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### TABLE OF CONTENTS

|     |        |   | PAGE  |
|-----|--------|---|-------|
| TH  | ESIS D | ECLARATION  | i     |
| AC  | KNOW   | LEDGEMENT   | ii    |
| TA  | BLE OI | F CONTENTS  | iii   |
| LIS | T OF F | IGURES  | vii   |
| LIS | T OF T | CABLES  | Х     |
| LIS | T OF A | BBREVIATIONS  | xi    |
| LIS | T OF S | YMBOLS  | xvi   |
| AB  | STRAK  | OTTO  | xvii  |
| AB  | STRAC  | т   | xviii |
| СН  | APTER  | LEDGEMENT<br>F CONTENTS<br>IGURES<br>ABLES<br>ABLES<br>ABREVIATIONS<br>YMBOLS<br>T  |       |
| 1.1 | Resear | rch background  | 1     |
|     | 1.1.1  | Cobalt-F75  | 1     |
|     | 1.1.2  | Cobalt-chromium-nickel (Co-Cr-Ni)   | 2     |
|     | 1.1,3  | Casting and powder metallurgy (P/M)   | 2     |
| 1.2 | Proble | em statements   | 3     |
|     | 1.2.1  | Determination of Co-Cr-Ni composition   | 3     |
|     | 1.2.2  | Casting versus powder metallurgy (P/M) method   | 6     |
|     | 1.2.3  | The improvement of cobalt-chromium (Co-Cr) properties<br>evaluated with casting and powder metallurgy fabrication<br>methods. | 8     |
|     | 1.2.4  | Physical properties   | 9     |
|     | 1.2.5  | Corrosion study   | 10    |

iii

### **CHAPTER 2 LITERATURE REVIEW**

| 2.1        | Bioma  | aterials   | 12 |
|------------|--------|--|----|
|            | 2.1.1  | Definitions of Biomaterials  | 12 |
|            | 2.1.2  | The properties of biomaterials   | 13 |
|            | 2.1.3  | Classifications of biomaterials  | 15 |
|            |        | The properties of biomaterials<br>Classifications of biomaterials<br>2.1.3.1 Metallic Biomaterials<br>2.1.3.2 Ceramic Biomaterials<br>2.1.3.3 Polymeric Biomaterials | 15 |
|            |        | 2.1.3.2 Ceramic Biomaterials   | 17 |
|            |        | 2.1.3.3 Polymeric Biomaterials   | 18 |
|            | 2.1.4  | Applications of biomaterials   | 21 |
| 2.2        | Fabric | ation of Biomaterials  | 22 |
|            | 2.2.1  | Fabrication of Metal Implant   | 22 |
|            | 2.2.2  | Powder metallurgy  | 24 |
|            |        | 2.2.2.1 Planetary ball mill  | 25 |
|            |        | 2.2.2.2 Sintering  | 26 |
| 2.3        | Bioco  | mpatibility of biomaterials  | 27 |
|            | 2.3.1  | Definition of biocompatibility   | 27 |
| $\bigcirc$ | 2.3.2  | In vivo and in vitro Test  | 29 |
|            |        | 2.3.2.1 <i>In vivo</i> test  | 30 |
|            |        | 2.3.2.2 In vitro test  | 31 |
| 2.4        | Cobal  | t-Chromium   | 33 |
| 2.5        | Nicke  | 1  | 39 |
| 2.6        | Cobal  | t-Chromium-Nickel  | 39 |
| 2.7        | Corros | sion behaviour   | 43 |

### **CHAPTER 3 EXPERIMENTAL PROCEDURE**

|   | 3.1                | Introduction  | 47 |
|---|--------------------|---|----|
|   | 3.2                | Raw material  | 49 |
|   | 3.3                | Raw material characterization   | 49 |
|   |                    | 3.3.1 Particle size analysis  | 50 |
|   |                    | 3.3.2 Phase analysis  | 50 |
|   |                    | <ul> <li>3.3.1 Particle size analysis</li> <li>3.3.2 Phase analysis</li> <li>3.3.3 Morphology analysis</li> <li>3.3.4 Elemental analysis</li> <li>Composite fabrication</li> <li>3.4.1 Mixing of Co-Cr-Ni powder</li> <li>3.4.2 Powder compaction</li> <li>3.4.3 Sintering</li> <li>Microstructural analysis</li> </ul> | 51 |
|   |                    | 3.3.4 Elemental analysis  | 52 |
|   | 3.4                | Composite fabrication   | 53 |
|   |                    | 3.4.1 Mixing of Co-Cr-Ni powder   | 53 |
|   |                    | 3.4.2 Powder compaction   | 55 |
|   |                    | 3.4.3 Sintering   | 56 |
|   | 3.5                | Microstructural analysis  | 58 |
|   |                    | 3.5.1 Optical microscope  | 58 |
|   | 3.6                | Physical properties testing   | 59 |
|   |                    | 3.6.1 Density   | 59 |
|   |                    | 3.6.2 Porosity  | 60 |
|   | 3.7                | Mechanical properties testing   | 61 |
| ( | $\hat{\mathbf{O}}$ | 3.7.1 Hardness  | 61 |
|   | 3.8                | Corrosion testing   | 63 |
|   |                    |   |    |

### **CHAPTER 4 RESULTS AND DISCUSSION**

| 4.1 | Chara | cterizations of raw materials      | 65 |
|-----|-------|------------------------------------|----|
|     | 4.1.1 | Morphology observation through SEM | 65 |
|     | 4.1.2 | Elemental analysis                 | 67 |

|     | 4.1.3 Particle size analysis  | 71  |
|-----|---|-----|
|     | 4.1.4 Phase analysis  | 73  |
| 4.2 | Microstructure after sintering  | 75  |
| 4.3 | XRD analysis for sintered samples   | 79  |
| 4.4 | Physical and mechanical properties  | 83  |
|     | 4.4.1 Porosity  | 84  |
|     | 4.4.2 Density   | 85  |
|     | 4.4.3 Shrinkage   | 87  |
|     | 4.4.4 Hardness  | 89  |
| 4.5 | Physical and mechanical properties<br>4.4.1 Porosity<br>4.4.2 Density<br>4.4.3 Shrinkage<br>4.4.4 Hardness<br>Corrosion behavior<br>4.5.1 Immersion test<br>4.5.2 Microstructure analysis | 90  |
|     | 4.5.1 Immersion test  | 90  |
|     | 4.5.2 Microstructure analysis   | 103 |
|     | APTER 5 CONCLUSION  | 110 |
| 5.1 | Conclusion  | 110 |
|     |   |     |
| RE  | FERENCES  | 112 |
|     |   |     |
| API | PENDIX A  | 117 |
| GL  | OSSARY  | 119 |
| LIS | T OF PUBLICATIONS   | 122 |

### vi

### LIST OF FIGURES

| NO      |   | PAGE |
|---------|---|------|
| 1.1     | The conceptual flow for powder metallurgy from the powder through<br>the processing to the final product.   | 4    |
| 1.2     | Presentation of the experimental alloys composition in ternary Co-<br>Cr-Ni system at room temperature.   | 5    |
| 1.3     | Venn diagram indicating the reasons for using powder metallurgy.  | 7    |
| 1.4     | Illustration of the fundamental idea underlying the improvement of<br>Cobalt-Chromium (Co-Cr) properties evaluated with casting and<br>powder metallurgy fabrication methods. | 9    |
| 2.1     | Plate and screws (18.8 steel) four and a half month after operation.  | 17   |
| 2.2     | Various application of different polymer composite biomaterial.   | 20   |
| 2.3     | Schematic depicting the ball motion inside the ball mill.   | 26   |
| 2.4     | Co-Cr phase diagram.  | 35   |
| 2.5     | Total hip prosthesis is composed of four components; a) femoral stem b) femoral head c) UHMWPE liner d) metal acetabular shell.   | 37   |
| 2.6     | Nail-plate fixation after displacement osteotomy at upper end of femur.   | 38   |
| 3.1     | Flow chart of experimental procedure.   | 48   |
| 3.2     | Photos for compacting and sintering process.  | 57   |
| $G_{3}$ | Heating profile for sintering process.  | 58   |
| 3.4     | Illustration of an arithmetic mean of the two diagonals, d1 and d2 in   | 62   |
| 4.1     | mm.<br>Scanning electron micrograph of cobalt at 500X magnification. Inset<br>illustrates the 5000X magnification of the SEM image.   | 66   |
| 4.2     | Scanning electron micrograph of chromium at 100X magnification.<br>Inset illustrates the 1000X magnification of the SEM image.  | 66   |
| 4.3     | Scanning electron micrograph of nickel at 500X magnification. Inset illustrates the 10000X magnification of the SEM image.  | 67   |

| 4.4  | EDS spectrum for raw cobalt powder.   | 68 |
|------|---|----|
| 4.5  | EDS spectrum for raw chromium powder.   | 69 |
| 4.6  | EDS spectrum for raw nickel powder.   | 70 |
| 4.7  | Particle size distribution for raw cobalt powder.   | 71 |
| 4.8  | Particle size distribution for raw chromium powder.   | 72 |
| 4.9  | Particle size distribution for raw nickel powder.   | 72 |
| 4.10 | Particle size distribution for raw nickel powder.<br>XRD plot for raw cobalt powder.                                    | 73 |
| 4.11 | XRD plot for raw nickel powder.   | 74 |
| 4.12 | XRD plot for raw nickel powder.   | 74 |
| 4.13 | The microstructure for a) Co9Cr10Ni b) Co4Cr5Ni c) Co4Cr23Ni d)<br>Co15Cr17Ni e) Co5Cr40Ni f) Co9Cr30Ni samples.        | 77 |
| 4.14 | The microstructure for g) Co20Cr5Ni h) Co20Cr23Ni i) Co37Cr5Ni j) Co28Cr10Ni k) Co50Cr samples.                         | 78 |
| 4.15 | XRD plot for Co50Cr and Co5Cr4Ni samples.   | 80 |
| 4.16 | XRD plot for Co4Cr23Ni, Co4Cr5Ni and Co20Cr5Ni samples.   | 81 |
| 4.17 | XRD plot for Co37Cr5Ni, Co20Cr23Ni and Co9Cr30Ni samples.   | 82 |
| 4.18 | XRD plot for Co9Cr10Ni, Co28Cr10Ni and Co15Cr17Ni samples.  | 83 |
| 4.19 | The bar chart for porosity result of 11 CoCr and CoCrNi compositions.   | 85 |
| 4.20 | The bar chart for density result of 11 CoCr and CoCrNi compositions.  | 87 |
| 4.21 | The bar chart of shrinkage for the 11 different CoCr and CoCrNi compositions.   | 88 |
| 4.22 | The bar chart of hardness for 11 CoCr and CoCrNi samples.   | 90 |
| 4.23 | Weight loss as a function of an immersion time plot for a) Co50Cr b)<br>Co5Cr40Ni c) Co4Cr23Ni and d) Co4Cr5Ni samples. | 92 |
| 4.24 | Weight loss as a function of an immersion time plot for a)<br>Co20Cr5Ni b) Co37Cr5Ni c) Co20Cr23Ni and d) Co9Cr30Ni     | 94 |

samples.

- 4.25 Weight loss as a function of an immersion time plot for a) 96 Co9Cr10Ni b) Co28Cr10Ni c) Co15Cr17Ni samples.
- 4.26 Corrosion rate (mpy) as a function of an immersion time plot for a) 99 Co50Cr and b) Co5Cr40Ni samples.
- 4.27 Corrosion rate (mpy) as a function of an immersion time plot for c) 100 Co4Cr23Ni d) Co4Cr5Ni e) Co20Cr5Ni f) Co37Cr5Ni g) Co20Cr23Ni and h) Co9Cr30Ni samples.
- 4.28 Corrosion rate (mpy) as a function of an immersion time plot for i) 101 Co9Cr10Ni j) Co28Cr10Ni and k) Co15Cr17Ni samples.
- 4.29 Microstructure before (left side) and 2 weeks after immersing (right 104 side) in sodium chloride solution following the lowest to highest mpy result for a) Co4Cr5Ni b) Co9Cr10Ni and c) Co4Cr23Ni.
- 4.30 Microstructure before (left side) and 2 weeks after immersing (right 105 side) in sodium chloride solution following the lowest to highest mpy result for d) Co15Cr17Ni e) Co50Cr and f) Co9Cr30Ni.
- 4.31 Microstructure before (left side) and 2 weeks after immersing (right 106 side) in sodium chloride solution following the lowest to highest mpy result for g) Co20Cr5Ni h) Co5Cr40Ni and i) Co28Cr10Ni.
- 4.32 Microstructure before (left side) and 2 weeks after immersing (right 107 side) in sodium chloride solution following the lowest to highest mpy result for j) Co20Cr23Ni and k) Co23Cr5Ni.
- 4.33 EDS for sample Co37Cr5Ni after immersion test. 108
- (4)34EDS for sample Co37Cr5Ni after immersion test.109

### LIST OF TABLES

| NO  |  | PAGE |
|-----|--|------|
| 2.1 | Materials for use in the body.   | 19   |
| 2.2 | Uses of Biomaterials.  | 21   |
| 2.3 | Notable developments relating to implants.   | 23   |
| 2.4 | Comparison of <i>in vivo</i> and <i>in vitro</i> test for biocompatibility                                     | 30   |
| 2.5 | The properties of cobalt, chromium and nickel.   | 40   |
| 2.6 | The composition (in atomic percent) of the experimental Co–Cr–Ni alloys and the Vickers hardness (30 N, 10 s). | 41   |
| 3.1 | Physical and chemical properties of Cobalt, Chromium and Nickel.   | 49   |
| 3.2 | The composition (in atomic percent) of the Co-Cr-Ni alloys.  | 54   |
| 3.3 | The compositions (in weight percent) of the experimental Co–Cr–<br>Ni alloys.                                  | 55   |
| 4.1 | Standard emf series of metals.   | 97   |
| 4.2 | mpy results for 11 series of CoCrNi composition.   | 102  |
|     | <i>r</i>   |      |

### LIST OF ABBREVIATIONS

| °C                              | Degree celcius                            |
|---------------------------------|---|
| AFNOR                           | Association Française de Normalisation    |
| Ag                              | Argentum                                  |
| Al                              | Aluminum                                  |
| Al-Zn-Mg                        | Aluminum-zink-magnesium                   |
| amu                             | Atomic mass unit                          |
| ASM                             | American Society for Microbiology         |
| ASTM                            | American Society for Testing and Material |
| at.%                            | Atomic percent                            |
| Au                              | Aurum                                     |
| BC                              | Before century                            |
| BC<br>bcc<br>BIS-GMA            | Base-centered-cubic                       |
| BIS-GMA                         | bis-phenol A glycidyl methacrylate        |
| BPR                             | Ball to powder ratio                      |
| BSE                             | Back-scattered electron                   |
|                                 | Carbon                                    |
| Cd                              | Cadmium                                   |
| CF                              | Carbon fibers                             |
| Co                              | Cobalt                                    |
| Co <sub>2</sub> Cr <sub>3</sub> | Cobalt2-chromium3                         |
| Co-Cr                           | Cobalt-chromium                           |

| CoCrMo  | Cobalt-chromium-molybdenum                       |
|---|--|
| Co-Cr-Ni  | Cobalt-chromium-nickel                           |
| CoCrWNi   | Cobalt-chromium-tungsten-nickel                  |
| CoNiCrMo  | Cobalt-nickel-chromium-molybdenum                |
| CoNiCrMoWFe   | Cobalt-nickel-chromium-molybdenum-tungsten-ferum |
| Cr  | Chromium   |
| Cr <sub>23</sub> C <sub>6</sub>                           | Chromium carbon<br>Chromium carbon               |
| Cr <sub>2</sub> C   | Chromium carbon                                  |
| Cr <sub>2</sub> Ni <sub>3</sub>                           | Chromium nickel                                  |
| Cr <sub>3</sub> B <sub>4</sub>                            | Chromium boron                                   |
| Cr <sub>3</sub> Ni <sub>2</sub>                           | Chromium nickel                                  |
| Cu  | Copper   |
| Ecorr   | Corrosion potential                              |
| EDS   | Energy dispersive spectroscopy                   |
| emf   | Electromotive force                              |
| Cu<br>E <sub>corr</sub><br>EDS<br>emf<br>E <sub>pit</sub> | Pitting potential                                |
| etc   | et cetera  |
| (fec  | Face-centered cubic                              |
| Fe  | Ferum  |
| FeNi <sub>3</sub>   | Ferum nickel                                     |
| Fig.  | Figure   |
| GF  | Glass fibers                                     |
| GFAAS   | Graphite furnace atomic absorption spectroscopy  |

| GPa                     | Giga pascal  |
|-------------------------|--|
| h                       | hour   |
| НА                      | Hydroxyapatite                                       |
| HAZ                     | Heat affected zone                                   |
| hcp                     | Hexagonal closed pack                                |
| Hg                      | Mercury  |
| HV                      | Hexagonal closed pack<br>Mercury<br>Hardness Vickers |
| HVOF                    | High velocity oxygen fuel                            |
| KF                      | Kevlar fibers  |
| LCP                     | Liquid crystalline polymer                           |
| Mg                      | Magnesium  |
| Мо                      | Molybdenum   |
| MPa                     | Mega pascal  |
| MPa<br>mpy<br>N<br>NaCl | Mils per year  |
| N                       | newton   |
| NaCl                    | Sodium chloride                                      |
| Ni                      | Nickel   |
| Ni <sub>3</sub> B       | Nickel boron   |
| Ni <sub>3</sub> C       | Nickel carbon  |
| NIH                     | National Institute of Health                         |
| nm                      | Nanometer  |
| P/M                     | Powder metallurgy                                    |
| Pb                      | Plumbum  |
|                         |  |

| PBIN                | Pacific basin information node                          |
|---------------------|---|
| PC                  | Polycarbonate   |
| Pd                  | Palladium   |
| PEA                 | Poltethylacrylate                                       |
| PEEK                | Polyetheretheketone                                     |
| PEG                 | Polyethyleneglycol                                      |
| PELA                | Block co-polymer of lactic acid and polyethylene glycol |
| PET                 | Polyethyleneterephthalate                               |
| PGA                 | Polyglycolic acid                                       |
| PHB                 | Polyhydroxybutyrate                                     |
| PHEMA               | Poly (20hydroxyethyl methacrylate)                      |
| PLDLA               | Poly (L-DL-lactide)                                     |
| PLLA                | Poly (L-lactic acid)                                    |
| PLLA<br>PMA<br>PMMA | Polymethylacrylate                                      |
| PMMA                | Polymethymethacrylate                                   |
| PP                  | Polypropylene   |
| PS                  | Polysulfone   |
| (Pt)                | Platinum  |
| PTFE                | Polytetrafluoroethylene                                 |
| PU                  | Polyurethane  |
| Rp                  | Polarization resistance                                 |
| rpm                 | Rotation per minute                                     |
| S                   | second  |
|                     |   |

|   | SCE   | Saturated calomel electrode                    |
|---|---|--|
|   | SEI   | Secondary electron imaging                     |
|   | SEM   | Scanning electron microscope                   |
|   | SiC   | Silicone carbide                               |
|   | SR  | silicone rubber                                |
|   | Т   | Temperature<br>Tantalum                        |
|   | Та  | Tantalum                                       |
|   | THA   | Total hip arthroplasty                         |
|   | Ti  | Titanium                                       |
|   | UMHWPE  | Ultra-high-molecular weight polyethylene       |
|   | wt.%  | Weight percent                                 |
|   | XRD   | X-ray diffraction                              |
|   | Zn  | Zink   |
|   | Zn<br>Zn-Mg<br>Zr-Sc                            | Zink-magnesium                                 |
|   | Zr-Sc   | Zirconium-scandium                             |
|   | αCo   | Alpha cobalt                                   |
|   | εCo   | Epsilon cobalt                                 |
| ( | Co <sub>x</sub> Cr <sub>y</sub> Ni <sub>z</sub> | Alloy composition for which subscripted        |
|   |   | letters/numbers are referred as atomic percent |
|   | CoxCryNi  | Alloy composition for which unsubscripted      |
|   |   | letters/numbers are referred as weight percent |
|   |   |  |

### LIST OF SYMBOLS

| %                  | Percent   |
|--------------------|---|
| μm                 | Mean size of particle (micro metre)                   |
| 20                 | Degree of diffraction angle 2 theta)                  |
| Å                  | Atomic radii (angstrom)<br>Arbitrary unit (intensity) |
| a.u.               | Arbitrary unit (intensity)                            |
| g                  | Amount of powder (gram)                               |
| g/cm <sup>3</sup>  | Density of solid (gram per centimetre cubic)          |
| g/mol              | Molecular weight (gram per mol)                       |
| kV                 | Current voltage (kilo Volt)                           |
| lb/in <sup>3</sup> | Density of a material (pound per inch cube)           |
| mg/cm <sup>3</sup> | Miligram per centimetre cubic                         |
| ml                 | Volume of ethanol                                     |
| mm                 | Arithmetic mean of a diagonal (milimeter)             |
| ten                |   |
| mm is tem is t     |   |
|                    |   |

#### Sifat Fizikal dan Kelakuan Kakisan ke atas Aloi Co-Cr-Ni Dihasilkan oleh Serbuk Metalurgi

#### ABSTRAK

Aloi berasaskan kobalt telah digunakan secara meluas dalam aplikasi bio-perubatan. Dalam kajian ini, 11 komposisi aloi kobalt-kromium-nikel (Co-Cr-Ni) yang berbeza-beza telah dihasilkan melalui kaedah metalurgi serbuk. Mikroskop imbasan elektron (SEM) bersama-sama dengan spektroskopi sinar-x penyerak tenaga (EDS) telah digunakan untuk pemerhatian morfologi dan unsur bahan-bahan mentah. Taburan saiz partikel untuk partikel kobalt, kromium dan nikel telah diperincikan menggunakan penganalisis partikel Malvern. Pembelauan sinar-x (XRD) telah dilakukan untuk mengkaji perubahan fasa bahan-bahan mentah. Serbuk mentah kobalt, kromium dan nikel telah dikisar menggunakan pengisar planet dan dipadatkan menggunakan penekan tangan ekapaksi kepada bentuk palet sebelum disinter menggunakan relau tiub di bawah persekitaran argon. Sampel-sampel telah disinter pada suhu 1000°C selama 2 jam. Ujian peratusan keliangan, ketumpatan, pengecutan dan kekerasan telah dijalankan untuk mengaitkan sifat-sifat fizikal dan mekanikal dengan komposisi aloi Co-Cr-Ni. Dimensi sampel sebelum dan selepas persinteran telah diukur dan peratusan pengecutan telah dikira. Pengukuran ketumpatan telah dijalankan melalui kaedah Archimedes sementara peratusan keliangan dikira berdasarkan data ketumpatan. Ujian kekerasan dijalankan menggunakan mesin kekerasan Vickers. Mikrostruktur dan perubahan fasa sampel tersinter masing-masing telah juga diperincikan menggunakan SEM dan XRD. Untuk memahami perkaitan di antara kerintangan kakisan dengan campuran komposisi Co-Cr-Ni, ujian rendaman telah dijalankan dalam alat rendaman air menggunakan larutan natrium klorida 0.9% sambil mengekalkan suhu pada 37°C. Ukuran pengurangan berat dan kadar kakisan telah dijalankan untuk mengkaji kerintangan kakisan sampel-sampel yang telah direndam. Keputusan telah menunjukkan bahawa peratusan keliangan sampel-sampel meningkat dengan penambahan kandungan Cr dan mengurang dengan penambahan kandungan Co. Ketumpatan dan peratusan pengecutan campuran meningkat dengan penambahan kandungan Co manakala menurun dengan penambahan kandungan Cr. Kekuatan meningkat dengan penambahan kandungan Co manakala menurun dengan penambahan kandungan Ni. Sampel dengan komposisi Co4Cr5Ni telah didapati mempunyai kerintangan kakisan yang paling tinggi selepas 30 hari direndam dalam larutan 0.9% natrium klorida. Sebaliknya, sampel dengan komposisi Co37Cr5Ni terbukti mempunyai kerintangan kakisan yang paling rendah.

#### Physical Properties and Corrosion Behaviour of Co-Cr-Ni Alloy Developed by Powder Metallurgy

### ABSTRACT

Cobalt-based alloys have been widely used in biomedical application. In this research, 11 different compositions of cobalt-chromium-nickel (Co-Cr-Ni) alloys were developed by powder metallurgy route. Scanning electron microscope (SEM) in conjunction with energy dispersive x-ray spectroscopy (EDS) was used for morphology and elemental observation of the raw materials. The particle size distribution of the Co, Cr and Ni particles were characterized using Malvern particle analyzer. X-ray diffraction (XRD) was carried out to analyze the phase transformation of raw materials. The raw Co-Cr-Ni powders were first milled using planetary mill and compacted using uniaxial hand press to a pellet shape before being sintered using tube furnace under argon atmosphere. The samples were sintered at 1000°C for 2 hours. Percentage of porosity, density, shrinkage and hardness test were carried out to correlate physical and mechanical properties with composition of Co-Cr-Ni alloys. The dimensions of the samples before and after sintering were measured and the percentage of shrinkage of the samples was calculated. Density measurement was carried out by Archimedes technique while percentage of porosity was calculated based on the density data. Hardness testing was performed using Vickers hardness machine. The microstructure and the phase transformation of sintered samples were also being characterized using SEM and XRD respectively. In order to understand a relationship of corrosion resistance with composition of Co-Cr-Ni alloy, an immersion test was executed in a water bath using 0.9% sodium chloride solution while maintaining the temperature of 37°C. Weight loss measurement and corrosion rate were carried out to analyze the corrosion resistance of the immersed samples. The results showed that the percentage of porosity of the samples increased with increasing Cr content and decreased with increasing Co content. The density and the percentage of shrinkage of the alloys increased with increasing Co content and decreased with increasing Cr content. Hardness increased with increasing Co content while decreased with increasing Ni content. Sample with composition of Co4Cr5Ni was found to have the highest corrosion resistance after 30 days immersed in 0.9% sodium chloride solution. In contrary, sample with composition of Co37Cr5Ni evidenced the lowest corrosion resistance.

#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 **Research background**

1.1.1 Cobalt-F75

, cted by or iconal copyright Cobalt-chromium-molybdenum (CoCrMo) alloys have superior tribological properties. CoCrMo alloys have two phases consisting of a cobalt alloy solid solution matrix and metal carbides. The material properties are related to the crystallographic nature of cobalt, the solid-solution-strengthening effect of chromium and molybdenum as well as the formation of extremely hard carbides, and the corrosion resistance is due to chromium. The mechanical properties are enhanced by the fine grained and homogeneous microstructure while the chemical composition is related to carbon content. The corrosion resistance of CoCrMo results from the formation of a thin passive oxide film on its surface. This oxide, consisting of a mixture of chromium and cobalt oxides which provides high corrosion resistance to the base alloy (Giacchi et al., 2010; Sinnett-Jones et al., 2005). The castable CoCrMo alloy has been used for many decades in dentistry and recently in making artificial joints. The wrought CoNiCrMo alloy is relatively new which is now used for making stems of prostheses for heavily loaded joints such as knee and hip (Wong et al., 2007).

#### 1.1.2 Cobalt-chromium-nickel (Co-Cr-Ni)

Cobalt, chromium and nickel are among most metals that were used to make alloys for manufacturing implants. Chromium improves the corrosion resistance of the alloys as well as stabilizing the hcp-structure of cobalt-matrix which is important to improve the mechanical properties, reduce the abrasive wear and lower the stacking faults energy. Nickel reduces a tendency to form stacking faults which the formation of stacking faults lessens the ductility of cobalt alloys. Therefore, by adding nickel to the alloys, the ductility of cobalt alloys can be improved besides stabilizing the fcc-structure of cobalt-matrix (Matkovic et al., 2004). Nickel as well as chromium strengthened the alloys when added to the pure cobalt matrix which is why their addition is the major consideration to improve the properties of pure cobalt alloys.

### **1.1.3** Casting and powder metallurgy (P/M)

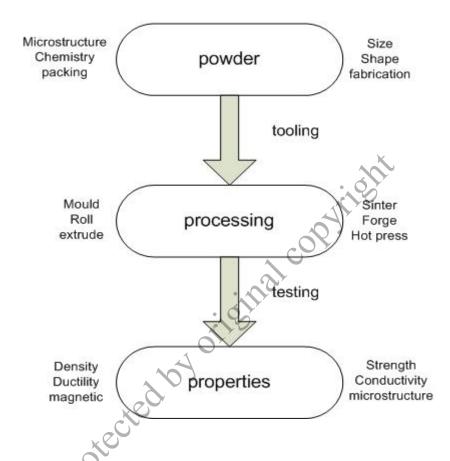
Casting is a process where an object or finished shape obtained by solidification of a substance in a mould. Powder is defined as a finely divided solid, smaller than 1mm in its maximum dimension. In most cases, the powders will be metallic, although in many instances they are combined with other phases such as ceramics or polymers. An important characteristic of a powder is its relatively high surface area to volume ratio. The particles exhibit behaviour that is intermediate between that of a solid and a liquid. Powders will flow under gravity to fill containers or die cavities, so in this sense they behave like liquids. They are compressible like a gas.

Powder metallurgy is the study of the processing of metal powders, including the fabrication, characterization, and conversion of metal powders into useful engineering components. The processing stage involves the application of basic laws of heat, work and deformation to the powder which change the shape, properties and structure of a powder into a final product (R.M. German, 1984). Fig. 1.1 shows the three main steps in the scheme of powder metallurgy.

# **1.2** Problem statement

#### 1.2.1 Determination of Co-Cr-Ni composition

From the previous investigation, the series of Co-Cr-Ni alloys were chosen due to their region in ternary Co-Cr-Ni diagram as shown in Fig 1.2. This region is located at the Co-based alloy as to avoid the region of toxicity.



Powder metallurgy processing

Figure 1.1: The conceptual flow for powder metallurgy from the powder through the processing to the final product (R.M. German, 1984).

Surv et al., (1978), Marti (2000) and Tkaczyk et al., (2009) explained that cobalt-base alloys may be generally described as non magnetic, wear, corrosion and heat-resistant (high strength even at elevated temperature). Many properties of the alloy originate from the crystallographic nature of cobalt, the solid-solution-strengthening effect of chromium and molybdenum, the formation of extremely hard carbides and the corrosion resistance imparted by chromium. Cobalt-base alloys are difficult to fabricate which is why their use has been limited, but continuous work led to the development of specialized casting methods. They reported that, the first medical use of cobalt-basealloys was in the cast of dental implants due to its excellent resistance to degradation in the oral environment. Various *in vitro* and *in vivo* tests have shown that the alloys are biocompatible and suitable for use as surgical implants. The use of Co alloys for surgical applications is mainly related to orthopaedic prostheses for the knee, shoulder and hip as well as to fracture fixation devices.

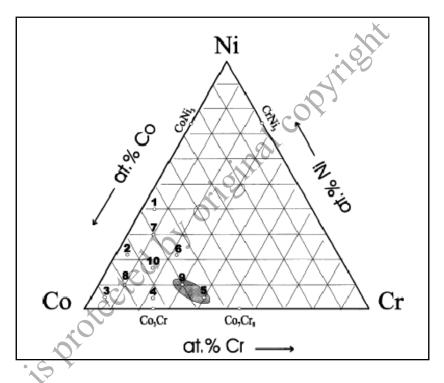


Figure 1.2: Presentation of the experimental alloys composition in ternary Co-Cr-Ni system at room temperature.

Sury et al., (1978), Marti (2000) and Tkaczyk et al., (2009) explained that cobalt-base alloys may be generally described as non magnetic, wear, corrosion and heat-resistant (high strength even at elevated temperature). Many properties of the alloy originate from the crystallographic nature of cobalt, the solid-solution-strengthening effect of chromium and molybdenum, the formation of extremely hard carbides and the corrosion resistance imparted by chromium. Cobalt-base alloys are difficult to fabricate which is why their use has been limited, but continuous work led to the development of specialized casting methods. They reported that, the first medical use of cobalt-basealloys was in the cast of dental implants due to its excellent resistance to degradation in the oral environment. Various in vitro and in vivo tests have shown that the alloys are biocompatible and suitable for use as surgical implants. The use of Co alloys for surgical applications is mainly related to orthopaedic prostheses for the knee, shoulder and hip as well as to fracture fixation devices.

#### 1.2.2

Casting versus powder metallurgy (P/M) method Hildebrand et al., (1989) and Matkovic et al. (2004) studied the influences of adding nickel and molybdenum on the microstructure and properties of as-cast cobaltchromium based alloys to be applied in biomedical. In contrary, the powder metallurgy technique was applied in this research. There are several benefits in using powder metallurgy instead of casting method. Venn diagram in Fig. 1.3 shows the reasons for using powder metallurgy. First of all, the low cost production of complex parts can be achieved via this method. Components for the automotive industry show the good example implementing this powder metallurgy activity. Within this economical part area laid productivity, tolerance and automation.

On the other hand, the fusion metallurgy which is casting method, both the precision and costs are very high. Furthermore, there are many problems and costs with segregation, machining, and final tolerance associated with casting which can be avoided through metal powder-based approaches. In Venn diagram, there is also unique property or unique microstructure justifications for using powder metallurgy