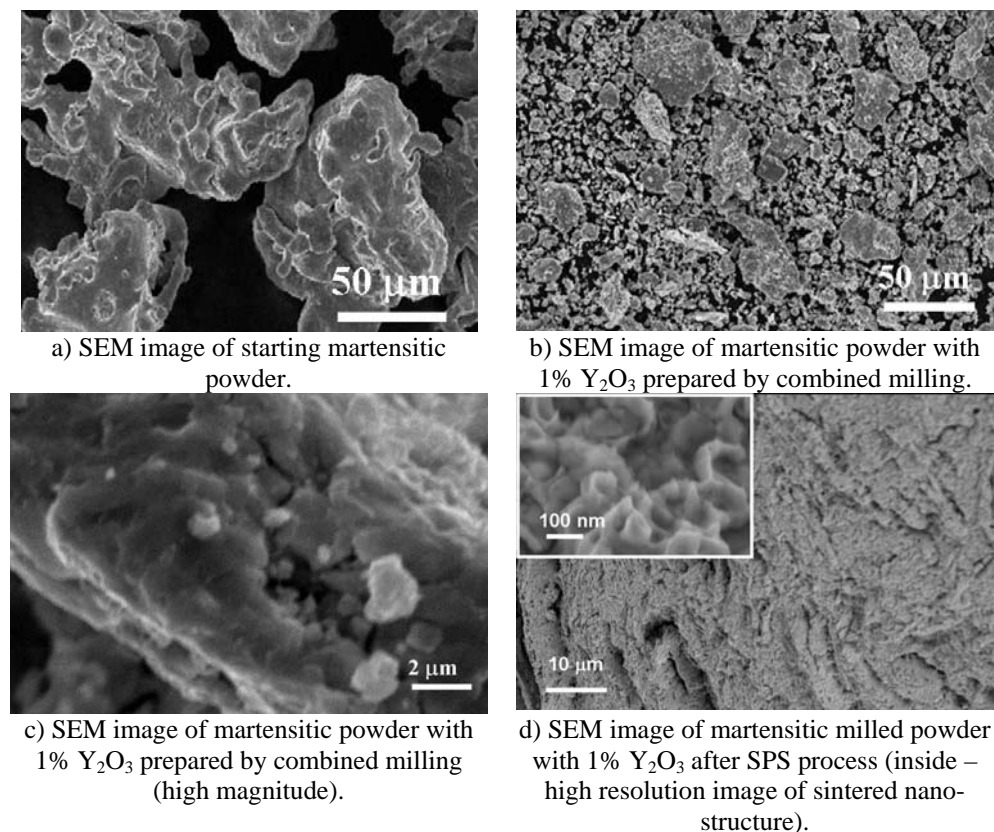


Fig.3. SEM images of martensitic powders.

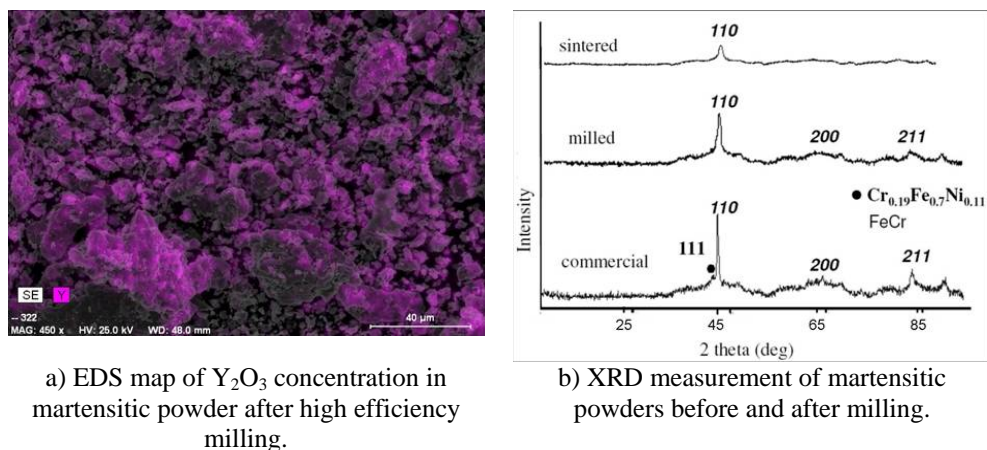


Fig.4. Structural investigation of martensitic ODS powders.

## Mechanical properties

The tensile strength measurements details are presented in Table 1. Martensitic ODS samples showed higher values than austenitic ODS samples.

Tab.1. Tensile strength measurements of SPS sintered ODS steels.

	Martensitic ODS + 1 wt.% Y <sub>2</sub> O <sub>3</sub>	Austenitic ODS + 1wt.% Y <sub>2</sub> O <sub>3</sub>
Rm [MPa], 20°C	832.1	638.95
Rm [MPa], 500°C	580.1	415.4
Bending strength [MPa]	1806.7	1210.8
R <sub>0.002</sub> [MPa]	29.68	24.97
Young modul [GPa]	95.2	80.9

The hardness of sintered ODS was measured with 5 and 10 N load. From these measurements, the hardness of martensitic ODS with 1% Y<sub>2</sub>O<sub>3</sub> addition is higher [HV (5 N) ~ 735 ± 29 and HV (10 N) ~ 849 ± 43] than the austenitic ODS with 1% Y<sub>2</sub>O<sub>3</sub> higher [HV (5 N) ~ 415 ± 18 and HV (10 N) ~ 516 ± 48]. One explanation is that the hardness decreases alongside the increasing Cr content.

## CONCLUSIONS

Two different types (austenitic and martensitic) of oxide dispersed (ODS) steels were produced by intensive milling together with spark plasma sintering. The structure of powders is considerably changed after high efficiency attritor milling consisting of a wet and dry process. The grain size of steel powders was reduced from the starting 100 µm to a few microns. The milled grains were stacked to 5-20 µm aggregates presenting a non-regular morphology at the same time. Dense samples showing nanostructural characteristics have been achieved after sintering at only 1210-1220 K for 5 minutes by spark plasma sintering. Grains of steel with 100 nm mean size have been observed by SEM in austenitic and with 100-300 nm in martensitic ODS. The martensitic ODS is twice as hard as the austenitic ODS. The combined milling resulted in hardness and bending strength increases.

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## REFERENCES

- [1] Ukai, S., Yoshitake, T., Mizuta, S., Matsudaira, Y., Hagi, S., Kobayashi, T.: J. Nucl. Sci. Technol., vol. 36, 1999, p. 710
- [2] Alamo, A., Regle, H., Pons, G., Bechade, LL.: Mater. Sci. Forum, vols. 88–90, 1992, p. 183
- [3] Mukhopadhyay, DK., Froes, FH., Gelles, DS.: J. Nucl. Mater., vols. 258–263, 1998, p. 1209
- [4] Sakasegawa, H., Tamura, M., Ohtsuka, S.: J. Alloys & Compounds, vol. 452, 2008, no. 1, p. 2
- [5] Zinkle, SJ., Ghoniem, NM.: Fusion Eng. Des., vols. 51–52, 2000, p. 55
- [6] Odette, GR., Alinger, MJ., Wirth, BD.: Annu. Rev. Mater. Res., vol. 38, 2008, p. 471
- [7] Guerin, Y., Was, GS., Zinkle, SJ.: MRS Bull., vol. 34, 2009, p. 10

- [8] Chen, CL., Tatlock, GJ., Jones, AR.: Mater. Sci. Forum, vols. 638–642, 2010, p. 3833
- [9] Duffy, DM.: Philos. Trans. R. Soc. A, vol. 368, 2010, p. 3315
- [10] Palm, M., Preuhs, J., Sauthoff, G.: J. Mater. Process. Technol., vol. 136, 2003, p. 114
- [11] Groza, JR., Ribaud, SH., Yamazaki, K.: J. Mater. Res., vol. 7, 1992, p. 2643
- [12] Groza, JR., Curtis, JD., Kramer, M.: J. Am. Ceram. Soc., vol. 83, 2000, p. 1281
- [13] Gang, JL., Grosdidier, T., Bozzolo, N., Launois, S.: Intermetallics, vol. 15, 2007, no. 2, p. 108
- [14] Zhang, L., Ukai, S., Hoshino, T.: Acta Materialia, vol. 57, 2009, no. 12, p. 3671