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OXIDATION BEHAVIOUR AND THERMAL ANALYSIS OF SPARK PLASMA SINTERED Co-BASED TERNARY SUPERALLOY

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ABSTRACT

Cobalt-based superalloys are currently used for gas-turbine vanes because of a combination of superior structural and thermal properties compared with nickel-base superalloys. Presently, superalloy fabrication is mostly done by casting, forming and arc melting. However, powder metallurgy brings unique advantages i.e. reduced machining, grain refinement and high-melting elements alloying. In this work, Co-based superalloy was prepared by spark plasma sintering (SPS) from high purity metallic powders of Co, W and Ta. The powders were vigorously mixed for 12 h, stacked in a graphite and compacted in vacuum furnace at 1000 and 1200 °C. The dwelling time of 10 and 15 min and heating rate of 150 °C/min were used. Structural characterizations of the superalloys were carried out using SEM-EDX and X-ray diffractometer, while thermal and oxidation tests were performed using Laser Flash Analyzer (LFA) and a high temperature furnace. Results indicated formation Co-rich main phase with dispersions of carbides and oxides phases of the metallic species within the material. Co-based superalloys sintered at 1000 °C have higher thermal conductivity (TC) at lower temperature range, while alloys sintered at 1200 °C exhibited proportional increase in TC values in the 700 – 1000 °C range. Cyclic oxidation resistance of the alloys increases with sintering temperature

Keywords: SPS; Superalloys; Co-W-Ta; Laser Flash Analyzer; Diffusivity; Carbides.

1. INTRODUCTION

Cobalt is one of the main elements for the few superalloys currently available. It is a crucial base element because it imparts to its alloys some very important properties, such as wear resistance, creep and fatigue strength at elevated temperatures. Notably, Co-based alloys exhibit higher stress capability at elevated temperatures and better hot corrosion resistance in contaminated gas turbine atmospheres than other superalloys types (Coutsouradis et al., 1987; Hahn and Özişik, 2012; Klarstrom et al., 2018). They also have better weldability and thermal fatigue resistance than Ni-based alloys. However, at ambient temperatures, Co-based superalloys have lower strength, ductility and fracture toughness. Cobalt alloys commonly contain 0.25%–1.0% carbon and grain boundary hardening usually occurs by precipitation of incoherent carbides during process or heat treatment. Meanwhile, alloying with any or combination of Ta, W, Nb, Cr and Mo provides the required solid solution strengthening (Klein et al., 2014; Klarstrom et al., 2018). Particularly, Ta is a high refractory element and it is uniquely identified as a good stabilizer, while W is known to be a good gamma prime (γ') former in superalloy system. With good hot corrosion resistance, oxidation and sulfidation resistance, co-based alloys are mostly applied in static parts such as vanes. Its lower strength properties due to strengthening limitations by solid solution or carbide precipitation makes Co-based alloys unusable for disk and blade applications (Donachie, 2002; Coutsouradis et al., 1987). Superalloys are often coated with special barrier material layer to enhance hot corrosion and oxidation resistance, and the process is somehow costly and may require specialized processes (Nicholls, 2003). Besides, it is well known that these coatings do not provide permanent remedy like the appropriate alloying and processes. Coating or no coating, system failure due to degradation by weak oxidation or hot corrosion resistance depends largely on the inherent physical properties of the alloy itself.

Co-based superalloys normally form continuous dense protective oxide layers in the form of CoO, Cr2O3, TaO, Ta2O3 and Al2O3, and these oxides are usually thermodynamically stable, thin, and with strong adherence to the surface (Tzvetkoff et al., 1995; Misra, 1986; Klarstrom et al., 2018). These allow for improved creep rupture characteristics above 1000 °C, weldability and thermal fatigue resistance (Davis, 1990; Davis, 2000). Since superalloys are mainly synthesized for high temperature applications, their creep, hot-corrosion and oxidation resistance are of primary importance (Reed, 2006). It is known that physical properties of materials can be tuned for enhanced performance not only through the alloying, but also through process technique. Most current studies on superalloys are focused on traditional arc melting and casting, while

attentions given powder metallurgy methods are still not adequate. Therefore, information on the effects of these non-traditional techniques on the alloy system are limited. Thermal conductivity is still one of the very important physical properties to assess an alloy for improved performance at high operational temperature (Ashby, 1989; Darolia, 1991; Miracle, 1993). To avoid surface degradation by local heating which could lead to alloy system failure, a reasonably high thermal conductivity is required. An alloy with a low thermal conductivity will be unable to curtail heterogenous temperature distribution which induces local melting and oxidation resistance failure. It is surprising that contrary to the extensive studies on thermal conductivity on intermetallic compounds (Terada et al., 1995; Terada et al., 2001; Terada et al., 2002; Terada et al., 2003), the available information for cobalt solid solutions is quite limited (Madelung and White, 1991). Cobalt has an advantage as a solvent material because of its wide solubility for many elements (Massalski, 1990; Okamoto, 2000). Hence, there are opportunities to improve the thermal conductivity property of cobalt alloys with an overall effect on their physical properties for improved performance at elevated temperature.

This work aimed to study the effects of the process parameters i.e. sintering temperatures and dwelling time on the thermal properties of cobalt ternary superalloy. Two no table highly refractory metallic elements, W and Ta were selected in optimized proportion as alloying additions to the base material Co to form a ternary combination. Spark plasma sintering technique was used to consolidate the green compact powder placed within graphite punches. Hence, microstructural and phase analysis of the sintered alloy samples were done, while the thermal characterizations were carried out using relevant methods.

2. MATERIALS AND METHODS

2.1. Experimental Procedure:

The Co-based superalloy samples were prepared using elemental powders of cobalt (1-3 µm), tungsten (2-3 µm) and tantalum (100 nm) with 99.9 % purity from TLS Technik GmbH. Powder composition for the samples was kept fixed at Co-15W-5Ta for the sintering. Holding time and sintering temperatures were varied accordingly (Table 1), while the sintering pressure and heating rate values were 50 MPa and 150 °C/min, respectively. In order to achieve the required homogeneity, the selected elemental powders were blended and mixed vigorously with 5 mm diameter stainless balls in a tubular mixer for 10 h. Subsequently, the mixed powders samples were stacked in a 30 mm graphite die with a 5 mm thickness and was compressed using graphite plungers. Consolidation was achieved using a spark plasma sintering equipment (SPS FCT Systeme GmbH model) under vacuum condition. The detail sintering profile is shown in Figure 1.

Table 1: Sintering parameters for the Co-based alloys

Sample	Sintering Temperature (°C)	Dwelling Time (min.)	Composition (wt. %)
CoWT1	1000	10	Co-15W-5Ta
CoWT2	1000	15	Co-15W-5Ta
CoWT3	1200	10	Co-15W-5Ta
CoWT4	1200	15	Co-15W-5Ta

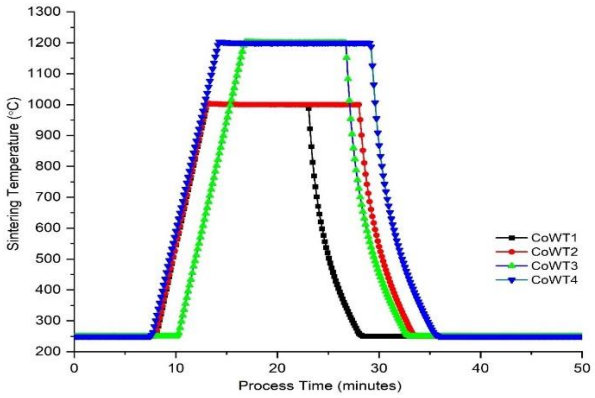

Figure 1. Sintering temperature profile of the Co-based alloys

2.2. Characterization Details:

The density values of the sintered alloys were determined using Archimedes principle, and the percentage densification of the samples was obtained relative to the theoretical densities calculated for the starting powder mixtures. The microstructural analysis was conducted on a field emission scanning electron microscope (FE-SEM: JEOL JSM 7600F) incorporated with an energy dispersive x-ray spectrometer (EDX). Crystallographic characteristic data for the alloys was acquired using the multiplatform PANalytical Empyrean X-ray diffractometer with Cu Kα radiation. Thermal conductivity was determined by a laser flash method on a disc specimen with dimensions of 10 mm x 10 mm x 5 mm. Cyclic oxidation experiment was done in a tubular furnace. For the cyclic oxidation experiment, the Co-based alloy samples were subjected to 10 heating cycles (3h/cycle) at 1000 °C. The samples were heated in an alumina boat, and the mass change was measured before and after every cycle using a high sensitive weighing balance.

3. RESULTS AND DISCUSSION

3.1. Compositional and Microstructural Analyses

The morphologies of samples prepared sintering temperature of 1000 ºC, at varied dwelling time are shown in Figures. 2(a) and (b), respectively. Despite the similar sintering temperature, the effect of the isothermal holding time on the morphology can be seen. There is a clear difference in term of phase distribution and transformation in the microstructure of the samples. CoWT1 exhibited a smoother morphology higher distributions of carbide phases. Meanwhile, for the sample sintered at 15 min dwelling time, a clear partitioning of major phases was identified, and with textured morphology. Network of phases was formed within the microstructure indicating diffusion and formation of phases with distinct structural characteristics within the system. Based on the EDX results, the Co-rich matrix phase is composed of intermetallics of the elemental constituents in combination with carbides. The white patches are tungsten-rich phases with carbide compounds, while the dark phase distributed within the structure are largely composed of Co_2C with tungsten. For sample CoWT2, a clear reduction or disappearance of dark phases is observed which indicates that at longer holding time, more transformation reactions occurred within the compacted powder material which led to increase in carbides, oxide, solid solutions and intermetallics formation. The lighter grey phase distributed within the main grey Co-rich phases is an intermetallics of near equal concentrations of Co and W with presence of carbides phases (Klarstrom et al., 2018). It is shown that higher holding time reduced the dominant carbides and favoured the formation of intermetallics through diffusion and reactions within main constituents.

The morphologies of samples CoWT3 and CoWT4 sintered at 1200 ºC are clearly distinguishable. Also, for 10 min holding time, more dark carbide phases are seen, but as dwelling time increased to 15 min, a drastic reduction in the appearance of dark phases is clearly noted. Though increase in dwelling time may not necessarily improve the mechanical properties of the alloys due to the deleterious grain growth, but the morphology and compositional analysis as shown in Figures 2 (c) and (d) indicated a drastic transformation in the structure and phases. Most especially for samples CoWT4, two main morphologies are observed, the smooth and textured phases. Though the sintering temperatures were below the melting point of any of the alloying elements, the slightly elevated and partitioned smoother Co-rich phase in samples CoWT2 and CoWT4 suggested plastic deformation within the material due to phase transformation by longer thermal loading (Srivatsan et al., 2001; Panigrahi et al., 2005; Smith et al., 1998). In contrast, samples prepared at 10 min dwelling time, are composed mainly of evenly distributed morphology with higher distributions of Co-rich carbides phases. It is then shown that longer holding time also promotes inter-particle plastic deformation. When the inter-particle contact is sustained for a longer period within the consolidated powder, the flow of current is sustained which causes the inter-particle zone to be heated faster than the particle interior. Hence, localized heating causes softening to occur at the particle contacts thereby causing plastic deformation which may be more intense in one sample than the other depending on the material.

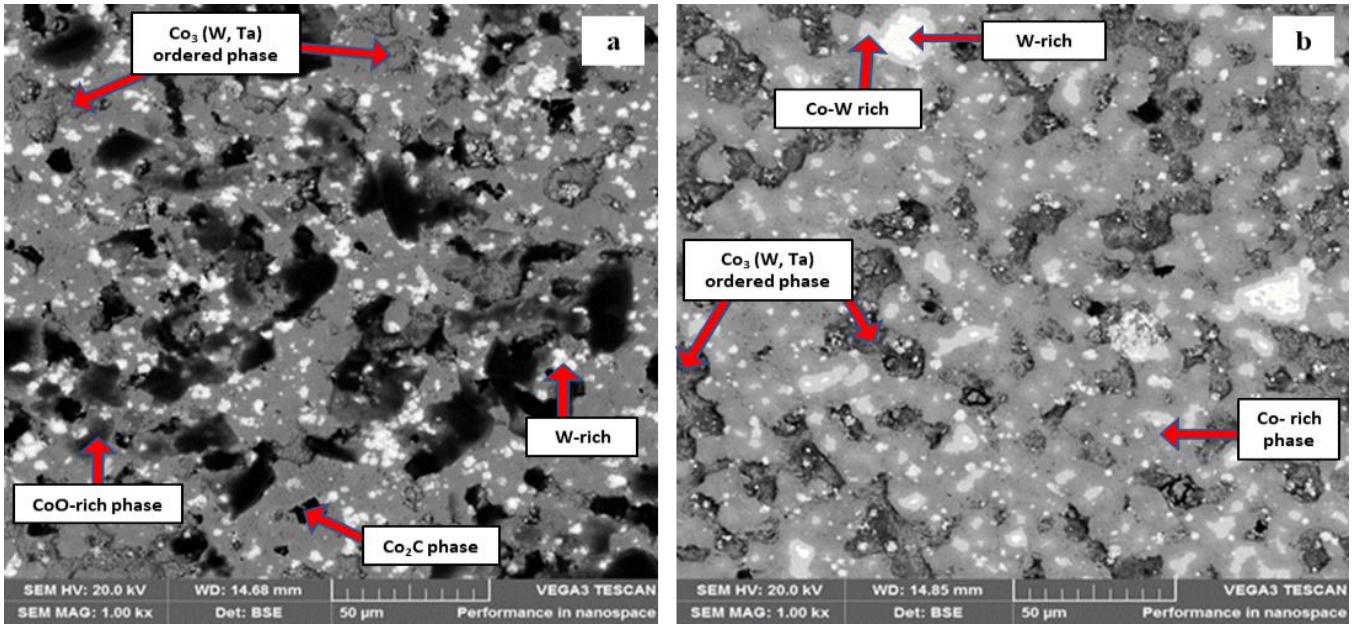

Figure 2. SEM micrograph and phase of sintered alloys (c) CoWT1 and (d) CoWT2

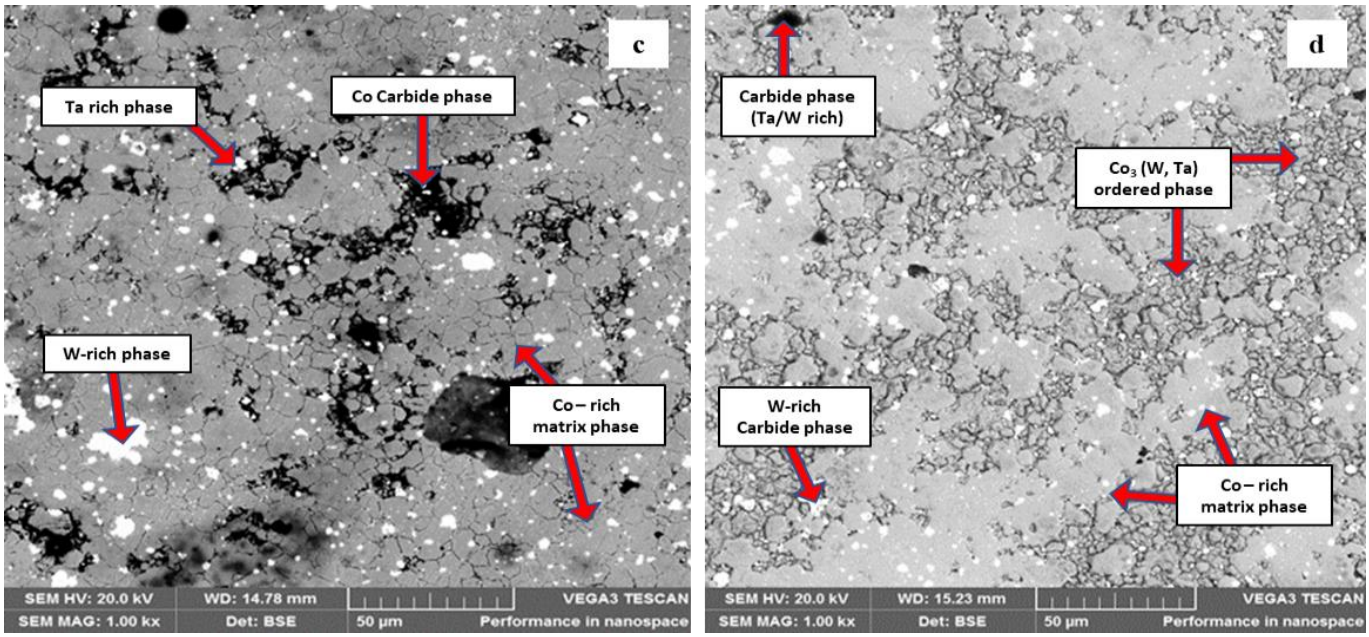

Figure 2. SEM micrograph and phase of sintered alloys (c) CoWT3 and (d) CoWT4

3.2. X-Ray Diffraction Properties

The diffraction spectra were used to study the crystallographic structure and orientations of the sintered Co-based ternary superalloy samples. The diffraction patterns are shown in Figure 3. The diffraction patterns show that the sintered alloys are polycrystalline in nature with the existence of well-defined peaks indicating different crystallographic orientations. The prominent peaks for each sample based on the preparation conditions show that the crystal have few preferred orientations

which are common to all the samples, and some that varied from sample to sample which invariably as a result of the formation new phases due to changes in sintering parameters. A close observation of the diffraction patterns revealed that Co, TaO and Ta_2O_5 are the prominent phases common to all the alloy samples. There are other few phases formed that are just peculiar to each of the sample due to different sintering conditions, and influenced by structural transformation due to thermal reactions and diffusions. It should be noted however that samples prepared at the same sintering temperatures (1000 °C or 1200 °C) exhibited almost similar crystallographic orientations. Remarkable phase transformation is observed as the sintering temperature increased from 1000 to 1200 °C. As some of the phases with prominent crystallographic peaks i.e. Co, TaO, Ta_2O_3, WC were observed in all samples sometimes at different crystallographic planes due to structural transformation that occurred within the material.

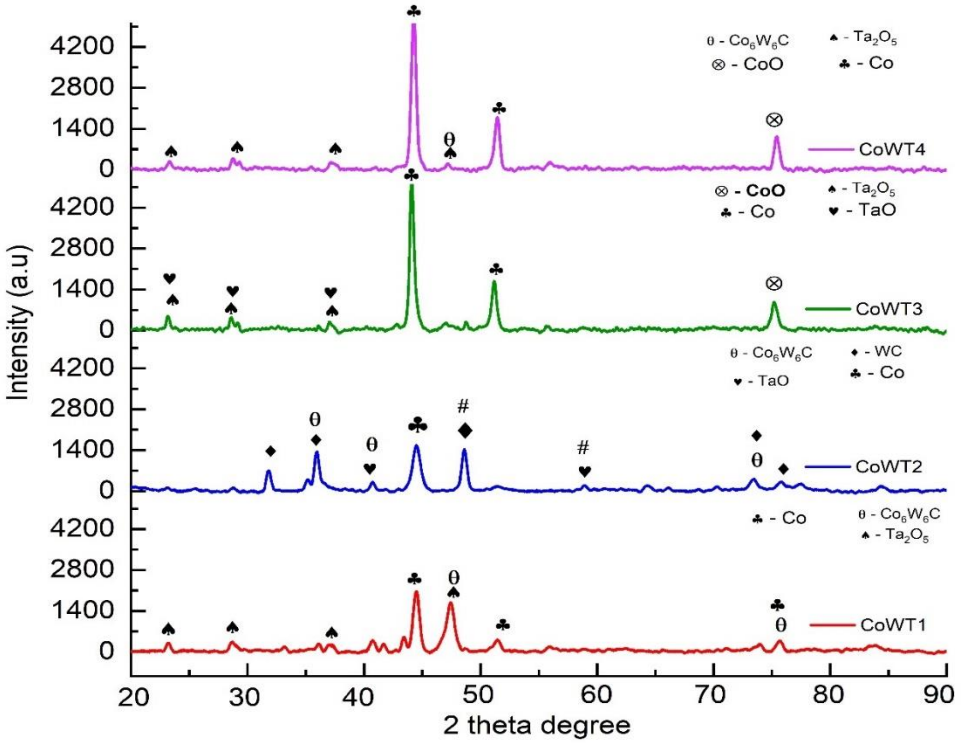

Figure 3. XRD Analysis results of Co-based ternary alloys samples

3.3. Thermal Analysis

Good thermal conductivity is one of the key parameters required for high-temperature structural applications of metallic materials. The thermal conductivity of the Co-based sample from 100 °C to 1000 °C are presented in Figure 4. With the common use of superalloys in operations involving elevated temperature, it is very important that their thermal conductivity is enhanced in order to properly manage high temperature conditions i.e. conduct excess heat away from the operational environment to avoid high thermal stress that can lead to material failure. Thermal conductivity data of the Co-based ternary alloys was obtained from the thermal diffusivity results determined by using LFA technique. It is observed that the thermal conductivity of the alloys varied with changes in their sintering parameters. Studies have shown that thermal conductivity of superalloys depends strongly on the chemical composition of alloy and the temperature (Zieliñska et al., 2010). In spite of having the same initial starting material composition, the sintering processing has a great influence on the final synthesized material. The clear differences in the thermal conductivity indicate that the alloys final composition variation is based mainly on sintering temperature. It is noted that samples CoWT1 and CoWT2 that were sintered at 1000 °C exhibited nearly the same thermal conductivity behaviour. As shown in Figure 4, a relatively high thermal conductivity values 245.26 and 465 W/mK were recorded at 300 °C for samples CoWT1 and CoWT2, respectively. A sharp drop in the thermal conductivity of the alloy is shown to occur at 300 °C after the highest values were attained. Though standardized data are still lacking on the thermal properties of most alloys, however from the available in literature, thermal conductivity of pure cobalt at ambient is taken at 45 W/mK, while those for Ta and W are recorded as 70 and 95 W/mK respectively (Valencia and Quested, 2008). Thermal conductivity of W is also given as 173 W/mK in other sources (Dean and Lange, 1999). It showed that tungsten has the highest thermal conductivity among the alloying elements. For the high value obtained for the alloy, there is a possibility that the addition of the W and Ta additively influenced the thermal conductivity of the alloy. However, beyond the initial increment, a sharp drop in values towards high temperature is observed, this behaviour is identified as the inherent properties of pure metals (Hahn and Özişik 2012). Hence, the thermal conductivity trend of the alloy sintered at 1000 °C exhibited a metallic behaviour. Which could indicate that though there was structural transformation and densification due to thermal load, there was limited transformation due to chemical reaction within the system at 1000 °C sintering temperature. The thermal conductivity behaviour of alloys is quite different from that of pure metals. For alloys, the density of the impurities and imperfections is very high, so the thermal conductivity increases proportionally with temperature. Samples CoWT3 and CoWT4, sintered at a higher temperature of 1200 °C, exhibited a typical behaviour of alloys, showed a much lower thermal conductivity value, but with a rather steep increase with temperature (Figures 4c and 4d). It showed that there were both structural and chemical transformations within the alloy, and these were also confirmed

from the crystallographic analysis. The ability to dissipate heat at elevated operational temperatures by superalloys is more desirable in order to reduce thermal fatigue due hot corrosion and oxidation. For high temperature heat dissipation, alloys prepared at 1200 °C will be more suitable.

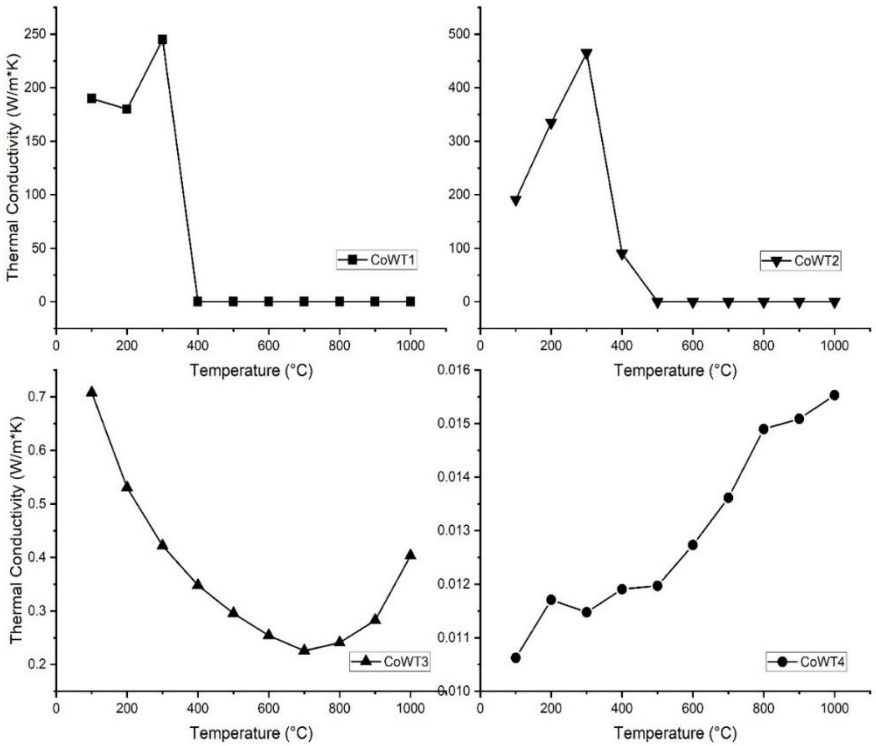

Figure 4. Thermal conductivity curve for sintered Co-W-Ta ternary alloy

3.4. Cyclic Oxidation Behaviour at 1000 °C

Figure 5 shows the isothermal cyclic oxidation kinetic curves of the Co-based sintered alloy samples. Notably, after the initial stage of fast oxidation, the curves show a parabolic time dependent behaviour of the weight gain for all the samples. It is observed the mass gained or change is dependent on both chemical and physical properties of the alloy. The alloy with the highest mass change and weight gain is sample CoWT2, sintered at 1000 °C, while sample CoWT4 sintered at 1200 °C has the lowest mass change. At low cycles, sample CoWT3 has almost the same oxidation kinetic behaviour with that CoWT4 with a slight divergence at higher cycle. With this similar oxidation resistance behaviour, it can be said that both alloys have the same physical attributes. that reduced the effects of high temperature oxidation attack. The oxidation behaviours exhibited by the samples are in strong agreement with the results obtained from other analysis. Formation of distinct phases and intermetallics in the alloy samples have been observed to have been formed as confirmed by crystallographic analysis, and this has attributed mainly to the varied sintering temperature and the dwelling time. The relative resistance to high temperature oxidation by the samples can be linked to their initial presence of oxide layers which inhibited further oxidation reaction on the surface of the alloys when exposed to high temperature. Generally, compare to other similar alloys investigated recently (Zhong et al., 2016), the mass gain or mass change values at mg range are much smaller than what was obtainable for other Co-based alloys. It is shown from the cyclic kinetic oxidation curves (Figure 5) that sample CoWT4 has the best oxidation resistance properties at 1000 °C.

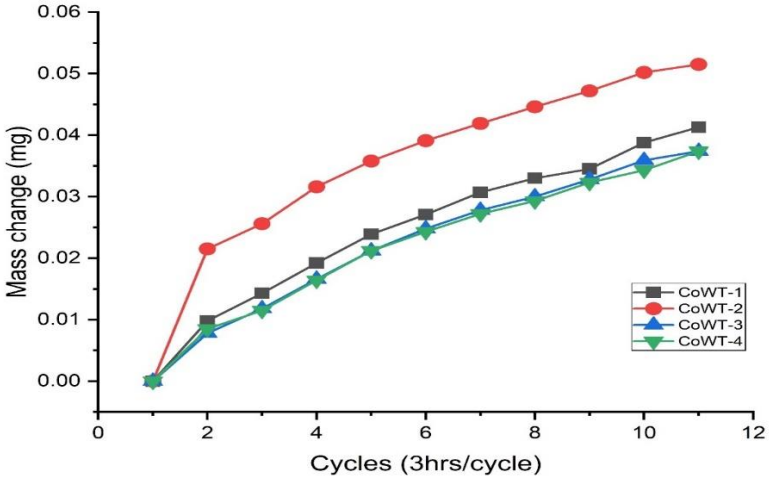

Figure 5. Mass gain against the number of cycles plot for Co-based superalloys subjected to cyclic oxidation test.

4. CONCLUSION

Co-based ternary superalloy samples of distinct physical properties have been prepared from fixed composition of high purity elemental powders of Co, W and Ta using the non-conventional powder metallurgy technique of spark plasma sintering. The distinct transformations observed in the alloys were attributed mainly to the sintering temperature and the isothermal holding time. Increase in crystallinity was observed in the alloys with the sintering temperature up to 1200 °C. Phase transformation and partitioning were observed at each sintering temperature when the holding time was increased to 15 min. The cyclic oxidation curves indicated that alloy samples prepared at 1200 °C have the higher oxidation resistance at 1000 °C. It is shown that Co-based alloy prepared at lower sintering temperature (1000 °C) exhibited high thermal conductivity (TC) at low temperature region and a sharp decrease beyond 300 °C similar to the behaviour of pure metals. Meanwhile Co ternary alloys (CoWT3 and CoWT4) prepared at 1200 °C have much lower TC at low temperature range, but with a characteristic steep proportional increase in TC at higher temperature region. With further material modifications, sintering at higher temperature (1200 °C) is more likely to favour alloys with the desired high TC at higher temperature.

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