PREPARATION OF NANO-OXIDE DISPERSED STEEL POWDERS BY POWDER METALLURGY

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Abstract: Nanostructured steels may be realized by two different methods. There is well-known the „top-down" method where taking account the grain size the technological step, like Severe Plastic Deformation (SPD) are developing from top to down. The other „bottom-up" method is starting from individual grains and is developing the product starting from bottom and ending at the top. The last method is considered the main approach of nanotechnology. In this work a summary of „bottom-up" methodology of preparation and examination of nanostructured steel powders is presented. Other steps of powder metallurgy (PM) as high efficient nano-milling, pressing and sintering will be also highlighted. High efficient attrition mills are on the basis of this work assuring grains with nanostructure and a narrow grains size distribution in the same time.

Keywords: oxide dispersed steel, powder metallurgy, high efficient attrition milling, sintering

Ferritic/martensitic steels (FMS) are a primary candidate for the advanced fast reactor cladding/duct materials as well as fusion DEMO plant first wall and blanket structural materials because of their advantage to radiation resistance up to high neutron dose as high as 200 dpa [1,2]. Their utilization is, however, limited to around 600 °C, which is due to inferior tensile and creep strength at higher temperatures. To achieve higher plant operation temperature for improved thermal efficiency, efforts have been made to improve high temperature properties by means of controlling alloying elements and heat-treatment with stabilized carbide precipitates in FMS, especially for application in the power-generation industry [3]. Oxide dispersion strengthened (ODS) FMS are promising materials with a potential to be used at elevated temperatures due to the addition of extremely thermally stable oxide particle dispersion into the ferritic/ martensitic matrix (Figure 1).

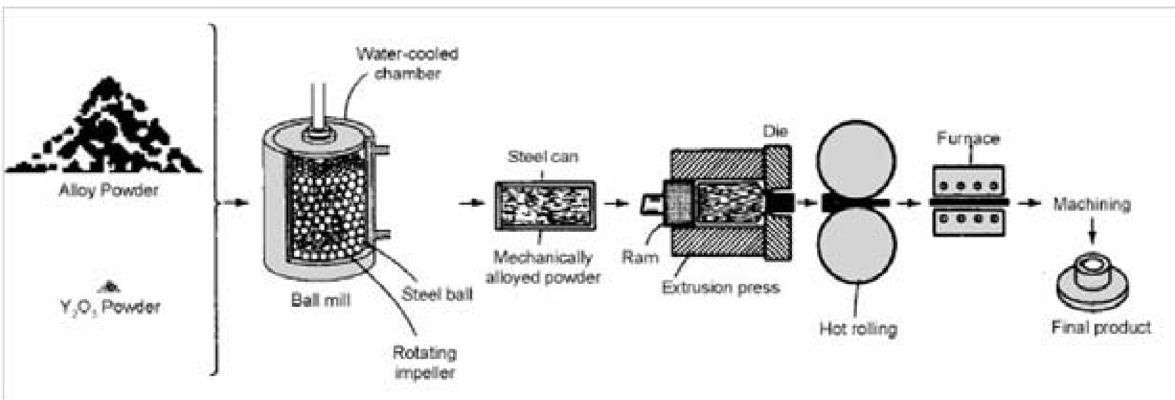

Figure 1. Schematic image of powder metallurgy and mechanical processing techniques

The development of ODS FMS has been conducted in the field of fast reactor fuel cladding application [4-8] and fusion reactor materials application [9-12]. A leading technology development of ODS FMS has been conducted in the Japan Nuclear Cycle Development Institute (JNC) particularly emphasizing fuel cladding application for fast reactors. This technological R&D is believed to extend the performance of reduced activation ferritic steels as a system applicable in fusion structural materials. The research and development of the ODS FMS, as a prospective cladding material for the advanced fast reactor, are being conducted since 1987 in JNC. Fundamental studies concerning optimization of mechanical milling (MM) processing as well as effects of alloying elements on the high-temperature mechanical strength had been carried out in cooperation with fabrication vendors [13,14].

Based on the results of those studies, the manufacturing of thin-walled cladding had been tried with hotextrusion and warm-rolling processes in 1990 [2]. This initial effort revealed that the manufactured claddings had not only degraded creep rupture strength in bi axial hoop direction in comparison with longitudinal uni-axial direction, which is so-called strength anisotropy, but also significantly poorer ductility in the hoop direction. Based on the fundamental study collaborated with Yoshinaga´s group of Kyusyu University, these unexpected mechanical properties of the manufactured ODS claddings were attributed to the grain boundary sliding among grains extremely elongated parallel to the rolling direction [15].

In order to make equi-axed and homogeneous grains, two kinds of approach had been experimentally explored using the extruded bars up to 1994: a to c phase transformation for martensitic 9Cr-ODS steels especially aiming at radiation resistant alloys and on the other side recrystallization processing for ferritic 12Cr-ODS steels aiming at corrosion resistant alloys [16-18]. From 1995 up to 2000, an extensive technological breakthrough has been accomplished for manufacturing thin-walled claddings to prevent crack initiation at an intermediate manufacturing process and for assuring both superior internal creep strength and ductility with homogeneous grain morphology on the basis of phase transformation and recrystallization processing [19-22].

The production processes of a thick-panel and largediameter pipe of ODS steels must be established to apply them to the heavy sections of future fusion first wall and blanket systems.

Figure 2 shows the proposed panel production process for fusion first wall application. A slab should be manufactured by HIP from the mechanical milled powders, and then a large-scale size panel can be directly produced by means of hot-rolling. The hot-rolling process should be necessary in the course of the production process, since the HIP products yield a uniform structure but their Charpy impact properties are degraded as described above.

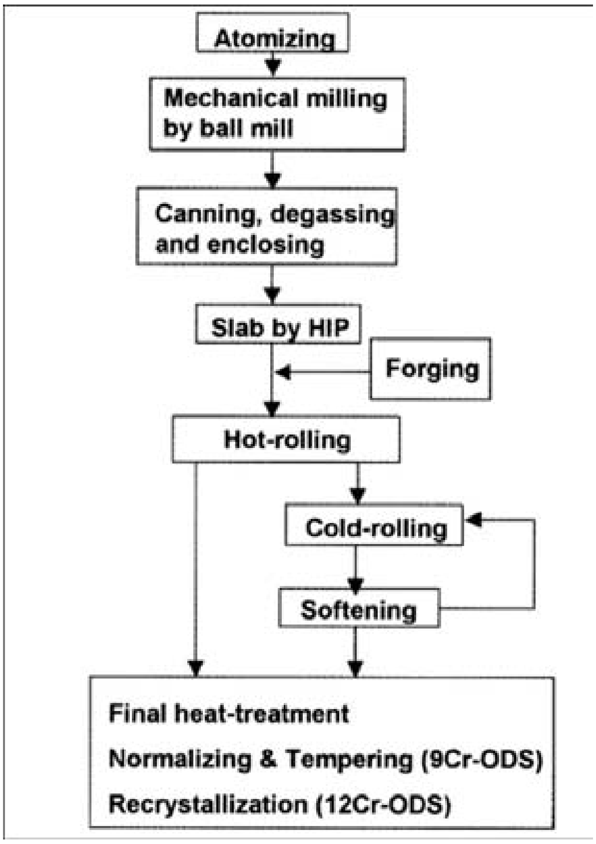

Figure 2. Proposed production process for fusion first wall panel [22].

As an alternative processing route, cold-rolling and subsequent heat-treatment are repeated to make the final panel in about 2 m x 2 m size and desired thickness with sufficiently dimensional accuracy. It is inevitable to soften the hardened cold-rolled panel by means of furnace cooling for martensitic 9Cr-ODS steels and recrystallization-annealing for ferritic 12Cr- ODS steels. The direct production of the final shape by hot-rolling would be applicable under certain circumstances. At the final stage, a heat-treatment to make equi-axed grains is necessary: a to c phase transformation for 9Cr-ODS steels and recrystallization processing for 12Cr-ODS steels. The large-scale equipment capable for production processing already exists in the steel industry.

2. RESULTS

2.1 High energy milling process

An efficient dispersion of ODS steels will be achieved by employing a high efficient milling process, namely the attritor milling (Figure 3). In this proposal the dry and wet coating process of fine ceramic particles is proposed by the help of mechano-chemical processes assured by attrition milling. The versatile attritor mill (available in our Department) can work in dry or in wet condition.

In the case of our model experiments, for some of the powder mixtures a high efficient attritor mill (Union Process, type 01-HD/HDDM) was employed. This apparatus allowed a higher rotation speed and a contamination free mixing process, because of ceramic (silicon nitride, zirconia) parts (tank, arm, balls) as in Figure 3.

Based on our former observations the attritor mill has more advantages to conventional planetary mill. In the wet process, the attritor may work at higher speeds as 4000 rpm in comparison to planetary mill, 500 rpm. The delta discs employed in the attitor, as well as the small media 0.1- 0.2mm assure a very efficient dispersion of IPs in the coating solution. In the following dry process a mechanical alloying process may be also involved.

a) b)

Figure 3. Attritor mills used in this study. a) vertical, b) horizontal alignment [23].

2.2 Pressing, shaping

The ODS samples were prepared by dry pressing machine (7 tons) (Figure 4).

Figure 4. Pressing tool.

2.3. Hot Isostatic Pressing (HIP)

The HIP process (Figure 5) provides a method for the fabrication of structural components from diverse powder materials. In the field of intermetallics it is a common technique to produce shaped componennts. The process is based on filling the powder mixture in a container. It most cases a steel can is applied as compartment. The container is evacuated to high vacuum and the temperature is elevated to remove air and moisture out of the material powders prior to processing.

After sealing the container, it is placed inside the HIP furnace. A high inert gas pressure is applied in the furnace going up to 2000 bar. The isostatic pressure as well as the elevated temperature is responsible for the compaction of the powder in the steel container. Similar to HP technique, elementary or pre-alloyed powders can be applied in this process. Due to the fact that the HIP method takes place at temperature up to 1800℃ very good densities close to the theoretical densities can be obtained by applying this technique.

Figure 5. Hot Isostatic Pressing (HIP).

2.4 Spark plasma sintering

SPS makes it possible to prepare fully densifed composites at comparatively lower temperature with substantial short holding. It also provides a means of precious modification of the kinetics of densification, reactions and grain growth that are involved in an entire sintering cycle. SPS has been applied with success to a wide range of ceramics (oxides, nitrides, carbides and composites). The SPS method is comparable to the conventional hot pressing process, where the precursor powders are loaded in a die and a uni-axial pressure is applied during the sintering. However, instead of using an external heating source, a current, which is typically a few thousands of ampers (and a few volts) can pass through the graphite die, the sample or both. Conduction along the die it represents basically resistance heating, i.e. the die also acts as a heating source. Conduction through the sample may generate breakdown, arcing, spark or plasma among powder particles that induce a fast densification process. By using the SPS method the densification of samples without considerable grain growth process can be achieved within few minutes. In MTA-MFA a FAST sintering apparatus will be developed.

2.5. Structural characterization of ODS steels

Structural characterization of starting austenit powder was performed by scanning electron microscopy (Figure 6).

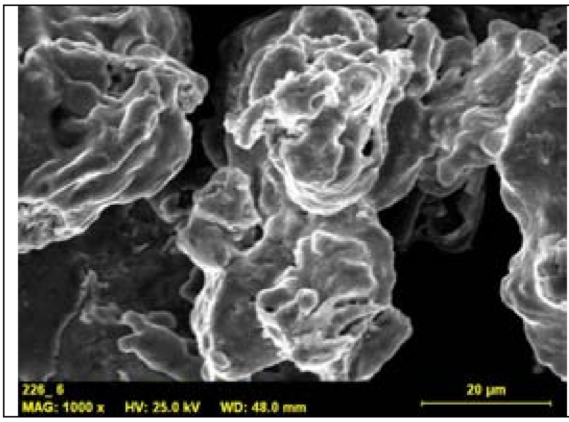

Figure 6. SEM image of starting austenit powder.

Structural analysis of austenitic sample with 1% Y_2O_3 prepared by dry milling at 600 RPM, for 5 hours are presented on following figures (Figures 7-9).

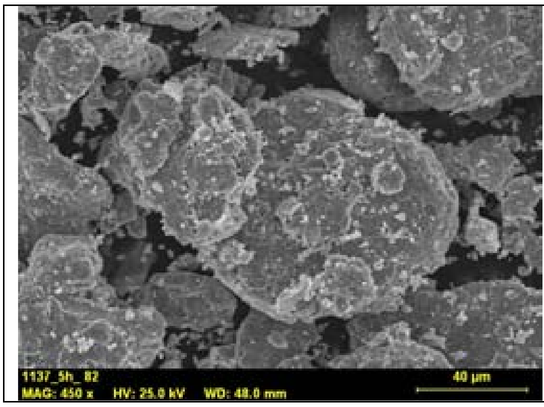

Figure 7. SEM image of austenitic sample.

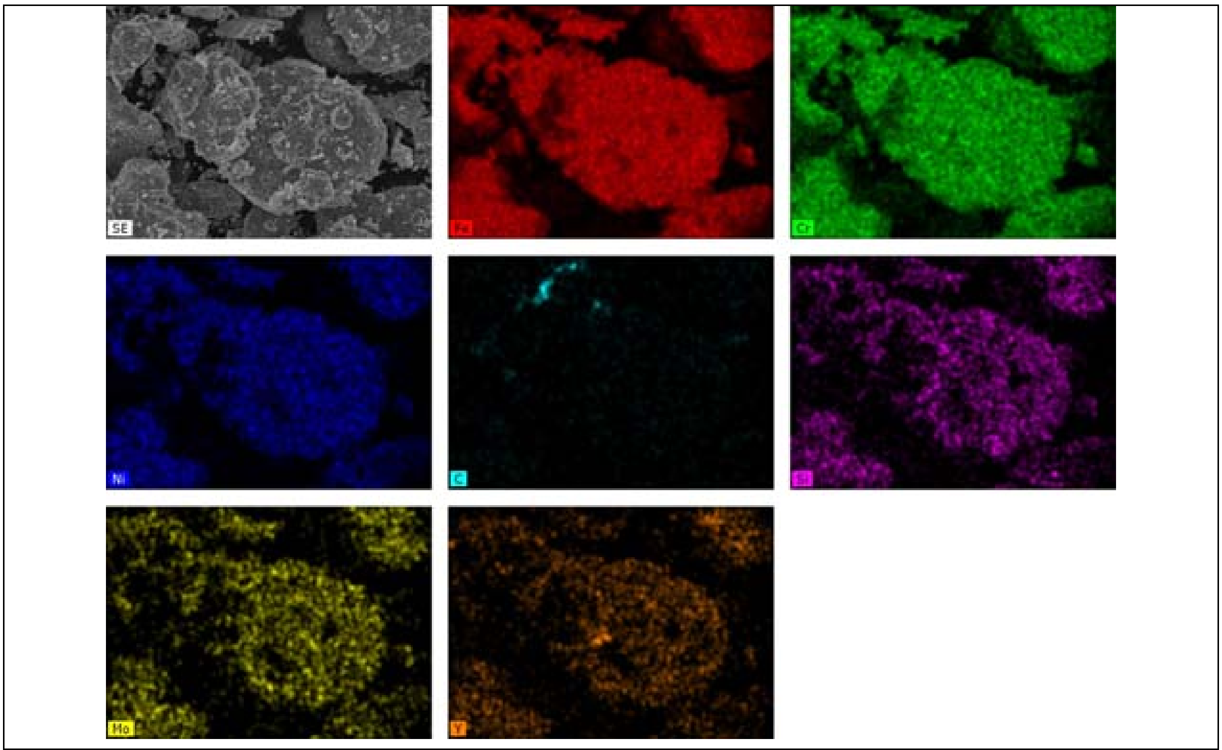

Figure 8. Map of elemental composition of austenitic sample.

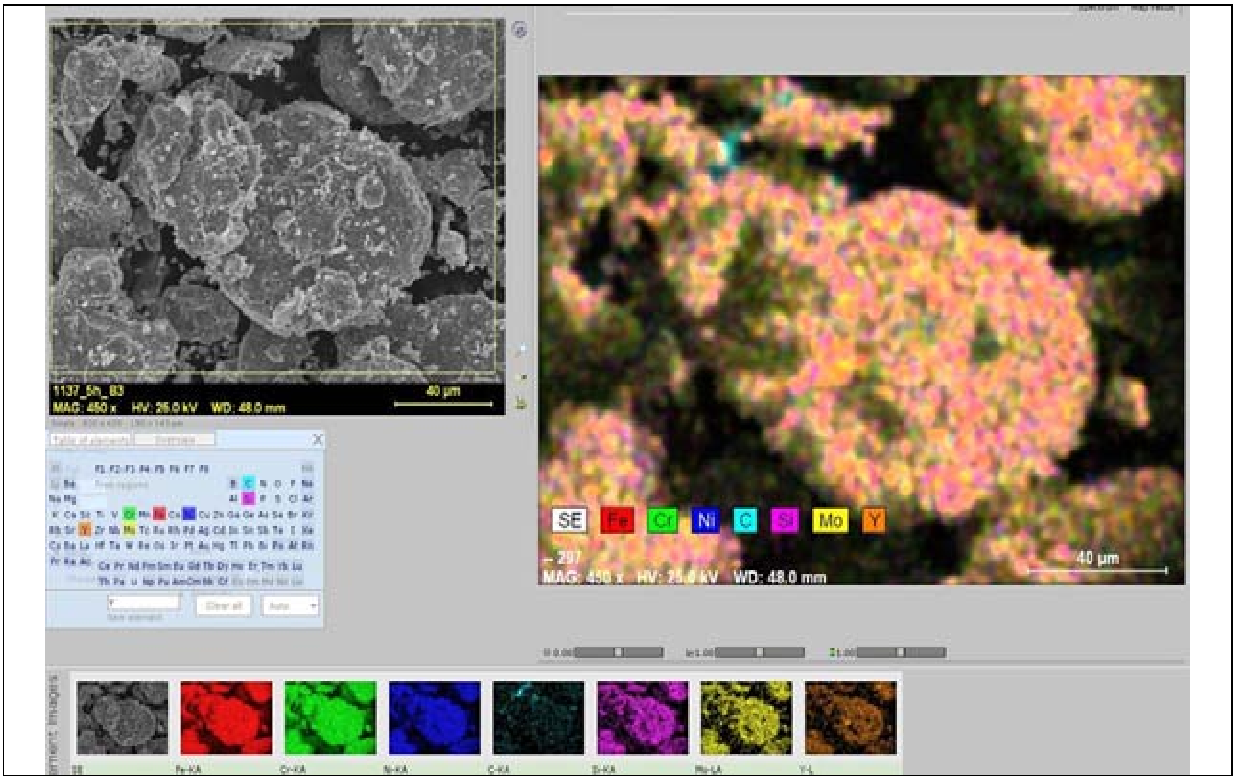

Figure 9. Map of all elements in austenitic sample.

Conclusions

Nanostructured steels may be realized by two different methods. There is well-known the „top-down" method where taking account the grain size the technological step, like Severe Plastic Deformation (SPD) are developing from top to down. The other „bottom-up" method is starting from individual grains and is developing the product starting from bottom and ending at the top. The last method is considered the main approach of nanotechnology. In this work a summary of „bottom-up" methodology of preparation and examination of nanostructured steels is presented. Other steps of powder metallurgy (PM) as high efficient nano-milling, pressing and sintering are used to prepare nanostructured steels. The first step of PM process, the high efficient attrition mills are on the basis of this work assuring grains with nanostructure and a good dispersion of oxide grains in the same time.

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