Microstructural Characterization of Magnetic Freeze Cast Scaffolds

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Freeze Casting: In the freeze-casting method, ceramic powders are mixed with water (Fig. 1a) and directionally frozen. As water freezes ice columns form and the ceramic particles are pushed between the columns forming lamellar walls (Fig. 1b). Then the frozen sample is sublimated to remove the ice (Fig. 1c), and sintered to strengthen the scaffolds (Fig. 1d)[1]. Since the ceramic columns, called **lamellar walls**, are aligned in ice growth direction, the maximum strength is in this direction.

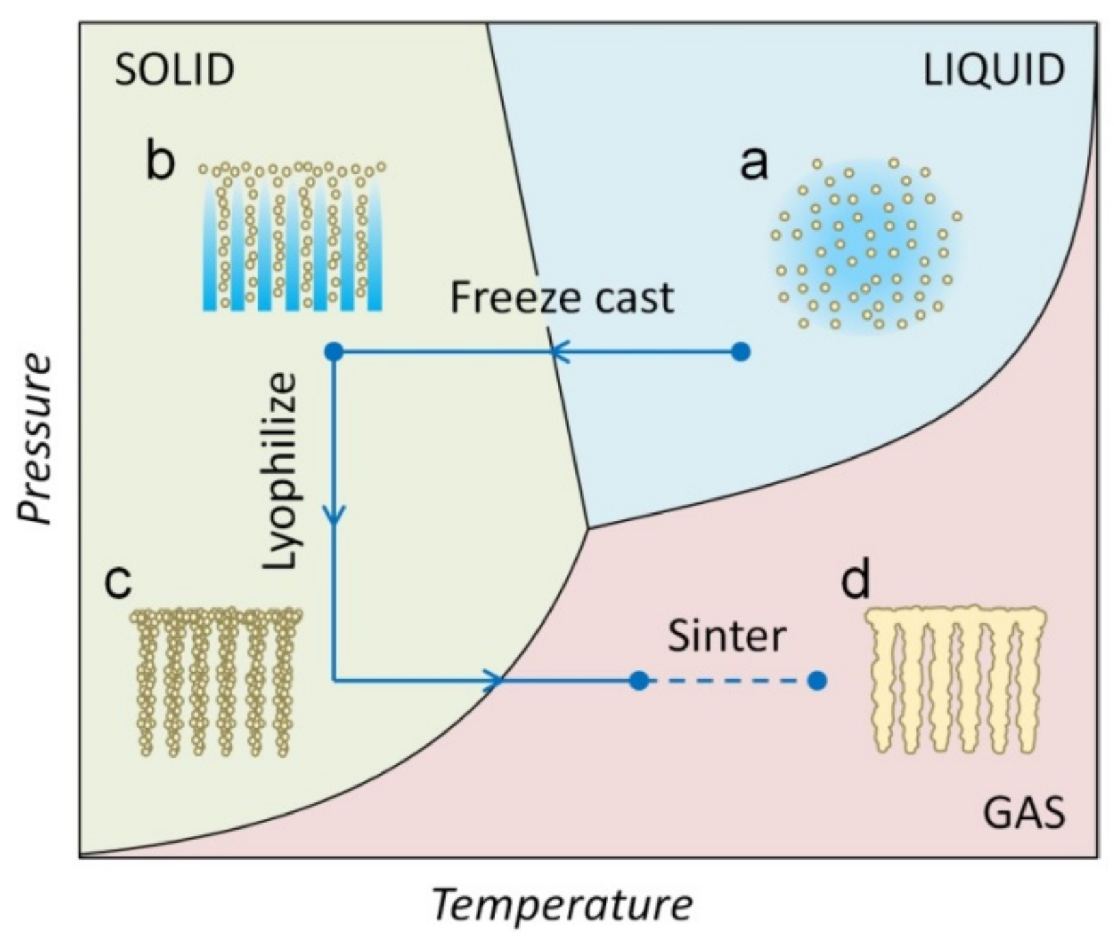

Fig. 1 Freeze casting process [1]

In literature [2] it is shown that the lamellar wall spacing and alignment are related to the scaffold strength. So, by controlling the lamellar wall spacing and alignment (or other microstructures), the mechanical properties of the scaffolds can be tailored.

Magnetic Freeze Casting: To enhance the strength of freeze cast scaffolds perpendicular to ice growth direction, an external magnetic field is applied (Fig. 2) in addition to adding Fe_3O_4 to slurry. This will align mineral bridges (Fig. 3) in the direction of the magnetic field, which enhances its strength in this direction. Ceramic particles with different magnetic susceptibilities, behave differently in a magnetic field. These particles are listed in Table 1. The TiO_2 structure was uniform in a magnetic field, while the others formed a biphasic structure.

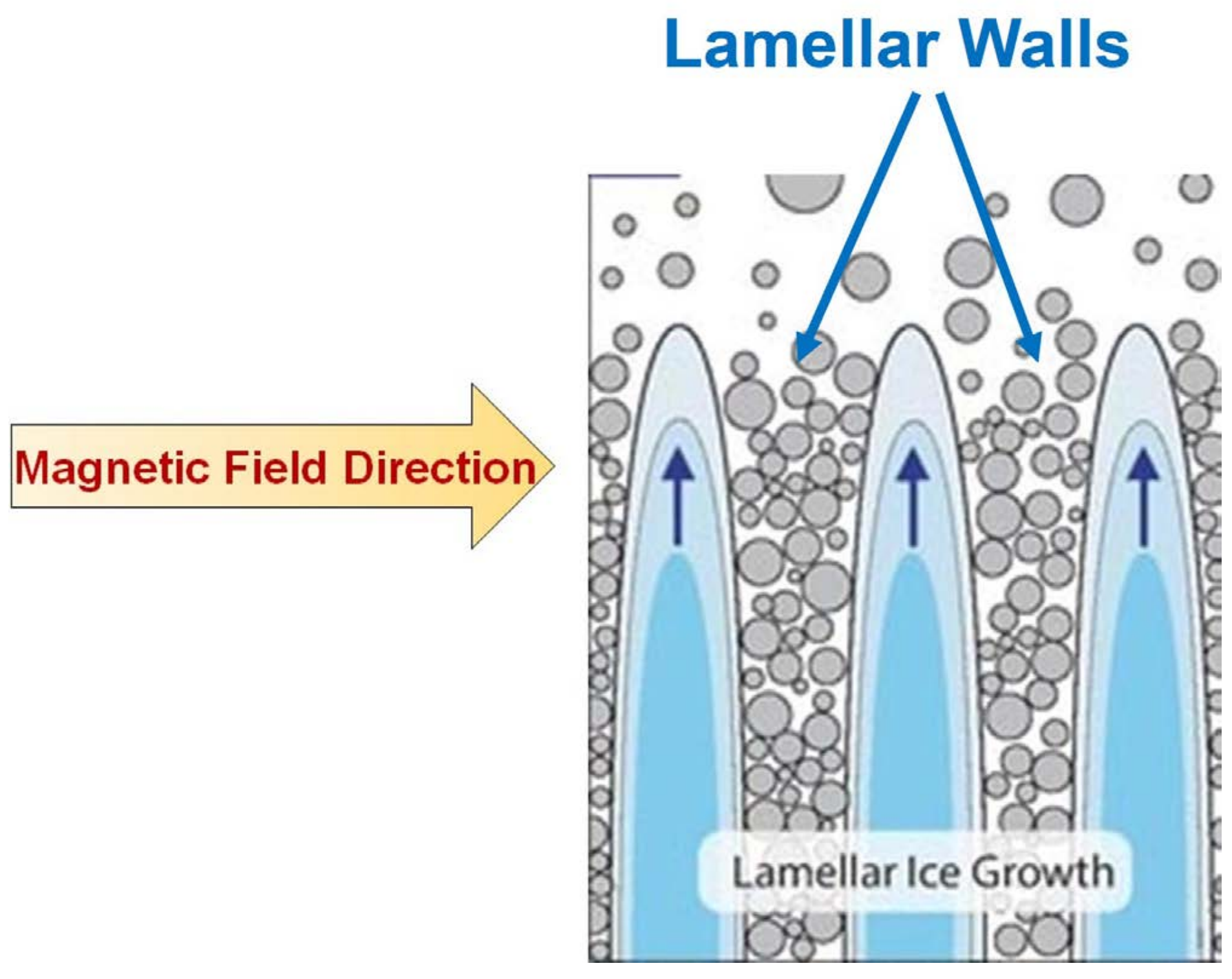

Fig. 2 Ice growth process

The different behaviors of these materials created different microstructures which could lead to a variety of different mechanical properties.

Table 1. Different ceramic particles that have been investigated for 3wt.% Fe_3O_4 and 10vol.% ceramics with a 10°C/min cooling rate.

Category	Material	Density (g/m^3)	Particle size (micron)	Magnetic susceptibility ($10^{-6}\,c.g.s$)	Image
Paramagnetic material	Titanium dioxide - **TiO2**	**4.26**	**0.20-0.50**	**+5.90**	
	Cerium oxide - **Ce2O3**	**7.65**	**1.00-3.00**	**+26.00**	
	Yttrium oxide - **Y2O3**	**5.01**	**0.05**	**+44.40**	
	Magnetite- **Fe3O4**	**4.95**	**<0.05**	**+3,586.00**	
Diamagnetic material	Aluminium oxide- **Al2O3**	**4.00**	**2.00-5.00**	**-37.00**	
	Hydroxyapatite - **HA**	**3.15**	**1.00-3.00**	**-46.00**	
	Zirconium dioxide – **ZrO2**	**5.89**	**0.20-0.50**	**-13.80**	

Characterizing: The first step was to characterize the microstructures of the scaffolds fabricated under different processing conditions. ImageJ software was used to characterize the microstructures. These characteristics are illustrated in Fig. 3. The results of these measurements are plotted in Fig. 6, which shows the processing conditions (magnetic field strength) and microstructures (mineral bridge length and orientation).

Processing Conditions
(concentration, freezing velocity...)
→
Microstructure
(Lamellar wall, mineral bridges)
→
Mechanical Properties
(Strength, toughness)

References:

[1] Deville S. "Freeze-casting of porous ceramics: A review of current achievements and issues". *Advanced Engineering Materials* 2008
[2] S. Flauder et al. "Structure and mechanical properties of B-TCP scaffolds prepared by ice templating with preset ice front velocities". *Acta Biomaterialia*, 2014
[3] M.M. Porter, P. Niksiar, J. McKittrick, "Microstructural control of colloidal ceramics by directional solidification under weak magnetic fields", Submitted to *Journal of the American Ceramic Society*
[4] S.S. L. Peppin et al. "Morphological instability in freezing colloidal suspensions". *Proceedings of Royal Society,* 2007

In fig. 4, the alignment of lamellar walls in different sections of the scaffolds are shown. Any attempt to align these sections in specific directions could increase the strength and stiffness of the scaffolds in the transverse direction.

Linear Instability Analysis:

When the freezing front velocity is slow, a planar ice front pushes the particles away and two separate phases are formed (Fig. 5(a)). Peppin et al.[4] derived Equation 1 by applying the conservation of mass law, using linear stability analysis. They solved Equation 1 numerically and showed that the freezing interface can become unstable due to constitutional supercooling. The wavelength of the of instabilities, $\boldsymbol{\alpha}$ (Fig. 5(b)) , which is the space between two adjacent lamellar walls, is related to the particle size, concentration, water latent heat, water density and temperature gradient. In turn, scaffolds with smaller lamellar spacing have a higher strength [2].

D is a mutual diffusion coefficient which depends on particle size, temperature and viscosity of the fluid. Z is ice growth direction, C_1 is the amplitude of perturbation, C is the concentration, and $\boldsymbol{\sigma}$ is growth rate of disturbance.

$$D(C)\frac{d^2c_1}{dz^2}+(1+2D_C\overline{C_Z})\frac{dc_1}{dz}+(D_C\overline{C_{ZZ}}+D_{CC}\overline{Cz^2}-\sigma-D\alpha^2)c_1=0 \qquad (1)$$

Research Plan: The relationship between different processing conditions and microstructure have been demonstrated under different magnetic fields, Fe_3O_4 concentrations and the mineral bridge lengths and orientations [3]. Data for different susceptibilities, magnetic field strengths, and particle sizes are also being gathered. Finding the relationship between the processing conditions and microstructural characteristics, which are listed in Table 2., is the next step. The candidate method is Dimensional Analysis.

Conclusion: By controlling the processing conditions, the mechanical properties of magnetic freeze cast scaffolds can be tailored. The magnetic susceptibility of the ceramics is going to be investigated to find its relationship with the other parameters on the microstructure of the scaffolds. Finding this relationship may provide the ability to fabricate materials with desired mechanical properties, just by adjusting the processing conditions.

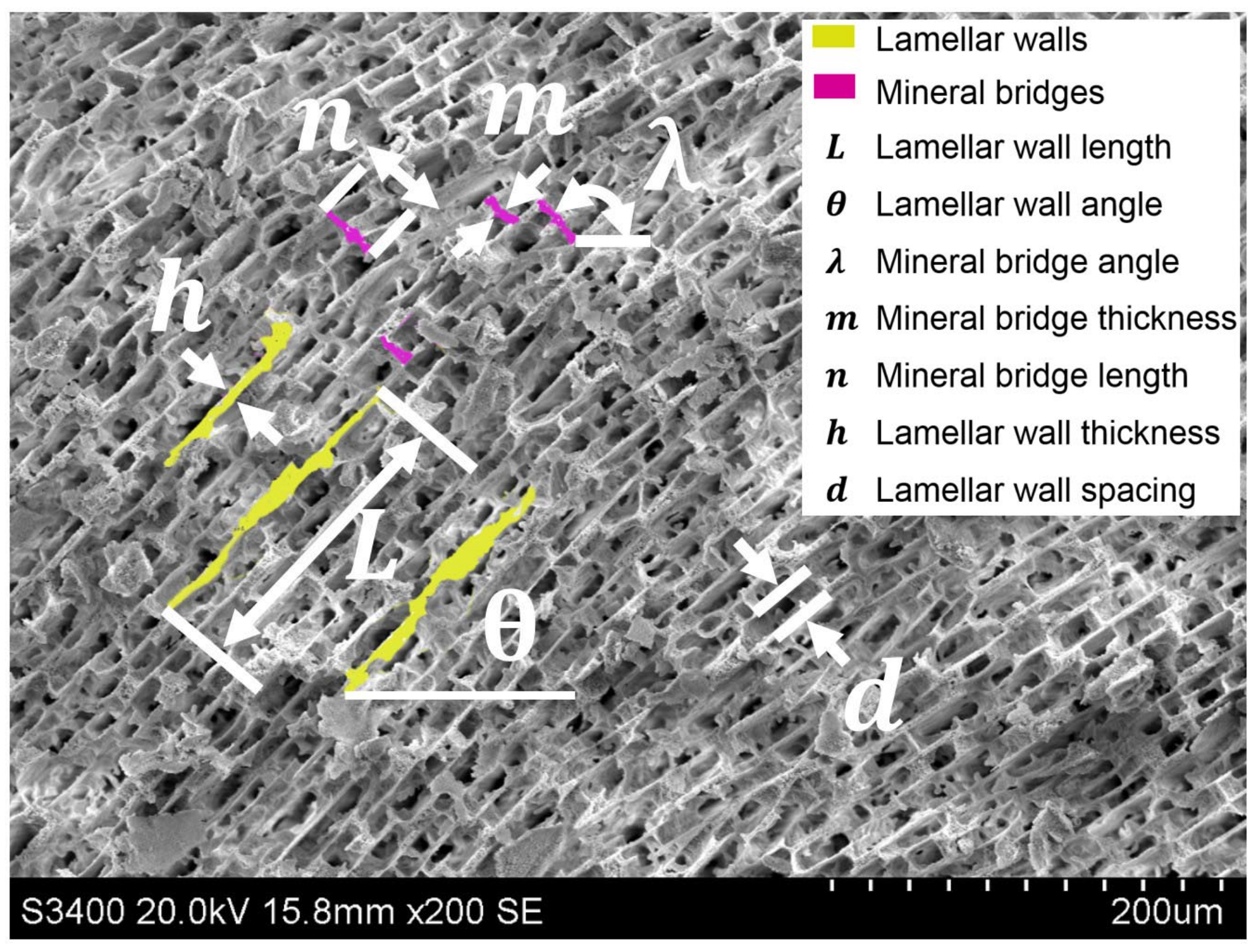

Fig. 3 Microstructural characteristics

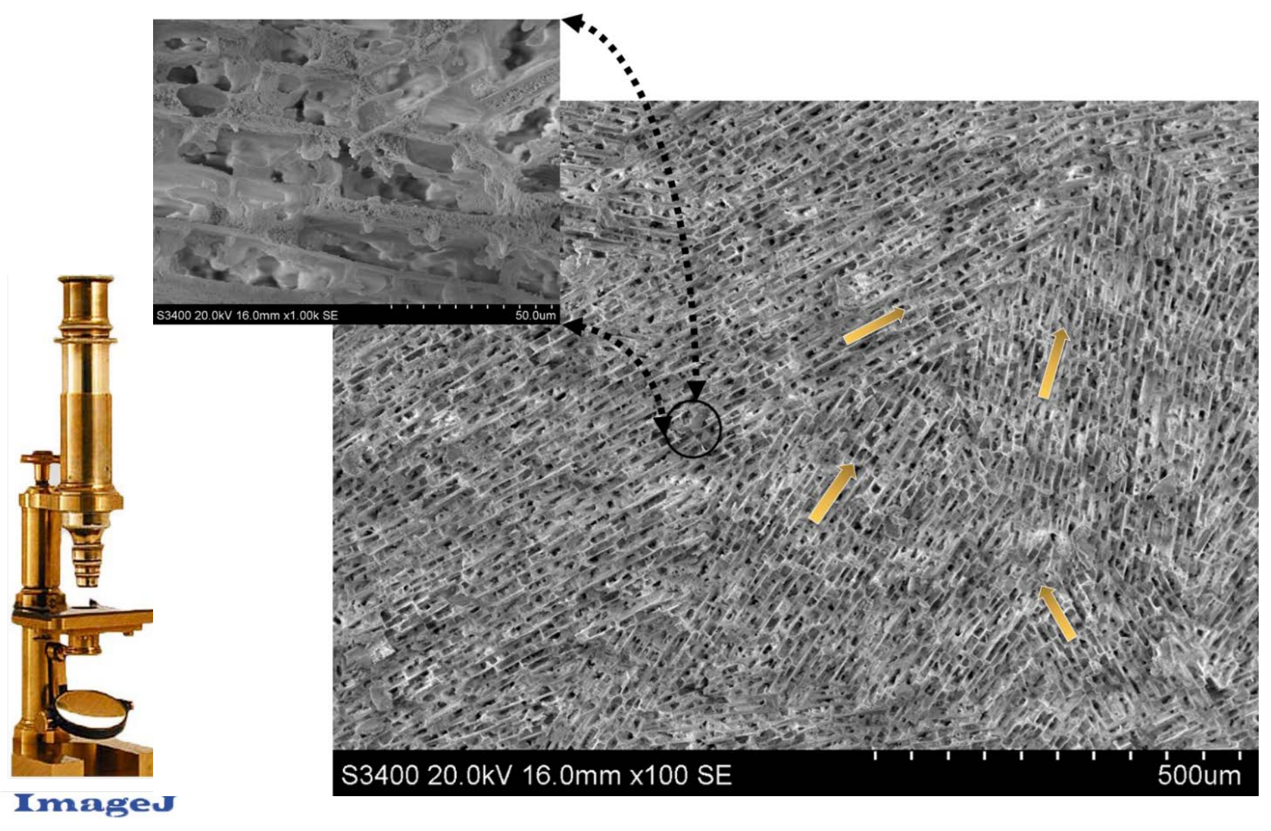

Fig. 4 Alignment of lamellar walls in several sections of a magnetic freeze cast scaffold

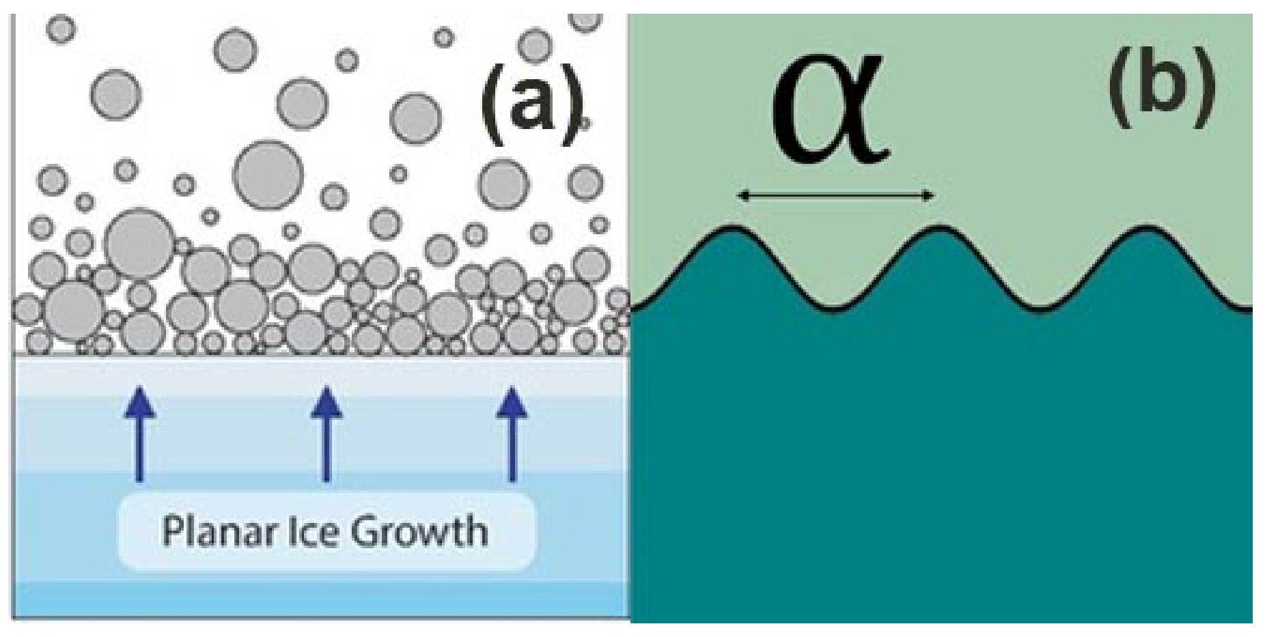

Fig. 5 Planar ice growth vs. lamellar wall pattern due to instabilities in the freezing front

Table 2. Controllable input and characteristic output variables in Magnetic Freeze Casting

Input processing conditions	Output microstructural characteristics
Particle density	Lamellar spacing
Particle size	Mineral bridge length
Particle concentration	Lamellar wall length
Latent heat of water	Mineral bridge thickness
Density of water	Lamellar wall thickness
Temperature gradient	Mineral bridge angle
Cooling rate	Lamellar walls angle
Magnetic field strength	
Magnetic susceptibility	
Viscosity	

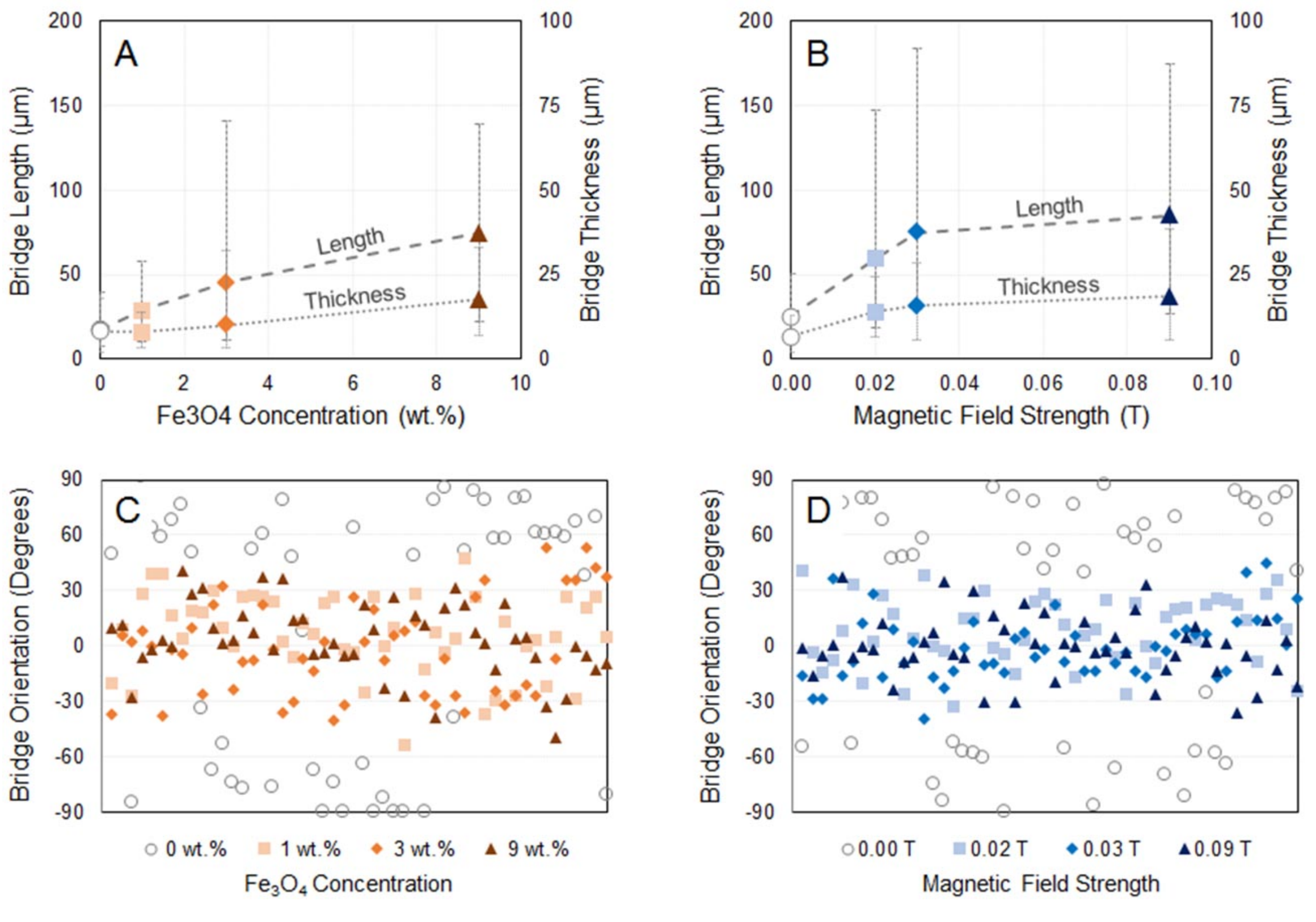

Fig. 6 Mineral bridge length and orientation vs. magnetic field strength and Fe_3O_4 concentration. [3]