

## Production and characterisation of Cr-Si-Ni-Mo steel foams

Ilven Mutlu\* & Enver Oktay

Istanbul University, Metallurgical and Materials Engineering Department, Istanbul, Turkey

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In this study, production of Cr-Si-Ni-Mo steel foams by space holder-water leaching technique in powder metallurgy is investigated. Cr-Si-Ni-Mo steel powders are mixed with different amounts of carbamide and then compacted at 180 MPa. Polyvinyl alcohol is used as a binder. The carbamide in the green compacts is removed by water leaching at room temperature. The foams having porosities ranging from 39 to 72 % are produced after sintering at temperatures between 1150 and 1250°C and times of 30 and 60 min in H<sub>2</sub> atmosphere. Young's modulus and compressive yield strength values of the steel foams are in the range of 0.20-5.21 GPa and 24-290 MPa, respectively. Increasing sintering temperature and sintering time enhanced the Young's modulus and compressive yield strength of the foams. The relationship between the Young's modulus and compressive yield strength with the relative density of the foams is found to obey a power law relation.

**Keywords:** Metal foams, Powder metallurgy, Cr-Si-Ni-Mo steel, Sintering, Space holder

Metal foams are a new class of engineering materials. They have low densities, high impact energy absorption, unusual acoustic properties, low thermal conductivity and high stiffness. Metal foams are widely used in thermal and sound insulation, lightweight constructions, vibration damping and in biomedical applications. The application depends on their macroscopic structure (pore size and porosity) as well as the mechanical properties (yield strength, Young's modulus and hardness). The ability to tailor the macroscopic structure of the foams as well as their microstructure is desirable and can determine their application<sup>1-8</sup>.

A wide range of methods are currently used in manufacturing metallic foams, including liquid foaming<sup>3</sup>, powder metallurgy<sup>3</sup>, electrochemical deposition, sintering of loose powders<sup>9</sup>, rapid prototyping<sup>10</sup>, slurry sintering and vapour deposition techniques<sup>3</sup>. In general, there are mainly two basic manufacturing methods for the metal foams: Liquid state processing and solid state (powder metallurgy) processing<sup>1-3</sup>. The liquid state based techniques have been used for the production of Al, Zn and Pb based foams due to low reactivity and low melting points. On the other hand, liquid state processing techniques for steel foams are more difficult to apply due to their high melting points. Solid state based powder metallurgy method can produce porous steel parts at

much lower temperatures<sup>6-8</sup>. Among the powder metallurgical metal foam production techniques, the space holder-sintering method can yield highly porous parts with desirable pore size, shape and volume using an appropriate space holder material. The space holder-sintering method consists of four sequential steps; mixing of the metal powder, polymeric binder and space holder, compaction of the mixture, removal of the space holder from the green body and sintering.

Sodium chloride<sup>11,12</sup>, carbamide<sup>4,6,13,14</sup>, carbonate<sup>15,16</sup>, magnesium<sup>17,18</sup> and several polymers<sup>2</sup> were used as space holder materials for manufacturing metal foams. However, there were certain drawbacks in the use of such materials. For example NaCl could cause undesirable corrosion to the base metal, while the removal of polymeric materials or carbonate release environmentally dangerous by-products during the decomposition. Additionally, they may leave residue and cannot be removed completely. Carbamide was successfully used to produce highly porous metal samples<sup>4,6,13,14</sup>. Powder metallurgy based space holder-sintering technique has been used to manufacture highly porous metals such as stainless steels<sup>4-8</sup>, titanium alloys<sup>4,18,19</sup>, magnesium<sup>13</sup>, Fe-26Cr-1Mo steel alloy<sup>12</sup> and superalloys<sup>4</sup>.

In the space holder-sintering technique, the crucial step is removal of the space holder from the green compacts. Wen *et al.*<sup>13</sup> manufactured 78% porous Ti and Mg foams by using space holder and sintering method. They used carbamide and ammonium

\*Corresponding author (E-mail: imutlu@istanbul.edu.tr)

hydrogen carbonate as space holder material and thermally removed the space holders at 200°C. Bakan<sup>6</sup> introduced a water leaching and sintering method to remove the space holder (carbamide) from AISI 316L stainless steel green compacts. Bakan removed the carbamide in water at room temperature. Later Gulsoy and German<sup>8</sup> removed carbamide from green specimens using the same method. Water leaching-sintering method is especially attractive because water is non-toxic and non-flammable. As an additional benefit, the equipment necessary for water leaching is very simple.

Steel foams compete with existing traditional solid non-porous materials and recently commercialised aluminium foams. Steel foams are promising materials for civil engineering and construction, crash protection, packaging and shipbuilding. The energy-absorption properties of steel foams are comparable with those of aluminium and their lower cost makes them potential competitors.

Ancorsteel 4300 alloy is a high performance Cr-Si-Ni-Mo steel alloy that simulates wrought steel compositions and can be processed at low sintering temperatures. Excellent strength, fatigue, and toughness characteristics in single press-single sinter condition provide a cost-effective alternative to alloys that require secondary heat treatments. Under a typical reducing atmosphere it contains low oxygen content. Other advantages of this alloy include good compressibility, high hardening capacity and dimensional stability<sup>20-22</sup>. King and Lindsley<sup>21</sup> manufactured high-density Cr-Si-Ni-Mo steel alloy specimens by powder metallurgy technique and determined the compressive strength and Young's modulus of the specimens. However, there is no study on highly porous Cr-Si-Ni-Mo steel alloy in the literature.

In this study, Cr-Si-Ni-Mo based steel alloy specimens having porosities in the range of 39-72% were produced using powder metallurgy based space holder-water leaching technique. The specimens were compressively tested in order to obtain a better understanding of compressive behaviour in the light of the microstructure examination.

### Experimental Procedure

Metal foams were produced by space holder-water leaching method using Cr-Si-Ni-Mo based Ancorsteel 4300 powders, which is a registered trademark of Hoeganaes, USA. Figure 1 shows scanning electron microscope (SEM), Jeol JSM 5600, image of the steel powder.

The powder premix consisted of 98.65% irregular shaped Ancorsteel 4300 steel powder, 0.75% Acrawax (lubricant) and 0.6% C. The chemical composition of the Ancorsteel 4300 powder was Fe -1.0% Ni, 1.0% Cr, 0.8% Mo, 0.1% Mn, 0.1% O and 0.6% Si. Apparent, tap and pycnometer (true) densities of the steel powder were determined to be 3.15 g cm<sup>-3</sup>, 3.94 g cm<sup>-3</sup> and 7.78 g cm<sup>-3</sup> respectively.

As a space holder material, carbamide was used for its very high solubility in water. Spherical carbamide particles, supplied by Merck, Germany, had a density of 1.34 g cm<sup>-3</sup>, melting temperature of 133°C, and solubility in water at 20°C of more than 1000 g L<sup>-1</sup>. Spherical carbamide particles were crushed and sieved to obtain the fraction of -1000+710 µm with irregular shape. The weight ratios of the steel powder to the carbamide were calculated to obtain defined porosities in the range of 40-70% in the specimens. The binder for green strength was polyvinyl alcohol (PVA), supplied by Merck, Germany. Initially, PVA solution, which consists of 2.5 wt% PVA and water, was added to the steel powder as a binder. The steel powder and 6 wt% PVA solution were mixed manually. Mixing of the steel and carbamide powders were performed in a Turbula mixer for 45 min. The mixture then compacted at 180 MPa into cylindrical specimens with a diameter of 12 mm and heights of 15-20 mm. The green specimens were immersed in distilled water at room temperature to leach the carbamide. About 90% of the carbamide was leached in 8-12 h, as confirmed by weighing the specimens before and after the space holder removal step.

Thermal debinding temperature of the PVA was determined to be 410°C by using thermo gravimetric

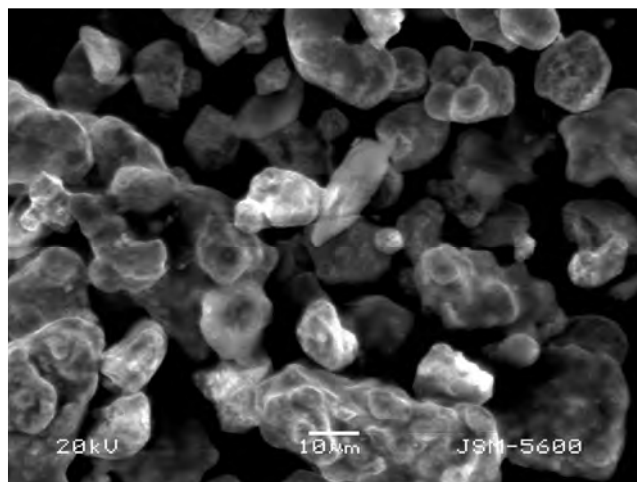


Fig. 1—SEM image of the Ancorsteel 4300 powder

analysis (TA, SDT Q600) at a constant heating rate of  $5^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere. The PVA in the green specimens was thermally removed as part of sintering cycle, which consisted of heating at a ramp rate of  $5^{\circ}\text{C min}^{-1}$  to  $410^{\circ}\text{C}$  with a dwell time of 40 min (debinding stage), followed by heating at rate of  $10^{\circ}\text{C min}^{-1}$  to sintering temperatures. The specimens were sintered at 1150, 1200 and  $1250^{\circ}\text{C}$  for times of 30, 45 and 60 min. The sintering cycle was performed in high purity hydrogen in a horizontal tube furnace (Lenton, UK).

Densities (total porosity) of the sintered specimens were determined from measurements of weight and dimensions of the specimens (geometric method). Open porosity was measured by mercury intrusion porosimeter (Quantachrome Poremaster). The pore morphology of the porous specimens was examined by using the SEM. Size, size distribution and shape of the pores were determined by using commercial image analyser software, Clemex Vision PE. The area of each pore on the SEM image was calculated, and then spherical diameter as pore size and sphericity as pore shape were determined.

For microstructural investigation, porous specimens were moulded, using Stuers, Epovac vacuum impregnation unit, into a resin to fill the pores. The moulded specimens were grinded, polished and then etched by Nital. The microstructures of the specimens were examined using Nikon, ME600 optical microscope.

Mechanical properties of the specimens were studied by the compression tests performed on a Zwick-Roell Z050 materials testing machine. Compression tests were carried out at a crosshead speed of  $0.5 \text{ mm min}^{-1}$ . The stress was calculated using the apparent cross-sectional area of the respective specimen, after which Young's modulus for each

specimen was determined from the slope of the corresponding stress-strain graph. Hardness was measured by using a Vickers micro-hardness tester (Clemex) using a test load of 50 gf. Before the hardness test the porous specimens were moulded, using Stuers, Epovac vacuum impregnation unit, into a resin to fill the pores.

## Results and Discussion

Cr-Si-Ni-Mo steel specimens with porosities ranging between 39 and 72% were produced by space holder-sintering technique. Total porosity of the foams consisted of 10-25% closed and 75-90% open porosity. Open porosity content increased with increasing total porosity. Open porosity content of 72 and 39% porous specimens was 10 and 25% respectively. The pore shape replicated the initial shape of the carbamide particles that were used to as space holder material. Porosities of the sintered specimens increased with increasing space holder content. Figure. 2 shows the 60 and 72% porous specimens.

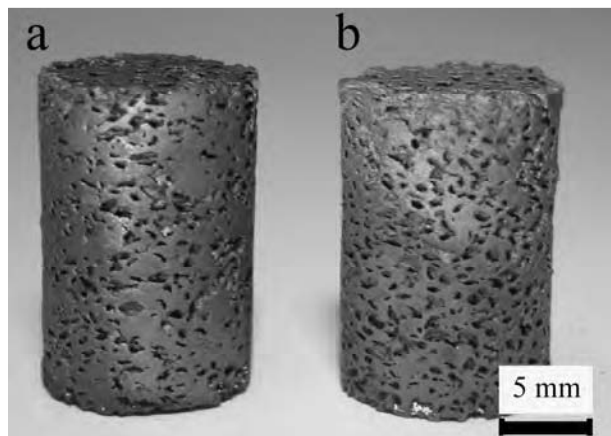


Fig. 2—Specimens sintered at  $1250^{\circ}\text{C}$  for 60 min (a) 60% porosity and (b) 72% porosity

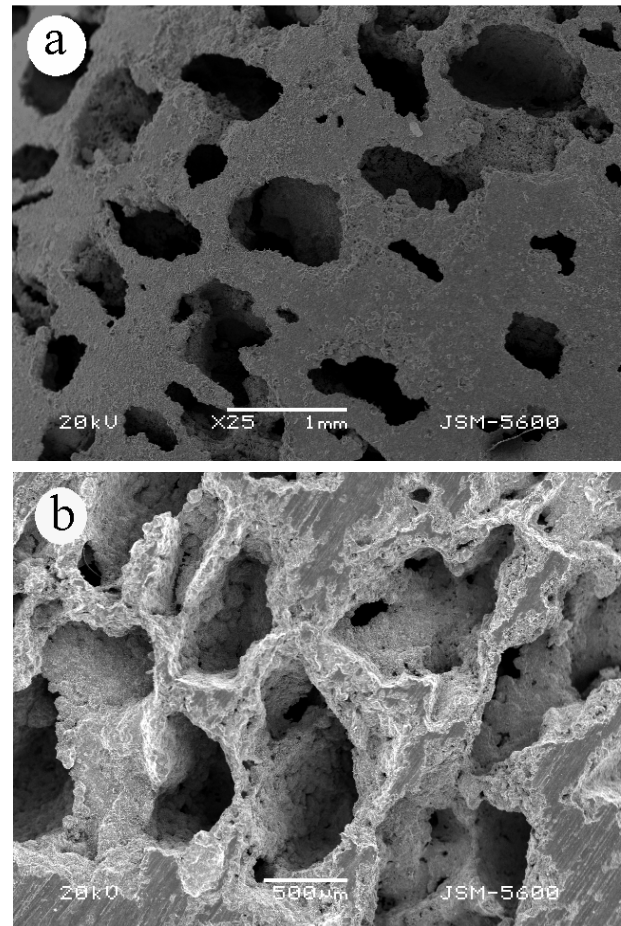


Fig. 3—SEM images of the 72% porous Cr-Si-Ni-Mo steel specimens (a) surface and (b) inner section

SEM images obtained from the surface and inner section of the sintered specimen having 72% porosity are provided in Fig. 3 and show a relatively uniform distribution of pores. Cell-walls separating each pore from its neighbouring can be clearly seen. In spite of sintering between the steel particles, the macro-pore framework remained with a small shrinkage. In all specimens, morphology of the final pores was similar to that of the carbamide powder particles. This suggests that pore structures can be designed by using proper size, shape and content of carbamide particles.

The SEM images of the porous specimens were also used to determine the mean pore size, size distribution and shape by the image analyser software. Figure 4 shows the pore size distribution in terms of spherical diameter. Mean pore size was  $\sim 607 \mu\text{m}$ . Mean sphericity of the pores and the carbamide particles was determined to be 0.56 and 0.62, respectively.

Optic microscope images from the cell walls of the highly porous Cr-Si-Ni-Mo steel specimens are shown in Fig. 5 and consist of martensite, bainite and pearlite. In the micrographs, the bright regions are martensite, and the darker regions are bainite. The images show that high levels of martensite can be obtained at moderate cooling rates ( $\sim 2.5^\circ\text{C s}^{-1}$ ). Some austenite is also present in the microstructure due to the presence of nickel. The amount of austenite and pearlite in the microstructure was quite low. In addition micro-pores are visible due to incomplete sintering. Increasing sintering temperature, sintering time and cooling rate increased the martensite content.

The compressive stress-strain curves of steel specimens, having porosities in the range of 39-72%, are illustrated in Fig. 6. Three distinct regions

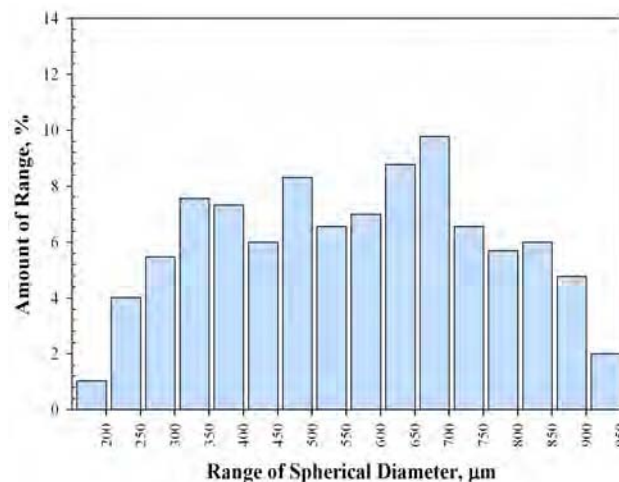


Fig. 4—Spherical diameter (pore size) distribution of 72% porous specimens

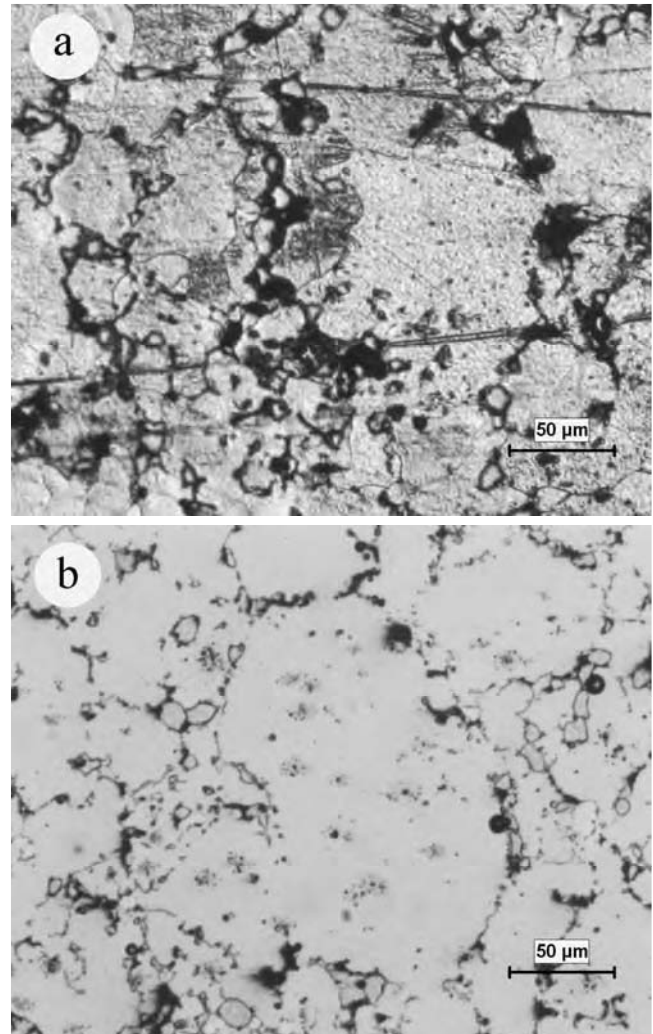


Fig. 5—Optic microscope images from the cell walls of the porous specimens (a) sintering at  $1150^\circ\text{C}$  and (b) sintering at  $1250^\circ\text{C}$

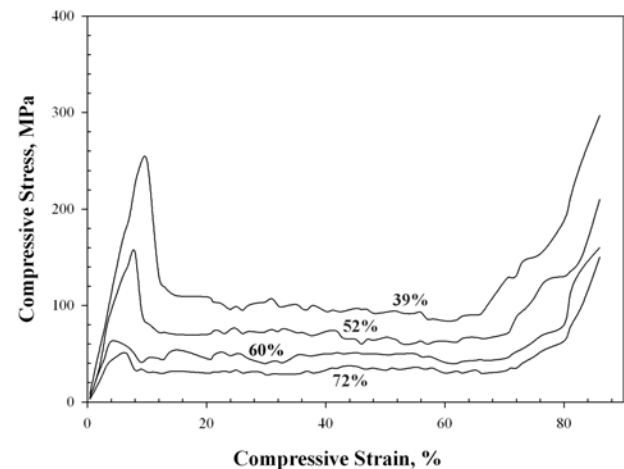


Fig. 6—Compressive stress-strain curves of the specimens having porosities in the range of 39-72% (sintering at  $1250^\circ\text{C}$  for 60 min)

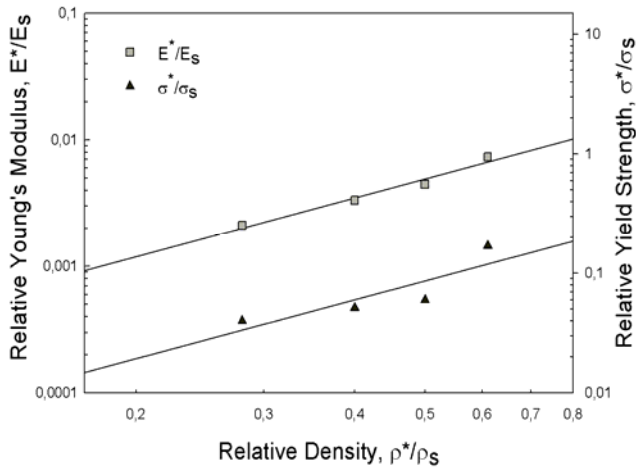


Fig. 7—Change of relative yield strength and relative Young's modulus with relative density of the porous specimens (sintering at 1250°C for 60 min)

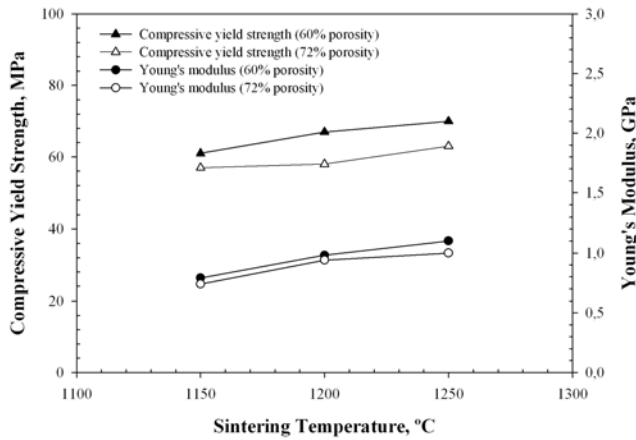


Fig. 8—Effect of sintering temperature on the Young's modulus and compressive yield strength of the porous Cr-Si-Ni-Mo steel specimens (sintering time: 60 min)

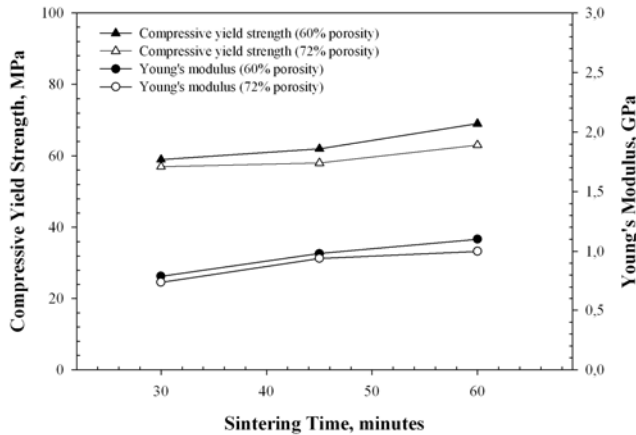


Fig. 9—Effect of sintering time on the Young's modulus and compressive yields strength of the porous Cr-Si-Ni-Mo steel specimens (sintering temperature: 1250°C)

characterized the curves; an elastic region where cell walls bending occur; a large plateau region and a densification region where the flow stress rapidly increases. The stress, after a first maximum, drops significantly as a result of the collapse of a pore layer. Once the cell edge collapses at the yield point, the collapsed edge has little ability to bear the load and bends easily by a low stress. The deformation mode, resulting from repeatable failure of the pore layers, gives rise to very uneven character of the stress-strain curve. At the end of the plateau region, stress starts to increase since the pores at the deformation zone have flattened and the material shows bulk-like properties. Compression tests of the porous specimens showed that the compressive yield strength values decreased and length of the plateau region increased with increasing porosity content. Compressive yield strength of specimens containing porosities in the range of 39–72% was observed to vary between 24–290 MPa. The resultant Young's modulus was between 0.20–5.21 GPa.

In Fig. 7, the data of relative compressive yield strength and relative Young's modulus of the 60% porous specimens were plotted against the relative density and given rise to the Eqs (1) and (2) for specimens sintered at 1250°C for 60 min.

$$\left(\frac{E^*}{E_s}\right) = 0.03 \left(\frac{\rho^*}{\rho_s}\right) \quad (R^2 = 0.94) \quad \dots (1)$$

$$\left(\frac{\sigma^*}{\sigma_s}\right) = 0.37 \left(\frac{\rho^*}{\rho_s}\right)^{1.73} \quad (R^2 = 0.93) \quad \dots (2)$$

where  $\sigma^*$ ,  $E^*$  and  $\rho^*$  are the compressive yield strength, Young's modulus and density of the porous specimens respectively, while  $\sigma_s$ ,  $E_s$  and  $\rho_s$  are the corresponding properties of the bulk non-porous Cr-Si-Ni-Mo steel alloy. The density, yield strength and Young's modulus of the bulk materials were taken as 7.81 g cm<sup>-3</sup>, 470 MPa and 207 GPa, respectively<sup>23</sup>. It is clear that the relative density mainly affects the yield strength and Young's modulus. The proportionality constants and the exponent values depend on foam characteristics, such as cell morphology, shape and arrangement of cell walls. Imperfections, such as broken walls, large pores, anisotropic pore structure and non-uniform foam density and micro-pores in cell walls significantly affect the mechanical properties.

Figure 8 shows the effect of sintering temperature and Fig. 9 shows effect of sintering time on the

Young's modulus and compressive yield strength of the porous specimens. Young's modulus and compressive yield strength increased with increasing sintering temperature and time. Increasing sintering time and temperature help densification of the cell walls that results increase in the Young's modulus and compressive yield strength. Hardness of the sintered and furnace cooled specimens was ~290 HV. Increasing the cooling rate to  $\sim 2.5^{\circ}\text{C s}^{-1}$  increased the hardness to ~350 HV.

### Conclusions

Cr-Si-Ni-Mo steel foams having porosities in the range of 39-72% with an average pore size of  $\sim 607\ \mu\text{m}$  was successfully fabricated using the space holder-water leaching technique in powder metallurgy. The final porosity was related to the added fraction of carbamide. Pore shape was similar to initial carbamide particle shape. Morphology of the pores can be controlled by selecting an appropriate carbamide particle type. In addition it is also possible to obtain a tailored pore size distribution in the highly porous specimen by using carbamide having a different particle size range. Microstructure of cell walls of the porous specimens consists of martensite, bainite and some pearlite. In this porosity range, Young's modulus and compressive yield strength of the specimens found to be in the range 0.20-5.21 GPa and 24-290 MPa, respectively and decreased with increasing porosity. Increasing sintering temperature and sintering time and decreasing porosity enhanced the Young's modulus and compressive yield strength. The relationship between the Young's modulus and compressive yield strength with the relative density of porous steel was found to obey a power law relation.

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