Metal Injection Molding of Co-28Cr-6Mo

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Abstract

Metal injection molding of gas- and water-atomized Co-28Cr-6Mo powders is evaluated. Sintering is conducted in different atmospheres to evaluate their effects on sintering response and carbon, nitrogen, and oxygen contents. The effects of hot isostatic pressing and heat treat on the mechanical properties are investigated. Properties are correlated to the interstitial content and microstructure. Optimized processing gives mechanical properties that exceed ASTM requirements for cast and wrought Co-28Cr-6Mo.

Introduction

Cobalt-chromium alloys are commonly used for surgical implants because of their high strength, superior corrosion resistance, non-magnetic behavior, and biocompatibility. Applications include prosthetic replacements of hips, knees, elbows, shoulders, ankles, and fingers; bone plates, screws, staples, and rods; and heart valves [1]. Material properties for various compositions and processing routes are covered by a number of ASTM specifications. Co-28Cr-6Mo is a common composition and can be cast (ASTM F75), wrought (ASTM F1537), or forged (ASTM F799). Due to the shape complexity of surgical implants, casting is often the selected processing route. For higher volume applications, metal injection molding (MIM) can compete favorably with castings on cost.

In addition to the property requirements summarized in these specifications, many implants must meet component-specific requirements. For example, femoral hip prostheses must meet specific fatigue property requirements as described in ASTM F2068. Fatigue properties are highly sensitive to porosity, so both cast and MIM components must usually be hot isostatically pressed (HIPed) to eliminate any remaining porosity to meet these requirements. Co-28Cr-6Mo, at low carbon levels typical of MIM, has a small grain size and high fatigue strength, but poor wear resistance. Higher carbon levels improve wear resistance, but can result in poor fatigue strength.

Carbon in Co-28Cr-6Mo can form grain boundary carbides, which are detrimental to mechanical properties, especially ductility [2,3]. Chromium carbides can form a eutectic that gives incipient melting as low as 1235°C [4]. To eliminate any grain boundary carbides, Co-28Cr-6Mo is generally solutionized by heating to above 1200°C. Rapid cooling then prevents carbide precipitation.

Nitrogen can be used instead of carbon to increase the strength of Co-28Cr-6Mo while maintaining good ductility [5]. Powder metallurgy methods are better suited to nitrogenizing than casting because the open pore structure during sintering facilitates uniform introduction of nitrogen as an interstitial solute. Nitrogen concentrations of up to 0.35% are soluble in Co-28Cr-6Mo at 1200°C with higher nitrogen levels resulting in the formation of chromium nitride second phase particles [6].

This work investigates nitrogenizing MIM Co-28Cr-6Mo by sintering in a nitrogen-containing atmosphere. The effects of subsequent thermal cycles, HIP and heat treat, on the mechanical properties are investigated for powders produced by water- and gas-atomization.

Experimental Procedures

Two pre-alloyed, -25 µm Co-28Cr-6Mo powders were selected for evaluation. One powder was produced by gas-atomization, the other by water-atomization. The characteristics of these powders are summarized in Table 1. Scanning electron micrographs showing the powder morphologies are given in Figures 1 and 2. Both powders show some satellite formation. The water-atomized powder also exhibits a few ligamental particles.

The chemical compositions of the powders are given in Table 2 in comparison to the ASTM F75 specification. The water-atomized powder has a high nitrogen content. Silicon and manganese contents are also relatively high, but are well within the specification limits.

Table 1: Powder characteristics

Powder	Water-atomized	Gas-atomized
Pycnometer density (g/cm^3)	8.2	8.3
Apparent density (g/cm^3)	2.6	3.8
Tap density (g/cm^3)	4.2	5.0
Particle size distribution		
d10 (µm)	3.9	3.9
d50 (µm)	9.6	8.9
d90 (µm)	17.9	15.8

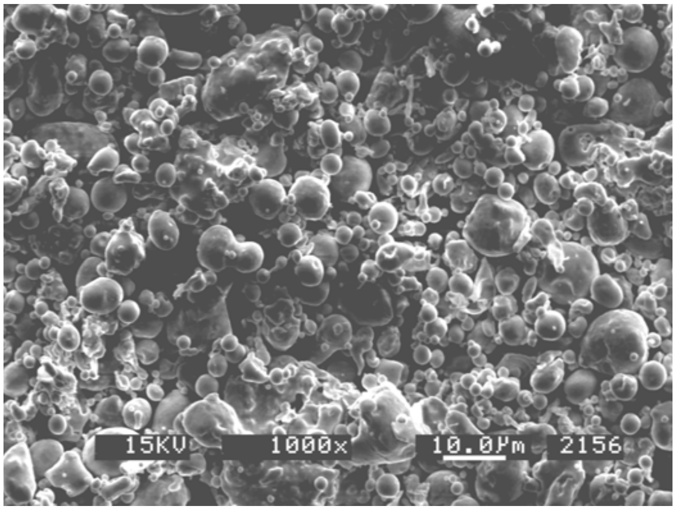

Figure 1: SEM of a water-atomized Co-28Cr-6Mo alloy powder.

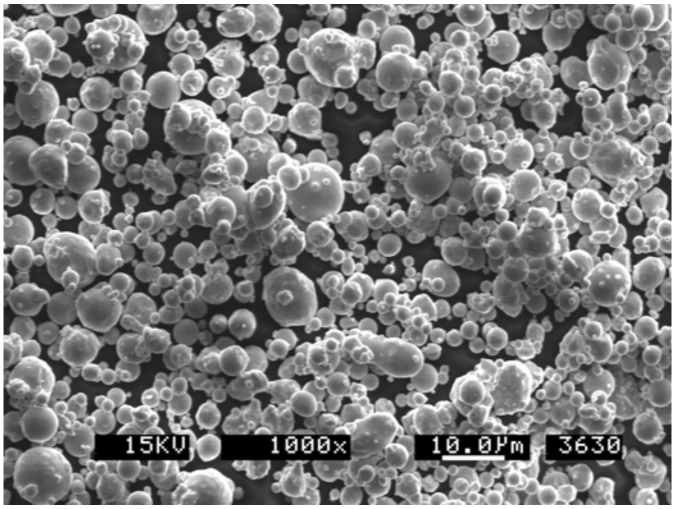

Figure 2: SEM of a gas-atomized Co-28Cr-6Mo alloy powder.

Table 2: Chemical compositions of prealloyed Co-28Cr-6Mo powders in comparison to ASTM F-75 specifications.

Element	F-75 spec	Water-atomized	Gas-atomized
Cr	27-30%	28.1%	28.1%
Mo	5-7	5.5	5.8
Ni	0-0.5	0.04	0.11
Fe	0-0.75	0.08	0.13
C	0-0.35	0.01	0.01
Si	0-1	0.78	0.38
Mn	0-1	0.66	0.01
W	0-0.2	N/R	N/R
P	0-0.02	0.004	N/R
S	0-0.01	0.005	0.003
N	0-0.25	0.246	0.049
Al	0-0.1	N/R	N/R
Ti	0-0.1	N/R	N/R
B	0-0.01	N/R	N/R
Co	balance	balance	balance

N/R – Not reported

Co-28Cr-6Mo is usually sintered slightly above its solidus temperature to achieve high sintered densities [7,8]; however, the solidus temperature varies depending on composition. Differential scanning calorimetry (DSC) was used to determine the solidus temperatures of the two powders. The DSC scans are given in Figure 3. The solidus of the gas-atomized powder was 1359°C, while that of the water-atomized powder was 1385°C.

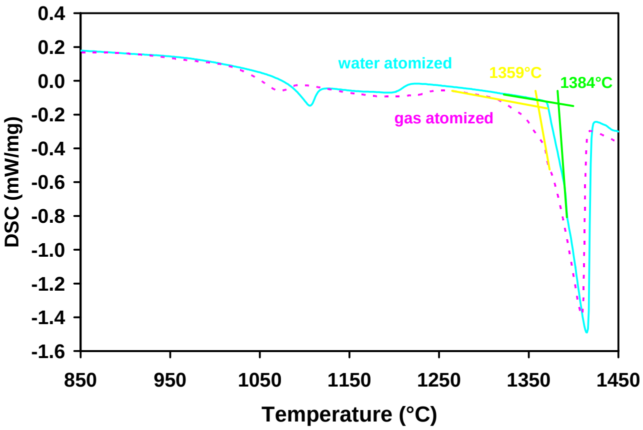

Figure 3: DSC scans of the Co-28Cr-6Mo powders.

The powders were mixed with a wax-polymer binder at a solids loading of 65 vol.% for injection molding. Test bars were injection molded and debound by a two-step process. First, the components were solvent debound to remove the wax portion of the binder. Then the parts were thermally debound and presintered by heating to 900°C in a 100% H_2 atmosphere.

The debound and presintered Co-28Cr-6Mo bars were sintered at 10°C/minute to temperatures ranging from 1320 to 1385°C. The hold time at the sintering temperature was 1 hour. Test bars were sintered in 100% H_2, 50% H_2/50% N_2 and 100% N_2. Samples were HIPed at 1200°C (2200°F) and 100 MPa (15 ksi) for 4 hours. After HIP, the test bars were solution heat treated at 1230°C for 2 hours and then water quenched.

Sintered densities were determined by Archimedes' technique of water displacement. The tensile strengths of sintered MIM test bars were measured using a MTS Systems Corporation Sintech 20/D universal testing machine with a 20000 lb (88.9 kN) load cell in accordance with MPIF Standard 50. Each sample was measured, placed in the tensile fixture, loaded at 2 mm/minute and monitored for fracture and ultimate tensile loading. Elongation was measured with a set of calipers. For metallography, the samples were mounted in Bakelite and polished to a 0.3 µm surface finish. The Co-28Cr-6Mo samples were etched with acetic glyceregia.

Carbon, oxygen, and nitrogen contents were measured using Horiba EMIA-8200 carbon/sulfur and EMGA-650 oxygen/nitrogen analyzers based on the infrared absorbance technique. An appropriate amount of each sample (0.1 g to 0.2 g) was either filed with a diamond file or cut. Samples for carbon testing were cut with an alumina blade while samples for oxygen/nitrogen testing were cut using a silicon carbide blade. Water was used as a coolant in both cases. The cut samples were cleaned with acetone prior to analysis. The samples for oxygen/nitrogen testing were mixed with tin granules, while the samples for carbon testing were mixed with tin and tungsten granules.

Results and Discussion

The effect of sintering temperature on the density of Co-28Cr-6Mo is shown in Figure 4 for samples sintered in 50% H_2/50% N_2. The gas-atomized powder gave higher sintered densities at all temperatures. The optimal sintering temperature was 1345°C for the gas atomized powder and 1385°C for the water-atomized powder. Additional test bars were sintered at these temperatures in 100% H_2. The density of the water-atomized powder increased slightly from 7.85 g/cm^3 to 7.99 g/cm^3, but the change in atmosphere had little effect on the density of the gas-atomized powder. The water-atomized powder was also sintered in 100% N_2, resulting in a density of 7.95 g/cm^3.

Test bars from both powders were sintered in H_2 and H_2/N_2 at their respective optimal temperatures. The water-atomized powder sintered in H_2/N_2 had the lowest density of the four groups, but was still 94.8% of the typical density of 8.28 g/cm^3 for ASTM F75. This density was sufficient to achieve a closed pore condition for containerless HIP. After HIP, the water-atomized samples had a density of 8.20 g/cm^3, while the gas-atomized samples had a density of 8.25 g/cm^3. A pore-free condition was likely achieved in both cases, with impurities in the powder resulting in lower theoretical densities.

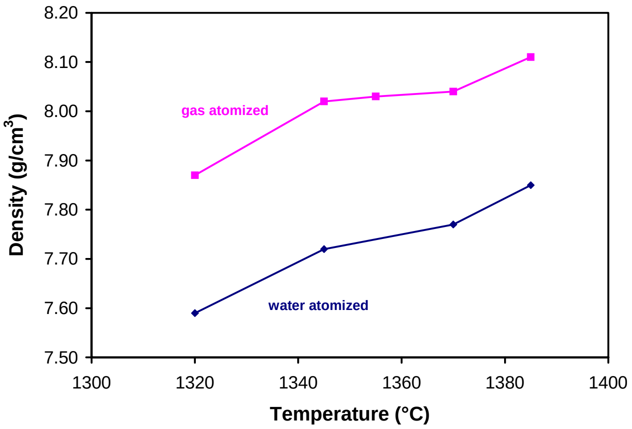

Figure 4: Effect of sintering temperature on the density of samples sintered in a 50/50 hydrogen/nitrogen atmosphere.

Microstructures of the nitrogen-sintered, water-atomized sample are shown in Figure 5 after sintering and after HIP and heat treat. The as-sintered sample shows some porosity and oxide inclusions. Etching results in clearly defined grain boundaries, indicating that they are chemically different from the rest of the grains. The HIPed and heat treated sample shows the oxide inclusions, but no porosity or grain boundaries.

Oxide inclusions were not present in microstructures of the gas-atomized samples, which had lower levels of silicon and manganese impurities. Grain boundaries were observed after HIP of the gas atomized powder, but not after heat treat. The lack of clearly defined grain boundaries indicates that impurities are in solution within the grains and are not segregated to the grain boundaries. Low carbon Co-28Cr-6Mo typically shows little grain boundary attack unless second phase particles are present in the matrix or at the grain boundaries [5].

Carbon, oxygen, and nitrogen contents are summarized in Table 3. Carbon contents were 0.04% or less in all cases. Sintering the water-atomized powder in 100% H_2 lowered its oxygen content from 0.26 to 0.17 wt.%, but this was still much higher than the oxygen content of the gas atomized powder sintered in 50% H_2/50% N_2. The higher oxygen content of the water-atomized powder is likely due to the higher levels of silicon and manganese impurities, which are more reactive and have greater tendency to form stable oxides.

Samples sintered in the hydrogen/nitrogen mix or in 100% nitrogen had nitrogen contents near the maximum limit of 0.25 wt.% for ASTM F75. Nitrogen likely segregates to the grain boundaries unless parts are solution heat treated and quenched.

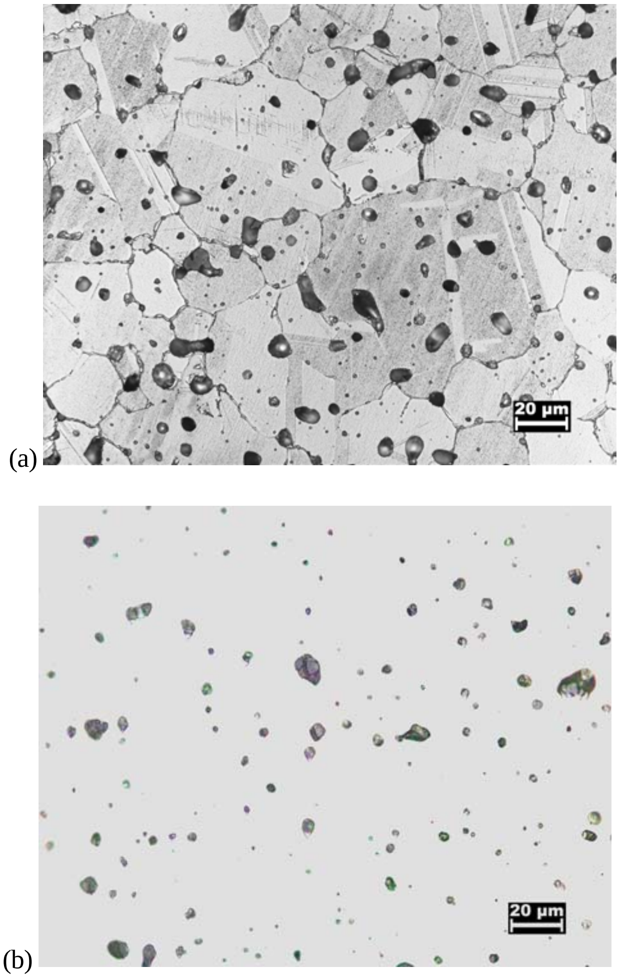

Figure 5: Micrographs of N_2 sintered Co-28Cr-6Mo (a) after sintering and (b) after HIP and heat treatment.

Table 3: Effect of sintering atmosphere on carbon, oxygen, and nitrogen contents of MIM Co-28Cr-6Mo after HIP and solution heat treatment.

	WA H_2	WA H_2/N_2	WA N_2	GA H_2/N_2
Carbon	<0.01%	<0.01%	0.02%	0.04%
Oxygen	0.17%	0.26%	0.29%	0.04%
Nitrogen	0.06%	0.23%	0.25%	0.26%

The mechanical properties of the gas-atomized and water-atomized test bars after sintering in H_2 or H_2/N_2, after HIP, and after heat treating are shown in Figures 6, 7, and 8. The ASTM specifications for cast (F75) and wrought (F1537) material are plotted for comparison. Both gas-atomized and water-atomized powders can meet F75 cast property requirements after sintering. Sintering in H_2/N_2 increases the yield and ultimate strengths for both the water-atomized and gas-atomized powders. This is expected from the solution-strengthening effect of the nitrogen.

As expected with the decrease in porosity, HIP increased the elongation of all the samples, and improved the yield strength and ultimate tensile strength of the water-atomized powder. However, HIP had little effect on the yield strength and ultimate tensile strength of the gas-atomized powder sintered in H_2. After HIP, the water-atomized powder sintered in H_2/N_2 meets F1537 wrought property requirements.

After heat treating, the gas-atomized powder sintered in H_2 meets F1537 wrought property requirements. Heat treat benefited the gas-atomized powder sintered in H_2, but had little effect on the other samples. The increase in ultimate tensile strength and elongation for the hydrogen-sintered, gas-atomized powder after heat treatment is surprising since this sample has the least amount of nitrogen to solutionize. Instead, heat treat was detrimental to the gas-atomized and water-atomized samples sintered in H_2/N_2 which have the most nitrogen to solutionize.

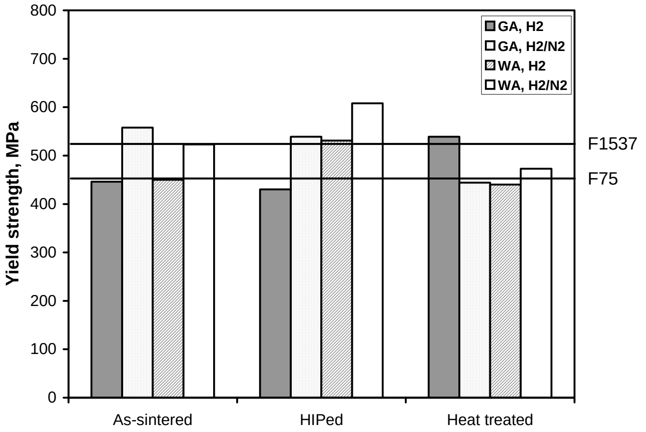

Figure 6: Comparison of the yield strength of MIM Co-28Cr-6Mo after each thermal process in comparison to ASTM specifications for cast and wrought material

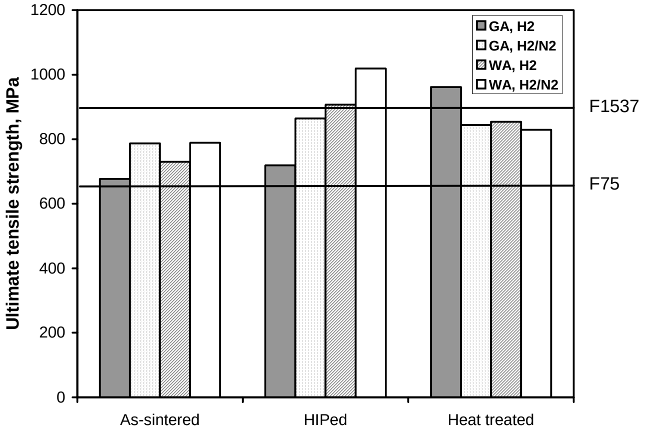

Figure 7: Comparison of the ultimate tensile strength of MIM Co-28Cr-6Mo after each thermal process in comparison to ASTM specifications for cast and wrought material.

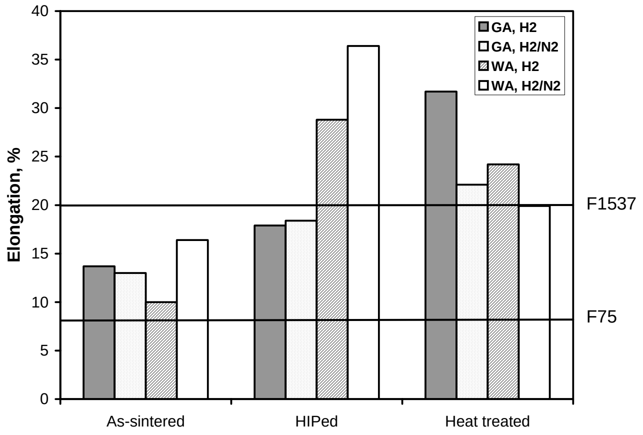

Figure 8: Comparison of the elongation of MIM Co-28Cr-6Mo after each thermal process in comparison to ASTM specifications for cast and wrought material.

In addition to the material specifications for static mechanical properties, many Co-28Cr-6Mo components have specific fatigue property requirements. Full density is essential since fatigue properties are highly sensitive to porosity. Typical fatigue property requirements can be met by the HIPed and heat treated gas-atomized powder, but the inclusions resulting from impurities in the water-atomized powder may prove detrimental to the fatigue strength.

Summary and Conclusion

Both water-atomized and gas-atomized Co-28Cr-6Mo powders can be injection molded and sintered to a closed pore condition. Sintering in a nitrogen or a hydrogen/nitrogen atmosphere results in nitrogenization, which can compensate for low carbon levels and increase the strength. Static mechanical properties of as-sintered Co-28Cr-6Mo exceed ASTM F75 requirements for cast material. Mechanical properties exceeding ASTM F1537 requirements for wrought material can be achieved after HIP of the water-atomized powder, and after HIP and heat treat of the gas-atomized powder. Solution heat treating keeps the nitrogen from segregating to the grain boundaries, but has a mixed effect on mechanical properties depending on the powder source. Impurities, such as manganese and silicon, in the water-atomized powder produce inclusions in the final microstructure, which may hinder fatigue properties.

Acknowledgements

The authors gratefully acknowledge Justin Brezovsky, Guneet Sethi, Rod Reber, and Mike Muscarella for their assistance with the experiments and testing performed during this research study.

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