Microstructures and Hardness of the High Chromium Oxide Dispersion Strengthened Alloy Fe-25Cr-Y2O3 Sintered by the Arc Plasma Sintering (APS)

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Abstract. High chromium ODS alloy has been developed for application as structural material in high temperature nuclear reactor. In the present study, Fe-25Cr-Y2O3 with dispersed 0.5 wt.% Ytria (Y2O3) were synthesized and characterized by means of various techniques as a function of milling time 1, 2 and 3 hours. The alloy synthesis was carried out by the Mechanical Alloying (MA) process and subsequent sintering by means the new plasma technique using the APS apparatus. Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) were conducted for morphology and phase analysis. Evaluation of the mechanical properties was studied based on the Vickers hardness measurement. SEM examination revealed that the sample after sintering by APS method at different milling duration exhibited some particle agglomeration and homogenized oxide dispersion that obviously strengthened the alloy. The XRD test, however, proved the formation of the main phase Fe-Cr. The alloy showed exceptionally high hardness of 193 VHR which is mainly due to the grain refining that increase by the increasing of the milling time.

1. Introduction

Oxide dispersion strengthened (ODS) ferritic alloy exhibits excellent strength, corrosion, hardness and radiation resistance at elevated temperatures. It is considered to be fitted for structural materials on the advanced and high temperature nuclear systems [1]. The excellent characteristics of this alloy has the origin in the special microstructures mainly consisting of fine grains and tiny oxide particles dispersed homogenously with high number density [2]. The nano oxide particle dispersoids that stable in high temperature can act as pinning point to inhibit dislocation movement that provide excellent creep strength and irradiation resistance [3-5]. It was found that the alloy of Fe-25 Cr steels will have excellent in high temperature oxidation by the formation a protective Cr2O3 layer on the surface that exhibited very satisfactory adhesion to the metallic core for all samples. It is clear that Chromium plays an important role in improving the high temperature oxidation resistance of the ODS alloy [6]. In our previous study reported, for achieving sufficient corrosion resistance in severe environment, a new series of high-Cr ODS ferritic steels have been developed to meet the requirements for advanced nuclear fuel claddings. ODS alloys are produced commonly by powder metallurgy and subsequent
densification via sintering at high temperature for several hours. However, mechanical alloying (MA) is a useful powder metallurgy processing technique involving mixing, coalescing, fracturing and remixing of powder particles in high-energy ball [3,7]. Densification process by sintering using conventional electric furnace is well-known to be very high energy and time consuming. At least since mid 80’s Spark Plasma Sintering (SPS) becomes popular for substituting the use of conventional furnace for the densification process. SPS uses high-pulsed DC current (~5000 Amperes) by 10 Volts to generate heat inside the sample body during relatively moderate time of period which is in the range of 30 minutes to one hour. However, beside of high energy demand SPS does not allows the application on samples with irregular shapes. In this place, APS is recognized as economically good alternative to SPS for solidification of powder green materials such as ODS alloy especially due to its simplicity, low power consumption and flexibility in using defined shape of specimens. APS uses plasma plume produced by dissociation of Argon gas which is exothermic process generating temperature higher than 2000°C. The plasma can be easily controlled in term of its diameter that allow process with high speed. Consolidation of ODS sample using the APS is much faster than the conventional way using heating furnace. For example to consolidate a 15mm diameter Zn-Mg alloy it was needed only 1 second at 1 Amperes. Detailed about APS is described elsewhere [8].

In the present study, Fe-25Cr based ODS alloy via powder metallurgy and sintering by APS method is produced with the aim to study the microstructure and mechanical properties of the alloy and their dependency to the preparation specially the milling time. The results were characterized by means of electron microscopy to reveal the characteristic microstructure.

2. Experimental

For this work, the Fe-Cr ODS alloy was produced with the composition Fe, 25 wt.% Cr and 0.5 wt.% of the dispersed particles Y₂O₃. This refers to standard ODS alloy exhibiting high temperature oxidation resistant with sufficient creep properties. The samples were prepared by mixing and milling all of the materials (Fe, Cr and Y₂O₃ powder) for 1, 2 and 3 hours in a high energy milling (HEM). After milling the samples were isostatic pressed with the compression load of 20 tons to get the sample coins as green material. The coins were then consolidated by sintering in the APS at 25 Amperes and 12 Volt for 4 minutes. The APS apparatus is shown schematically in Figure 1.

![Figure 1. The Arc Plasma Sintering Device (APS).](image-url)
The microstructure and composition of the alloys were studied by means of Scanning Electron Microscopy (SEM) coupled with the Energy Dispersive Spectroscopy (EDX). The EDX spectrums illustrated the chemical composition of the samples. The EDX mapping was performed to show and evaluate the distribution of the alloying element of Fe, Cr and the dispersion of Yttria inside the matrix. The XRD test was conducted to study the phases formed during the APS sintering process. The mechanical properties of the consolidated samples were then studied using the Vickers micro hardness (HV) measurement.

3. Results and Discussion

Microstructures of the sintered ODS alloy samples with dispersion of 0.5 wt.% Yttria were presented in Figure 2. The figures were taken from top view as secondary electron images to increase the contrast of the different phases occur. The alloy generally consists of large Fe-Cr alloy matrix phase seen as bright areas and the dark Cr dominated second phases as also confirmed by the EDX measurement. The small bright particles distributed almost homogenously throughout the image area are Yttrium oxides which appear as individual particle but also as agglomerates of some particles. As also observed in our recent investigation, an area of inter-diffusion zone was detected in the matrix-Cr-rich phase interface. This elucidates the fact that the alloying process has been begun with the formation of two single primary Fe and Cr phases followed by the process of interdiffusion the same elements in both direction [9]. Obviously, one can see the grain refining in a function of milling time. The mean grain size of the sample milled for 3 hours is in the range between 2 and 15 μm, whereas those of the sample milled for 1 hour between 2 and 50 μm. The part of fine grains definitely increases with the milling time.

The number of porosity seems to decrease with the grain refining following the rise of the milling time. The porosity falls consequently from about 15 % on the sintered sample milled for 1 hour to circa 10 % on the sintered sample after 3 hours milling. This is by far acceptable because the APS method is press less sintering process which lefts some porosity on its product.

The presence of large single Cr-rich phase can be explained as a result of large different of particle size of the start material. As a Cr-source was used Cr-powder purchased from Aldrich company with initial grain size in average about 60 μm while Fe powder much more smaller (less than 30 μm). Because the alloying process is known to be diffusion driven phenomena, it may happen that during 4 minutes sintering even at high temperature not enough time for Cr atoms to escape their bonding on the Cr particle surface to diffuse toward Fe matrix to at last form Fe-Cr alloy.

![Figure 2. SEM images of the sintered ODS alloy milled (a) 1 hour, (b) 2 hour and (c) 3 hours.](image_url)
milling time has caused homogenize of Yttria presumable due to particle size reduction and intensive mixing during milling. The mean grain size and oxide distribution were similar to those found in the samples sintered by the Spark Plasma Sintering method, which is often reported as a crucial requirement for producing a compact materials with strength and good ductility [10].

EDX mapping again reveals the retained Cr-particle, which remains exist after the sintering process as mentioned before. Figure 3 demonstrate this in undisputed manner the existent of retained Cr particle. The Cr-K line intensity image in the Figure 3a which represents the Cr-rich phase meets deflected zone in the Fe-K intensity in the Figure 3b.

The excess of O-K intensity as present in the images on all the samples correlated directly to Yttrium oxides, which forms agglomeration mainly in the grain boundaries. The most part of O-intensity seems to distributed homogenously on the entire observable surface area inside the grain and grain boundaries. This indicates to the homogenous distribution single Yttrium particles.

**Figure 3.** EDX mapping of the ODS alloy prepared by 1 hour milling.
The XRD investigation was performed to study the phase formation during the ODS alloy sintering process. Figure 6 shows the diffraction pattern of sintered ODS alloy samples after 1 hour milling. In general, during time set the alloy was already dominated by the Fe-Cr phase as confirmed by the observation of the microstructure and measurement of elemental composition by the SEM-EDX presented above. Detailed analysis of the occurrence of this Fe-Cr phase can be taken in the easiest way by observation of the first and most intense peak of the XRD pattern which is cropped from the image and presented in Figures 6b. By increasing of milling time the full-width at half-maximum (FWHM) of the peak become wider. This confirmed the grain refining that strengthened the microstructure observation by the SEM described before. More detailed analysis in the first peak of all samples showed that this is actually a superimposing of Fe-Cr and Fe peaks due to the similarity of the crystal parameters. But the peak of the Fe part is quite small so that it can be concluded the most phase dominated by Fe-Cr phase. The alloying process which drive the formation Fe-Cr phase is mostly completed even though the very short sintering time. These development caused the improvement of the mechanical properties that can be observed on the results of the hardness measurement.

Figure 4. EDX mapping of the ODS alloy prepared by 2 hours milling.

Figure 5. EDX mapping of the ODS alloy prepared by 3 hours milling.
The hardness tests on samples with variation of milling time is given in Figure 7. The ODS steel alloy sample showed significant increase of hardness value from around 170 VHN after 1 hour to 176 VHN after 2 hours milling. But the hardness raises to ca. 193 HVN after milling 3 hours. Increasing the milling time will increase the hardness with not linear shape (depletion to linear path as indicated in the image) which is assumed to be caused by the grain refining in one hand and by the more homogenous distribution of oxide particles at longest milling on the other hand.
Figure 7. Vickers Hardness of the ODS alloy Fe-25Cr-0.5 Y_2O_3 with milling time variation.

4. Conclusion

From this study, it can be concluded that with APS method high Chromium ODS alloy can be produced with sufficiently quality. Due to the low DC current plasma generation, the heat applied to the sample can be exactly defined and controlled. This significantly simplify the handling of the sintering process compared to the conventional method using furnace even using commercially available SPS method. Electron microscopy investigation found that the sample after sintering with APS at different milling duration exhibited some particle aglomeration and homogenized oxide dispersion that obviously improve the strength of the alloy. The XRD test, confirmed the complete alloy formation of the Fe-Cr matrix phase even after sintering process for only 4 minutes. The alloy showed exceptionally high Vickers Hardness of 193 VHR which is mainly due to the grain refining and homogenous distribution of Yttrium oxides following the milling time.

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