Optimization of process parameters for spark plasma sintering of nanostructured SAF 2205 composite

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**Abstract**

This research optimized spark plasma sintering (SPS) process parameters in terms of sintering temperature, holding time and heating rate for the development of a nano-structured duplex stainless steel (SAF 2205 grade) reinforced with titanium nitride (TiN). The mixed powders were sintered using an automated spark plasma sintering machine (model HHPD-25, FCT GmbH, Germany). Characterization was performed using X-ray diffraction and scanning electron microscopy. Density and hardness of the composites were investigated. The XRD result showed the formation of FeNi$_{0.068}$. SEM/EDS revealed the presence of nano-ranged particles of TiN segregated at the grain boundaries of the duplex matrix. A decrease in hardness and densification was observed when sintering temperature and heating rate were 1200°C and 150°C/min respectively. The optimum properties were obtained in composites sintered at 1150°C for 15 min and 100°C/min. The composite grades irrespective of the process parameters exhibited similar shrinkage behavior, which is characterized by three distinctive peaks, which is an indication of good densification phenomena.

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1. Introduction

Duplex stainless steels (DSS) is a prominent member of the stainless steel family, which combines the properties of both austenitic and ferritic classes of stainless steel because of the near balance of austenite and ferrite phases present in its microstructure [1–5]. They have been successfully utilized in aerospace, chemical, power generation and biomedical industries and other demanding engineering applications due to...
possibility of attractive properties such as high corrosion resistance, good mechanical strength and ductility, abrasion resistance, erosion resistance and a very good weldability [6–9].

Conventional DSS alloys suffer considerable loss in wear and mechanical strength at high temperatures. Such limitations in mechanical properties limit their use in structural applications in many industrial sectors [10,11]. One promising approach to improve the elevated temperature properties as well as the mechanical, wear and oxidation properties of stainless steels is by reinforcing it with ceramic dispersoids [12].

The dispersion strengthened steels have attracted considerable attention due to their ease of fabrication, lower costs, and attractive physical and mechanical properties. Traditionally, reinforced steels have been produced by several processing routes such as powder metallurgy, conventional casting and reactive sintering techniques [13]. All these techniques are based on the addition of ceramic reinforcements to the steel matrix, which may be in molten or powder form [14,15]. Among these fabrication techniques for synthesizing the composites, spark plasma sintering (SPS) has attracted much attention, because of its low energy consumption and very short sintering time [16,17].

Spark plasma sintering (SPS) is a versatile technique used to rapidly fabricate a number of materials including metals [18], ceramics [19,20] and composites [21]. In the SPS method, starting powders are placed in a graphite die, and a uniaxial pressure is applied during sintering. The heating is accomplished by spark discharges in voids between the particles. Due to these discharges, the particle surface is activated and purified, and a self-heating phenomenon is generated between the particles. As a result, heat-transfer and mass-transfer can be completed instantaneously. Therefore, SPS technique can be used for sintering ceramic particulates reinforced composite quickly to its full density at relatively low temperature [22].

Several works have been reported for the SPS of stainless steel based composites [13,14,21,22] but nano particle dispersion strengthening of duplex stainless steels has received little attention from researchers. Also, the challenge to obtain fully dense or near-full dense composites and avoid grain growth with nano particles is of great importance and could be carefully resolved by appropriate selection of sintering process parameters to meet demanded mechanical properties and wear resistance [23,24]. However, it is imperative to state that this article presents the first set of data for our research which seeks to develop nano structured duplex stainless steel composites with varying TiN additions via spark plasma sintering (SPS). SPS process parameters such as sintering temperature, holding time, and heating rate were varied in this research using 2205-5TiN with the aim to obtain the best combination of parameters in terms of densification and hardness.

## 2. Materials and methods

2205 DSS (average particle size 22 μm, 96% pure, supplied by Sandvik Osprey Ltd, UK) and TiN (average particle size of 20 nm, 97% purity, supplied by Nanostructured & Amorphous Materials, Inc., USA) powders were utilized as the starting materials for this research. The chemical compositions of the powders are presented in Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF 2205</td>
<td>≤0.03</td>
<td>≤1.0</td>
<td>≤2.0</td>
<td>≤0.03</td>
<td>≤0.015</td>
<td>22</td>
<td>5</td>
<td>3.2</td>
<td>0.18</td>
<td>–</td>
<td>Bal</td>
</tr>
<tr>
<td>TiN</td>
<td>0.03</td>
<td>&lt;0.003</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&lt;0.001</td>
<td>–</td>
<td>21.91</td>
<td>77.83</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

The powders were mixed in a dry environment using the TURBULA Shaker Mixer T2F at a mixing speed of 72 rpm for 8 h to ensure homogeneous mixing of powders. The morphology and phases of the mixed powders were examined with a field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL, Japan) and X-ray diffraction (XRD) respectively.

The appropriate amount of mixed powders required in producing 20 mm diameter and 5 mm thick 2205-5%TiN nano structured composites were poured into a graphite die and then sintered using an automated spark plasma sintering machine (model HHPD-25, FCT GmbH, Germany). To ensure easy removal of sintered products and reduction of temperature in-homogeneities, graphite sheets were used to shield the powders from the die, upper and lower punches [25]. The mixed powders were sintered at different temperatures, times and heating rate as presented in Table 2. The composites were sintered in vacuum and sintering pressure was maintained at 50 MPa throughout the whole process [25].

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Sintering temp (°C)</th>
<th>Holding time (min)</th>
<th>Heating rate (°C/min)</th>
<th>Exp. density (g/cm³)</th>
<th>% porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1000</td>
<td>10</td>
<td>100</td>
<td>7.31</td>
<td>4.07</td>
</tr>
<tr>
<td>B</td>
<td>1100</td>
<td>10</td>
<td>100</td>
<td>7.49</td>
<td>1.72</td>
</tr>
<tr>
<td>C</td>
<td>1150</td>
<td>10</td>
<td>100</td>
<td>7.51</td>
<td>1.44</td>
</tr>
<tr>
<td>D</td>
<td>1200</td>
<td>10</td>
<td>100</td>
<td>7.47</td>
<td>1.94</td>
</tr>
<tr>
<td>E</td>
<td>1150</td>
<td>5</td>
<td>100</td>
<td>7.44</td>
<td>2.28</td>
</tr>
<tr>
<td>F</td>
<td>1150</td>
<td>15</td>
<td>100</td>
<td>7.53</td>
<td>1.16</td>
</tr>
<tr>
<td>G</td>
<td>1150</td>
<td>15</td>
<td>50</td>
<td>7.46</td>
<td>2.02</td>
</tr>
<tr>
<td>H</td>
<td>1150</td>
<td>15</td>
<td>150</td>
<td>7.48</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Upon removal of the sintered products from the graphite die, sand blasting was used to remove the graphite contaminations on the surface of the products. The relative densities of the samples were measured by Archimedes principle. The relative density was calculated with reference to the theoretical density of the starting powders constituents using the rule of mixtures.

The samples were prepared for metallographic examination following standard procedures prescribed for grinding and polishing for stainless steels [26]. The phases present in the sintered specimen were characterized by X-ray diffraction (XRD) using a PANalytical Empyrean model with Cu Kα radiation and analyzed using Highscore plus software. The samples were etched using carpenters reagent for 20 s and the microstructure was analyzed using a scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) incorporated with an EDX detector (Oxford X-Max) with INCA X-Stream2 pulse analyzer software, and Back Scattered Electron (BSE) detectors.

The Vickers microhardness (HV) at room temperature was measured by a microhardness tester (Future-tech) at a load (P) 100 gf (1.0 N) and a dwell time of 10 s. Three repeat tests were carried out on the samples to ensure reliability of the data generated.

3. Results and discussion

In this section, the influence of sintering temperature, holding time and heating rate on phase evolution, microstructure, densification behavior and hardness is discussed with a view to optimize process parameters for fabricating 2205 DSS-TiN composites.

3.1. Phase and microstructural analysis of the sintered composites

The variations in sintering conditions for optimization of sintering temperature, holding time and heating rate for the TiN dispersion strengthened 2205 DSS are presented in Table 2. Fig. 1a shows that the nano particles of the TiN were evenly distributed in the 2205 matrix. The XRD result (Fig. 1b) of the mixed powders shows that only peaks corresponding to TiN and phases containing iron, chromium, and nickel, which are the main constituent of DSS 2205 phases are detected in the patterns. The main components of the DSS (Fe, Cr, Ni) in the periodic table of the elements lie next to each other. Therefore, they have similar characteristics, and their lattice parameters are very similar [22].

The XRD result of the sintered composites with sintering temperature, holding time and heating rate (Table 2, A–H) is presented in Fig. 2. It is observed from the XRD result that there is a phase change, and a new phase of iron nitride with chemical formula FeN_0.068 was formed. There were slight changes in relative intensity of peaks which is obviously due to the difference in sintering parameters of temperature, time and heating rates as given in Table 2.

![Fig. 1 - SEM (a) and XRD (b) results of the mixed 2205 duplex stainless steel and TiN powders.](image-url)

![Fig. 2 - XRD result of sintered DSS 2205-TiN composites under different sintering conditions as shown in Table 2.](image-url)
Fig. 3 – Characterization of sintered DSS 2205-5%TiN: (a) nano clusters of TiN, (b) SEM/EDX, (c) neck formation at powder surface and (d) TiN at grain boundaries.

The prevention of grain growth and detainment of the nano particles of TiN in the duplex matrix forms the objective of this research. Fig. 3 shows the results of SEM examinations of the microstructures of the sintered 2205 DSS-5TiN composite at very high magnification. The particle sizes were taken at this magnification and were noted to be in the nano range (white regions, Fig. 3a). The EDS result of Fig. 3b shows that the examined regions mainly contained nano particles of TiN (Figs. 3b1). It is observed that, the microstructures were different from cast structures as characteristic features of the austenite and
ferrite phases were distinct. It is however possible to clearly separate the content of phases in the tested composites. This suggests that the incorporation of nano particles in the crystal structure of iron changes its network parameters [22]. Fig. 3d shows a homogeneous distribution of TiN in the steel matrix with a general tendency of the reinforcing TiN phase to locate itself at the vicinity of grain boundaries in the matrix.

Microstructural examinations from previous studies have shown that the favored sites for the formation of phases are grain boundaries and the reinforcement/matrix interface [27]. The phase of iron nitride formed in the XRD result (Fig. 2) is obviously due to the diffusion of iron and nitride at the grain boundary as indicated in the EDS result (Fig. 3b1). It is worthy to state that during the SPS process, non-equilibrium conditions exists in the material, which has a significant influence on diffusion and the reactions taking place during sintering. The formation of FeN0.068 phase in the studied composites is as a result of intense phenomena taking place during SPS (surface activation, diffusion, surface melting, necking between the particles of sintered powder, and plastic flow [28]). During sintering, mass transport increases and eventually results in

Fig. 4 – Effect of sintering temperature variation on the densification and hardness of DSS 2205-5TiN.

Fig. 5 – Microstructures of composites with 5% TiN sintered at (a) 1000, (b) 1100, (c) 1150 and (d) 1200 ºC.
formation of neck and better bonding between powder particles (Fig. 3c) [29].

3.2. Optimization of sintering temperature

Three initial temperatures of 1000, 1100 and 1200 °C were selected for the optimization of the sintering temperature in terms of densification and micro-hardness (sintering conditions reported in Table 1) of the nano-structured 2205-TiN composites. A decrease in hardness and densification was observed when sintering temperature was increased from 1100 °C to 1200 °C. It was thought that the hardness and density could further be improved if the temperature was above 1100 °C; this led to the consideration of sintering temperature 1150 °C.

Fig. 4 confirmed similar trend in behavior for densification and micro-hardness with increase in sintering temperature. It is evident from the figure that the maximum densification and micro-hardness was achieved at 1150 °C. The increase in densification could be attributed to improved powder contact (nano and micro powders interaction) and decrease in porosity level obtained at 1150 °C (Table 2). It is however imperative to state that high density accompanied with moderate grain size could contribute to considerable increase in microhardness which is in correlation with our investigations. A reduction in density and hardness was however noted with an increase in sintering temperature to 1200 °C. The decrease in densification and hardness at 1200 °C may be as a result of localized melting of powders. Similar trend in result of reduction in densification and hardness with further increase in temperature was reported by [25], while optimizing process parameters for Fe-18Cr-2Si nano structured alloy. The authors suggested that partial melting of stainless steel powders could occur at 1200 °C.

Fig. 5 compares the microstructures of 2205 DSS and TiN composites at different sintering temperatures. The reinforcing TiN phase was uniformly distributed in the duplex matrix. The grains were also observed to grow with increasing sintering temperature. At 1150 °C (Fig. 5c), numerous fine nitride precipitates were detected within the grains boundaries with a higher packing density and an increase in the number of necks which indicates improved sintering. The presence of these precipitates accumulated within the grain boundaries could significantly retard the grain boundary mobility and dislocation movement [30]. In SPS the high sintering temperature enhances consolidation through thermal diffusion.

3.3. Optimization of holding time

The next parameter to be optimized was holding time in terms of densification and hardness at an optimized sintering temperature of 1150 °C as discussed in the previous section. The effect of holding times (5, 10 and 15 min) on densification and micro-hardness of the composites is presented in Fig. 6. The result shows an increase in densification and hardness with increase in holding time. The increase in densification at 15 min is mainly because of increased heat flux, which ultimately reduced the porosity in the composites. This is in accordance with earlier reports that demonstrated an increase in density with increasing holding time, but they also stressed the drawback of grain growth at longer holding times [22,31]. We could not increase the holding time beyond 15 min as prolonged holding time could give rise to further grain growth which may adversely affect the properties of the composites. It was also not economical to increase the holding time beyond 15 min since a densification of about 99% was achieved.

Fig. 7a–c shows the microstructure of the sintered specimens at different holding times of 5, 10 and 15 min. Significant changes were observed in the composite microstructure. The grains were noticed to increase with increasing holding time. It is however observed that, longer sintering time promoted the formation of precipitates within the grain boundaries. These precipitates were absent in the composite sintered at holding time 5 min but increased from 10 to 15 min holding time. X-ray diffraction of the precipitates obtained revealed that nitrides were the main types of precipitates in the microstructure. It is noteworthy to state that these precipitates are inherent resistance to dislocation movement and further grain growth. It is a fact that grain growth kinetics is governed by grain boundary mobility and the key factors responsible for grain boundary mobility in materials are grain boundary segregation, solute drag, pore drag, chemical ordering, and secondary phase (precipitates) [31]. It is therefore recognized that the increase in hardness and density with holding time could as a result of the combined pinning effect of this precipitates and segregation of nitrogen atoms to grain boundaries.

3.4. Effect of heating rate

It became necessary to optimize the heating rate for sintering of the composites after the optimization of sintering temperature and holding time at 1150 °C and 15 min respectively. Fig. 8 shows the effect of heating rates (50, 100 and 150 °C/min) on the densification and hardness of the composites. As can be seen from Fig. 8, with the increase in heating rate from 100 °C/min to 150 °C/min, the densification and hardness.
considerably decreased from 98.82 to 97.86 g/cm³ and 308.46 to 302.5 HV, respectively.

The result indicated that low heating rate promoted the elimination of pores; consequently a higher density is achieved even with a high heating rate of 100 °C/min. However, when the heating rate was too rapid (150 °C/min), the lack of the particle rearrangement and large temperature hysteresis between the heater and powders could be the reason for the high porosity level obtained [32]. Again, low heating rate allows longer time for atomic diffusion, which is a critical sintering factor. The implication is that more atoms move to points of contact between powder particles to form sintering necks. When the necks grow, the pore sizes are reduced. This results in an increase in density of the sintered products.

The drop in densification at heating rate of 150 °C/min is an indication that the high heating rate could not provide sufficient time for homogenization of the microstructure and allow for improvement of the composite packing density. The formation and neck growth during sintering have been reported to largely depend on local distribution of the current density [18]. The highest densification and hardness were achieved at 100 °C/min of heating rate and was chosen as the optimized heating rate to sinter the composites at 1150 °C.

3.5. Shrinkage behavior of the composites

The shrinkage behavior of the DSS 2205 and TiN composites during sintering was evaluated; the shrinkage rate versus time of the sintered grades is presented in Figs. 9 and 10. The figures also illustrate the densification phenomena taking place during sintering of the composites. It is observed that all

![Fig. 7 - Microstructures of composites with 5% TiN addition at 1150 °C at holding time of (a) 5 min, (b) 10 min and (c) 15 min.](image)

![Fig. 8 - Effect of heating rate on the densification and hardness of DSS 2205-5TiN.](image)

![Fig. 9 - Shrinkage rate versus time for the 2205 DSS/TiN sintered at different temperatures.](image)
Fig. 10 – Shrinkage rate versus time for the 2205 DSS/TiN sintered at 1150 °C at different holding times.

the composite grades irrespective of the sintering conditions exhibited similar shrinkage behavior, which is characterized by three distinctive peaks (1, 2 and 3). For the samples sintered at different temperatures (Fig. 9), there was an increase in shrinkage rate and localized deformation with increase in temperature up to 1150 °C; however, a slight drop in peak was observed with further increase of sintering temperature. It is noted that densification and hardness were observed to drop at 1200 °C (Fig. 4). This could be attributed to the delay in the start of the localized deformation as observed in Fig. 9.

Diof and Molinari [17] reported that the first peak is attributed to the initial rearrangement or relative movement of the powder particles which is due to the application of pressure and movement of the lower and upper punches. The second peak is linked to localized deformation at contact point, while the third peak represents bulk deformation of the sintered product. The degree of densification is a function of the intensity of the peaks and the extent of deformation of the particles.

Fig. 10 shows the shrinkage behavior of the composites sintered at 1150 °C and at different holding times. The peaks were observed to increase with holding time, which indicates an increased densification and displacement rate. A delay in localized deformation was observed for the grade sintered for 5 min. This result of the shrinkage rate is in agreement with our earlier report on the relative densities and hardness of the samples.

4. Conclusion

DSS 2205-5%TiN composite has been synthesized by SPS. SPS process parameters in terms of sintering temperature, holding time and heating rate were optimized. The results can be concluded as follows:

1. The hardness, density and microstructure of the sintered composites largely depend on the SPS process parameters.
2. The XRD results indicated that there was a phase change; iron nitride with chemical formula FeN0.068 was formed.
3. The SEM/EDS revealed the presence of nano ranked particles of TiN evenly distributed at the grain boundaries of DSS matrix.
4. A decrease in densification and hardness was observed when sintering temperature and heating rate were 1200 °C and 150 °C/min, respectively.
5. The density and hardness results indicated that the optimum properties were obtained at sintering temperature of 1150 °C, holding time 15 min and heating rate of 100 °C/min.
6. All composite grades displayed similar shrinkage behavior irrespective of the sintering conditions.

Conflicts of interest

The authors confirm that there is no conflict of interest.

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