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Structure–property relationships in a CoCrMo alloy at micro and nano-scales

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ABSTRACT

This investigation considered the multiscale tribo-mechanical evaluations of CoCrMo (Stellite®21) alloys manufactured via two different processing routes of casting and HIP-consolidation from powder (Hot Isostatic Pressing). These involved hardness, nanoscratch, impact toughness, abrasive wear and sliding wear evaluations using pin-on-disc and ball-on-flat tests. HIPing improved the nanoscratch and ball-on-flat sliding wear performance due to higher hardness and work-hardening rate of the metal matrix. The cast alloy however exhibited superior abrasive wear and self-mated pin-on-disc wear performance. The tribological properties were more strongly influenced by the CoCr matrix, which is demonstrated in nanoscratch analysis.

1. Introduction

Although their hardness decreases as temperature increases, the cobalt based wear and corrosion resistant Stellite® alloys generally retain their wear resistance at high temperatures, where they also resist oxidation. They perform particularly well in lubrication starved or high temperature wear situations [1]. Originally developed by Elwood Haynes and patented in 1907 [2], many variations on the original CoCrWC and CoCrMoC alloys are now in common use. They generally contain 25–33 wt% Cr, 4–18 wt% W/Mo, and 0.1–3.3 wt% C. Microstructurally, they consist of a CoCr(W,Mo) solid solution (with trace amounts of Ni, Fe, Si, Mn) containing one or more carbide phases. The solid solution matrix provides toughness whilst the carbides provide hardness and wear resistance as well as some strengthening. Cr is the principal carbide former, with W and Mo also playing a role. The relative amounts of W, Mo, Cr and the atomic ratio [W+Mo+Cr]:[C] strongly influence the types of carbides that form. Whilst the room temperature hardness is primarily a function of the carbide content, the hot hardness is more dependent on solid solution strengthening of the Co-based matrix by W and/or Mo [3].

Stellite 21 was developed in the mid-1930s. It consists of a CoCrMo alloy matrix containing dispersed hard carbides which strengthen the alloy and increase its hardness and wear resistance, but also decrease the ductility. The type, shape, size and distribution of the carbides is strongly influenced by the processing history of the alloy, and hence the mechanical properties and tribological performance are strongly dependent on the manufacturing route and any subsequent heat treatments. Due to the low carbide content relative to other similar alloys, the Co-based alloy matrix dominates the wear and corrosion properties, giving it excellent resistance to cavitation, galling, high-angle erosion and metal-to-metal sliding wear, but relatively low resistance to hard particle abrasion and low-angle erosion. The matrix can work harden considerably during wear or even during machining. Stellite 21 can be cast, powder metallurgically processed, or applied as a weld hardfacing. It is recommended for applications involving a combination of the above-mentioned wear mechanisms, combined with corrosion and/or high temperature service, such as valve trim for petrochemical and power generation. As a weld deposit it has been widely used in the building up of forging or hot stamping dies, due to its relatively good impact resistance [4].

The present authors have previously reported findings concerning the influence of a change in the manufacturing route from casting to HIPing in Stellite alloys containing between 4.6 and 16.5% W and between 0.7 and 2.4% C [5–8]. Compared with the cast alloys, the HIPed alloys had relatively finer, more rounded and homogeneously distributed carbides, which resulted in an excellent combination of tribo-mechanical properties, i.e. an improvement in ductility, fracture toughness, and fatigue life, without

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compromising the hardness, strength and wear resistance. The emphasis in the current investigation is to consider if a similar improvement in performance of a low-carbon cobalt-based alloy containing Mo can be achieved by altering the manufacturing route from casting to HIPing.

Whilst the carbide content is the main differentiator between Stellite 21 and the alloys previously investigated (Stellite 4, Stellite 6 and Stellite 20), the fact that the alloy contains Mo instead of W can also influence the properties [5–8]. Firstly, it has been reported that replacement of W in Stellite 6K by Mo [9] or additions of Mo to Stellite 6 [10] result in changes in the carbide morphology and an increased volume fraction of carbides in the microstructure. This is ascribed to the fact that the atomic weight of Mo is roughly half of that of W, and hence the same mass percentage in an alloy translates to roughly twice as many Mo atoms as W atoms [9,10]. Mo also has a greater affinity for C than does W, thereby favouring the formation of carbides in the cast alloy [9]. Secondly, the corrosion behaviour of CoCrMo alloys is different to that of CoCrW alloys. For example, alloying with Mo rather than W improves the aqueous corrosion resistance in complex or reducing acidic environments [11].

Previous research on the tribological performance of Stellite 21 alloys has focused on the influence of alloying elements at room and elevated temperatures [12–15]. Huang et al. [12] investigated the influence of Mo content and heat treatment on the sliding wear resistance and concluded that both factors influenced the performance. Radu et al. [13] modified the composition of Stellite 21 alloy by adding yttrium and concluded that the addition of yttrium markedly enhanced the mechanical properties of the oxide scale on Stellite 21 and its adherence to the substrate, which benefited the high-temperature wear performance of the alloy in air. The benefit of oxide scale on the wear resistance of Stellite 21 was more pronounced in air than in an argon environment. However, the oxide scale became less protective as the wearing force was increased. The influence of manufacturing process has also been previously investigated in terms of cladding and surface coatings. Aoh et al. [14] investigated the wear behaviour of clad layers of Stellite 6 and 21 for hot rolling mill rollers and concluded that the elevated temperature sliding wear performance of Stellite 6 was superior to that of Stellite 21. Persson et al. [15] investigated the room temperature self-mated dry sliding performance of Stellite 21 and concluded that during high load dry sliding, a Co-enriched tribofilm is created which exhibits low friction and high galling resistance. The tribofilm evolved via face-centred cubic (fcc) to hexagonally close-packed (hcp) phase transformation under strain.

Investigations relating to the tribological performance of Stellite 21 alloy manufactured via HIP-consolidation are however limited in the published literature. This paper provides microstructural and tribo-mechanical comparisons of cast and HIPed Stellite 21 alloys via Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) spectrometry, X-Ray Diffractometry (XRD), hardness, abrasive wear, nanoscratch, and sliding wear evaluations.

2. Experimental test procedures

2.1. Materials and microstructure

Table 1 summarises the chemical compositions of the Stellite 21 alloys. The alloys were produced by casting and by HIP-consolidation of gas-atomised powders, respectively. The sieve analysis of the powder used for HIPing is summarised in Table 2. The powder was encapsulated in an air-free steel can and subjected to 100 MPa isostatic pressure at 1200 °C for 4 h, followed by slow furnace cooling.

Table 1
The chemical compositions of Stellite 21 alloy (wt%).

Stellite	Co	Cr	Mo	C	Fe	Ni	Si	Mn
Stellite 21 (Cast)	Balance	28.48	6.03	0.26	0.51	0.24	0.65	0.48
Stellite 21 (HIPed)	Balance	27.80	5.5	0.28	1.55	2.74	1.66	0.82

Table 2
The sieve analysis of the Stellite powders (wt%).

Stellite powder	+38 μm	+20 μm	−20 μm
Stellite 21	0	50.5	49.5

The microstructure of the powder and alloys was observed via SEM using a Secondary Electron (SE) imaging and also Back-scattered Electron (BSE) imaging detector. The chemical compositions of different phases developed in the powders and alloys were determined via both EDX and XRD with Cu-K_α radiation (wavelength = 1.5406 Å). A commercially available open source software (ImageJ) was used to analyse the area fractions of each phase identified from the SEM images.

2.2. Hardness, modulus and impact toughness measurements

The Vickers macro- and micro-hardness of the alloys was measured using an Avery hardness tester under a load of 294 N, and a Mitutoyo (MVK-H1) micro-hardness tester under a load of 2.94 N, respectively. Five macro-hardness and ten micro-hardness measurements were conducted on each alloy. Spacing between measurements was maintained to ensure that neighbouring indents did not influence the hardness values as per BS-EN ISO 6507-1:1997 [16]. Nano-hardness and modulus measurements were performed using a calibrated nanoindentation system (NanoTest™ – Micro Materials Limited, UK) equipped with a standard Berkovich nanoindenter tip. Measurements were performed at room temperature (~23 °C) in load control at loads of 50 mN and 5 mN to investigate the influence of nanoindentation load on measured hardness and modulus. The indentation procedures were programmed as three segments of trapezoidal shape with 10 s loading, 5 s hold and 10 s unloading segments. Eighteen measurements were performed on each alloy at 50 mN load, and ten measurements at 5 mN load. Indentation hardness and modulus results were based on the real time load–displacement curve and were analysed using the Oliver and Pharr method [17]. Further details of the various measurement techniques and analysis in the nano-indentation method can be found in earlier publications [18–20].

Tensile tests were conducted according to BS-EN 10002 [21] on the HIPed specimens only, using an Instron® tensile testing machine (30 kN load cell, 5567 series). Dumbbell shaped test specimens of 25 mm gauge length and 4 mm diameter were used in this investigation. Three tests were conducted at a loading rate of 0.05 mm min^{-1}. The Charpy impact tests were conducted on unnotched alloy samples with dimensions of 10 mm × 10 mm × 55 mm, using an Avery Charpy impact tester at an impact rate of 5 m s^{-1}. Three tests were conducted on each alloy.

2.3. Nanoscratch sliding wear tests

The nanoscratch tests were conducted to investigate the micromechanics of plastic deformation and resulting wear of the individual metal matrix and carbide phases. Nanoscratch (sliding wear) tests were performed with a sphero-conical diamond indenter of 10 μm tip radius and 60° apex angle using the