

# Microstructure and Mechanical Properties of Nano-Y<sub>2</sub>O<sub>3</sub> Dispersed Ferritic Steel Synthesized by Mechanical Alloying and Consolidated by Pulse Plasma Sintering

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## Abstract

Ferritic steel with composition of 83.0Fe-13.5Cr-2.0Al-0.5Ti (alloy A), 79.0Fe-17.5Cr-2.0Al-0.5Ti (alloy B), 75.0Fe-21.5Cr-2.0Al-0.5Ti (alloy C) and 71.0Fe-25.5Cr-2.0Al-0.5Ti (alloy D) (all in wt %) each with 1.0 wt% nano-Y<sub>2</sub>O<sub>3</sub> dispersion were synthesized by mechanical alloying and consolidated by pulse plasma sintering at 600, 800 and 1000 °C using 75 MPa uniaxial pressure applied for 5 min and 70 kA pulse current at 3 Hz pulse frequency. X-ray diffraction, scanning and transmission electron microscopy and energy disperse spectroscopy techniques have been extensively used to characterize the microstructural and phase evolution of all the alloys at different stages of mechano-chemical synthesis and consolidation. Mechanical properties in terms of hardness, compressive strength, yield strength and Young's modulus were determined using micro/nano-indentation and universal testing machine. The present ferritic alloys record very high levels of compressive strength (850-2850 MPa), yield strength (500-1556 MPa), Young's modulus (175-250 GPa) and [nanoindentation](#) hardness (9.5-15.5 GPa) and measure up to 1-1.5 times greater strength than other oxide dispersion strengthened ferritic steel (< 1200 MPa). These extraordinary levels of mechanical properties can be attributed to the typical microstructure comprising uniform dispersion of 10-20 nm Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> or Y<sub>2</sub>O<sub>3</sub> particles in high-alloy ferritic matrix.

**Keywords:** Nano-Y<sub>2</sub>O<sub>3</sub> dispersed ferritic steel; mechanical alloying; microstructure; mechanical property; pulse plasma sintering

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## 1. Introduction

There is a growing technological interest in nano-oxide dispersed ferritic steels for applications as heat exchanger parts, superheater tubes, and similar structural components in thermal or fast-breeder nuclear reactors [1-4]. Though ferritic steels possess excellent oxidation and corrosion resistance, dispersion of nanometric rare-earth oxide like  $Y_2O_3$  or  $CeO_2$  further enhance the creep strength at elevated temperature. Usually austenitic or ferritic steels tend to undergo a marked loss in creep strength at temperatures above 600 °C. However, nano-oxide dispersed ferritic steels can be used at much higher temperature. The excellent high temperature oxidation and hot corrosion resistance of ferritic steels is attributed to high Cr (and also Al) content conducive for the formation of stable, dense and tightly adherent  $Cr_2O_3$  or  $Al_2O_3$  protective oxide film. This oxide film/layer forms during the final heat treatment of the mill products [5]. The high stability of oxide dispersoids within the alloy matrix allows retention of usable strength at temperatures almost up to 90 % of its solidus temperature [6,7]. In comparison, conventional ferritic steels can be used only up to an operating temperature of 550-600 °C. Carbide strengthened steels are not safe in the above mentioned application because carbon can leach out or dissolve in liquid sodium environment in fast-breeder nuclear reactor. The usual melting and casting route is not suitable for developing nano-oxide dispersed high-alloy ferritic steels due to significant difference in melting points, density, solubility and chemical reactivity of the concerned components. In this regard, mechanical alloying involve mutual dissolution of an elemental powder blend by high energy planetary ball milling is an inexpensive, convenient and effective method of producing such nano-oxide dispersed high Cr-Al-Ti ferritic alloy/steel at ambient

temperature [4]. Indeed, oxide dispersion strengthened steels produced by mechanical alloying with  $Y_2O_3$  dispersion have recorded higher creep resistance and elevated temperature tensile strength compared to traditional ferritic/martensitic steels of similar compositions [8–11].

However, the mechanically alloyed powders are not suitable for structural and engineering applications, unless bulk components can be produced from such powders. Several possible routes exist which can be utilized to consolidate mechanically alloyed powders into bulk or finished components like hot extrusion [12], cold compaction and pressure-less sintering [13], high pressure sintering [14,15], equi-channel angular pressing [16,17], laser sintering [18], hot isostatic pressing [19] and pulse plasma sintering [20]. The last one is quite suitable to develop dense isotropic, homogeneous and near-net shape solid bodies from mechanically alloyed powders with dispersion of ultrafine and light oxide particles. During this particular sintering process, an electric field is applied ( $\sim 600$  MW) to activate and heat the powder mass by high current discharge pulses. The process is characterized by very high thermal efficiency and is quite similar to other plasma assisted sintering processes like spark plasma sintering and field assisted sintering, but differs in terms of the quantum of energy delivered and crucible design [21,22]. During the short pulses, the powder compact is subjected to cycles of very rapid heating and cooling with very short holding time at the sintering temperature, lower than that used in normal spark plasma sintering [23]. However, studies on pulse plasma sintering of nano-oxide dispersed mechanically alloyed ferritic steel are rather limited. Furthermore, composition of the ferritic steel itself needs optimization in terms of relative proportion of Fe and Cr with minor addition of Ti and Al. Hence,

extensive studies are warranted to optimize both alloy composition and consolidation process for manufacturing components from ferritic steel powders with nanometric oxide dispersion that can offer the desired range of mechanical and physical properties at ambient and elevated temperatures. Recently, we have explored consolidation of the same set of mechanically alloyed ferritic steels by high pressure sintering at 600-1000 °C under 8 GPa uniaxial pressure [24] and hot isostatic pressing at 600-1000 °C under 1.2 GPa uniaxial pressure [25,26].

In the present investigation, a series of nano-Y<sub>2</sub>O<sub>3</sub> dispersed ferritic steel powders (with varying Fe and Cr contents) was synthesized by mechanical alloying and consolidated using pulsed plasma sintering at different temperatures. Subsequently, the density, microstructures, hardness, compressive deformation and failure modes of the present steels have been extensively investigated to arrive at a conclusive microstructure-property-process parameter correlation and assessment of the present steels for possible application as structural components in nuclear reactors.

## **2. Experimental Procedure**

Four different elemental powder (>99.9 wt% purity and 30-80 μm size) blends with initial composition of 83.0Fe-13.5Cr-2.0Al-0.5Ti (alloy A), 79.0Fe-17.5Cr-2.0Al-0.5Ti (alloy B), 75.0Fe-21.5Cr-2.0Al-0.5Ti (alloy C), and 71.0Fe-25.5Cr-2.0Al-0.5Ti (alloy D) (all in wt %) each with 1.0 wt % nano-Y<sub>2</sub>O<sub>3</sub> addition/dispersion were subjected to mechanical alloying by high energy ball milling in a multi vial Fritsch PM400 planetary ball mill, operated at 300 rpm using a new set of stainless steel vials and balls (10 mm

diameter). Milling was conducted with a ball to powder ratio of 10:1 in wet (toluene) medium to avoid agglomeration of powders and ensure maximum yield of milled product. The identity and sequence of phase evolution in different stages of mechanical alloying of all the alloys were monitored by X-ray assisted diffraction and reported elsewhere [in our earlier studies](#) with the same set of alloys [25-26].

Following mechanical alloying, the milled powders were consolidated in a vacuum chamber (vacuum level  $\approx 5.5 \times 10^{-3}$  Pa) by spark discharges that occur between the particles across the pores present in the green compact. Figure 1 shows the schematic representation of the apparatus for this pulse plasma sintering. Similar technique was reported elsewhere by Michalski et al. [27,28]. Prior to sintering, the nano-size powder was subjected to preparatory cold compaction under a pressure of 200 MPa. The preforms of powder mixture were placed in a graphite die (diameter 20 mm and height 15 mm), between two punches to which electrical energy was delivered from a battery of capacitors (300  $\mu$ F) each. The powder preforms were heated by high-current discharge pulses, generated periodically from the capacitor battery, charged to a minimum of 10 kV.

The duration of each pulse was several hundred microseconds with high electric current intensity (in few tens of kA). Figure 2 shows the thermal cycle and load variation at different temperature during pulse plasma sintering process. Before the onset of sintering, the chamber was pumped down to a pressure  $5.5 \times 10^{-3}$  Pa. The process was carried out by a two-stage method; firstly the powder compacts were loaded to 30 MPa pressure at 500 °C for 3 min so as to remove the absorbed gases within the powder particles or around their surfaces. After degassing, the compacts were further heated to

the final sintering temperature in between (600 °C and 1000 °C) with a uniaxial pressure of 75 MPa applied for 5 min (shown in Figure 2). The temperature on the surface of the graphite die was measured using Ahlborn IR AMIR 7838-51 pyrometer. During sintering, the temperature and heating rate of the samples were varied by controlling the pulse discharge energy and the pulse repetition frequency.

As already stated, the identity and sequence of phase evolution/transformation during mechanical alloying and/or pulse plasma sintering (at appropriate stages) were determined by using a Panalytical X'Pert Pro-diffractometer with Co- $K_{\alpha}$  (0.179 nm) radiation. The density was determined by using a helium pycnometer (AccuPyc 1330) [29]. Morphology, size, shape and distribution of the phases in the sintered components and surface damage in worn tracks were studied using a field emission gun assisted scanning electron microscopy (FESEM, Zeiss, Supra 40 V). Electron transparent thin foils were prepared for transmission electron microscopy studies initially by mechanical polishing followed by argon ion thinning using a GATAN precision ion mill for about 30 min. Selected foils prepared from alloys sintered at 1000°C were examined under a JEOL JEM 2100 high resolution transmission electron microscope (HRTEM) operated at 200 kV, using both bright and dark field as well as high resolution lattice imaging mode. Selected area diffraction (SAD) analysis was conducted to identify the phases present in the milled/sintered product. Qualitative information on chemical compositions at different locations was obtained using the energy dispersive spectroscopy (EDS) units (Oxford, UK) equipped with an ultra-thin window and attached to both the FESEM and HRTEM.

Mechanical properties in terms of [nanoindentation hardness](#) and elastic/Young's modulus were determined from nano-indentation test on selected sintered samples using standard nano-indentation hardness (TriboIndenter with MultiRange NanoProbe, Hysitron) with a Berkovitz indenter at 200 mN load. Each hardness value was measured from an average of 15 point measurements for nano-indentation and repeated 3-5 times at equivalent locations to ensure precision. [The nanoindentation experimental data were converted into Young's/elastic modulus \( \$E\$ \) and Poisson's ratio \( \$\nu\$ \) by the standard equation:](#)

$$1/E_r = (1-\nu_i^2)/E_i + (1-\nu_s^2)/E_s \quad (1)$$

where  $E_r$  = reduced elastic modulus calculated from the experimental data (average),  $\nu_i$  = Poisson's ratio of diamond indenter tip (0.07),  $E_i$  = elastic modulus of diamond (1140 GPa),  $\nu_s$  = Poisson's ratio ODS ferritic alloy (0.294) and  $E_s$  = elastic modulus of the ODS ferritic alloy.  $E_s$  reported here is evaluated by considering the elastic properties of the ODS alloys and not the indenter.

Compression tests were carried out at a strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$  at room temperature using a universal testing machine (Zwick/Roell Z 250). The dimension of the cylindrical specimens for compression test was 4.0 mm diameter and 6.0 mm height to maintain height/diameter = 1.5 (ASTM standard). The fracture surfaces of the ferritic alloys subjected to compression tests were studied using an FESEM.

### 3. Results and Discussions

Figure 3 to Figure 6 show the results of XRD analysis of alloys A, B, C and D consolidated by pulse plasma sintering at 600 °C, 800 °C and 1000 °C, respectively. A close scrutiny of the XRD profile of each alloy reveals that BCC-Fe(Cr) phase is the predominant constituent of the all the sintered product along with intermetallic phases like  $\text{Fe}_{11}\text{TiY}$  and  $\text{Al}_{9.22}\text{Cr}_{2.78}\text{Y}$  and mixed oxide phase like  $\text{Y}_2\text{Ti}_2\text{O}_7$ . Prior to sintering, the present alloys were synthesized from elemental powder blends of pre-determined composition by mechanical alloying for different cumulative time periods (0 to 40 h). XRD of the as-milled powders clearly reveal that the milled product in each case is a single phase body centre cubic (BCC) solid solution indicating that Cr, Al and Ti completely dissolve in Fe in course of high-energy ball milling for 30-40 h. The amount (1.0 wt %)  $\text{Y}_2\text{O}_3$  is too small to produce separate peaks in the XRD patterns. The detailed characterization of the four alloys during synthesis by mechanical alloying was recently reported elsewhere by Karak et al. [25-26], and hence not repeated here. [Yet it is relevant to point out that during mechanical alloying solute elements like Cr, Ti, and Al gradually dissolve in the bcc-Fe matrix/lattice and the lattice parameter of bcc-Fe gradually increases in all the four alloys up to about 10 h of milling indicating possible effects of solid solution strengthening.](#)

Figures 7 (a, b) show the bright field and corresponding dark field TEM image of alloy A sintered at 600°C. These micrographs clearly confirm the presence of 10-20 nm ultrafine  $\text{Y}_2\text{Ti}_2\text{O}_7$  particles distributed uniformly in the matrix. Figures 8 (a, b) show the bright field image and corresponding SAD pattern of alloy A sintered at 1000°C. Figure 8(a) evidences the presence of  $\text{Y}_2\text{Ti}_2\text{O}_7$  particles (10-20 nm) as well as [Al<sub>9.22</sub>Cr<sub>2.78</sub>Y](#) and

$\text{Fe}_{11}\text{TiY}$  intermetallic phases along the grain boundary and grain boundary triple point. The details analysis of bulk SAD patterns (Figure 8(b)) confirms the presence of corresponding phases, namely, the (110), (200) and (211) planes for the BCC Fe-Cr phase, (222) for the  $\text{Y}_2\text{Ti}_2\text{O}_7$  mixed oxide phase, (040) for the  $\text{Al}_{9,22}\text{Cr}_{2,78}\text{Y}$  and (321) for the  $\text{Fe}_{11}\text{TiY}$  intermetallic phases, respectively. The calculated interplanar spacing ( $d$ ) of BCC Fe-Cr phase matches with the standard  $d$ -values of 0.2020 nm for (110), 0.1430 nm for (200) and 0.1010 nm for (220) planes, respectively. Similarly, the measured  $d$ -values of  $\text{Y}_2\text{Ti}_2\text{O}_7$  mixed oxide match with the standard values of 0.2914 nm for (222) and 0.2115 nm for (321) planes in  $\text{Fe}_{11}\text{TiY}$ , and 0.2257 nm for (040) planes in  $\text{Al}_{9,22}\text{Cr}_{2,78}\text{Y}$  intermetallic phases, respectively.

It may be noted that distribution of nano- $\text{Y}_2\text{O}_3$  or  $\text{Y}_2\text{Ti}_2\text{O}_7$  is quite uniform though varying in size within a narrow range. This size variation may arise as these particles could be both ex-situ  $\text{Y}_2\text{O}_3$ , or, in-situ  $\text{Y}_2\text{Ti}_2\text{O}_7$  phases produced during sintering. It may be pointed out that presence of such ultrafine oxide is desirable to induce resistance to grain boundary sliding at elevated temperature (creep deformation). It is apparent that increase in sintering temperature from 600 °C to 1000 °C leads to significant grain growth (Figure 7a vis-à-vis Figure 8a). This is due to enhanced diffusion activity at higher sintering temperature (1000 °C) which can be easily estimated through the usual Arrhenius relation as follows:

$$D = D_0 \exp (-E/RT) \quad (2)$$

where  $D$  is the diffusion coefficient at an isothermal temperature ( $T$ ),  $D_0$  is the pre-exponential factor and  $E$  is the activation energy. The standard values for diffusional kinetic analysis are:  $D_0 = 3.56 \times 10^{-6} \text{ m}^2/\text{s}$  and  $E = 185 \text{ kJ/mol}$  at 600 °C [30] and  $D_0 = 2.1$

$\times 10^{-4} \text{ m}^2/\text{s}$  and  $E = 240 \text{ kJ/mol}$  at  $1000 \text{ }^\circ\text{C}$  [31], respectively. Accordingly, the calculated values of diffusion coefficients from equation (2) at  $600 \text{ }^\circ\text{C}$  and  $1000 \text{ }^\circ\text{C}$  are  $3.45 \times 10^{-6} \text{ m}^2/\text{s}$  and  $1.97 \times 10^{-4} \text{ m}^2/\text{s}$ , respectively. Assuming the steady state isothermal growth dominated by volume diffusion of Cr in  $\alpha\text{-Fe}$ , the diffusion distance ( $X$ ) covered at time ( $t$ ) at these reference temperatures, calculated as per the relation:  $X = (Dt)^{-1/2}$  is found an order of magnitude larger at  $1000 \text{ }^\circ\text{C}$  ( $\approx 190 \text{ }\mu\text{m}$ ) than that at  $600 \text{ }^\circ\text{C}$  ( $\approx 30 \text{ }\mu\text{m}$ ). It is obvious that average grain size at  $1000 \text{ }^\circ\text{C}$  will be significantly higher at  $1000 \text{ }^\circ\text{C}$ , compared to that at  $600 \text{ }^\circ\text{C}$  or at  $800 \text{ }^\circ\text{C}$  as per usual growth kinetics relation.

The grain coarsening kinetics during isothermal sintering of oxide dispersed strengthened alloys may follow the usual grain growth kinetic relation [32]

$$d^n - d_0^n = kt \quad (3)$$

where  $d$  and  $d_0$  are average grain diameter at a given time and initial time period,  $n$  is the power exponent, and  $K$  is temperature dependent rate constant, respectively  $K$  in turn is a function of diffusion coefficient ( $D$ ) of the growth controlling species, equilibrium solubility of the precipitate/solute in the matrix ( $C_e$ ) and the concerned matrix-precipitate/dispersoid interfacial energy ( $\sigma$ ).

The coarsening rate during sintering can be studied by volume-controlled coalescence of particles driven by curvature, as described by the Lifshitz-Sloyzov-Wanger theory [33,34]. In the present case coarsening of these nanocrystalline oxide dispersed strengthened alloys can be expressed as

$$d^3 - d_0^3 = kt \quad (4)$$

The nanometric oxide particles ( $Y_2Ti_2O_7$ ) can act as a pinning agent during the course of high temperature deformation or use of oxide dispersed alloys. This pinning or frictional action can be correlated to a simple Zener pinning [33] type of strengthening mechanism expressed as

$$d = 2/3(r / f_r) \quad (5)$$

where  $d$  is the grain size,  $r$  is the particle radius and  $f_r$  is the volume fraction of the dispersed particle. There is no substantial difference in size between the particles residing within the grain and those along the boundary. These particles can offer significant strengthening at elevated temperature provided they are harder than the matrix and do not dissolve in or react with the matrix.

Figure 9 shows the variation of bulk density and porosity of the sintered samples, measured by pycnometer, as a function of sintering temperature for the four different alloys. As sintering temperature rises the density increases and porosity decreases in all the present alloys. It is apparent that the maximum density is attained by sintering at the highest temperature (1000 °C) in all the four alloys. By the same logic, lowest density is obtained by consolidation at the lowest temperature (say, 600 °C). This is due to incomplete grain bridge formation or welding at low temperature. Similar results were obtained by several researchers in the past while sintering powders of diverse composition and history, e.g., by Roy et al. [35] in  $Al_{65}Cu_{20}Ti_{15}$  alloy, Yang et al. [36] in WC-ZrO<sub>2</sub>-VC ceramic composites, Zhao *et al.* [37] in cubic boron nitride and Ardestani et al. [38] in W-20-40 wt% Cu composite powder. Thus the sintering behaviour of the present set of alloys during pulse plasma sintering follows the usual sintering mechanism

as observed in conventional long duration at elevated temperature and by pressureless sintering.

Figure 10 shows the variation of the Young's modulus and [nanoindentation](#) hardness of the sintered products of all the four alloys as a function of the sintering temperature. [The difference in hardness values in micro and nano measurements due to 'indentation size effect' which details described by Mukhopadhyay and Paufler \[39\]](#) .It is apparent that pulse plasma sintering of all the alloys at 1000 °C yields the highest [nanoindentation](#) hardness and Young's modulus. This enhanced strength at higher temperature may be attributed to stronger diffusional bond and structural integrity achieved due to greater diffusional activity, despite grain growth, at 1000 °C than that obtained at 600 °C or at 800 °C. Based on the observations from the plots in Figures 9 and 10, it is possible to infer that the maximum Young's modulus and [nanoindentation](#) hardness is obtained under the processing condition that yields the highest density. Obviously, the density, Young's modulus and hardness of the alloys sintered at low temperature (say, 600 °C) are lower for the condition that yields incomplete densification. However, the increase in hardness and Young's modulus on pressing at the higher temperature can probably be attributed to the densification of matrix as well as pinning of the grain boundary by the uniform distribution of  $Y_2Ti_2O_7$ . Similar results were obtained by Roy *et al.* [35], Yang *et al.* [36], Zhao *et al.* [37] and Ardestani *et al.* [38].

Figure 11 shows the typical stress versus strain curves generated through compression tests of the alloy A consolidated by pulse plasma sintered at different temperatures. The tests at each temperature were repeated three times to ensure that the results were reproducible. From the stress-strain curves, it is observed that failure has

occurred in the plastic regime after yielding. It appears that the extent of plastic deformation increases from 4.5 % to 11.8 % with increase in sintering temperature from 600 to 1000 °C. As discussed earlier, the porosity of all the alloys is the maximum after sintering at 600 °C and the minimum at 1000 °C (shown in Figure 9). The maximum compressive strength of 2850 MPa and yield strength of around 1545 MPa was obtained in the alloy D sintered at 1000 °C with the corresponding plastic strain of 8.4 %. These results of mechanical properties are summarized in Table 1. The strength values of the current alloys are significantly higher than that of commercial ODS alloy MA957 ( $\approx$  1400 MPa) as well as ODS EUROFER ( $\approx$  1500 MPa), as reported by Klueh et al. [40] and de Castro et al. [41], respectively. The compressive strength of the present alloys with a lower density has been found greater than that of the maximum compressive strength ( $\approx$  2203 MPa) of tungsten alloy (93W-4.9Ni-2.1Fe (wt %)) reported by Zhang et al. [42]. Lee et al. [43] have achieved the maximum compressive strength of partially stabilized zirconia (PSZ) dispersed ODS tungsten heavy alloys (93W-5.6 Ni-1.4Fe (wt %)) in the order of 1000 MPa, which is much lower than that of the present ferritic alloys.

The extremely high mechanical strength of these alloys can be attributed to at least three different strengthening mechanisms namely dispersion hardening, solid solution hardening and grain refinement (Hall-Petch effect) [44]. Since the present alloys are sintered at reasonably high temperature, it is anticipated that strengthening effect due to grain refinement even if present in the as-milled condition, may not be retained after sintering at elevated temperature due to grain coarsening. In other words, strengthening

due to dispersion hardening and solid solution effects would be dominating factors compared to grain refinement effect in the present alloys.

The total strength ( $\tau$ ) can be expressed by the generally accepted relation [45-50]

$$\tau = \tau_s + \tau_d \quad (6)$$

where  $\tau_s$  and  $\tau_d$  represent the critical resolved shear stress of the solid solution (matrix) and dispersion hardening, respectively. The general equation for solid solution strengthening has the form

$$\tau_s = \alpha G \varepsilon^m c^n \quad (7)$$

where  $G$  is the matrix shear modulus,  $\varepsilon = (r_{matrix} - r_{solute}) / r_{matrix}$  is the misfit strain based on radius ( $r$ ) of concerned species (matrix or solute),  $c$  is the atomic fraction of solute and  $\alpha$  is a constant,  $m$  and  $n$  depend on assumptions made about solute spacing and statistical averaging of the solute-dislocation interactions [51]. For the mean solute spacing,  $m = 1$  and  $n = 0.5$ , Friedel statistics (Fleischer model) yield  $m = 1.5$  and  $n = 0.5$  and the Labusch analysis [51] in the limit of strong localized interactions yields  $m = 1.33$  and  $n = 0.667$ .

Dispersion strengthening in the current ferritic steel is primarily dependent on the volume fraction, particle size and interparticle spacing of fine nano-Y<sub>2</sub>O<sub>3</sub> or Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> in the matrix. Beside the ex-situ nano-Y<sub>2</sub>O<sub>3</sub>, several in-situ mixed oxide (Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) or intermetallic Fe<sub>11</sub>TiY and Al<sub>9.22</sub>Cr<sub>2.78</sub>Y particles have also been detected in the sintered microstructure (Figures 3-7). The size and distribution of these ultrafine phases are determined by nucleation, growth and coarsening rates during pulse plasma sintering. The essential parameter governing the variation in nucleation rate is chemical driving force, while that governing growth and coarsening is the prevailing diffusion rate.

Strengthening ( $\tau_d$ ) through the dispersed particles (when the size of the dispersoids or second-phase particles is less than the grain size) is governed by the Orowan mechanism [52]. The critical stress for Orowan process  $\tau_d$  is a function of volume fraction of second phase particles  $f$  and average radius  $r$  of the spherical incoherent particles and sintering temperature ( $T$ ).

$$\tau_d = k'Gb / \lambda \quad (8)$$

where,  $G$  is the shear modulus of the matrix,  $b$  is the magnitude Burgers vector of the dislocation,  $\lambda$  is the interparticle spacing and  $k'$  is a numerical constant.

$$\lambda = 4(1-f)r / 3f \quad (9)$$

The strengthening mechanism of these alloys are very much complex. Hardening of the current alloys not only depends on dispersion, solid solution and grain boundary strengthening but also on precipitation hardening due to presence or precipitation of intermetallic phases in the microstructure. Analysis of the XRD patterns (Figures 3 to 6) and TEM images (Figures 8 (a, b)) confirm the presence of intermetallic ( $\text{Fe}_{11}\text{TiY}$  and  $\text{Al}_{9.22}\text{Cr}_{2.78}\text{Y}$ ), which are likely to contribute to increasing the strength of the ferritic matrix by precipitation strengthening.

Figures 12 (a, b) show the low and high magnification views of the fracture surface generated during compression tests carried out on the alloy A consolidated at 1000 °C by pulse plasma sintering. These fractographs confirm that void formation precede fracture during compression test and suggest that the failure is not totally brittle in nature. Figure 12a reveals evidence of some dimple formation along with interfacial decohesion of the  $\text{Y}_2\text{Ti}_2\text{O}_7$  particles from the Fe-Cr alloy matrix during localized plastic

deformation. The small size (nanometric scale) and uniform distribution of dispersoids seem to restrict the slip process within the matrix during bulk deformation. As suggested by Hawk et al. [53], higher plastic deformation and ductility can arise only through a dislocation climbing process over the intermetallic dispersoids in such dispersion strengthened matrix. Such interactions affect the matrix deformation behaviour resulting in an increased flow stress but decreased capacity for strain hardening. The mechanical properties (nanoindentation hardness, compressive strength, elastic/Young's modulus) are functions of the sintering temperature. This trend is confirmed by the level of improvement of mechanical properties of all the alloys as the sintering temperature increases from 600 to 1000 °C. The mechanical properties (Table 1) of alloy D sintered at 1000° C are the best. It is interesting to note that the percent elongation decreases with increase in Cr content of all the alloys. The compressive strength of the current alloys is maximum for alloy D (Table 2) consolidated by hot isostatic pressing at 1000 °C as compared to that obtained after consolidation by other two techniques namely, high pressure and pulse plasma sintering. It is important to note that our earlier studies showed that the same alloys following sintering by hot isostatic pressing [25,26] and high pressure sintering [24] were very strong but fairly brittle. However, the same alloys seem to yield comparable or higher compressive strength with marginally higher ductility following consolidation by pulse plasma sintering. Thus, it is interesting to note that the same set of mechanically alloyed powders with identical composition and microstructural state can eventually produce widely different mechanical properties when sintered by different techniques using the optimum process parameters.

#### **4. Conclusions**

The present study suggests that pulse plasma sintering is a promising technique for consolidation of mechanically alloyed powders of nano-Y<sub>2</sub>O<sub>3</sub> dispersed Fe-Cr-Al-Ti ferritic alloys. Density, hardness and compressive stress of all the alloys increase with increase in sintering temperature. The present ferritic alloys record extremely high ranges of compressive strength (850-2850 MPa), yield strength (525-1545 MPa), Young's modulus (175-250 GPa) and [nanoindentation](#) hardness (8.5-17.5 GPa) and measure up to 1.5-2 times greater compressive strength with a lower density (~ 7.4 Mg/m<sup>3</sup>) than other oxide dispersion strengthen ferritic steel (< 1200 MPa) or tungsten based alloys (< 2200 MPa). The novelty of the present consolidation route lies in the unique microstructure comprising uniform distribution of 10-20 nm Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> or Y<sub>2</sub>O<sub>3</sub> particles, recommended for grain boundary pinning and creep resistance. Substantial grain coarsening occurs in all the alloys consolidated at 1000 °C as compared to that at 600 °C or at 800 °C due to greater extent of volume diffusion of Cr in  $\alpha$ -Fe at this higher temperature. These mechanical properties compare well with those from the same set of alloys consolidated by high pressure sintering [24] and hot isostatic pressing [25, 26], earlier reported by us. However, the extent of plastic deformation prior to failure recorded in the present study is higher than that obtained in the earlier studies based on other consolidation methods.

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### **Figure Captions**

Figure 1: The schematic representation of the apparatus for pulse plasma sintering

Figure 2: Schematic of thermal cycle and load variation at different isothermal temperature during pulse plasma sintering

- Figure 3: XRD patterns of alloy A consolidated by pulse plasma sintering at different temperatures
- Figure 4: XRD patterns of alloy B consolidated by pulse plasma sintering at different temperatures
- Figure 5: XRD patterns of alloy C consolidated by pulse plasma sintering at different temperatures
- Figure 6: XRD patterns of alloy D consolidated by pulse plasma sintering at different temperatures
- Figure 7: (a) Bright field and (b) dark field TEM image of alloy A sintered at 600 °C
- Figure 8: (a) Bright field TEM image and (b) corresponding SAD patterns of alloy A sintered 1000 °C
- Figure 9: Variation of density and porosity as function of sintering temperature used for pulse plasma sintering
- Figure 10: Variation of [nanoindentation](#) hardness and Young's modulus as function of sintering temperature used for pulse plasma sintering
- Figure 11: The variation of engineering stress with strain of alloy A at different sintering temperature by pulse plasma sintering
- Figure 12: FESEM images of the fracture surfaces generated during compression tests carried out on the alloy A consolidated by pulse plasma sintering at 1000 °C (a) low and (b) high magnification

### **Table Captions**

- Table 1: Summary of mechanical properties of alloys A, B, C and D sintered by pulse plasma sintering (PPS) at different temperature
- Table 2: Comparison of compressive strengths of alloys A, B, C and D consolidated at 1000 °C by high pressure sintering (HPS), hot isostatic pressing (HIP) and pulse plasma sintering (PPS) techniques.