Chemical Redistribution and Microstructural Evolution of ODS Fe-Cr Powders During Mechanical Alloying

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The oxide dispersion strengthened ferritic steel powders with chemical composition of Fe-14Cr-3W-0.3Y ₂O₃ were mechanically alloyed from elemental powders in a planetary ball mill. Microstructural and chemical changes at different milling times were investigated by electron microscopy (SEM-EDS) and X-ray diffraction analysis (XRD). It was observed that morphology and structure of powders have experienced many stages during milling, and a quantitative mechanism was proposed. The initiation and evolution of the alloy formation started somewhere around 32 h of mechanical alloying (MA). According to microscopy and XRD analysis, in the first MA stages, milling chiefly has resulted in severe plastic deformation and grain refinement of powders, while in the later stages, alloying was progressed. It seems that 32 hours of milling are necessary to initiate the alloying process of Fe with Cr, but 78 h are not sufficient for completely dissolving W into á-Fe matrix retarding the Fe-Cr-W solid solution formation.

Keywords: ODS ferritic alloys, mechanical alloying, microstructure

Oxide dispersion strengthened (ODS) steels are promising structural materials for Generation IV nuclear fission systems and fusion reactors due to their excellent resistance at high mechanical stress and temperature [1-7]. The dispersion and high density of homogenous nanoscale oxide particles inside a ferritic matrix provide higher operating temperatures, a strengthening effect and a trap for the insoluble helium produced by transmutation reactions [8, 9]. It is known that rare-earth oxides, especially yttria, increase oxidation and creep resistance. ODS steel properties depend on the size and distribution of the oxide phase. Generally, an ODS steel is produced by mechanical alloying of Fe-based alloy or elemental powders with Y₂O₂ powder by high-energy ball milling, using various milling devices and MA parameters. The chemical and physical characteristics of the milled powders depend on the mechanical alloying parameters, such as: type of device, size and number of balls, the ball-to-powder ratio (BPR), rotation speed (rpm), the milling atmosphere, the milling medium (wet or dry), processing temperature and others [10,11]. However, extensive studies show that it is not easy to achieve a uniform distribution of Y₂O₃ during mechanical alloying, leading to inhomogeneous distributions of oxide particles. During the development of ODS materials, it has been known that it is important to adjust the milling parameters and consolidation temperature for improving microstructural homogeneity and, accordingly, the dispersion strengthening of the ODS steels [12]. Optimizing the processing method affects the uniformity and grain size of the alloys as well as their performance in extreme environments.

In spite of numerous studies, there is still a lack of systematic research comparing morphology, size distribution and other characteristics of ODS ferritic steel powders produced by ball milling method under various powder metallurgy conditions [13]. Dousti et al. [14] proposed five stages to the milling process of ODS ferritic alloys. The first stages involve the formation of core-rim particles with large Fe particles in the middle, cold welding and formation of clusters with transition to equiaxed particles with lamellar structures inside them. Further milling leads to severe refining and transition to plate-like particles and fracture and re-welding of these, advancing up to homogenization. Mechanical alloying produces nanograin structures and high dislocation densities in the processed powders. During consolidation, the grains grow or recrystallize, and the dislocations partially recover, depending upon the processing temperature and the presence of nanoclusters [9]. MA powders need consolidation by hot-isostatic-pressing (HIP), spark plasma sintering or hot extrusion [15, 16].

The present study focuses on understanding of the microstructural evolution of a ODS steel during mechanical alloying. Based on the results, a qualitative mechanism for the milling process is proposed.

Experimental part

The ODS powder with chemical composition of Fe-14Cr-3W-0.3Y $_{2}O_{3}$ (in wt.%) was prepared by mechanical alloying using high-purity metal powders with different average particle size (APS) (supplied by Alfa Aesar, USA) of Fe (99.9%Fe, APS < 50 µm), Cr (99.95%Cr, APS < 10 µm), Ti (99.95%Ti, APS < 44 µm), W (99.95%W, APS < 1 µm) and Y₂O₃ (99.995%Y₂O₃ APS 50-70 nm). The powder mixture was mechanically blended for 10 min before milling. The mechanical alloying was performed in a high-purity argon atmosphere using a planetary ball mill, Pulverisette 7 (Frisch). The milling equipment was used with a set of stainless steel vessels and balls. The milling was conducted at room temperature with BPR 10:1, in wet media (anhydrous alcohol – 1 mL to 5 g of mixed powder) to avoid excessive cold welding and oxidation during the milling process. The powders were milled up to 78 hours, at a rotation speed of 250 rpm.

Microstructural and chemical changes at different milling times (10, 32, 50 and 78 h) were investigated. Milled powder samples were characterized by X-ray diffraction

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(XRD) using an X'Pert PRO MPD PANalytical diffractometer with CuK α -radiation (λ =0.1542 nm) followed by crystallite size and lattice strain calculation using Warren-Averbach method. X-ray diffraction line profile analysis is an adapted tool to characterize the behaviour of powders under mechanical alloying process. Warren-Averbach method is one of the most powerful methods to separate crystallite size and lattice distortion effects on the diffraction line broadening [17-20].

Powder morphology and elemental distribution were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a Hitachi SU5000 microscope with Schottky field-emission.

Results and discussions

Microstructure evolution and chemical redistribution during MA process

It has to be pointed out that the mechanical alloying process is statistical in nature, and each particle may have a unique processing history. Accordingly, each interval of milling time can comprise few features specific to different mechanical alloying stages [14].

Investigation of the scanning electron images of the samples milled up to 78 h (fig 1) reveals that particles pass by different milling stages. The initial particle size lies in the 1 μ m to 44 μ m range. In the early milling period (0-32 h) the internal microstructure of powders suffers severe plastic deformation. Due to the impact of balls, particles become flat since iron has very high ductility. Upon further milling, plate-like particles stack forming layered structures. The area and thickness of these layers grew forming lamellar structures (10 h). By applying more impacts, particles agglomerate forming large clusters. The morphology of the lamellar structures at 32 h MA illustrates



Fig. 1. SEM images (secondary electrons) of powders milled for (a) initial powders and after different milling times: (b) 10 h, (c) 32 h, (d)-(e) 50 h and (f) 78 h.

that cold-welded particles still retain their identity and loosely bound to each other. Formation of the lamellar structure inside the particles is necessary to progress alloying in the MA process.

In this stage, diffusion is enhanced by severe plastic deformation involving the advancing of the alloying process. However, some authors consider that shear displacement is the mechanism leading in the milling process, and they do not accept the role of diffusion in MA. To progress towards homogenization of powders in MA, the deformability of components and their welding are necessary conditions [14]. When ductile particles start to weld, the brittle oxide particles are trapped between the layers at the instant of the ball collision. As a result, fragmented reinforcement oxide will be placed at the interfacial boundaries of the welded particles resulting in the formation of composite particles. As welding is the predominant mechanism at this stage, the particles change their morphology by congestion of the lamellar particles. Deformation, welding and solid dispersion harden the material and increase the fracture of structures reducing the particle size and favouring formation of equiaxed morphology (50 h). Prolonging the MA process up to 78 h, welding and fracture reach equilibrium, promoting the formation of composite particles with randomly oriented interfacial boundaries. At the steady state, the microstructure suffers great refinement to nanograins, and the layered structures are no longer visible [21]. To achieve the critical balance between welding and fracturing, the surface of the deforming particles needs to be modified by addition of a so-called process control agent (PCA). The normal range of PCA used in the mechanical alloying process is about 1-5% of the total powder charge [22].

The mechanical alloying atmosphere has no significant influence on the morphology and size distribution of the ODS steel powder particles. However, the elemental powders processed by MA in a very pure argon atmosphere can contain higher amounts of oxygen and carbon than the powders processed in a pure hydrogen atmosphere [23, 24].

The effect of morphology changes on homogenization can be understood by comparing the composition in some locations at different milling times. EDS mapping (fig.2) shows Cr and W distribution in Fe matrix of Fe-14Cr-3W- $0.3Y_{2}O_{3}$ (wt.%) powders processed by MA after 10, 32, 50 and 78 h. The maps show points rich in Cr and W until 50 h MA but at 78 h, the powder seems to be more homogeneous. The chemical composition of the powders processed by MA is presented in table 1. The EDS analysis



Fig. 2. EDS mapping of Fe, Cr and W elements in Fe-14Cr-3W-0.3 Y_2O_3 powders milled for different hours (10-78 h)

 Table 1

 CHEMICAL COMPOSITION OF POWDERS AT

 DIFFERENT MILLING TIMES

Elements (in wt.%)				
MA time	Fe	Cr	W	Y
10h	83.01	16.56	0.43	-
32h	87.09	12.39	0.28	0.24
50h	83.75	13.82	2.45	-
7 8h	82.24	14.94	2.82	-



depicts that Cr might completely dissolve and redistribute in Fe matrix, and its weight percentage almost reached to the nominal one. However, EDS mapping shows that distribution of W even in this long time of milling was not homogeneous, yet.

The presence of reinforcement Y203 particles mixed with ductile elemental powders classifies the mechanical alloying process to a ductile-brittle component system [10]. In figure 3 is proposed one possible scheme of the mechanical milling process of this system processed under the given conditions. A quantitative mechanism is proposed in order to evidence the various milling stages of the ODS milling process. This mechanism shows that the MA process mainly consists of five stages. As presented in the illustration, these stages are: I- agglomeration of the elemental particles and formation of clusters with large Fe particles in the middle part (fig.1a and fig.2), II - deformation/flattening of the ductile particles and fragmentation of the brittle ones (fig.1b), III - the ductile particles start to weld forming lamellar structures, which trap brittle particles inside and with continued milling these structures suffer fragmentation (fig.1c), IV - severe refining of internal layered structures and random re-welding of plate-like particles (fig.1d,e), V - welding and fracture mechanisms reach equilibrium, promoting the formation of composite particles in the nanometer range (fig.1f).

XRD analysis of the MA powders

In order to validate the proposed mechanism, the X-ray diffraction analysis was useful. X-ray diffraction patterns of the mechanically alloyed Fe-14Cr-3W-0.3Y, O, (wt.%) steel powders for different milling times are presented in figure 4. These patterns are characterized by three main peaks of (110), (200) and (211) planes referring to á-Fe and the peaks of unalloyed tungsten. The Fe and Cr peaks are situated very close, and they are observed in the initial mixt powder, whereas they have mostly disappeared in the MA processed material. However, the remaining W peaks in the XRD pattern of the 78h milled powder reveals the hard dissolution rate of this element into Fe matrix, which retards the Fe-Cr-W solid solution formation. XRD analysis combined with the SEM-EDS results can suggest that 78 h time of processing is sufficient to obtain a wellblended microstructure with relatively uniform and fine size distribution, but a longer milling time or higher energy is needed to obtain the Fe-Cr-W solid solution.

The (110) peak typical to Fe matrix of the initial and milled is presented in figure 5. The XRD analysis on the ball milled powders show that the diffraction peaks became substantially broadened after 78 h of milling. Peak broadening is attributed to diminution of crystallite size and introduction of defects and microstrain during the milling process.

Fig. 3. Illustration of powder

microstructure evolution in the mechanical alloying process.





Fig. 5. Typical XRD peak shifts and broadening of the Fe matrix during MA process

The collisions of milling balls induce severe plastic deformation of the powder particles which leads to work hardening and ultimately fracture. Prolonged processing conducts to the reduction in particles and crystallite size, and increases the defect density which manifest in broadening of the diffraction peaks. This gradual reduction of the crystallite size and increase in the lattice strain is confirmed by Warren-Averbach analysis of the diffraction patterns. In the early stages of MA a rapid decreasing of the crystallite size to about 23 nm was observed and further milling proceeds relatively slow and powders reach an average crystallite size of about 9 nm (fig.6). Figure7





Fig. 7. Variation of lattice strain with MA time

shows the variation of the lattice strain with the milling time; it may be noticed that there is an increase of lattice distortion up to 1%.

Comparing the diffraction line profiles after different milling hours, a shift of the typical (110) peak of the Fe matrix towards a lower angle is observed (fig.5). This shift can be due to lattice parameter increase which expends the Fe matrix. In a study, Khatikar et al. [25] reported a lattice parameter increase during pure iron milling for 20 h and suggested that mechanical milling increases defect density and also increases surface energy of crystal due to reduction in size, which might lead to expansion of the cell.

Conclusions

On the basis of the results, the following conclusions can be drawn:

The milling of Fe-14Cr-3W-0.3Y₂O₃ (wt.%) ODS powder mainly consists of five stages. Morphology of particles varied from loosely bound deformed primary powders (stages I and II) to lamellar packed structures, which suffer cold-welding and fragmentation (stage III), followed by deformation, re-welding and increased fracture that favour particle size diminution and equiaxed morphology formation (stage IV). Finally, by prolonged milling the welding and fracture reach equilibrium, promoting composite particle formation with a nanostructure (stage V).

In the first stages (from beginning to 32 h), the milling process resulted in severe plastic deformation, while in the later stages (after 32 h), particle refinement and alloying were progressed. It seems that powder alloying induced by mechanical milling is limited before the formation of layered structure. It is believed that the lamellar inner structure of the formed particles produces more interfaces between elemental components in the microstructure helping diffusion. Additionally, it could be that the strain induced in powders processed by MA determines enough dislocations and grain boundaries density to start diffusion in solid state.

The collision-induced dissolution rate of the Cr into the Fe matrix is higher than that of the W. The poor dissolution of W particles retards the Fe-Cr-W solid solution formation. Higher process energy is necessary to obtain the solid solution.

In the mechanical alloying process a change of crystal lattice takes place by increasing the network defects and deformation. During milling, there was a gradual decrease in the crystallite size combined with an increase of the lattice strain. Given the fact that the concentration of Y_2O_3 is low, it is hard to characterize the microstructural evolution of the oxide dispersions by the analysis techniques used for this study.

This work will be used in parameter optimization to obtain ODS ferritic steels by mechanical alloying in Pulverisette 7 planetary ball mill.

References

1.LIU, D.H., LIU, Y., ZHAO, D. P., WANG, Y., FANG, J.H, WEN, Y.R., LIU, Z.M., Trans. Nonferrous Met. Soc. China, **20**, 2010, p. 831;

2.KARAK, S.K., MAJUMDAR, J.D., WITCZAK, Z., LOJKOWSKI, W., CIUPINSKI, L., KURZYDLOWSKI, K.J., MANNA, I., Metall. Mater. Trans. A, **44A**, 2013, p. 2884;

3.AUGER, M.A., DE CASTRO, V., LEGUEY, T., MONGE, M.A., MUNOZ, A., PAREJA, R., J. Nucl. Mater., **442**, 2013, p. S142;

4.RAJAN, K., SARMA, V. S., KUTTY, T.R.G., MURTY, B.S., Mater. Science & Engineering A 558, 2012, p. 492;

5.RAHMANIFARD, R., FARHANGI, H., NOVINROOZ, A. J., MONIRI, S., Metall. Mater. Trans. A, **44A**, 2013, p. 990;

6.ROGOZHKIN, S. V., BOGACHEV, A. A., KIRILLOV, D.I., NIKITIN, A. A., ORLOV, N. N., ALEEV, A. A., ZALUZHNYI A. G., KOZODAEV, M. A., The Phys. Metals Metallography, **115**, no.12, 2014, p. 1259;

7.ROUFFIE, A.L., WIDENT, P., L. ZIOLEK, DELABROUILLE, F., TANGUY, B., CREPIN, J., PINEAU, A., GARAT, V., FOURNIER, B., J. Nucl. Mater., **433**, 2013, p. 108;

8.DAI, L., LIU, Y., MA, Z., DONG, Z., YU, L., J. Mater. Science, **48**, 2013, p. 1826;

9.ALINGER, M.J., ODETTE, G.R., HOELZER, D.T., Acta Materialia, 57, 2009, p. 392;

10.SURYANARAYANA, C., Progress Mater. Science, 46, 2001, p. 1;

11.SURYANARAYANA C., AL-AQEELI, N., Progress Mater. Science, 58, 2013, p. 383;

12.KIM, J. H., BYUN, T.S., LEE, J.H., MIN, J. Y., KIM, S.W., PARK, C. H., LEE, B. H., J. Nucl. Mater., **449**, 2014, p. 300;

13.OKSIUTA, Z., Acta Mechanica et Automatica, 5, no.2, 2011, p.74; 14.DOUSTI, B., MOJAVER, R., SHAHVERDI, H.R., MAMOORY, R.S., J. Alloys Compd., 577, 2013, p. 409;

15.BOULNAT, X., PEREZ, M., FABREQUE, D., DOUILLARD, T., MATHON, M.H., DE CARLAN, Y., Metall. Mater. Trans. A, **45A**, 2014, p. 1485;

16.ZHANG, H., HUANG, Y., NING, H., WILLIAMS, C.A., LONDON, A. J., DAWSON, K., HONG, Z., GORLEY, M. J., GROVENOR, C.R.M., TATLOCK, G.J., ROBERTS, S.G., REECE, M. J., YAN, H., GRANT, PS., J. Nucl. Mater., **464**, 2015, p. 61;

17. MITTEMEIJER, E.J., WELZEL, U., Z. Kristallogr., **223**, 2008, p. 552; 18. VIVES, S., GAFFET, E., MEUNIER, C., Mater. Science and Engineering, **A 366**, 2004, p. 229;

19.ICHIKAWA, R.U., MARTINEZ, L.G, IMAKUMA, K., TURRILLAS, X., Published in: Blucher Physics Proceedings, **1**, no. 2, 2014; DOI: 10.5151/ phypro-ecfa-049; and presented at Conference: IV Workshop of Applied Crystallography to Materials Science and Engineering, Vitoria-ES, Brazil, **1**, may 2014;

20.STANCIULESCU, M., ABRUDEANU, A., GALATANU, A., CARLAN P., MIHALACHE, M., Rev. Chim. (Bucharest), **68**, no.5, 2017, p. 1109

21.CANAKCI, A., OZSAHIN, S., VAROL, T.L, Powder Technology, **228**, 2012, p. 26;

22.NOURI, A., WEN, C., Critical Reviews in Solid State and Mater. Science, **39**, 2014, p. 81;

23. OKSIUTA, Z., BALUC, N., Nucl. Fusion, 49, 2009, 055003;

24. MURAMATSU, Y., WAMIKAWA, S., OHTAGUCHI, M., OKADA, H., ABE, F., Mater. Transactions, **46**, no.3, 2005, p. 681;

25.KHATIRKAR, R.K., MURTY, B.S., Mater. Chem. Phys., 123, 2010, p. 247.

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