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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
bcc	Base-centered-cubic
BIS-GMA	bis-phenol A glycidyl methacrylate
BPR	Ball to powder ratio
BSE	Back-scattered electron
C	Carbon
Cd	Cadmium
CF	Carbon fibers
Co	Cobalt
Co_2Cr_3	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
$Cr_{23}C_6$	Chromium carbon
Cr_2C	Chromium carbon
Cr_2Ni_3	Chromium nickel
Cr_3B_4	Chromium boron
Cr_3Ni_2	Chromium nickel
Cu	Copper
E_{corr}	Corrosion potential
EDS	Energy dispersive spectroscopy
emf	Electromotive force
E_{pit}	Pitting potential
etc.	et cetera
fcc	Face-centered cubic
Fe	Ferum
$FeNi_3$	Ferum nickel
Fig.	Figure
GF	Glass fibers
GFAAS	Graphite furnace atomic absorption spectroscopy

GPa	Giga pascal
h	hour
HA	Hydroxyapatite
HAZ	Heat affected zone
hcp	Hexagonal closed pack
Hg	Mercury
HV	Hardness Vickers
HVOF	High velocity oxygen fuel
KF	Kevlar fibers
LCP	Liquid crystalline polymer
Mg	Magnesium
Mo	Molybdenum
MPa	Mega pascal
mpy	Mils per year
N	newton
NaCl	Sodium chloride
Ni	Nickel
Ni_3B	Nickel boron
Ni_3C	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)
PMA	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
T	Temperature
Ta	Tantalum
THA	Total hip arthroplasty
Ti	Titanium
UMHWPE	Ultra-high-molecular weight polyethylene
wt.%	Weight percent
XRD	X-ray diffraction
Zn	Zink
Zn-Mg	Zink-magnesium
Zr-Sc	Zirconium-scandium
αCo	Alpha cobalt
εCo	Epsilon cobalt
$Co_xCr_yNi_z$	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)
2θ	Degree of diffraction angle 2 theta)
Å	Atomic radii (angstrom)
a.u.	Arbitrary unit (intensity)
g	Amount of powder (gram)
g/cm^3	Density of solid (gram per centimetre cubic)
g/mol	Molecular weight (gram per mol)
kV	Current voltage (kilo Volt)
lb/in^3	Density of a material (pound per inch cube)
mg/cm^3	Miligram per centimetre cubic
ml	Volume of ethanol
mm	Arithmetic mean of a diagonal (milimeter)

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

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.

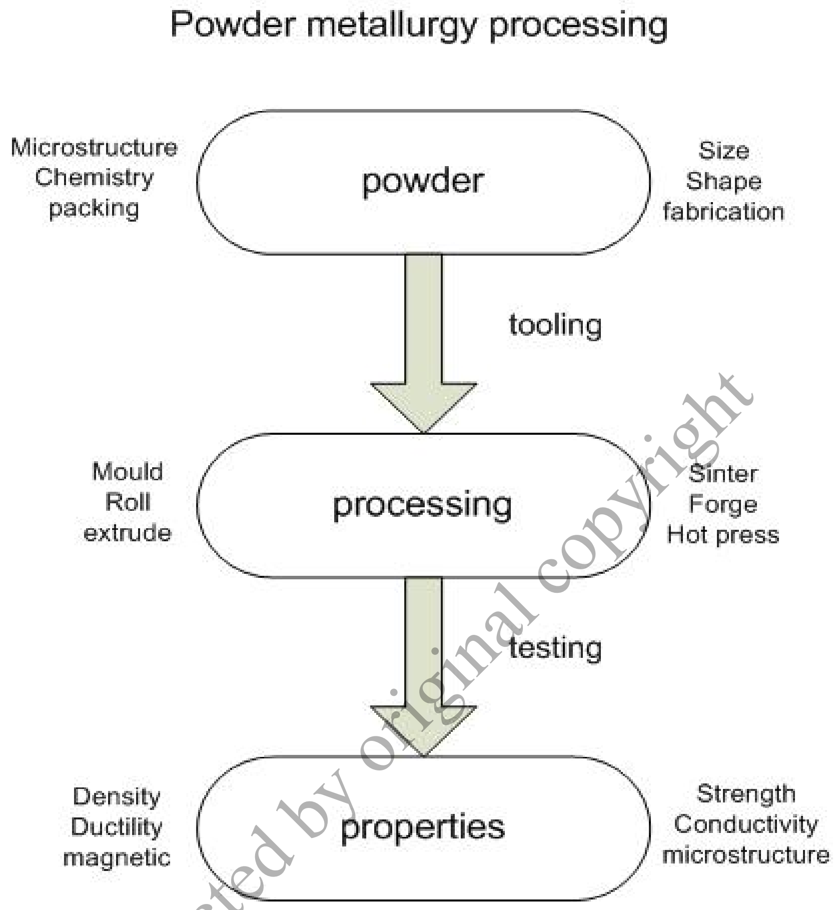

Figure 1.1: The conceptual flow for powder metallurgy from the powder through the processing to the final product (R.M. German, 1984).

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-base-alloys 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.

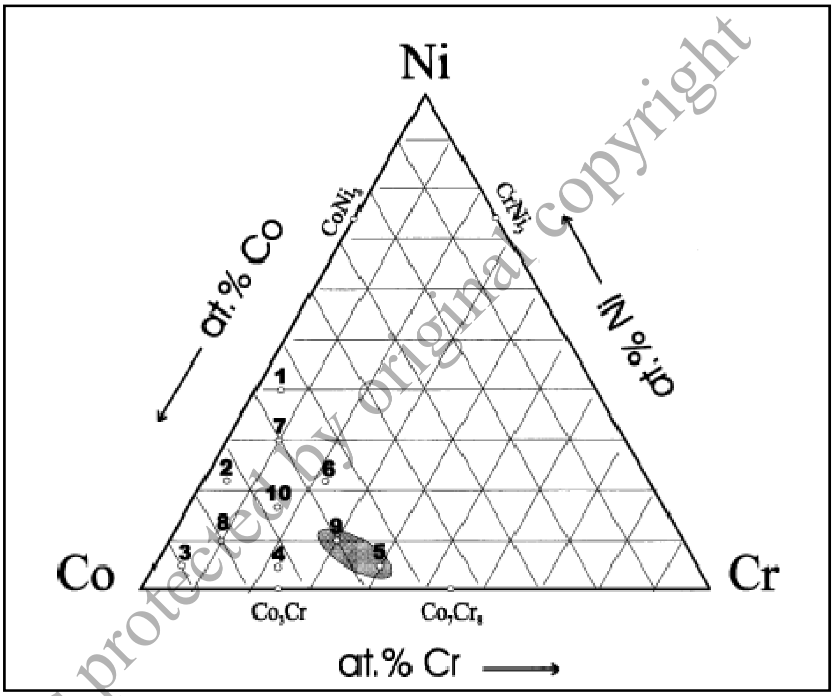

Figure 1.2: Presentation of the experimental alloys composition in ternary Co-Cr-Ni system at room temperature.

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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 cobalt-chromium 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