Effect of Nanosize Yittria and Tungsten Addition to Duplex Stainless Steel During High Energy Planetary Milling

A K Nayak, R Shashanka, D Chaira*

Department of Metallurgical and Materials Engineering, National Institute of Technology Rourkela, Rourkela-769008, Odisha, India

*E-mail: chaira.debasis@gmail.com, Phone: +91(661)2462561

Abstract. In this present investigation, elemental powders of duplex stainless steel composition (Fe–18Cr–13Ni) with 1 wt. % nano yittria and tungsten were milled separately in dual drive planetary mill (DDPM) for 10 h to fabricate yittria dispersed and tungsten dispersed duplex stainless steel powders. The milled powder samples were characterized by X-Ray diffraction and scanning electron microscopy (SEM) to study the size, morphology and phase evolution during milling. The gradual transformation from ferrite to austenite is evident from XRD spectra during milling. The crystallite size and lattice strain of yittria dispersed duplex stainless steel after 10 h milling were found to be 7 nm and 1.1% respectively. The crystallite size of tungsten dispersed duplex stainless steel was 5 nm. It has been observed from SEM analysis that particles size has been reduced from 40 to 5 μm in both cases. Annealing of 10 h milled powder was performed at 750°C for 1 h under argon atmosphere to study phase transformation in both yittria and tungsten dispersed duplex stainless steel. The XRD analysis of annealed stainless steel depicts the phase transformation from α-Fe to γ-Fe with the formation of oxides of Y,Fe and Cr. The differential scanning calorimetry analysis was conducted by heating the milled powder from room temperature to 1200°C under argon atmosphere to investigate the thermal analysis of both the stainless steel powders.

Keywords: Mechanical alloying; DDPM; Annealing; Phase transformation; DSC

1. Introduction

Demands of stainless steel has been increased in various fields because of its properties like high corrosion resistance, good toughness, low thermal expansion, high energy absorption, weld-ability and high strength [1]. Based upon their crystalline structure and properties, stainless steels can be divided as austenitic stainless steel, ferritic stainless steel, martensitic stainless steel and duplex stainless steel. Duplex stainless steel contains almost equal proportions of ferrite and austenite phases in its structure which has made it to have very good toughness, high corrosion resistance, low thermal expansion, high energy absorption, weld-ability and high strength compared to single phase austenitic and ferritic stainless steel, hence used in chemical, oil, petrochemical, marine, nuclear power, paper and pulp industries [1-4].
The structural components in super thermal plants and nuclear reactors are subjected to high operating temperatures. Oxide dispersion strengthened (ODS) steels are considered most suitable materials because of their ability to retain mechanical strength and resist oxidation/corrosion under extreme conditions of temperature and pressure [5]. Rare earth oxides, particularly yittria is known to increase the creep resistance and oxidation resistance. The properties of the ODS steel is dependent upon the size and distribution of the oxide phase in a given proportion.

Phaniraj et al. prepared mechanically alloyed austenitic steels (Fe–20Ni–14Cr–2.5Mo–2Mn–2.5Al-wt. %) dispersed with 0, 0.5 and 5 wt. % yittria and tested their cyclic oxidation behavior at 800°C in air. They found that addition of yittria improves the resistance to scale spallation but higher yittria content does not affect the oxidation rate of the alloy significantly [6]. Xu et al. synthesized ODS 304 austenitic steel (0.35 wt. % Y₂O₃) by mechanical milling and consolidated by hot isostatic pressing for 3 h at 1423 K under a pressure of 200 MPa. They concluded that the tensile and yield strength of ODS alloy were greatly improved compared with 304 austenitic steel, but the ductility reduced due to coarse oxide particles both at room temperature and high temperatures [7]. Torralba et al. also investigated the mechanical response of ODS ferritic steels (pre-alloyed grade of Fe–20Cr–5Al and Fe–14Cr–5Al–3W with the addition of Ti and Y₂O₃ as reinforcements) by mechanical alloying followed by spark plasma sintering at 1200°C and 64 MPa. They reported enhanced tensile properties of ODS alloys as compared to pre-alloyed alloys [8]. Olaniran et al. fabricated oxide dispersed duplex stainless steel (2205) dispersed with partially stabilized Zirconia (3 mol. % yittria) by hot press sintering machine for 30min at 30MPa at the temperature 1100°C in argon gas environment and demonstrated that addition of chromium and nickel can enhance densification and corrosion property of duplex stainless steel composites [15].

On the other hand, tungsten is used for preparation of super duplex stainless steel which exhibits better pitting corrosion resistance and mechanical properties. Tungsten is an effective element for solid solution strengthening for providing the required mechanical properties and for enhancing the stability of the ferrite phase. However, the addition of tungsten can result in a loss of ductility [8-10]. Xu et al. added tungsten in the ODS steel to stabilize the tensile property at high temperatures [7].

In the present work, an effort has been made to synthesize yittria dispersed and tungsten dispersed (both 1 wt. %) duplex stainless steel (Fe-18Cr-13Ni) through mechanical alloying of elemental powder particles in dual drive planetary mill (DDPM).

The dual drive planetary mill (DDPM) is a specially designed planetary mill meant for the preparation of nano-structured powders in bulk amount. Shashanka et al. showed that for synthesis of nano-structured stainless steel powders a specially designed DDPM required only 10 h as compared to 40 h milling in Fritsch pulverisette planetary mill because of its high acceleration field [12]. The DDPM consists of a gyratory shaft and cylindrical jars. Both shaft and jars rotate simultaneously with different speeds and in opposite directions. The details of mill fabrication and mechanism can be found elsewhere [12].

2. Materials and Methods

Powder compositions of Fe–18Cr–13Ni (wt. %) was selected from Schaeffler diagram to prepare duplex stainless steel by high energy planetary milling. Elemental powders of Fe (99.5% pure), Cr (99.8% pure), Ni (99.5% pure) was milled with 1 wt. % Y₂O₃ (99.5% pure) and 1 wt. % W (99.7% pure) separately in dual drive planetary mill (DDPM) for 10 h to obtain yittria dispersed and tungsten dispersed duplex stainless steel powders. The milling media of the DDPM consists of 1 kg stainless steel balls of 8 mm diameter. The milling was conducted at room temperature with 6:1 ball-to-powder weight ratio in both jars under toluene atmosphere (wet milling) to prevent oxidation. In the DDPM, the angular velocity of the vials and the supporting main shaft were 620 and 275 rpm respectively. Milled powder samples were then characterized by X-ray diffraction (XRD) in a Philips PANalytical diffractometer using filtered CuKα-radiation (λ = 0.1542 nm) followed by crystallite size and lattice strain calculation using
Williamson–Hall method. Powder morphology was investigated by scanning electron microscopy (SEM) using JEOL JSM-6480LV. Annealing of yittria and tungsten dispersed duplex stainless steel powders was carried out at 750 °C for 1 h under argon atmosphere to study the phase transformation. Thermal behavior of final powder samples were studied using differential scanning calorimetry (DSC) Netzsch, Germany. During DSC study, the powder samples were heated from room temperature to 1200°C at a heating rate of 10 °C/min in argon atmosphere.

3. Results and discussion

3.1. XRD analysis of milled powders

Fig. 1 (a) and (b) presents XRD patterns of tungsten dispersed and yittria dispersed duplex stainless steel respectively milled for various times. The XRD patterns of starting powder show sharp crystalline diffraction peaks of elemental Fe, Cr and Ni, while peaks corresponding to W or Y₂O₃ are not detectable owing to their low concentration. It also can be noticed that the peaks corresponding to the starting materials tend to broaden or disappear by increasing milling time. Such behaviour is attributed to considerable increase in structural defects, increased lattice strain, refined grain size and migration of Cr and Ni into lattice of Fe to form solid solution during milling [11]. The collisions and friction during milling resulted in the increase of the local temperature which facilitated diffusion of alloying atom into the matrix [7]. Increase in milling time increases the phase transformation from α-Fe to γ-Fe and after 5h both austenite and ferrite peaks resolve in to (111) and (110) planes of Fe as shown in Fig. 1 (a) and (b). Both 10h milled samples show highly broadened diffraction peaks. It has been widely accepted that during mechanical alloying, the enthalpy of the components increases due to defects introduction and increased internal energy. This could act as the driving force for solid-state amorphization and phase transformation during MA [11].

Fig. 2 (a) and (b) shows the XRD spectra of 10 h milled samples of tungsten dispersed and yittria dispersed duplex stainless steel scanned slowly (1°/min) in the range of 40 to 55°. In this figure, tungsten dispersed duplex stainless steel showed distinct peaks of austenitic and ferritic phase while intensity of austenitic one is more, which confirms transformation from ferritic to austenitic phase. But in case of Y₂O₃ dispersed duplex stainless steel, there is no distinct austenitic and ferritic peaks. Hence it may be concluded that tungsten helps in rapid transformation from ferrite to austenite than yittria. It is also found that limited transformation from ferrite to austenite takes place during milling as milling energy is not sufficient for transformation. However, annealing of milled powder accelerates the transformation [2,12, 13].

3.2. Crystallite size and lattice strain calculation

The broadening of X-Ray diffraction peaks occurs mainly due to instrumental errors, decrease in particle size and increase in lattice strain during milling. The crystallite size and lattice strain can be calculated using Williamson-Hall method by de-convoluting the size and strain by calculating XRD peak width as a function of 2θ [2,12]. The Williamson-Hall equation is given as follows:

\[ \beta \cos \theta = \frac{0.944}{D} + 4\eta \sin \theta \] (1)

Where, \( \beta \) is the full width half maxima (FWHM), \( D \) is the crystallite size and \( \eta \) is the lattice strain.

The crystallite size and strain of tungsten and yittria dispersed duplex stainless steels were calculated from Williamson–Hall method and represented graphically in Fig. 3 (a) and (b) respectively. From the graph it is confirmed that as milling time increases, the crystallite size decreases and it attains a saturation level after 10 h, where further refinement of crystallite size is quite difficult. But lattice strain increases
continuously with milling due to continuous contact between powder–ball-jar surfaces. The crystallite size of tungsten dispersed and yittria dispersed duplex stainless steel decreases from 101 to 5 nm and from 99 to 7 nm respectively. Similarly, the lattice strain increases from 0.36 to 0.7 % for 5 h tungsten dispersed and from 0.5 to 1.1 % for 10 h yittria dispersed duplex stainless steel milled samples respectively.

Fig. 1: XRD spectra of (a) tungsten dispersed and (b) yittria dispersed duplex stainless steel from 0 to 10 h

Fig. 2: Slow scan range XRD spectra of (a) tungsten dispersed and (b) yittria dispersed duplex stainless steel after 10 h of milling
Fig. 3: Variation of lattice strain and crystallite size with milling times of (a) tungsten dispersed and (b) yttria dispersed duplex stainless steel

3.3. XRD analysis of annealed sample in argon atmosphere

Fig. 4(a) and (b) shows the XRD traces of 10 h DDPM milled 1wt. % tungsten dispersed and 1wt. % yttria dispersed Fe–18Cr–13Ni powders after subsequent heat treatment at 750°C for 1 h in argon atmosphere followed by furnace cooling to room temperature. The XRD spectra after annealing in argon atmosphere exhibit the strong diffraction peaks of austenite (γ) and peaks of ferrite (α) and weak oxide peaks in both cases. However, annealed yttria dispersed sample showed more oxide peaks than tungsten dispersed due to steel containing yttria oxide. The presence of Y₂O₃ produces higher amount of oxides containing Y, Fe and Cr as also referred by Phaniraj et al. [6]. The intensity of austenitic peaks is higher as compared to 10h milled powder as phase transformation is favoured during annealing due to supply of heat energy to the powders[12].

Fig. 4: XRD traces of annealed sample of 10h milled (a) tungsten dispersed and (b) yttria dispersed duplex stainless steel heat treated in argon atmosphere at 750°C for 1h
3.4. Scanning electron microscopy
Fig. 5 (a) and (b) shows the SEM micrographs of 0 h and 10 h milled tungsten dispersed duplex stainless steel powders and Fig. 4 (c), (d) represents SEM micrographs of yittria dispersed duplex stainless steel milled for 0 h and 10 h respectively. From the figures, it is clear that before milling elemental powder particles were large and irregular in shape of size 40-50 μm, but after 10 h of milling particles become fine and spherical of size 5-10 μm. At the start of milling, the elemental powder particles become flat flakes due to ductile nature of Fe. As the milling proceeds, two or more flakes get cold welded together and this leads to increase in particle size. The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents [14]. With further increase in milling time the particles get work hardened and fragmentation results into fine and spherical stainless steel powders.

Fig. 5:- SEM images of 1wt. % tungsten dispersed duplex stainless steel milled for (a) 0h (b) 10h and 1 wt. % yittria dispersed duplex stainless steel for (c) 0h and (d) 10h respectively
3.5. Thermal analysis

Fig. 6 (a) and (b) shows the DSC graphs of 10 h milled tungsten dispersed and yttria dispersed duplex stainless steels heated with the heating rate of 10°C/min respectively. It shows exothermic peaks with peak temperature of 755 and 486°C for tungsten dispersed and yttria dispersed duplex stainless steel respectively. The exothermic peaks represent crystal growth, lattice strain release and amorphous to crystalline phase transition during annealing [12]. In the DSC graphs, $T_p$ stands for the peak temperature of the broad exothermic peak which is the crystallization temperature. Sherif et al. found a single exothermic peak corresponding to an amorphous-crystalline phase transformation with crystallization temperature 970°C with an enthalpy change of crystallization 16.88 kJ/mol during DSC analysis of mechanically alloyed Fe-18Cr-8Ni powders. They confirmed it with bright field imaging (BFI) which showed the formation of large polycrystalline grains with sharp grain boundaries [16]. The change in enthalpy is found to be 192.79 KJ/mol and 157.92 KJ/mol from DSC analysis of tungsten dispersed and yttria dispersed duplex stainless steel respectively. Shashanka et al. reported exothermic peak at 841°C with an enthalpy change of 62.35 KJ/mol by performing DSC analysis (heating rate 10°C/min) of partial amorphous powder of duplex stainless steel (Fe-18Cr-13Ni) prepared by milling in DDPM [2]. It also can be seen from DSC graph of yttria dispersed stainless steel that weak exothermic peaks are present at around 750°C. The appearance of these peaks may be due to the formation of oxides of Y, Fe and Cr which is evidenced by the XRD plots of annealed samples of 10 h milled yttria dispersed duplex stainless steel powders. Kimura et al. observed exothermic peaks at 927°C during DSC analysis of mechanically milled Fe-24Cr-15Y$_2$O$_3$ powder mixture due to the formation of YCrO$_3$ and Y$_2$O$_3$ [17]. Lei Dai et al. performed DSC analysis of 100 h mechanically milled Fe-9Cr-15Y$_2$O$_3$ powder mixture and showed exothermic peak formed at 620°C due to growth of Y$_2$O$_3$ nano-crystals [18].

![DSC graphs](image)

Fig. 6.- DSC graphs of (a) tungsten dispersed and (b) yttria dispersed 10 h milled duplex stainless steel after heating to 1200°C under argon gas
4. Conclusions
From the present study the following conclusions can be drawn:

1. The irregular and large elemental powders reduced to fine and spherical particles of size 5-10 μm after 10h of milling in both tungsten and yittria dispersed duplex stainless steels.
2. The XRD spectra of 10h milled samples showed highly broadened peaks due to high lattice strain and reduced particle size during milling. The lattice strains were 0.7 % upto 5h milling for tungsten dispersed and 1.1 % upto 10h milling for yittria dispersed duplex stainless steels. The crystallite sizes of 10h milled samples were 5 nm and 7nm for tungsten dispersed and yittria dispersed duplex stainless steels respectively.
3. Annealing in argon atmosphere enhanced ferrite to austenite transformation almost equally in both cases.
4. DSC analysis showed broadened exothermic peaks caused by reduction of lattice strain, crystal growth and crystallization of amorphous milled powder during heating.

References

[1] R. Shashanka, D. Chaira, Optimization of milling parameters for the synthesis of nano-structured duplex and ferritic stainless steel powders by high energy planetary milling, Powder Technology 278 (2015) 35–45.
[2] R. Shashanka, D. Chaira, Development of nano-structured duplex and ferritic stainless steels by pulverisette planetary milling followed by pressureless sintering, Materials Characterization 99 (2015) 220–229.
[3] L.A. Dobrza´nski, Z. Brytan, M.A. Grande, M. Rosso, E.J. Pallavicini, Properties of vacuum sintered duplex stainless steels, Journal of Materials Processing Technology 162–163 (2005) 286–292.
[4] R. Shashanka, D. Chaira, B.E. Kumara Swamy, Electrocatalytic Response of Duplex and Yttria Dispersed Duplex Stainless Steel Modified Carbon Paste Electrode in Detecting Folic Acid Using Cyclic Voltammetry, Int. J. Electrochem. Sci., 10 (2015) 5586 – 5598.
[5] S.K. Karak, J. Dutta Majumdar, Z. Witczak, W. Lojkowski, I. Manna, Microstructure and mechanical properties of nano-Y2O3 dispersed ferritic alloys synthesized by mechanical alloying and consolidated by hydrostatic extrusion, Materials Science & Engineering A 580 (2013) 231–241.
[6] M.P. Phaniraj, Dong-Ik Kim, Jae-Hyeok Shim, Young Whan Cho, Cyclic oxidation of yttria dispersed austenitic stainless steels, Corrosion Science 52 (2010) 3573–3576.
[7] Yingli Xu, Zhangjian Zhou, Ming Li, Pei He, Fabrication and characterization of ODS austenitic steels, Journal of Nuclear Materials 417 (2011) 283–285.
[8] José M. Torralba, Luz Fuentes-Pacheco, Nerea García-Rodríguez, Mónica Campos, Development of high performance powder metallurgy steels by high-energy milling, Advanced Powder Technology 24 (2013) 813–817.
[9] T. Narita, S. Uka, S. Ohtsuka, M. Inoue, Effect of tungsten addition on microstructure and high temperature strength of 9Cr ODS ferritic steel, Journal of Nuclear Materials 417 (2011) 158–161.
[10] F. Abe, H. Araki, T. Noda, M. Okada, Microstructure and toughness of Cr-W and Cr-V ferritic steels, Journal of Nuclear Materials 155–157 (1988) 656–661.
[11] T. Haghir, M.H. Abbasi, M.A. Golozar, M. Panjepour, Investigation of α to γ transformation in the production of a nanostructured high-nitrogen austenitic stainless steel powder via mechanical alloying, *Materials Science and Engineering A* 507 (2009) 144–148.

[12] R. Shashanka, D. Chaira, Phase transformation and microstructure study of nanostructured austenitic and ferritic stainless steel powder prepared by planetary milling, *Powder Technology* 259 (2014) 125–136.

[13] M.H. Enayati, M.R. Bafandeh, Phase transitions in nano-structured Fe–Cr–Ni alloys prepared by mechanical alloying, *Journal of Alloy and Compounds* 454 (2008) 228–232.

[14] C. Suryanarayana, Mechanical alloying and milling, *Prog. Mater Sci.* 46 (2001) 1 – 184.

[15] O. Olaniran, B. O. Adewuyi, J. A. Omotoyinbo, A. E. Afolabi, D. Folorunso, A. Adegbola, E. Igbamen, Development of oxide dispersion strengthened 2205 duplex stainless steel composite, *Leonardo Electronic Journal of Practices and Technologies* ISSN 1583-1078 (2015) 129-140.

[16] M. Sherif El-Eskandarany, H.A. Ahmed, Morphological and structural studies of amorphous Fe$_{74}$Cr$_{18}$Ni$_8$ alloy prepared by the rod-milling technique, *Journal of Alloys and Compounds* 216 (1994) 213-220.

[17] Yuuji Kimura, Setsuo Takaki, Shinichi Suejima, Ryuji Uemori, Hiroshi Tamehiro, Ultra Grain Refining and Decomposition of Oxide during Super-heavy Detormation in Oxide Dispersion Ferritic Stainless Steel Powder, *ISIJ International* Vol. 39 (1 999) 176-182.

[18] Lei Dai, Yongchang Liu, Zhizhong Dong, Size and structure evolution of yttria in ODS ferritic alloy powder during mechanical milling and subsequent annealing, *Powder Technology* 217 (2012) 281–287.