Synthesis of nano-structured duplex and ferritic stainless steel powders by planetary milling: An experimental and simulation study

Shalabh Gupta, R. Shashanka, D. Chaira*

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

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

Abstract. Nano-structured duplex and ferritic stainless steel powders were prepared by planetary milling of elemental Fe, Ni and Cr powder compositions (duplex: 69Fe-18Cr-13Ni and ferritic:82Fe-17Cr-1Ni) in a dual drive planetary mill for 10 hours. The feasibility for solid solution formation of Cr and Ni in Fe matrix were studied. The samples were collected at regular time intervals and characterized for their morphological and phase analysis using X-Ray diffraction (XRD) and scanning electron microscopy (SEM). It has been observed that as the milling time increases crystallite size decreases and lattice strain increases. Thermodynamic aspects of milled stainless steel powders were performed using Miedema model. The theoretical values $\Delta H$, $\Delta S$ and $\Delta G$ of and were calculated and were found to be -14.32kJ/mol, 6.93J/mol and -16.39 kJ/mol for duplex stainless steel and -2.81kJmol, 4.35Jmol and -4.11 kJ/mol for ferritic stainless steel respectively.

Keywords: Stainless steel; planetary milling; Miedema model; thermodynamic parameters

1. Introduction

Powder metallurgy route for preparation of stainless steel has been the cause of much scientific attention due to its capability of producing components with a wide range of mechanical properties which are near-net shaped by making use of various alloy selections and processing options. Although powder metallurgy route can be used for different grades of stainless steel powder production but among them duplex and ferritic stainless steels are being extensively studied because of versatility of their applications. Conventionally, duplex stainless steels are used in orthopaedic applications such as medical implants or as surgical cutting tools and applications where high toughness levels are in compatibility with cryogenic applications and creep resistance [1]. Many processing methods have been adopted in order to improve the structure and properties of stainless steel. Methods like hydrostatic extrusion, equi-channel angular pressing, high pressure torsion and mechanical alloying are being used for the structural refinement of metals and alloys [2]. Among all methods mechanical alloying proves to be one of the best powder metallurgy routes to refine the particle size to nano level. Therefore, specially designed dual drive planetary mill (DDPM) was used to prepare nano-structured stainless steel. This high-energy milling is one of the most promising from industrial view point because it involves the use of comparatively less inexpensive equipment for the synthesis of bulk nano-structured powder production; in fact. This has many common aspects with mixing, fine grinding
and comminution of materials. Alloy formation takes place by diffusion during planetary milling of elemental powder particles which leads to atomic level alloying often accompanied by nano sized structured meta-stable phase transformation [3–5]. The high density of dislocations and grain boundaries created in powders and micro segregation of solute at these defects may lead to the formation of extended solid solutions [6]. Thermodynamic parameters are very important to predict the solid solution formation during planetary milling. Very few literatures are available so far regarding calculation of thermodynamic parameters for the binary systems such as Ti–Al, Ti–Ni, Al–Ni and Al–Ni–Ti using Miedema model [7, 8]. In the present study, we have made an attempt to evaluate the various thermodynamic parameters of ternary system (Fe–Ni–Cr) during planetary milling. Here, our main intention is to predict various thermodynamic parameters during synthesis of nano-structured stainless steel by planetary milling.

2. Experimental
The elemental powder compositions of Fe–18Cr–13Ni (duplex) and Fe–17Cr–1Ni (ferrite) were selected and milled in a specially designed DDPM for 10 h under toluene atmosphere to prevent oxidation. The milling media of the DDPM consist of 600 g stainless steel balls (10 mm diameter) and ball to powder weight ratio of 6:1 was maintained during milling. The angular velocity of the supporting main shaft and jars were kept at 275 and 725 rpm respectively to attain 75 % critical speed. Milled stainless steel powders were characterized by using X-ray diffraction (XRD) in a Philips PANalytical diffractometer using filtered Cu Kα-radiation (λ = 0.1542 nm). Williamson–Hall method was used to calculate crystal size and lattice strain of the milled powders. Morphological analysis of the milled powders was performed by scanning electron microscopy (SEM) using JEOL JSM-6480LV model. Thermodynamic parameters (ΔS, ΔH and ΔG) of stainless steel powders for both compositions were calculated by simulation method using Miedema model.

3. Results and discussions
3.1 Thermodynamic analysis using Miedema model
Considering the formation of disordered A (B, C) solid solution from a mixture of pure A, B and C elements.

Here, ΔHms and ΔSy are the enthalpy and entropy of mixing respectively. T is the temperature at which a solid solution is formed.

ΔSy can be calculated with the assumption of configurational entropy of mixing:

\[ ΔS_y = -R(x_a \ln x_a + x_b \ln x_b + x_c \ln x_c) \] (1)

Where, \( x_a, x_b \) and \( x_c \) are mole fractions for A, B and C in the mixture.

According to Miedema semi-empirical model, the entropy of a solid solution formation consists of three terms for a ternary system:

\[ ΔS = -R(x_a \ln x_a + x_b \ln x_b + x_c \ln x_c) \] (2)

Total enthalpy for formation of solid solution is

\[ ΔH_{Total} = ΔH_{chemical} + ΔH_{elastic} + ΔH_{structural} \] (3)

Where, \( ΔH_{chemical} \), \( ΔH_{elastic} \) and \( ΔH_{structural} \) are the chemical, elastic and structural contributions due to atomic mixing, mismatch in size and the difference in valance electrons and crystal structure of solute and solvent atoms, respectively. The complete form of \( ΔH_{chemical} \) is as follows:

\[ ΔH_{chemical} = \sum_{i,j} \delta_{ij} f_{ij}(T) \]

Where, \( \delta_{ij} \) is the atomic mixing parameter and \( f_{ij}(T) \) is the configurational entropy of mixing.
\[ \Delta H_{\text{chemical}} = \frac{2f(C^s)(X_A V_A^3 + X_B V_B^3/2)^2 \left[ P(\varepsilon^2 + Q(\Delta n_{ws})^{2/3} \right]}{(n_{ws}^A - 1/3 + (n_{ws}^B)^{-1/3}} \] (4)

Where \( X_a \) and \( X_b \) are the mole fractions of elements A and B; \( \varepsilon \), \( V \) and \( n_{ws} \) are work function, molar volume and electron density of constituents, respectively. \( P \) and \( Q \) are empirical constants and \( f(C^s) \) is the concentration function that for solid solution is given by

\[ f(C^s) = C_A^s C_B^s \] (5)

\[ C_A^s = \left( \frac{X_A V_A^3}{X_A V_A^3 + X_B V_B^3} \right)^2 \] (6)

\[ C_B^s = \left( \frac{X_B V_B^3}{X_A V_A^3 + X_B V_B^3} \right)^2 \] (7)

\[ \Delta H_{\text{elastic}} = x_b \Delta E_{\text{A in B}} + x_a \Delta E_{\text{B in A}} \] (8)

Where \( \Delta E_{\text{A in B}} \) and \( \Delta E_{\text{B in A}} \) are the elastic energy caused by dissolving A in B and B in A, respectively and can be estimated by

\[ \Delta E_{\text{A in B}} = \frac{2K_a G_b (\Delta V)^2}{3K_b V_b + 4G_b V_a} \] (9)

\[ \Delta E_{\text{B in A}} = \frac{2K_b G_a (\Delta V)^2}{3K_b V_a + 4G_a V_b} \] (10)

Where \( \Delta E_{\text{A in B}} \) and \( \Delta E_{\text{B in A}} \) are the elastic energy caused by ‘A’ dissolving in ‘B’ and ‘B’ dissolving in ‘A’ respectively. Where \( K \) and \( G \) are bulk and shear modulus respectively.

\( \Delta S_{\text{structural}} \) was neglected as the value is negligible compared to other two enthalpies.

Table 1 shows the list of various parameters used for Fe, Cr and Ni.
Gibb’s free energy for formation of solid solution was calculated by using the following equation:

\[ \Delta G = \Delta H_{Total} - T \Delta S \]  \hspace{1cm} (11)

Here temperature ‘T’ for formation of solid solution is assumed 300K.

Table 2 shows the value of different thermodynamic parameters calculated using Miedema model. It is observed from the table that \( \Delta G \) for duplex stainless steel is higher than ferritic stainless steel. The reason is due to diffusion of higher amount of alloying element in duplex steel than ferritic steel.

Table 1. Values of different parameters for Fe, Ni and Cr

| Parameter                          | Fe  | Cr  | Ni  |
|------------------------------------|-----|-----|-----|
| Molar Volume \( (V^{2/3}) \) \( (\text{cm}^3) \) | 3.7 | 3.7 | 3.5 |
| Electron density \( (n_{rel}^{1/3}) \) \( (\text{d.u.})^{1/3} \) | 1.77| 1.73| 1.75|
| Work function \( (\epsilon) \) \( (\text{V}) \) | 4.93| 4.65| 5.2 |
| K \( (\text{GPa}) \)             | 170 | 160 | 180 |
| G \( (\text{GPa}) \)              | 82  | 115 | 76  |

Table 2. Values of thermodynamic parameters calculated using Miedema model

|          | \( \Delta H \) \( (\text{kJ/mol}) \) | \( \Delta S \) \( (\text{J/mol}) \) | \( \Delta G \) \( (\text{kJ/mol}) \) |
|----------|---------------------------------|---------------------------------|---------------------------------|
| Duplex   | -14.32                          | 6.93                           | -16.39                         |
| Ferrite  | -2.81                           | 4.35                           | -4.12                          |

3.2 X-Ray diffraction study

Fig. 1 (a) and 1 (b) represents the XRD spectra of duplex and ferritic stainless steel powders milled at 0, 2, 5 and 10 h respectively in DDPM using ball to powder weight ratio of 6:1. The sharp crystalline peaks of elemental Fe, Cr and Ni start broadening continuously with milling and gradually move into the Fe lattice. It is evident from both the graphs that intensity of individual elements (Fe, Cr, Ni) decreases gradually with milling. After 10h of milling the duplex stainless steel show strong austenite peaks along with weak ferrite peaks as shown in Fig. 1 (a). In case of ferritic stainless steel, low intense austenite peaks are present along with strong ferrite peaks. Increase in milling time increases the phase transformation from \( \alpha \)-Fe to \( \gamma \)-Fe and after 10h both austenite and ferrite peaks resolve in to (111) and (110) planes as shown in Fig. 1 (b). This phase transformation is due to the higher degree of defects and refinement of particles in nano-crystalline size.
Fig. 1 XRD spectra of 0 to 10h milled (a) Austenitic stainless steel (b) Ferritic stainless steel powders

The XRD spectra show broadening of XRD peaks with the milling time due to instrumental errors, decrease in crystalline size and lattice strain [9]. Crystal size and lattice strain of both the stainless steels were calculated using Williamson-Hall method [10] by de-convoluting the size and strain by calculating XRD peak width as a function of 2θ. Williamson-Hall equation is as follows,

$$\beta \cos \theta = \frac{0.94 \lambda}{D} + 4 \eta \sin \theta$$

(8)

Where, D is crystallite size, β is full width half maxima (FWHM) and η is lattice strain. During milling crystallite size decreases and strain increases with milling time due to the formation of more defects during milling. Refinement of crystallite size reaches a saturation level at higher milling time and further refinement becomes quite difficult. Due to more and more interaction of powder-ball, powder-powder and powder-jar surface, the lattice strain increases continuously even after 10h of milling. The crystallite size of duplex and ferritic stainless steel decreases from 43 to 6 nm and from 52 to 7nm respectively. Similarly, the lattice strain increases from 0.06 to 1.06 % in case of duplex and from 0.32 to 1.03 % in case of ferritic stainless steel respectively.

3.3 Scanning electron microscopy
Fig. 2 (a) and 2 (b) depicts the SEM micrographs of 0h and 10h milled duplex stainless steel powders. Similarly, Fig. 2 (c) and 2 (d) represent SEM micrographs of ferritic stainless steel milled for 0h and 10h respectively. From the figures it is confirmed that the elemental powder particles are large and irregular in shape before milling but as milling starts particles start to form flat flakes and cold welded due to ductile nature of Fe. Finally particles are work hardened and fragmented in to smaller particles as shown the figure. This refinement of particle size reaches a saturation and further refinement of particles become more difficult after 10h.
Fig. 2 SEM images of austenite stainless steel powder milled for (a) 0h (b) 10h; and ferritic stainless steel powder milled for (c) 0h (d) 10h respectively

Energy dispersive spectroscopy (EDS) analysis was carried out to study the elemental composition of stainless steel powders after 10 h of milling. Fig. 3 (a) and 3 (b) depicts the EDS spectra of duplex and ferritic stainless steel powders after 10 h of milling. From the spectra it is evident that there is no much variation in initial elemental composition and final alloy composition.
Fig. 3 EDS spectra of (a) duplex and (b) ferritic stainless steel after 10 h of milling

4. Conclusions
The following conclusions can be made from the present investigation:
1. The austenitic composition was showing ferritic phase till 2 h of milling and becomes austenite after 5 h in DDPM.
2. Austenite phase becomes more dominant at higher milling time
3. The powder particles were of micron range and of random size before milling and as milling starts there will be slight increase in the particle size due to the repeated welding of ductile iron during milling. As milling continues, particles become strain hardened and spherical. After 10 h of milling the crystallite size reduced to 6 and 7 nm in case of austenitic and ferritic stainless steel respectively. The lattice strain goes on increasing in both cases.
4. Thermodynamic parameters (ΔH, ΔS and ΔG) were calculated by using Miedema model and the values found to be -14.31kJ/mol, 6.93J/mol and -16.39kJ/mol for duplex and -2.81kJ/mol, 4.35J/mol, 4.11kJ/mol for ferritic stainless steel respectively.
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