Correlation between ultrasound velocity, density and strength in metal-ceramic composites with added hollow spheres

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Abstract. Ultrasound velocity is known as a non-destructive predictor of strength in some construction materials like concrete. In multi-phase materials, where the physical properties of components differ by orders, the strength prediction becomes more ambiguous due to more complicated interactions between the components. As an example of such material, sintered metal-ceramic composites with added hollow spheres were taken. The matrix was a mixture of powdered iron and clay, where hollow admixtures were cenospheres or microspheres of fly ash. By varying the iron-to-clay ratio, sintering temperature and cenospheres content, 17.4% variation of the bulk density ρ and 35.3% variation of the compression strength σ were achieved. Ultrasound velocity C was measured in cylindrical specimens and showed 8.6% variation. All mentioned parameters positively correlated with each other. The relationship between C and σ had expressed non-linear character. Normalization of the relationship by ρ helped improving the C-σ correlation. The non-linear monotonous function $C = ρ^{-2} \cdot σ^{-4}$ provided the closest correlation with the Spearman rank correlation coefficient 0.942 and the Pearson linear correlation coefficient 0.943. The hollow spheres content was the main determinant of density ρ in this material.

1. Introduction

Innovative materials offer growth of application opportunities in machinery, construction, transport and other fields. During the recent decades, promising expectations have been assigned to a diversity of types of syntactic foams [1]. Metal matrix composites and metal/ceramic composites are designed to reduce weight and costs of products maintaining high strength properties [2]. Addition of hollow particles such as fly ash cenospheres into metal matrix composites and syntactic foams may significantly reduce the total weight of the composite and increase its impact absorption properties [3]. On the other hand, the addition of hollow particles results in decrease of the mechanical strength as the effect similar to increased porosity [4]. The trade-off between the achieved lightweight, low costs and the necessary strength is an important issue in designing of the syntactic foams with hollow fillers.

Non-destructive evaluation of the mechanical properties of syntactic foams and strength prediction can be valuable components of the material development and testing. Ultrasonic examination based on measuring of quantitative parameters of ultrasound propagation, the most commonly, ultrasound velocity also called as ultrasound pulse velocity and speed of sound has proven itself in different testing applications. The most widely the method has been used for examination of cementitious materials, particularly, concretes [5]. Correlations between ultrasound velocity and compression strength of concretes are well established and are put into testing standard and serve as a basis for ultrasonic testing [6]. Usually, this correlation is of a non-linear type that is explained by both non-linear dependences of
ultrasound velocity on the elasticity modulus (as follows from the theory of elasticity and experiment, the velocity is proportional to the square root of the elasticity modulus [7] and of the elasticity modulus versus the strength [8]. Various authors offer empirical dependences of the strength on the velocity, the most commonly described by the equation: \( \sigma = a \exp(b \cdot C) \), where \( \sigma \) is strength, \( C \) is ultrasound velocity; \( a \) and \( b \) are empirical coefficients for different compositions and conditions, such as dry or wet [9].

There were attempts to apply ultrasonic measurements for properties characterization in syntactic foams. Influence of volume fraction of different components, particularly, micro-balloons on ultrasound longitudinal and shear wave velocities and attenuation has been demonstrated [10]. However, the creation of a generalized strength prediction model based on the ultrasonic parameters is difficult due to complex influences of the composition, structure, and interaction between components in the multiphase material. The inclusion of cenospheres - hollow gas-filled particles in a high concentration may create unexpected effects.

The purpose of the study was to test the applicability of ultrasound velocity measurements for the strength prediction in metal-ceramic composites with hollow particles (cenospheres) and investigate the empirical correlation. The variables that affected density and strength of the material were the metal-ceramic ratio, the presence or absence of the cenospheres content, and the sintering temperature, i.e. the factors related to composition, structure and manufacturing technology.

2. Materials and methods

2.1. Composite specimens

The purpose of material selection was to provide such range of specimens, where the variation of strength was determined by influence of three independent factors: composition of the metal-ceramic base, bonds between the metal and ceramic components and presence of hollow particles as a low density filler. Previous attempts have demonstrated the feasibility of fabrication of such metal-ceramic syntactic foams with cenospheres with compression strength varying in the range 150-340 MPa [11]. In the present study, two variations of the metal-ceramic compositions were laid – with the weight ratios of raw iron powder to clay 1:1 and 2:3. The ceramic materials was natural homogenised illite red clay from Liepa deposition (Lode JSC, Liepa, Latvia). The homogenised clay was dried at 105 °C for 24 h, milled with a RETSCH PM 400 (Retsch, Haan, Germany) ball mill for 15 min, and sieved to limit the particle size to <100 \( \mu \)m. The bonds within the ceramic component and between the ceramic and metal components were affected by gradual variation of sintering temperature. Four grades of sintering temperature were applied – 1050, 1100, 1150 and 1180 °C, stopped at the maximum above which burning of clay was possible. The hollow particles were cenospheres – waste or byproduct of coal burning at thermal power plants presenting hollow air-filled spheres obtained from Biotecha Latvia Ltd (Riga, Latvia). The cenospheres are typically sized 0.1 – 0.3 mm in diameter with a silica wall 10 – 30 microns thick and have bulk density in the range of 0.4 – 0.8 g/cm\(^3\). Chemical and grading compositions for the applied clay and cenospheres were described in details in the previous studies of the authors [11, 12]. Cenospheres were uniformly mixed to one part of specimens with the weight ratio to the rest metal-ceramic content of 2:5, while another part of specimens contained no cenospheres. Introduction of cenospheres had the purpose to reduce total bulk density of the composite making it more lightweight, but compromising the material strength to some extent. The groups of specimens were designated according to the ratios of bulk weights of three components in raw mixtures before sintering: M, C and S, where M – is metal (iron) powder; C – is clay or ceramic component; and S – is cenospheres content. Four basic groups were formed: MCS 4-6-4; MCS 5-5-4; MCS 4-6-0; and MCS 5-5-0 with corresponding ratios of M, C and S components. Two first groups contained cenospheres and two last groups were composed only of metal and ceramics. Each group was divided into subgroups by 4 mentioned grades of sintering temperature. Each subgroup contained 5 identical specimens. Thus, the total number of specimens reached 4x4x5 = 80. The sintered specimens had cylindrical shape with a diameter 19 mm and a height in the range of 16-20 mm depending on the shrinkage during sintering.
2.2. Ultrasonic testing

Ultrasonic velocity was determined by conventional pulse time-of-flight measurements using through transmission. The experiment layout is presented in figure 1. To generate and receive ultrasonic signals, a pair of miniature custom-made piezoelectric transducers was used. The excitation pulse was a two-period tone-burst sine enveloped by the Gauss function. The working frequency of 500 kHz coincided with one of resonant frequencies of the transducers. It was selected by the following reasons. Due to the presence of hollow particles and pores in the volume, the material exhibited high attenuation of ultrasound at frequencies approaching to 1 MHz and higher. It caused weak detection of the first arrival of ultrasonic signals masked by noises and being under the level of resolution. By decrease the frequency much lower 500 kHz, the ultrasonic wavelength becomes comparable with the specimen’s size that may cause undesirable manifestations of geometrical dispersion of the velocity. Ultrasonic wavelength at 500 kHz was in the range of 4-8 mm that is smaller than the specimens’ size but several times larger than the elements of internal structure – sintered metal-ceramic clusters and cenospheres – allowing to consider the medium as a continuous one.

Ultrasound velocity was calculated as \( C = \frac{D}{(t - dt)} \), where \( D \) was the specimen’s diameter, \( t \) – time-of-flight, and \( dt \) – time delay in the transducers measured at zero base. Pulse repetition time of 1 millisecond was chosen sufficient to ensure that all reverberation from multiple reflections was damped. Time-of-flight \( t \) was measured by the first arrival of the pulse and related to the fastest propagating longitudinal wave mode. Other parameters of the testing device were the following: excitation voltage 140 V peak-to-peak, sampling rate 30 MS/s, ADC 10-bit, averaging number 32, and tuneable amplification. Measurements were repeated 4 times in each specimen with replacing the transducers. The average reproducibility of ultrasound velocity was 25 m/s in specimens without cenospheres and 35 m/s in specimens containing cenospheres.

2.3. Density and strength testing

Because the specimens’ shape was a regular cylinder, it allowed determination of the bulk density by simple weighting specimens in the air and measurement of the diameter and height at several locations. After passing ultrasonic testing, the specimens were statically loaded by compression to the maximum force, after reaching of which the destruction occurred. For compression tests, a universal testing machine of Instron, model 8801, was used. Strain rate was 0.01kN/s. Compression strength was determined as the ratio of the maximum force to the specimen’s cross-section.

3. Results and discussion

The summarized data in all specimens’ dataset, including average values of ultrasound velocity, compression strength and bulk density with some statistical estimates are presented in Table 1. The data
shows the variance of all parameters, where compression strength has the highest relative variation and ultrasound velocity has the lowest one. According to the skewness estimations, the data distribution is approximately symmetric for ultrasound velocity and density (<0.5 in absolute value), but strength has a moderate positive skewness with upper values more dispersed than lower ones. Low values of kurtosis (<3 in absolute value) indicate that the values distribution is uniform for all parameters with no outlier data problems. Variation coefficients of the parameters in subgroups of specimens of the similar composition and sintering temperature (n=5) are the measures of data deviation in conditionally identical specimens. On the average in the subgroups, it was 1.99% for ultrasound velocity, 6.25% for compression strength and 1.39% for bulk density. The ratios of variation coefficients in the entire dataset of specimens to the same in subgroups was 4.3 for ultrasound velocity, 5.7 for compression strength and 12.5 for bulk density. Therefore, ultrasound velocity and compression strength had close relative variability caused by the factors of composition and sintering temperature, but it was 2-3 times higher for density.

**Table 1.** Ultrasound velocity, compression strength and bulk density in specimens’ dataset (n=80).

| Parameter, measurement units | Average value | Standard deviation | Variation coefficient (%) | Skewness | Kurtosis |
|------------------------------|---------------|-------------------|--------------------------|----------|----------|
| Ultrasound velocity (m s⁻¹)  | 3270 ± 280    | ± 8.6             | 0.05                     | − 0.91   |
| Compression strength (MPa)   | 183 ± 64      | ± 35.3            | 0.56                     | − 0.50   |
| Bulk density (g cm⁻³)         | 3.82 ± 0.66   | ± 17.4            | 0.31                     | − 1.01   |

**Figure 2.** Bulk density ρ (a), compression strength σ (b) and ultrasound velocity C (c) in groups of MCS specimens’ groups differing by their composition and sintering temperature T.

Influence of the varied factors – composition and sintering temperature on three studied parameters – ultrasound velocity, compression strength and bulk density is illustrated in figure 3 (a-c). The following common trends were revealed. All the parameters increased by increase of sintering temperature, reaching maximum at the highest temperature of 1180°C. The explanation of this fact is strengthening of bonds in the sintered components till achievement of the maximum strength and stiffness of the ceramic component. Simultaneous compaction of the material caused the increase of its density. In the relation to the specimens’ composition, all the examined parameters were higher in the specimen’s groups of higher iron content due to a higher strength, stiffness and density of iron comparing to ceramics. Addition of cenospheres in the composites had a similar effect to the introduced porosity explained by the hollow structure and low strength of cenospheres. It caused the compromised strength of the composite in the whole, as well as lower ultrasound velocity and lower density. Despite the common trends to increase with sintering temperature and increase of iron content, the changes of
each parameter had their individual peculiarities according to changes of sintering temperature and composition. It was caused, firstly, by a complex nature of the mutual dependences, and secondly, by unaccounted factors related to measurement such as non-uniformity of the specimens by the volume. Additional effects on strength can be caused by a complex interference between the components with sharply differing properties – metal powder particles, clay and cenospheres. Such effects were found for metal-cement composites with additives that manifested in voids and tiny cracks on the boundaries between the components [13].

The strength of correlation between the parameters was quantified by the Pearson product-moment correlation coefficient as the measure of linear dependence and by the Spearman’s rank correlation coefficient (Spearman’s rho), the measure of the relationship described by a monotonic function, including a nonlinear one. Cross-correlations between the examined parameters presented in Table 2 show that all the parameters are positively correlated.

| Table 2. Cross-correlations between ultrasound velocity (C), compression strength (Ϭ) and bulk density (ρ) by Pearson and Spearman. |
|---|---|---|---|---|
| Type of correlation | Pearson |  | Spearman |   |
| Parameter | Ϭ | ρ | Ϭ | ρ |
| C | 0.875 | 0.886 | 0.894 | 0.867 |
| Ϭ | - | 0.816 | - | 0.781 |

The Pearson and Spearman correlation coefficients ranging between 0.8 and 0.9 show close dependences between the parameters. Increase of ultrasound velocity is due to both increase of strength and density. The discrepancy with the theory of elasticity teaching that ultrasound velocity is inversely proportional to the square root of the density [7] is explained by the positive correlation of the density with the strength. The specimens containing cenospheres are less dense and mechanically weaker than...
the specimens without it. The same relates to the specimens sintered at lower temperature in comparison to those sintered at higher temperature. In the majority of construction materials such as concrete, plastics and metal alloys, the strength positively correlates with the elasticity modulus. According to the theory of elasticity and the practice of ultrasonic testing, speed of sound is directly proportional to the square root of the elasticity modulus [7]. Hence, the increase of ultrasound velocity accompanying the increase of density occurs due to associated effects of the increment of the strength and elasticity modulus rather than the increase of density.

Correlations fields of ultrasound velocity $C$ and bulk density $\rho$ (a) and compressional strength $\sigma$ (b) are presented in figure 3 (a, b). In order to find closer correlations and bring the dependences to a linear character that is more convenient for the strength prediction, varying degrees of strength $\sigma$ and combinations of products $\sigma$ with bulk density $\rho$ at varying degrees were tried to correlate with $C$. The results of these trials are presented in Table 3. By increasing the negative degree of $\sigma$ and applying its product with $\rho$, the Pearson linear correlation coefficient increased reaching its maximum of 0.943 for the dependence $C = \sigma - 4 \rho - 2$. The results demonstrated the possibility of creation of a strength prediction model for metal-ceramic composites with hollow fillers increasing the inner porosity based on measurements of ultrasound velocity related to the longitudinal wave and bulk density of the material. At a constant ratio of metal and ceramic contents, the material density will be determined by the content of hollow inclusions.

Table 3. Correlation between ultrasound velocity ($C$) and mathematical expressions of compression strength ($\sigma$) and bulk density ($\rho$) by Pearson and Spearman.

| Type of correlation | Expressions of $\sigma$ and $\rho$ |
|---------------------|----------------------------------|
|                     | $\sigma$ $\sigma^{-2}$ $\sigma^{-4}$ $\rho \sigma$ $\rho \sigma^{-2}$ $\rho^{-2} \sigma^{-4}$ |
| Pearson             | 0.875 0.895 0.902 0.907 0.934 0.943 |
| Spearman            | 0.894 0.904 0.904 0.942 0.938 0.938 |

4. Conclusion

The study has demonstrated a non-linear character of dependence of ultrasound velocity on strength and density in sintered metal-ceramic composites with hollow fillers, where sintering temperature and the material composition were variables. The strength prediction model for such materials based on measurement of velocity of the longitudinal ultrasonic wave has to account bulk density in order to provide the closest correlation.

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References

[1] Duarte I and Ferreira J M F 2016 Materials 79 1
[2] Karakulov V V and Smolin I Y 2016 International Conference on Physics of Cancer Proceedings (Tomsk) vol 1760 (AIP Publishing LLC) 020024
[3] Santa Maria J A, Schultz B F, Ferguson J B, Gupta N and Rohatgi P K 2014 J Mater Sci 49 1267
[4] Orbulo I N and Ginsztler J 2012 Acta Polytechnica Hungarica 9 43
[5] Malhota V M and Carino N J 2004 Handbook on nondestructive testing of concrete (Boca Raton: CRC press) p 384
[6] British Standards Institution 2004 EN 12504-4 Testing concrete – determination of ultrasonic pulse velocity
[7] Krautkrämer J and Krautkrämer H 1990 Ultrasonic testing of materials (Berlin: Springer-Verlag) p 497
[8] Jurowski K and Grzeszczyk S 2015 Procedia Engineering 108 584
[9] Panzera T H, Christoforo A L, Cota F P, Borges P H R and Bowen C R 2010 Ultrasonic pulse velocity evaluation of cementitious materials Advances in Composite Materials - Analysis of Natural and Man-Made Materials ed P Tesinova (Rijeka: Intech) chapter 17 pp 411-436
[10] Mylavarapu P and Woldesenbet E 2008 J. Cellular Plastics 44 203
[11] Rugele K, Lehmhus D, Hussainova I, Peculevica J, Lisnanskis M and Shishkin A 2017 Materials 10 828
[12] Shishkin A, Mironovs V, Zemchenkov V, Antonov M and Hussainova I 2016 Key Engineering Materials 674 35
[13] Mironov V, Pundiene I, Tatarinov A and Baroninsh J 2015 Construction Science (Riga: Riga Technical University) 16 16