IN VITRO CORROSION ANALYSES OF HEAT TREATED COBALT-CHROMIUM ALLOYS MANUFACTURED BY DIRECT METAL LASER SINTERING

Corresponding author:

Frank Alifui-Segbaya

School of Dentistry and Oral Health

Griffith University, Griffith Health

Queensland, 4222, Australia

Email: f.alifui-segbaya@griffith.edu.au

ABSTRACT

Purpose: Heat treatments are indicated as necessary in complex intra-oral framework production by additive manufacturing to remove accumulated thermal stresses. However, heat treatments have been linked to corrosion in cast dental alloys. Currently, there are few publications on this subject for laser sintered dental alloys required for academic review. This research paper compared corrosion data obtained from additive manufactured heat-treated and non heat-treated cobalt-chromium alloy.

Design/Methodology/Approach: Five rectangular specimens (n=5), each with a total surface area of 10.27cm² were fabricated for the two groups. Specimens were immersed in artificial saliva suspended by a nylon thread for 42 days at 37°C. Readings for cobalt, chromium and molybdenum ions released into solution were obtained using an atomic absorption spectrometer at 1, 4, 7, 14, 21, 28, 35, and 42 day intervals at a detection limit of one part per million. Test methods are in accordance with ISO 10271.

Findings: Results showed a higher ion release in the heat-treated sample, statistically significant at 99% confidence level ($P<0.01$). A two-way Anova test conducted showed that there was a main effect of day and a main effect of finish, and there was also a significant interaction between these factors.

Originality/value: The study concludes that, although ion release in both samples was within the safe level recommended by ISO for the three major alloying elements, heat-treatment indeed contributed extensively to the reduced corrosion resistance in the laser sintered cobalt-chromium alloy. Further biocompatibility tests are recommended.

INTRODUCTION

The construction of cobalt-chromium (Co-Cr) denture frameworks to carry artificial teeth in the mouth has for many years been restricted to the 'lost wax' process where molten alloys are caused to flow into heated hollow moulds formed by burnt-out wax patterns. With the extensive advancement of computer aided technologies in dentistry, there is significant scope to replace the traditional casting technique with layer manufacturing techniques such as Additive Manufacturing (AM) in complex intra-oral framework production (Williams et al., 2006; Gao et al., 2009). Metal AM technology is a digitally driven process that uses either electron beams or laser beams to fuse metallic powders, in a layer-by-layer fashion into three dimensional (3D) objects. However, the laser manufacturing system have been routinely used to process many different alloys (Collins, 2012) including Co-Cr-Mo for denture frameworks. The AM technique may well provide fitting accuracy, reduced tooling and labour time and low cost restorations (Renishaw Plc, 2012). The few publications on the clinical performance of AM Co-Cr alloys claim they have the potential to further exhibit good corrosion resistance, biocompatibility and sustainable mechanical properties (Vandenbroucke and Kruth, 2007; Jevremović et al., 2011; Alifui-Segbaya et al., 2013).

Heat treatment has been used to improve the mechanical properties of cast alloys (Brantley and Alapati, 2012). AM parts fabricated by selective laser melting (SLM) also employ heat treatment for reduction of internal stresses but improvement in their mechanical properties such as the breaking elongation and the fatigue performance is also possible (Thöne et al., 2012). Currently, heat treatment is required for AM Co-Cr removable denture frameworks but may not be necessary for metallic

substructures for ceramic and composite veneers unless their span exceeds 2 units. This post-treatment technique is completed by simply putting the Co-Cr denture frameworks in an argon atmosphere at a prescribed temperature/time period. However, previous studies (Supreetha et al., 2010; Al-Hity et al., 2007; Craig, 1985; Sorensen et al., 1990) have linked heat treatments of cast alloys to increased corrosion.

Corrosion is described as the unintentional wearing down of metal or alloy surfaces (Poljak-Guberina et al., 2002). Nevertheless, it is an inevitable chemical process in Co-Cr alloys due to their large number of alloying elements that make them exhibit a non-homogenous microstructure (Guertsen, 2002; Roach, 2007). Likewise, ionization of any alloy can occur regardless of an alleged corrosion resistance (Geis-Gerstorfer, 1994; Smith and Williams, 1982). Corrosion causes dental alloys to release free equated or complex metal ions which may then come into contact and react with cells in the immediate environment or be distributed throughout the human body (Yfantis et al., 2007). Metal ions released from a Co-Cr denture framework have been detected in tongue scrapings, saliva (Sternberg, 1982) plaque and in the gingiva adjacent to these alloys (Guertsen, 2002). As a result of these, corrosion analyses of dental alloys are considered fundamental tests since ion release has been closely linked with biological reactions such as allergy and toxicity (Schmalz and Garhammer, 2002). The release of metal ions can also lead to poor aesthetics and compromise the physical properties of dental alloys (Johansson et al., 1989; Wataha, 2000). Since Co-Cr denture frameworks are physically wide, presenting a large surface area and interact actively with corrosion inducers such as abrasion from foods, liquids and toothbrushes, continuous saliva flow, temperature fluctuation and varying pH (Gil et al., 1999; Can, 2007) they are liable to release more metallic

ions than fixed partial denture substructures partially veneered with ceramic or composite (Wataha, 2000).

If the adverse oral or systemic effects of corrosion on cast alloys due to heat treatment are anything to go by, then it is prudent that laser-sintered alloys also undergo stringent and repeated corrosion tests in various corrosion environments to ascertain their safety and endurance, as few published data are available on this subject for academic reflection. The research described here seeks to compare the corrosion properties of EOS SP2 AM Type 4 alloy in EN ISO 22674:2006 standard (EOS GmbH, Electro Optical Systems, Robert-Stirling - Ring, 82152 Krailling, Munich, Germany) in non heat-treated and heat-treated forms for in vitro ion release in accordance with BS ISO 10271.

MATERIALS AND METHODS

The AM Co-Cr alloy, EOS SP2, include the following alloying constituents, Co (63.2% by weight), Cr (24.4%), Mo (5.2%), W (5.2%), Si (0.9%) (3T RPD Ltd, 2008, EOS GmbH, Electro Optical Systems, Robert-Stirling - Ring, 82152 Krailling, Munich, Germany). The alloy is designed to be formed into substructures in an EOSINT M270 Direct Metal Laser Sintering Machine (DMLS). Two test samples were prepared for the corrosion test in accordance with ISO 10271 specifications. There were five specimens in each group, heated (HRx) and non-heated (NHRx) samples. The number (n=5) exceeds ISO's minimum recommendation for this test. Currently, no powdered alloy is offered specifically for removable partial denture (RPD) frameworks.

DMLS Heat and Non-Heat Treated Specimens production:

SolidWorks CAD data was used to design a rectangular prismatic plate with dimensions 50mm x 20mm x 1.8mm. The CAD data was sent to Renishaw (New Mills, Wotton-Under-Edge, Gloucester GL12 8JR, UK) for test piece production in EOS SP2 alloy by DLMS. The plates to be heat treated were placed on a steel plate put inside a gas box connected to an Argon supply with a flow rate of approx 8L per/min. The temperature was raised to 450°C and held for approximately half an hour and increased to 750°C and held again for approximately 45 minutes. The plates were then left in the furnace overnight to cool. They were sent to The National Centre for Product Design & Development Research (PDR) at, Cardiff Metropolitan University (UWIC) where they were accurately measured and cut to the required size of 42mm x 10mm x 1.8mm. No further changes were made to plates. Each specimen had a total surface area of 10.27cm², this exceeds the minimum of 10cm² recommended (EN ISO 22674: 2006; BS ISO 10271: 2001)

All specimens were ultrasonically cleaned separately in ethanol (99.8+% analysis Certified AR, Fisher Scientific UK Ltd Bishop Meadow Road, Loughborough, Leicestershire, LE11 5RG) for 2 minutes, rinsed with Optima-LCMS grade water (Fisher Scientific UK Ltd Bishop Meadow Road, Loughborough, Leicestershire, LE11 5RG) and dried with oil-free air. During each test, specimens were suspended with a very thin nylon thread (Geis-Gerstorfer et al; 1991) and immersed completely in test tubes containing an artificial saliva solution of 0.1M NaCl (analytical grade) and 0.1M lactic acid (analytical grade) with a pH of 2.3±0.1, again in compliance with the ISO. The pH of the freshly prepared sample solutions was measured with a Jenway pH meter (Bibby Scientific Limited, Staffordshire ST15 0SA, U.K.) before immersion of samples and repeated on residual sample solutions after each elapsed immersion

time period. The pH remained virtually the same i.e. pH of 2.3±0.1, before and after immersion of alloys samples. The test tubes were sealed to prevent evaporation of solution and maintained at 37°C in a water bath for 1, 4, 7, 14, 21, 28, 35 and 42 days thus performing time dependence test (BS ISO/DIS 10271). The volume of solution to surface area of each alloy was at a ratio of 1ml of solution per 1cm² of sample surface area as prescribed by the standard. For each specimen group, additional test tubes were used to hold reference solutions (10 ml 0.1M saline lactic acid without immersed specimens) tightly sealed and maintained in parallel with the solutions containing the specimens until the elapsed period. After each time period, specimens were removed from test tubes with plastic tongs, rinsed with distilled water and placed into new test tubes with freshly prepared solutions for subsequent repetition of the tests as described above.

Each sample solution was analysed quantitatively with a flame atomic absorption spectrometer (FAAS) for cobalt (Co), chromium (Cr) and molybdenum (Mo) ions after day 1, 4, 7, 14, 21, 28, 35, and 42 of sample immersion in the solution. Co, Cr and Mo are the major alloying elements of the alloys under test and as such the ion release of these elements only was studied. Calibration of the atomic absorption spectrometer was achieved with standard solutions. The calibration table below shows the wavelengths at which the elements were detected with the atomic absorption spectrometer. R squared (R2) is the coefficient of determination. The calibration curves were used to determine the concentrations of the unknown quantities in the analytes by comparing them to the known quantities in the standard solutions.

Table1: Atomic Absorption Spectrometer Parameters for Elemental Release Analysis

		R^2 of the calibration curves							
Element	Wavelength (nm)	Day 1	Day 4	Day 7	Day 14	Day 21	Day 28	Day 35	Day 42
Cobalt	240.7	0.9996	0.9972	0.9971	0.9999	0.9995	0.9998	0.9999	0.9999
Chromium	357.9	0.9994	0.9992	0.9998	0.9998	0.9989	0.9993	0.9989	0.9996
Molybdenum	313.3	0.9702	0.9839	0.9796	0.9918	0.9921	0.9945	0.9877	0.9783

All elements had a detection limit of 1 part per million (ppm) and required a linear calibration equation

The sample solutions were analysed for these elements at a detection limit of 1 part per million (ppm). To determine substance loss after each time period, sample solutions were shaken on an MS2 Minishaker (IKA-Werke GmbH & Co. KG, D-79219, Staufen) before aspirated directly into a flame Unicam 969 Solaar atomic absorption spectrometer (AAS) (Unicam Limited, York Street, Cambridge, CB1 2SX, U.K.). Triplicate absorbance readings per element in each sample solution were made and these readings were used to determine the mean concentration of the different elements (Co, Cr and Mo) in ppm. An average of 8ml of sample solution was found to be enough for analysing the concentration of the three elements in each test tube. The reference solutions, which served as blanks, were used to establish the impurity level for each element of interest in the sample solution.

Statistical Analysis of Test Results: A two-way Anova test was conducted to investigate (i) the effect of day and (ii) treatment on as-received samples.

RESULTS

Table 1 shows the daily and total release of metallic elements from the tested samples into artificial saliva solution. There was a higher ion release (16.47 µg/L) in HRx sample compared to the small amount of 0.63µg/L released in NHRx sample after 42 days. Corrosion trends of HRx and NHRx AM alloy samples are reported in **Figure 1.** Elapsed time on the x-axis is plotted against the release rate per day on the y-axis. The data and graph presented in this study are in accordance with BS ISO 1027:2001 and BS/DIS ISO 10271:2009 recommendations and have been widely used in similar documented studies (Alifui-Segbaya et al., 2013, Yfantis et al., 2007, Al-Hiyasat et al., 2002, Can et al., 2007, Geis-Gerstorfer et al., 1991) to report their research findings. The HRx corrosion curve shows a higher ion release between day 1 and 14 and a steady decline thereafter. The NHRx corrosion curve appears to show a somewhat erratic release of ions, which could be due to the fact that the readings obtained, were at the lower limit of detection of the apparatus used. In **Table 2,** the sum of elemental release from HRx and NHRx alloy samples into artificial saliva solution after 42 days is shown. **Figure 2** shows a chart that compares the sum of Co, Cr and Mo released from HRx and NHRx alloy samples into artificial saliva solution. The sum of Co-Cr-Mo released per square centimetre (µg/cm²) after 42 days is also reported in Figure 2.

Statistical analysis of test results showed that there was a main effect of day, (P<0.01) and a main effect of finish, (P<0.01) there was also a significant interaction between these factors, (P<0.01).

Table 1. Element release *(Mean±SD)* from HRx and NHRx alloy samples into artificial saliva solution

	Day 1	Day 4	Day 7	Day 14	Day 21	Day 28	Day 35	Day 42	**Total**
HRx	4.3± .98	4.6± 1.00	2.5± .40	2.58 ± .57	0.9± .16	0.50 ± .06	0.49 ± .09	0.34 ± .10	**16.47± 1.50 µg/L**
NHRx	0.29± .07	0.00± .00	0.06± .04	0.08 ± .03	0.05 ± .00	0.00 ± .00	0.13 ± .03	0.02 ± .02	**0.63±0.78 µg/L**

**Key:** HRx = Heat-treated sample   NHRx = Non-heat treated sample

Table 2. The sum *(Mean ± SD)* of elemental release from HRx and NHRx alloy samples into artificial saliva solution after 42 days

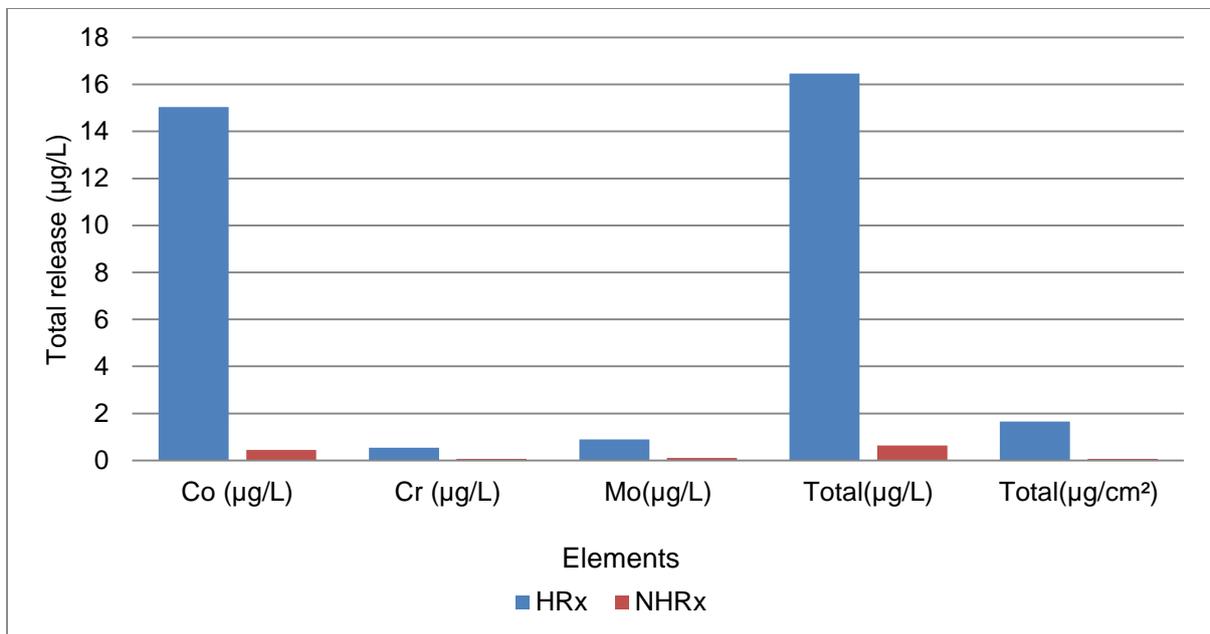| Sample	Co (µg/L)	Cr (µg/L)	Mo (µg/L)	Total* (µg/L)	Total** (µg/cm²)
HRx	15.04± 1.33	0.54± 0.15	0.89± 0.32	16.47± 1.49	1.65± 0.15
NHRx	0.45± 0.06	0.07± 0.06	0.11± 0.06	0.63± 0.08	0.06± 0.01

*Sum of Co-Cr-Mo released after 42 days

** Sum of Co-Cr-Mo released per square centimeter after 42 days

Key: HRx = Heat-treated sample   NHRx = Non-heat treated sample
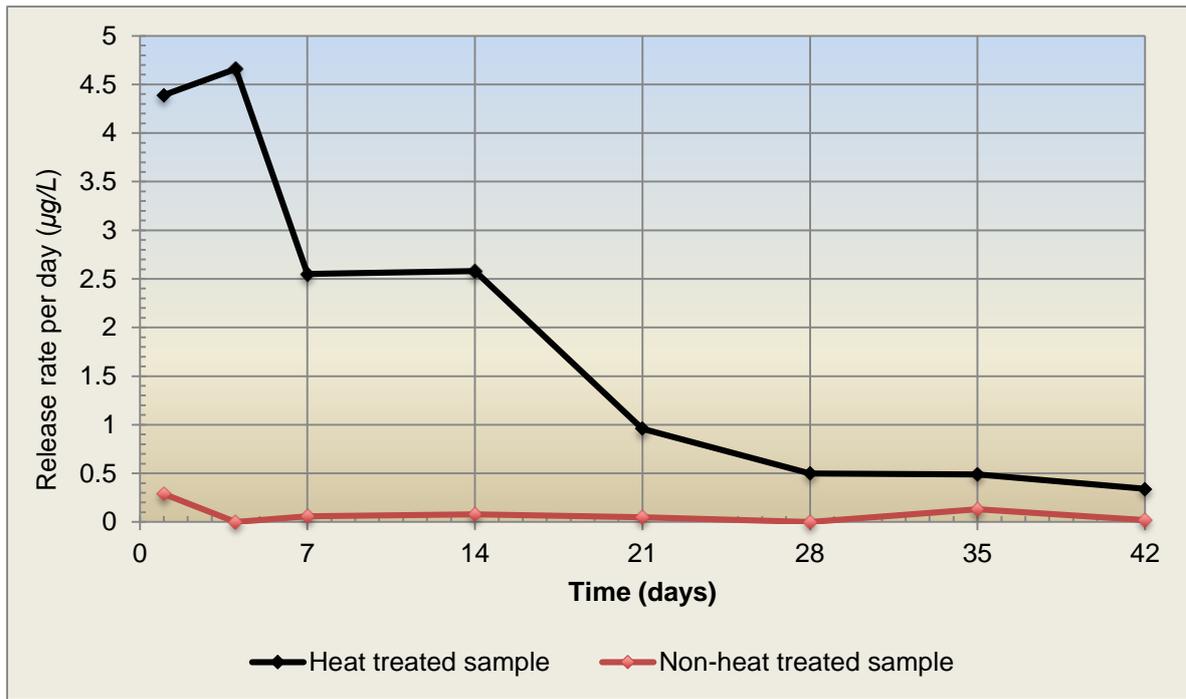
Figure 1: Corrosion trends of AM Co-Cr HRx and NHRx alloy samples

Figure 2: Total release of Co, Cr and Mo from HRx and NHRx alloy samples into artificial saliva solution

DISCUSSION

The *in vitro* corrosion behaviour of dental alloys is dependent on several parameters, which include composition, and treatment of alloys, pH, the clinical situations of rest and chewing simulated in the test design and instrumentation (Brune, 1986; Yfantis et al., 2007). The reduced corrosion resistance of the HRx alloy recorded in this study may be primarily due to the change in the microstructure that occurred at high temperature during the heat treatment process (Supreetha et al., 2010). This is in agreement with a study by Thöne et al. (2012) that confirmed enlarged grain size and microstructure pattern change in HRx SLM alloys. According to Ghiban et al. (2008), heat treatment of Co-Cr dental alloys will produce consequent decrease in their corrosion resistance.

Another parameter that might have provoked a higher ion release in the HRx sample is the 'as built' surface condition of the alloy. A study by Alifui-Segbaya et al. (2013) on the same HRx Co-Cr alloy used in this study showed a significantly larger corrosion resistance in polished and electrobrightened samples. In both tested alloy samples, the total ion release was below 1 µg/L after 42 days. Thus, the surface condition of AM Co-Cr alloy could be classified as an important corrosion parameter.

The HRx corrosion curve in Figure 1 shows almost two-third of the total ion release occurred within the first fourteen days of immersion after which there was a steady decline in the daily ion release - an indication of good passivation (Yfantis et al., 2007). This is identical to trends seen in another study (Geis-Gerstorfer, 1991) where Co-Cr-Mo cast alloys exhibited corrosion curves that flattened out between 7 to 14 days. Through passivation, the surface of an alloy may be transformed (by the

formation of metal oxide film) into a state by which corrosion is greatly inhibited (Schmalz and Garhammer, 2002).

The release of metal ions through oral corrosion may have several biological and clinical effects such as cytotoxicity, tissue lesions metallic taste, sensitization or carcinogenesis (Smith and Williams, 1982) depending upon the amount and nature of released cations. Although there is evidence that the three elements tested in this study, which form the bulk of the alloying elements, could trigger biologic response in excess quantities (Guertsen, 2002), one would not anticipate that the amount of ion released during the first week would lead to any adverse effects, based on the fact that the total ion release is lower than the limit of $200\mu gcm^2$ within 7 ± 0.1 days, specified in the EN ISO 22674:2006. The likely biological reactions from excess metallic elements are discussed in relevant literature.

The total release of cobalt ions from HRx samples was higher (>25) than chromium. Previous studies (Yfantis *et al.*, 2007; Al-Hiyasat *et al.,* 2002) also reported low chromium release from cobalt-chromium alloys. This finding also confirms that metal ion release from alloys is not generally proportional to alloy composition (Wataha and Lockwood, 1998). The corrosion trends of the NHRx sample show ion release below one ppm - an indication of its resistance to the corrosive medium.

CONCLUSION

If AM techniques are to be fully adopted in denture framework production, full characterisation of material properties is required to ensure compliance with appropriate medical device regulation and specific ISO standards.   This paper

presents appropriate testing of AM-produced Co-Cr samples. Together with previous research that demonstrates the technical feasibility of designing and producing complex dental framework designs using AM, this research provides further evidence that can support the development of AM techniques as an alternative to casting. As technology developers and researchers optimise technical parameters of the production process, this will enable AM techniques to be integrated into an optimised design and production environment that could offer economical benefits, more predictable manufacturing standards and improved device design. The test procedures used within this study are in compliance with ISO 10271 static immersion test for dental alloys. This study concludes that heat-treatment of the AM Co-Cr (EOS SP2) alloy increased its susceptibility to 'in vitro' corrosion. Further biocompatibility tests are recommended.

REFERENCES

- 3T RPD Ltd. (2008), "Cobalt-Chrome Alloy", available at: www.3trpd.co.uk/pdf/Dental%20Cobalt%20Chrome%20alloy%20 (accessed 25 February, 2011)

- Al-Hity, R. R., Kappert, H. F., Viennot, S., Dlard, F. and Grosgogeat, B. (2007), "Corrosion resistance measurements of dental alloys, are they correlated?" *Dental Materials*, Vol. 23 No. 6**,** pp. 679-687.

- Al-Hiyasat, A. S., Bashabsheh, O. M. and Darmani, H. (2002), "Elements Released from Dental Casting Alloys and Their Cytotoxic Effects", *The International Journal of Prosthodontics*, Vol. 15**,** pp. 473-478.

- Alifui-Segbaya, F., Foley, P. Williams, R.J. (2013) "The corrosive effects of artificial saliva on cast and rapid manufacture-produced cobalt chromium alloys", Rapid Prototyping Journal, Vol. 19 Iss. 2, pp. 95-99.

- Brantley, W.A. and Alapati, S.B. (2012), "Heat Treatment of Dental Alloys: A Review available at http://dx.doi.org/10.5772/52398 (accessed 3 November, 2012).

- British Standards Institute (2001), *BS ISO 10271: Dental metallic materials – Corrosion test methods,* British Standards Institute, London.

- British Standards Institute (2006), *BS ISO 22674:2006: Dentistry – Metallic materials for fixed and removable restorations and appliances,* British Standards Institute, London.

- British Standards Institute (2009), *BS ISO/DIS 10271: Dental metallic materials – Corrosion test methods,* British Standards Institute, London.

- Brune, D. (1986), 'Metal release from dental biomaterials', *Biomaterials*, Vol. 7, pp. 163-175.

- Can, G., Akpinar, G. and Aydin, A. (2007), "The Release of Elements from Dental Casting Alloy into Cell-Culture Medium and Artificial Saliva", *European Journal of Dentistry,* Vol. 1**,** pp. 86-90.

- Collins, C. (2012). Laser and Electron Beam Powder Bed Fusion, available at http://www.mtadditive.com/articles/laser-and-electron-beam-powder-bed-fusion (accessed 15 March, 2013)

- Craig, R.G. (1985). *Cast and Wrought Base Metal Alloys. In Restorative Dental Materials* (7th edn). CV Mosby, St. Louis.

- EOS e-Manufacturing Solutions (n.d.), "Dentistry", available at: http://www.eos.info/en/applications/medical/dentistry.html (accessed 6 November, 2010)

- Gao, B., Wu, J., Zhao, X. and Tan, H. (2009), "Fabricating titanium denture base plate by laser rapid forming", *Rapid Prototyping Journal,* Vol. 15 No. 2, pp. 133-136.

- Geis-Gerstorfer J, Sauer K, Passler, K. (1991), "Ion Release from Ni-Cr-Mo and Co-Cr-Mo Casting Alloys", *International Journal of Prosthodontics,* Vol. 4, pp. 152-58.

- Geis-Gerstorfer, J. (1994), "In vitro corrosion measurements of dental alloys", *Journal of Dentistry*, Vol. 22, pp. 247-251.

- Geurtsen, W. (2002), "Biocompatibility of dental casting alloys, *Critical* Reviews in *Oral Biology & Medicine",* Vol. 13 No. 1, pp. 74-84.

- Ghiban, B, Boriun, C, Cosmeleata, G, Ciuca, S, N. Ghiban, Carceanu, I. (2008), "Structural Characteristics of Some Cobalt Dental Alloys after Heat Treaments'' European Cells and Materials, Vol 16. Suppl. 1, pp.35

- Gil, F. J., Sánchez, L. A., Espiás, A. and Planell, J. A. (1999), "In vitro corrosion behaviour and metallic ion release of different prosthodontic alloys", *International Dental Journal*, Vol. 49, pp. 361-367.

- Guertsen, W. (2002), "Biocompatibility of dental casting alloys", *Critical Reviews in Oral Biology & Medicine*, Vol. 13 No.1, pp. 71-84.

- Jevremović, D.P., Kojić, V., Bogdanović, G., Puškar, T., Eggbeer. D., Thomas, D. and Williams, R. (2011), "A selective laser melted Co-Cr alloy used for rapid manufacture of removable partial denture frameworks - initial

screening of biocompatibility", *Journal of the Serbian Chemical Society,* Vol. 76 No. 1, pp. 43-52

- Johansson, B. I., Lemons, J. E. and Hao, S. Q. (1989), "Corrosion of dental copper, nickel, and gold alloys in artificial saliva and saline solutions" *Dental Materials*, Vol. 5**,** pp. 324-328.

- Poljak-Guberina, R., Knezović-Zlatarić, D. & Katunarić, M. (2002). Dental Alloys and Corrosion Resistance. Acta Stomatol Croat, 36 br 4, pp. 447-450.

- Renishaw Plc (2012) "*Additive Manufacturing*", available at http://www.renishaw.com/en/additive-manufacturing--15239 (accessed 24 January, 2012).

- Roach, M. (2007), "Base Metal Alloys Used for Dental Restorations and Implants", *Dental Clinics of North America,* Vol. 51 Iss. 3, pp. 603-627..

- Schmalz, G. and Garhammer, P. (2002), "Biological interactions of dental cast alloys with oral tissues", *Dental Materials, Vol.* 18 Iss. 5, pp. 396-406.

- Smith, D. C. and Williams, D. F. (eds.) (1982), *Biocompatibility of Prosthodontic Materials,* CRC Press, Florida.

- Sorensen, J. A., Engelman, M. J., Daher, T. and Caputo, A. A. (1990), "Altered corrosion resistance from casting to stainless steel posts", *The Journal of Prosthetic Dentistry*, Vol. 63 No. 6, pp. 630-637.

- Sternberg, T. (1982), "Release of cobalt from cobalt chromium alloy constructions in the oral cavity", *Scandinavian journal of dental research,* Vol. 90, pp. 472-479.

- Supreetha, S.N., Ravindra, K. and Murali, H. (2010), "Effect of Heat Treatment on the Corrosion Behavior of Nickel Chromium (Wiron 99) Alloys" IJDA, 2(1)

- Thöne, M., Leuders, M, Riemer, A. Tröster, T and Richard, H.A. (2012). Influence of heat-treatment on Selective Laser Melting products – e.g. Ti6Al4V, available at http://utwired.engr.utexas.edu/lff/symposium/proceedingsArchive/pubs/Manuscripts/2012/2012-38-Thoene.pdf (accessed 20 March 2013)

- Vandenbroucke, B. and Kruth, J.P. (2007), "Selective laser melting of biocompatible metals for rapid manufacturing of medical parts", *Rapid Prototyping Journal,* Vol. 13 No. 4, pp.196 - 203.

- Wataha, J. C. (2000), "Biocompatibility of dental casting alloys: a review", *The Journal of Prosthetic Dentistry,* Vol. 8 No. 2, pp. 223-234.

- Wataha, J. C. and Lockwood, P. E. (1998). Release of elements from dental casting alloys into cell culture medium over 10 months. Dental Materials, 14 No. 2, pp. 158-163.

- Wataha, J. C., Lockwood, P. E. and Nelson, S.K. (1999), "Initial versus subsequent release of elements from dental casting alloys", *Journal of Oral Rehabilitation,* Vol. 26 No. 10, pp. 798-803..

- Williams, R.J., Bibb, R., Eggbeer, D. and Collis, J. (2006), "Use of CAD/CAM technology to fabricate a removable partial denture framework", *Journal of Prosthetic Dentistry,* Vol. 96 No. 2, pp. 96-99.

- Yfantis, C., Yfantis, D., Anastassopoulou, J. & Theophanides, T. (2007). Analytical and Electrochemical Evaluation of the in vitro corrosion behaviour of Nickel-chrome and Cobalt-chrome casting alloys for metal-ceramic restorations. European Journal of Prosthodontics and Restorative Dentistry, 15 (1), pp. 33-40.

ACKNOWLEDGEMENTS