Effect of nickel powder particle size on the microstructure and thermophysical properties of spark plasma sintered NiCrCoAlTiW-Ta superalloy

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Abstract. The spark plasma sintering technique (SPS) was used to consolidate admixed elemental powder in order to fabricate NiCrCoAlTiW-Ta superalloy. Nickel which is the key element that formed the matrix powder particle size was varied in the range of 3-44, 45-106 and 106-150 µm. The effect of varying the starting powder particle size, on the formation of intermetallic phases was investigated. Also, important thermophysical properties in the development of superalloys for high temperature applications were investigated by using laser flash machine, in the range of 100-800 °C. The constituents of the microstructure for the sintered alloy includes, the gamma (γ) matrix phase (Ni), precipitated intermetallic gamma prime (γ') phase Ni3(Al, Ti) and the precipitated solid solution strengthening elements (Cr and W). There was an increase in the density with decreasing powder particle size. Also, the average grain size increased with increasing powder particle size. The thermophysical properties obtained, which include thermal conductivity and diffusivity increase with increasing temperature. Non-linear behaviour and inflection points were observed as the temperature increases due to short range order and disorder phenomenon which is associated with superalloys. The powder particle size has little or no significant effect of the thermophysical behaviour as the pattern observed were almost the same.

1. Introduction
NiCrCoAlTiW-Ta alloy belongs to the class of nickel based-superalloy that has been extensively used in gas/steam turbines. This is largely due to the appreciable mechanical properties and structural stability strength that the alloy posed when used for high-temperature applications. The alloy is unique due to its high specific Young’s modulus, coupled with excellent oxidation, corrosion, creep and fatigue resistance properties. Oil and gas, chemical, power generation and aerospace industries, etc are great beneficiaries of the outstanding qualities of this alloy. Valuable components and equipment like heat exchanger, valve, turbine blade, driller and gas-cooled reactors have been developed by using NiCrCoAlTiW-Ta alloys. The microstructure formation of superalloy is quite complex, and this is due to the combination of different constituent elements with different material properties. Often, some major microstructural phases are developed in superalloys due to the reaction between powder elements during sintering [1, 2]. For NiCrCoAlTiW-Ta alloy, the constituent phases that are normally present include the matrix gamma (γ) phase, the ordered intermetallic gamma prime (γ’) phase and the precipitate disordered solid solution...
strengthening phase. These phases have a face-centered cubic crystal structure which aid structural stability at ambient and high-temperature environments. A numbers of literature provide substantial information on the evolution of the three phases and their influence on the resulting material properties [3-5]. The fluctuation in temperature applied to the alloy while in service, especially turbine blades often cause thermal shock to the material. The shock is often due to thermally induced stresses, which leads to extensive thermal and stress gradients in the alloy. Consequently, a potential thermal gradient is developed which pose a threat to the efficiency and life span of a turbine system.

Hence, a careful selection of both processing routes and alloy composition has helped in reducing the occurrence of material and microstructural defects. By using spark plasma sintering (SPS) technique for the fabrication of superalloys, the limitations such as fluctuating mechanical properties across the bulk volume of the resulting alloy, which are largely due to chemical and structural heterogeneities are addressed. It has been reported that the wide variation in the particle size and shape of the starting elemental powder contribute to material densification [6, 7]. This in turn has significant effect on the thermal and material responses of the alloy when in service. A number of methods such as hot press, selective laser melting, spark plasma sintering (SPS) and injection moulding are available in powder metallurgy (PM), and among these, SPS technology is used in this study. SPS is a PM technique which consolidates powder by the simultaneous application of direct pulsed current and uniaxial force [8, 9]. Using this technique, an electric current density is supplied to induce high temperature within the green powder via the Joule heat effect thereby resulting in the sintering of the powder. SPS technique is a fast sintering process that densifies material in one single operation. The detailed SPS mechanism, advantages and disadvantages have been reported in the literature [10, 11]. This study is aimed at developing NiCrCoAlTiW-Ta superalloy via SPS technique and investigating the effect of the varied starting powder particle size (nickel matrix) on the microstructure and thermal properties of the sintered alloy.

2. Experiment
The sintering of NiCrCoAlTiW-Ta superalloy was carried out by combining seven elemental powders in accordance with the stoichiometric composition standard of the superalloy [12]. The elements that make up the composition include; nickel which constitutes 64.58 wt% of the alloy, with 99.8% purity (varied over three powder particle sizes: 3-44 µm, 45-106 µm and 106-150 µm). Others are chromium (16 wt%, 99.9% purity), cobalt (8.3 wt%, 99.8 purity), titanium (3.4 wt%, 99.8 purity), aluminium (3.4 wt%, 99.9% purity), tungsten (2.6 wt%, 98.5 purity) and tantalum (1.72 wt%, 98.5% purity). All the elements were supplied by TLS-TechnikGmbH (Ni, Ti and Co) Sigma Aldrich (Cr, Al and Ta) and Alfa Aesar (W) companies. They were weighed by using an electric weighing machine to accuracies of ±0.001, poured into a plastic container and pre-alloyed in a tubular mixer. The pre-alloyed process was done over a period of 10 hours at a speed of 49 rpm. The green powder was poured into the graphite die with 30 mm diameter. The thickness of the samples was fixed at 5 mm for each of the alloys. Prior to sintering, 0.2 mm thick graphite paper was used to line the interior of the graphite die and the faces of the punches that made contact with the green powder. The purpose of the graphite paper was to prevent reaction between the graphite die and the powder at high temperature and to enable easy removal of the alloy after sintering. The parameters used for the sintering process are, 1100 °C sintering temperature, 32 MPa pressure, 100 °C/min heating rate and 5 min holding time. It was ensured that the process was done in a vacuum atmosphere. At the completion of the sintering process, the furnace was switched off and the temperature was allowed to cool down to room temperature before the alloy was removed. A sand blasting process was carried out to remove carbon deposited on the surface of the sintered alloy from the graphite paper. The material was later sectioned into smaller pieces for metallographic investigations. Series of emery paper was used (320, 600, 800 and 200 grit size) to remove patches and scratches on the surface of the test samples. The samples were polished by using diamond paste and etched afterwards. The etchant used was kalling reagent (2 g of CuCl2, 50 ml of HCl, 25 ml of HNO3, and 200 ml of H2O). The microstructure was investigated by using a scanning electron microscope (SEM) (JEOL JSM-7600F SEM) equipped with an EDS detector with INCA X-Stream2 pulse analyzer software. Polarized optical microscope was used to calculate the average grain size of the sintered alloys and this follows ASTM E112 standard [13].
Chemical phases present in the alloy were analyzed by X-Ray diffraction (XRD), PANalytical Empyrean model with CuKα radiation. The thermal properties of the sintered alloys were also evaluated. The density and thermal diffusivity values used in this study were measured by the Archimedes method and NETZSCH model 427 laser flash diffusivity respectively. The specific heat capacity used was taken from the literature [14, 15]. The thermal diffusivity study was conducted from 100 - 800 °C and the thermal conductivity properties was calculated by using equation 1. The dimensions of the sample used on the laser flash equipment is 10 mm x 10 mm x 4 mm.

\[ \lambda = \rho \cdot C_p \cdot a \]  

Where: \( \lambda \) - thermal conductivity (w/(m.k))
\( \rho \) - Bulk density (g/cm³)
\( C_p \) - Specific heat capacity (j/(g.k))
\( a \) - Thermal diffusivity (mm²/s)

The laser flash analysis (LFA 427) procedure used in this study was in accordance with ASTM E-1461 standard and the thermal diffusivity measurement was conducted under a nitrogen environment. Graphite solution (Al₂O₃-graphite) was used to coat the surface of the test sample to facilitate fast absorption of the flashlight. This, in turn, leads to heat emission on the backside of the test piece, which is recorded by an attached sensor and the values were recorded.

3. Results and discussion

3.1 Relative density and average grain size

The relative density and the average grain size of the sintered NiCrCoAlTiW-Ta superalloy is presented in figure 1. These were for the three sintered alloys (106-150 and 45-106 and 3-44 μm initial powder particle sizes) and their porosities were observed to be 11.27 %, 8.43 % and 3.9 % respectively. The highest relative density of 96.1% was observed for an alloy with 3-44 μm as the initial powder particle size. The theoretical density was calculated to be 7.894 g/cm³. Decrease in the average grain size was observed with decreasing powder particle sizes. The biggest average grain size was obtained for alloy with fine particle size. This implies that finer particles size are closely packed with reduced initial porosity between powder compact. This enhances densification of the sintered alloy. The increase in the average grain size suggest that the sintered alloy keep memory of the starting powder particle size [16]. This means that localized deformation of particles (plastic flow) during densification could not reduce the coarser particle size to form grains of the same size with alloy of finer particle. Further work is in progress to establish particle behaviour and densification kinetics during the sintering process of NiCrCoAlTiW-Ta superalloy. However, relatively dense NiCrCoAlTiW-Ta superalloy with refine grains can be produced via SPS technique.
3.2 Microstructure analysis
SEM images of NiCrCoAlTiW-Ta superalloy samples, sintered at 1100 °C with the three different starting powder particles sizes, are given in figure 2. The EDX graphs adjacent to the SEM image show the elemental composition of the sintered alloys and their respective weight percent. The sintering has resulted in the formation of different phases and grain shapes. The three different colours on the SEM images, light grey, dark grey and the white dotted patches that are heterogenosly distributed within the microstructures. Further analysis shows that the light grey area represents the γ + γ′ phase, the dark grey represents precipitated chromium-rich zones and the white represent the precipitated tungsten solid solution. Careful observation shows that chromium precipitates were largely formed on the grain boundary of the γ matrix and γ′ intermetallic phases. However, the overlap observed in the formation of the γ matrix phase and the γ′ intermetallic phase is expected since these phases are both know to be face center cubic crystal structures. Hence, the γ′ intermetallic phase forms precipitates within the γ matrix phase due to the similar cubic lattice and the closeness in their lattice parameters. The XRD results also confirmed the presence of the overlapped phases that was observed on the microstructure. An increase in average grain size was observed with increasing powder particle sizes. The effect of this observations was captured in section 3.1. Apart from chromium, tungsten was also observed to form precipitated solid solution strengthened elements within the microstructure, and this is sparsely distributed within the structure of the sintered alloys. Tungsten is known as a hard metal with high melting temperature and by forming solid solution strengthened precipitate in the alloy, the strength of the sintered alloy is improved. Idowu et al. [17], in their study on cast IN738LC superalloy observed the formation of precipitated γ and γ′ phase alongside the formation of solid solution strengthened elements. These results are similar to that obtained in this study.
Figure 2. SEM images of spark plasma sintered NiCrCoAlTiW-Ta superalloy on the left, with EDX analysis results on the right. (a) Ni-matrix powder particle size (3-44 µm) (b) Ni-matrix powder particle size (45-106 µm) (c) Ni-matrix powder particle size (106-150 µm).

3.3 XRD analysis

Figure 3 shows the XRD patterns for the starting powder and the three sintered (different particle size range of matrix) samples. The XRD analysis on the SPS solid samples shows the formation of gamma (γ) matrix phases with prominent peaks observed at 42, 52 and 76° 2θ diffraction angles. In general, the gamma (γ) matrix phase is the dominant phase that is present in all the sintered samples. The pre-alloyed powder has sharp minor peaks reminiscent of the constituent elements. Intermetallic phases were not present in the pre-alloyed powder, since there was no reaction yet between powder particles. The analysis of the three sintered alloys shows the presence of intermetallic phases. This was formed from the application of thermal energy which triggered chemical reaction within the structure of the sintered alloy. In addition, the type of secondary intermetallic phase formed was gamma prime (γ') phase (Ni₃Al and Ni₃Ti). These two γ' phases overlap in the peak with the highest intensity at 42° angle 2θ, while at 52 and 78° diffraction angles, they are separated respectively for Ni₃Al and Ni₃Ti. The intensity of the peak formed at angle 42° angle 20 was observed to decrease with decreasing starting powder particle size. Marginal decrease was observed with the peak formed at 42° angle 20, for alloy with c and d. This suggests that there was an increased formation of intermetallic precipitate phase, with decreasing starting powder particle sizes [18]. This is due to reduction in the volume of matrix elements (nickel) that dissociated to form secondary phases [19]. For this reason, it was considered that more intermetallic phases were present in the alloy sintered with smaller initial powder particle size.
Figure 3. XRD patterns of NiCrCoAlTiW-Ta samples (a) Pre-alloyed powder and b-c is the spark plasma sintered superalloys; (b) Ni-matrix powder particle size (3-44 µm) (c) Ni-matrix powder particle size (45-106 µm) (d) Ni-matrix powder particle size (106-150 µm).

3.4 Thermal diffusivity and thermal conductivity measurement

The response of the thermal diffusivity and thermal conductivity of the sintered NiCrCoAlTiW-Ta superalloys as a function of temperature is shown in figure 4. Table 1 shows the data as obtained from the laser flash analyzer, while the specific heat capacity data used were from the literature [14]. In general, figure 4 shows that the thermal diffusivity, conductivity and specific heat capacity increased with increasing temperature for the three sintered alloys. For sample with 3-44 µm initial powder particle sizes (figure 4a), there is a slight decrease in the thermal properties between 200 and 300 °C. Thereafter, the thermal properties start to increase with increasing temperature. A plateau pattern was observed in the thermal behaviour of alloy with 106-150 µm initial powder particle size (figure 4c) with increasing temperature. The points where the patterns deviate from linear progression with increase in temperature is referred to as an inflection point, and this is more pronounced in sample C (106-150 µm initial powder particle size). The point of inflection was observed at 600 °C for sample B. Several reasons can be responsible for the deviation in the patterns as the temperature increases, especially the occurrence of inflection points. For this type of alloy, the deviation is attributed to phase transformation and structural adjustment. The structural reconfiguration is a result of atom redistribution which causes disorder in the matrix phase [20]. Also, at high temperature state, dissolution of precipitated γ’ intermetallic and γ matrix phases might occur which may equally lead to inflections. However, it was reported that chromium precipitate at high temperature, usually above 477 °C, while it depletes at a temperature above 800 °C [20]. The absorption of heat will create thermal stress within the microstructure which is also a factor that could result in inflection due to the precipitation of chromium along grain boundaries (figure 1). Similar reports in the literature [20-22], stated that the occurrence of inflection point was as a result of dissolution of γ’ intermetallic precipitates, which usually occur at high temperatures.
Figure 4. Thermal diffusivity, thermal conductivity and specific heat of NiCrCoAlTiW-Ta superalloy: (a) Ni-matrix powder particle size (3-44 µm), (b) Ni-matrix powder particle size (45-106 µm), (c) Ni-matrix powder particle size (106-150 µm).

Table 1: Thermal diffusivity, thermal conductivity and specific heat of spark plasma sintered NiCrCoAlTiW-Ta superalloy as a function of temperature

| Temperature, °C | Thermal diffusivity, mm²/s | Specific heat, J/(g·K) [14, 15] | Thermal conductivity, W/(m·K) |
|----------------|----------------------------|----------------------------------|------------------------------|
| 100            | 4.93                       | 0.461                            | 17.24                        |
| 200            | 6.16                       | 0.502                            | 23.47                        |
| 300            | 6.05                       | 0.523                            | 23.10                        |
| 400            | 6.55                       | 0.544                            | 27.04                        |
| 500            | 6.97                       | 0.544                            | 28.76                        |
| 600            | 7.51                       | 0.586                            | 33.38                        |
| 700            | 8.01                       | 0.586                            | 35.60                        |
| 800            | 8.61                       | 0.628                            | 40.99                        |

(b) Ni (45-106 µm) particle size. Density: 7.229 g/cm³

100  4.19  0.461  13.96
200  4.31  0.502  15.65
300  4.60  0.523  17.37
400  4.93  0.544  19.40
500  5.24  0.544  20.62
600  5.73  0.586  24.27
700  6.01  0.586  25.47
800  6.37  0.628  28.90
Ni (106-150 µm) particle size. Density: 7.004 g/cm³

| 100  | 5.25  | 0.461  | 16.94 |
|------|-------|--------|-------|
| 200  | 5.37  | 0.502  | 18.90 |
| 300  | 5.34  | 0.523  | 19.58 |
| 400  | 5.74  | 0.544  | 21.88 |
| 500  | 5.93  | 0.544  | 22.60 |
| 600  | 6.34  | 0.586  | 26.03 |
| 700  | 6.61  | 0.586  | 27.14 |
| 800  | 6.97  | 0.628  | 30.68 |

4. Conclusions
NiCrCoAlTiW-Ta superalloy with strengthening intermetallic and precipitated solid solution phase were established by using Spark Plasma Sintering. Also, the thermal conductivity was calculated from the knowledge of thermal diffusivity, heat capacity and alloy density over temperatures of 100-800 °C. Highly dense alloys were achieved for the sintered alloys with relative densities in the range 88 – 96%. The alloy with starting powder particle range between 3-44 µm has the highest relative density of 96.1% and the least density of 88.73% was obtained for alloy with 106-150 µm starting powder particles (coarser). The starting powder particle sizes was observed to have significant effect on the density of the sintered product, even at the same processing parameters. The non-linear pattern observed from the thermophysical properties is due to atomic redistribution and short-range order/disorder phenomena which are known to occur in the Ni–Cr alloy system. The variations in the thermophysical properties are not so significant, however, the thermal conductivity of the superalloys depends on temperature and the phases formed. Thermal conductivity and diffusivity were discovered to increase with increasing temperature.

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