

WC/Co-Ti Kompozitlerinin Isıl ve Elastik Özelliklerinin Ultrasonik Dalga Hızı ile İlişkisi

Vildan ÖZKAN BİLİCİ¹, İsmail H. SARPÜN², M. Selami KILIÇKAYA³

¹Department of Physics, Afyon Kocatepe University, Faculty of Science and Literature, Afyonkarahisar, Turkey

²Department of Physics, Akdeniz University, Faculty of Science, Antalya, Turkey

³Department of Physics, Eskişehir Osmangazi University, Faculty of Science and Literature, Eskişehir, Turkey

*Corresponding author: vildanozkan@aku.edu.tr

Geliş Tarihi: 21.03.2019; Kabul Tarihi: 11.05.2019

Özet

Anahtar kelimeler

Kompozit; Young's Modülü; Darbe-Yankı; Daldırma; Isıl İletkenlik

Bu çalışmada, çeşitli kompozitler üretmek ve fiziksel özelliklerini ortaya koymak amaçlanmıştır. Toz metallurjisi ile WC-Co-Ti seramik-metal kompozitinin hazırlanmasında tungsten karbür (WC) tozu ve bağlayıcı faz olarak da kobalt (Co) ve titanyum (Ti) tozu kullanılmıştır. WC-Co-Ti kompozitlerinde mekanik dalga hızını ölçmek için iki farklı ultrasonik tahribatsız teknik kullanıldı. Çalışmada %60 ile %80 oranında farklı WC_x içeriği ve 3:1, 1:1 ve 1:3 gruplarında Co/Ti içeriği ile çeşitli numuneler yapıldı. İncelenen malzemelerde WC_x içeriği standart tahribat analizi kullanılarak belirlenmiştir. Üretilen kompozitlerin Young modülü (E) ve ultrasonik hızları, ultrasonik darbe-yankı metodu ve daldırma metodu ile ölçüldü. Numunelerin termal iletkenliği, sıcak disk yöntemi ile ölçülmüştür. İki farklı yöntemle elde edilen ultrasonik dalga hızları ile Young's modülü değerleri ve ısı iletkenlik arasındaki ilişki, fiziksel olarak incelenmiş ve sonuçlar literatür ile karşılaştırılmıştır.

The Relationship of Thermal and Elastic Properties with Ultrasonic Wave Velocity of WC/Co-Ti Composites

Abstract

Keywords

Composite; Young's Modulus; Pulse-Echo; Immersion; Thermal Conductivity

In this study, it is aimed to produce various composites and reveal their physical properties. Tungsten carbide (WC) powder and the two of cobalt (Co) and titanium (Ti) powders as binder phase have been used for the preparation of WC-Co-Ti ceramic-metal composite with powder metallurgy. Two different ultrasonic non-destructive techniques were employed to measure the mechanical wave velocity in WC-Co-Ti composites. The study was performed on various specimens with different WC_x content at the range from 60 to 80% and Co/Ti content in 3:1, 1:1 and 1:3 groups. The WC_x content in examined materials was determined using the standard destructive analysis. The Young modulus (E) of the produced composites and the ultrasonic velocity measured through ultrasonic pulse-echo method and immersion method. Thermal conductivity of samples has been measured via hot disk method. The relation between the Young modulus' values with ultrasonic wave velocity, which is obtained through two different methods and thermal conductivity has been physically examined and the results have been compared with the literature.

© Afyon Kocatepe Üniversitesi

1. Introduction

A non-destructive testing technique, which is an ultrasonic technique, is used to qualitatively or/and quantitatively evaluate the physical and elastic

properties of materials. Cracks, defects, faults and irregularities in the material can be detected by ultrasonic testing (Bouda et al., 2003; Krautkramer, 1977; Markham, 1957). The some material shows a

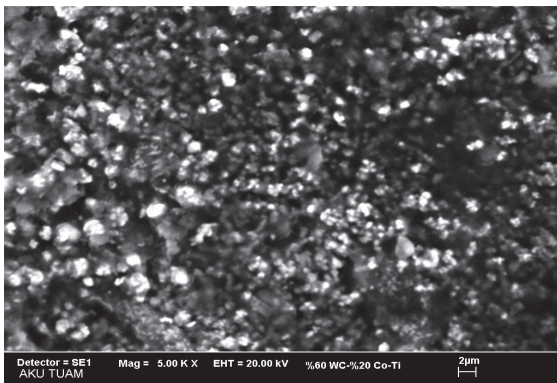
distinctly anisotropic response which somewhat complicates the experimental tests for the mechanical and physical characterization, especially if conventional testing techniques are used. Many difficulties can be overcome by adopting some non-destructive experimental approaches like, for example, the ultrasonic immersion techniques with pulse-echo. In particular, this ultrasonic experimental approach allows for the determination of all the elastic constants characterizing the mechanical response of a composite material starting from the measurement of the velocity of ultrasonic waves along suitable directions of propagation (Castellano et al., 2014-2016). Cemented carbides consist of the hard carbide phase (WC, TiC, and B₄C) and a transition metal binder (Co, Ni, Ti, Fe). Due to their high hardness (especially in high temperature), strength, excellent wear resistance and low thermal coefficient, cemented carbides are widely used for a variety of machining, cutting, drilling and other applications (Kursawe et al., 2001; Genga et al., 2013; Guo et al., 2008; Xu, 2011). The compatibility between the hard tungsten grains and the ductile cobalt and nickel binder phase enables the composites to have unique and superior combinations of mechanical properties (Hongsheng et al., 2012; Mohammadzadeh et al., 2015). Due to their technological importance these composites of WC have been subject to a great deal of investigation in order to optimize the compositions, the processing leading to the highest mechanical properties and a reduction of the manufacturing cost compared with the production method such as welding, plastic forming, extrusion, injection, casting (Fernandes et al., 2008). The possibility of complete or, at least, partial substitution of cobalt with nickel or other metals, alloys and composite in sintered WC-Co, WC-Ni and WC-Co-Ni cemented carbides has been investigated for years (Voitovich et al., 1996; Zhang et al., 2005; Krishnaveni et al., 2006; Shon et al., 2009). Tungsten cemented carbide was used to designate a metal matrix composite constituted by hard ceramic particles, normally WC, into a metallic matrix. Conventional tungsten carbide hard metal alloys consist of tungsten carbide with a soft and

ductile metal Co as the binder phase. Also cobalt wets tungsten carbide well and has good mechanical properties (Fernandes et al., 2011; Konyashin et al., 2014; Gao et al., 2018). Recently, tungsten carbide (WC) reinforced metal matrix composites such as WC-Co (Zhong et al., 2011), WC-Ni (Zhang et al., 2015), WC-Fe (Zhong et al., 2016), WC-CoNi (Tarrago et al., 2015), WC-CoCr (Hong et al., 2016), WC-CoCu (Gu et al., 2007) and WC-Al (Lekatou et al., 2015) were obtained by adding components such as Ti, Ni, Cr, Al, Ta and Nb beside the Co matrix to improve the bonding properties (Ekroth et al., 2000). In this study, WC-Co-Ti composite samples obtained in 3:1, 1:1 and 1:3 groups using the powder metallurgy technique. Moreover, the research carried out a series of experimental tests to explore the characteristics and properties of the same sintering temperatures on different specimens with varying amounts of Co and Ti. Evaluation of thermal and elastic properties of composite materials obtained in this study was investigated by using ultrasonic and thermal hot-disk techniques. We have examined the relationship between thermal and elastic properties of WC / Co-Ti composites with ultrasonic wave velocity, as they provide information about the study of ultrasonic wave propagation in metals, alloys and composites on the microstructure, mechanical and physical properties of the material.

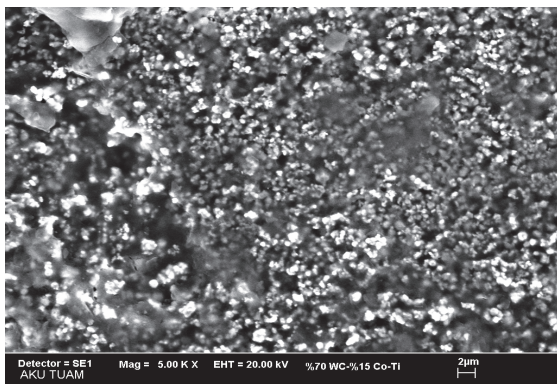
2. Materials and Methods

In this study, Tungsten carbide (WC) powders of 10 µm particle size with 99.5 % purity, Cobalt (Co) and Titanium (Ti) powders of -325 mesh particle size with 99.5 % -99 % purity were used in the form of powders and also were both provided from Alfa Aesar Company (Massachusetts, ABD). One of the purposes of this work is to reinforce WC ceramic powders with Co-Ti. Co and Ti powders were added in the mixture directly. In the experimental study, the samples were prepared through three different compositions. Co/Ti ratios were taken in 3:1, 1:1 and 1:3 groups depending on WC_x volume ratio. All the samples were mixed homogeneously for 24 h in a mixer following the weighing. The mixture was shaped by single axis cold hydraulic pressing using high strength steel die of 15 mm diameter and 5

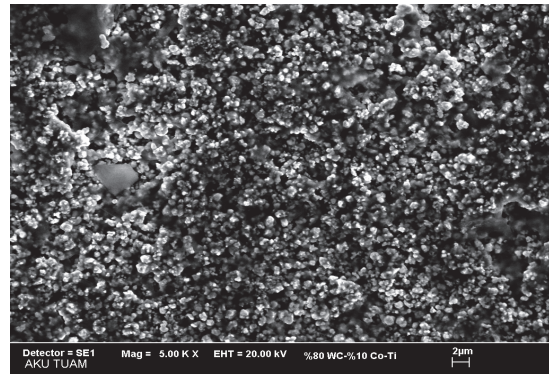
mm height. A pressure of 305,9 kg/cm² was used for compacting all the powder mixtures. The cold pressed samples underwent sintering at 1000 °C for 2 h in a traditional tube furnace using Argon gas atmosphere. The samples were cooled in the furnace after sintering and their longitudinal and transverse ultrasound velocity Young's modulus and thermal conductivity measurements were carried out using ultrasonic non-destructive testing which are pulse-echo and immersion methods for the longitudinal and transverse ultrasound (ultrasonic) velocity measurements and hot disk method for thermal conductivity measurements, respectively. Sintered composite samples were characterized using Leo 1430 VP equipped with Röntec energy dispersive X-ray (EDX) model scanning electron microscopy (SEM). Figure 1 shows the SEM microanalyses images of WC-Co-Ti composites.



(a)



(b)



(c)

Figure 1. SEM pictures of a) WC_{0.6}+Co_{0.2}+Ti_{0.2} b) WC_{0.7}+Co_{0.15}+Ti_{0.15} c) WC_{0.8}+Co_{0.1}+Ti_{0.1} samples.

In this study, a system combining immersion and pulse method was developed to measure the pass times of the samples in water and both the longitudinal and transverse ultrasound velocities of the samples. In pulse-echo method, a transducer serves as both a receiver and a transmitter. The ultrasound wave obtained by applying very short electrical signals to the transducer is sent to the material. As the ultrasound wave moves through the material, the same transducer starts to operate as a receiver. When the ultrasound wave reflected from the back wall of the sample reaches the transducer, the mechanical vibrations are converted into electrical signals. Velocity measurements were obtained by reflection peaks from the front and back surface of the ultrasound wave sent to the sample by the transducer. The determination of transmission velocity of ultrasonic waves through the composites were performed by a Panametrics 5800 model Olympus brand computer-controlled pulser-receiver (PR) and digital oscilloscope with Sonatest SLH4-102 T/R transducer probe to measure longitudinal velocities and GE Inspection Technologies MB-4Y T/R transducer probe to measure transverse velocities at the frequency of 4 MHz at the room temperature. Sonatestsonagel-W was used as interface between the transducers and composite samples, given the smoothness of the composite surfaces. In immersion testing, the transducer probe is placed in the water tank, above the test object, and a beam of sound is projected. When an ultrasound wave emitted within the water used in

the experimental setup strikes a solid object so that it normally has a certain angle of incidence, the incoming wave is divided into a transverse and longitudinal wave within the sample. Thus, necessary measurements were made over transverse and longitudinal waveforms. When the sample was placed between each of the Z4K53342-2324 transducer probe at the frequency of 5 MHz were obtained by combining pulse-echo and immersion methods. Density of all the sintered WC-Co-Ti composite samples was measured with Archimedes principle, later Young's modulus have been obtained with using calculated densities, ultrasonic longitudinal and transverse velocity. Young's modulus in medium can be found by the following equation (1):

$$E = \rho V_T^2 \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \quad (1)$$

where V_L is the longitudinal wave velocity (m/s), V_T is the transverse wave velocity (m/s) and ρ is density. The thermal conductivity measurements of the WC-Co-Ti composite samples were obtained using the hot disk method to investigate the relationship between the Young's modulus and thermal conductivity. The well-established Hot Disk Thermal Constants Analyzer method allows rapid, accurate and non-destructive testing of thermal conductivity of most material types, all in a single measurement and also conductivity and diffusivity are tested directly. The sensors used in this test method which is sandwiched between two insulating specimen halves (Figure 2). In this study, using the basic theory of measuring the thermal conductivity of the heated plane sensor, the conductivity values have been read from the system (Ashraf, 2014; Yi, 2005).

transducers, the time taken for the wave passing through the track and the time taken for the wave moving between the transducers in the water between the transducers were taken and the speed in the water was determined. In this study, transverse and longitudinal ultrasonic measurements of GE Inspection Technologies

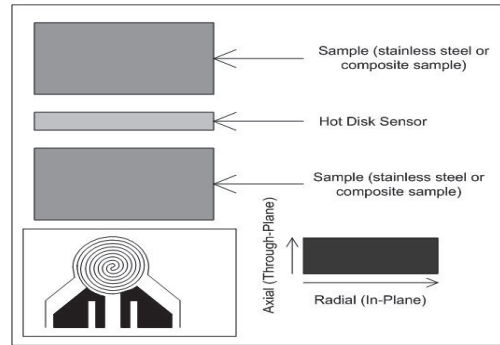


Figure 2. Schematic of samples and sensor for the Hot Disk.

3. Results and Discussion

Young's modulus and thermal conductivity of the prepared ceramic-metal composite material was physically tested. Experimental results obtained with ultrasound velocities, elastic modulus, thermal conductivity and density values belong to the samples prepared by adding Co and Ti binder into WC powder are given in Table 1. The variations in longitudinal and transverse ultrasound velocity with Young's modulus and thermal conductivity of WC-Co-Ti samples are shown in Figs. 3 and 4. When WC-Co-Ti composite samples obtained in 3:1, 1:1 and 1:3 groups is examined, there is a linear increase in the longitudinal and transverse ultrasound velocities.

Table 1. Ultrasound velocities, elastic modulus, thermal conductivity and density values of WC-Co-Ti composite sample.

Sample	Pulse-Echo Method			Immersion Method			Thermal Conductivity (W/mK)	Density (g/cm ³)
	V_L (m/s)	V_T (m/s)	E (GPa)	V_L (m/s)	V_T (m/s)	E (GPa)		
WC _{0.6} +Co _{0.3} +Ti _{0.1}	4942	2249	94.2	4933	2362	102.5	6.82	6.8
WC _{0.6} +Co _{0.2} +Ti _{0.2}	5313	2501	110.4	5104	2532	111.4	6.98	6.5
WC _{0.6} +Co _{0.1} +Ti _{0.3}	5871	2721	133.2	5839	2870	145.8	7.59	6.6
WC _{0.7} +Co _{0.225} Ti _{0.075}	4633	2467	112.5	4777	2489	115.6	3.48	7.1
WC _{0.7} +Co _{0.15} Ti _{0.15}	5138	2636	123.0	4982	2683	125.0	4.40	6.7
WC _{0.7} +Co _{0.075} Ti _{0.225}	5653	2824	140.4	5281	3076	155.3	5.29	6.6
WC _{0.8} +Co _{0.15} +Ti _{0.05}	4438	2626	113.7	4586	2509	108.5	3.20	6.7
WC _{0.8} +Co _{0.1} +Ti _{0.1}	4934	2759	139.5	4747	2870	143.8	3.38	7.2
WC _{0.8} +Co _{0.05} +Ti _{0.15}	5380	2941	140.2	4915	3307	149.7	3.68	6.3

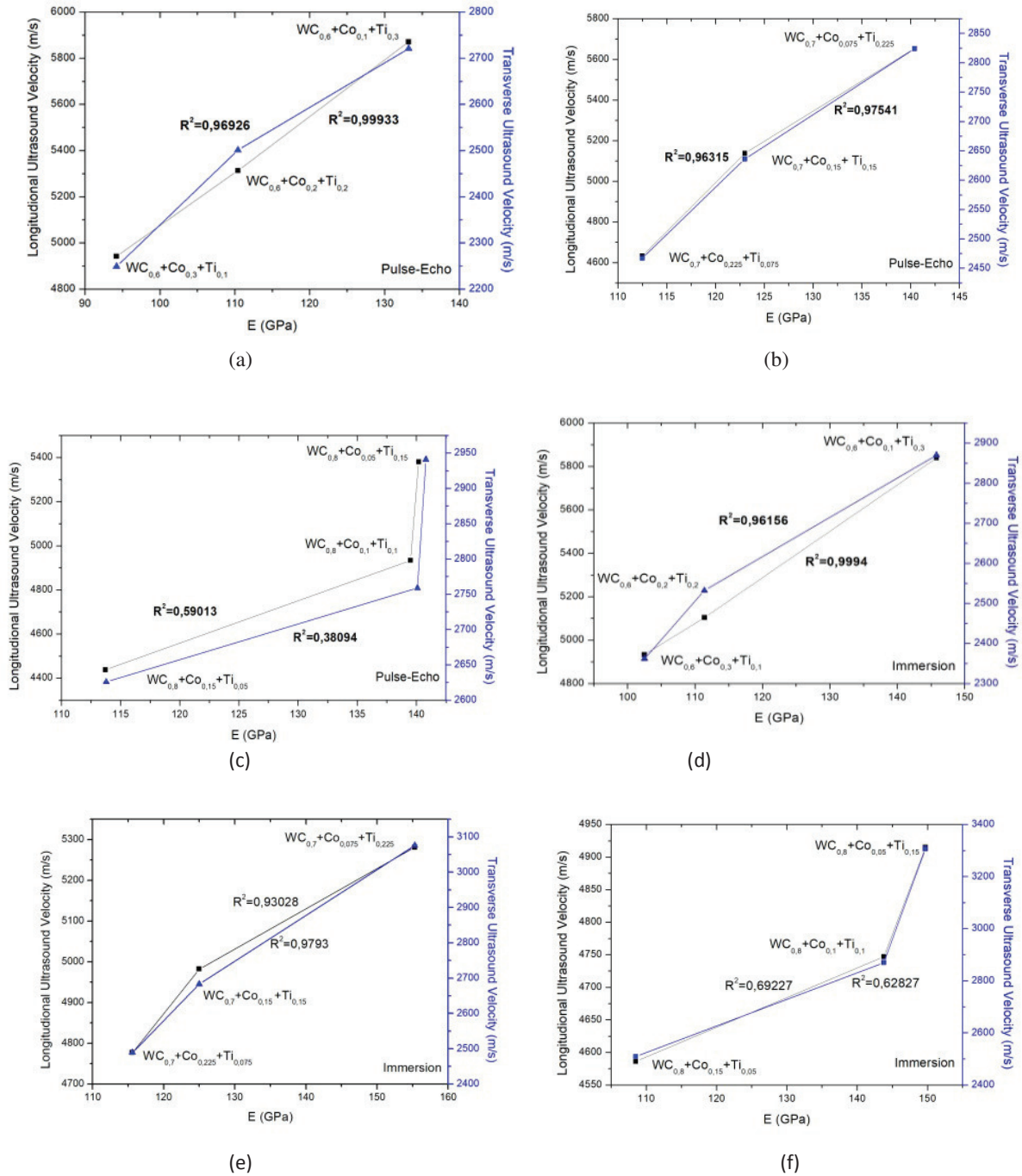


Figure 3. Variation in longitudinal and transverse ultrasound velocity with Young's modulus (a-c) Pulse-echo method and (d-f) Immersion method.

However, the situation is different when examined according to WC rate. A comparison showed that the results obtained for the wave velocity from pulse-echo and immersion method are in good agreement, indicating that both techniques can be considered as a quantitative non-destructive tool of mean grain size content evaluation. The results are presented in the form of linear relationships of wave velocity versus tungsten content in the composite materials. While longitudinal ultrasound wave velocity values of WC-Co-Ti composite sample decrease depending on WC_x volume ratio, there is an increase in transverse ultrasound wave velocity values. By considering size of WC particles in the structure, arrays of atoms in the strands in the longitudinal wave measurement performed parallel to the axis being smaller than the other

binding phases will effect homogeneous distribution, thus longitudinal wave velocity in the matrix element are observed to decrease. In addition, BiliciÖzkanet al. (2018) have investigated the relationship between thermal and elastic properties of WC-Fe-Ti composites in another study.They observed a modest increase in Young's modulus and thermal conductivity, as in WC-Co-Ti composites. Also,In Figures 5.a-c, Young modulus, as calculated depending onultrasound velocities and densities as previously described and thermal conductivity linearly increases. R^2 value of fit line in Figure 5.c is lower than the others. It is caused by Young modulus values of $WC_{0.8}+Co_{0.1}+Ti_{0.1}$ and $WC_{0.8}+Co_{0.05}+Ti_{0.15}$ compositions, being very close to each other for both ultrasound methods.

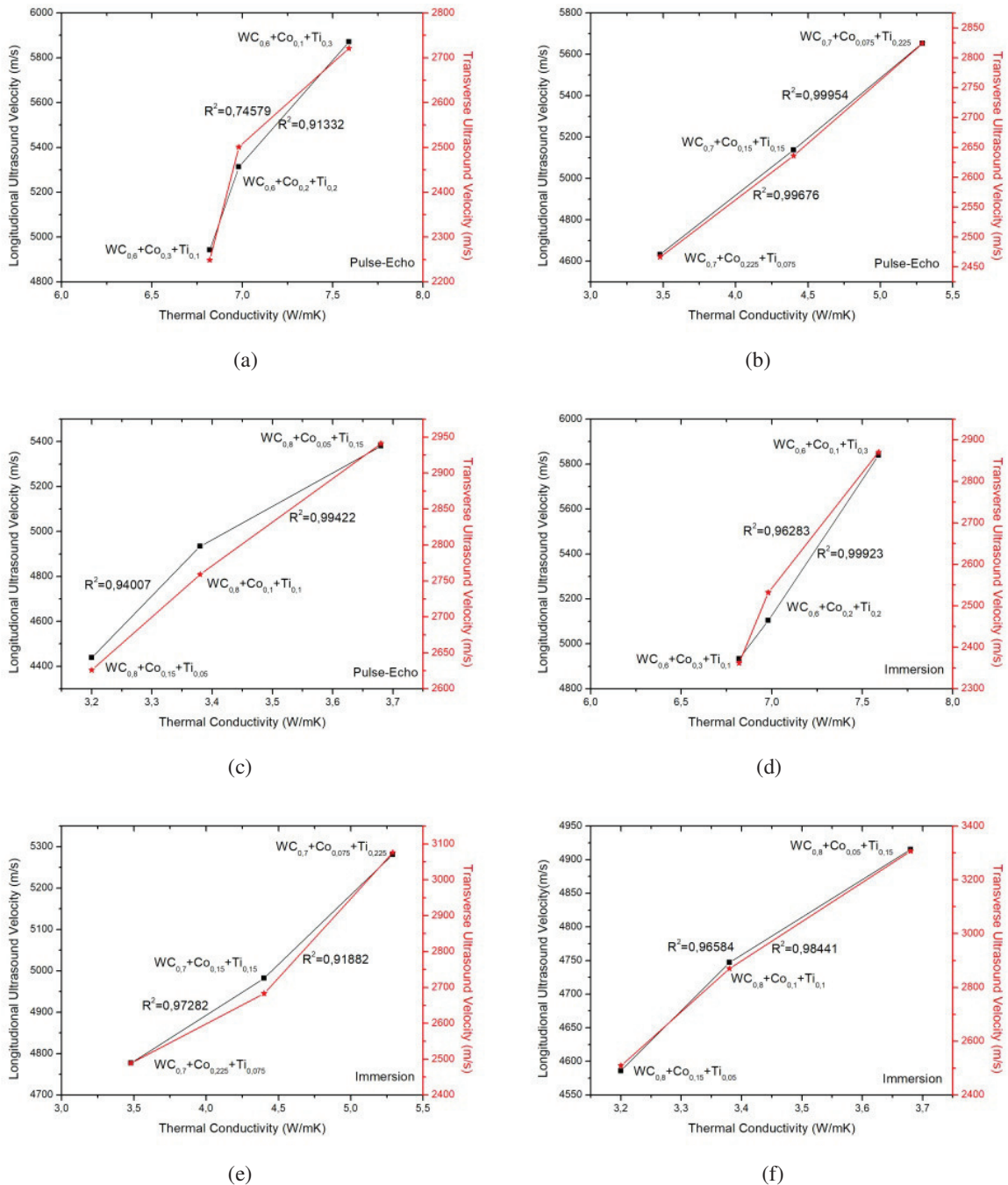


Figure 4. Variation in longitudinal and transverse ultrasound velocity with thermal conductivity (a-c) Pulse-echo method and (d-f) Immersion method.

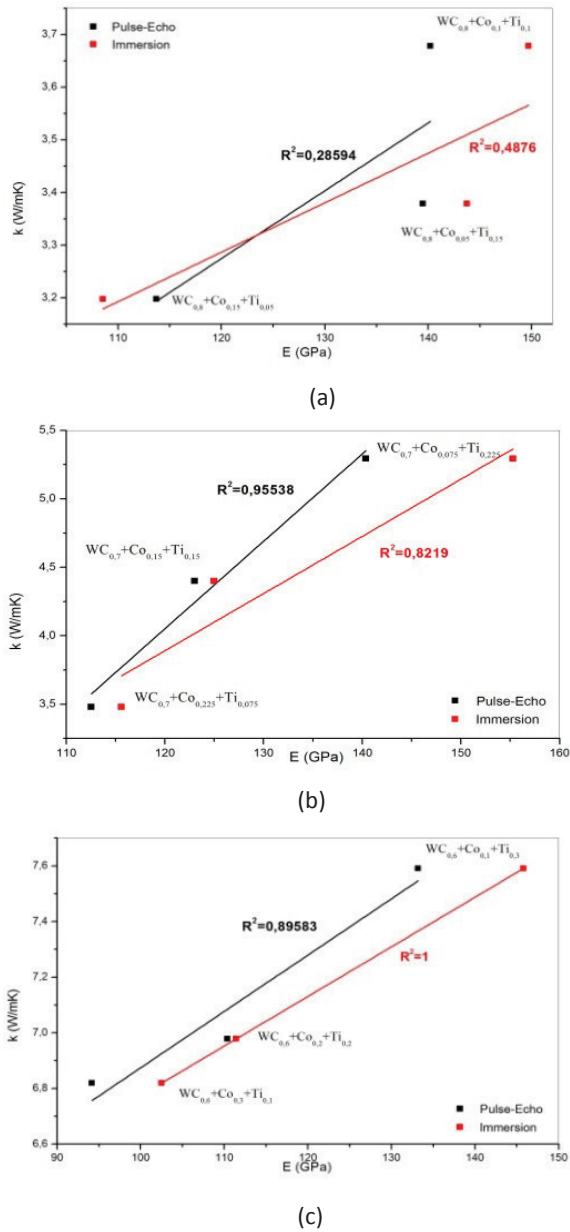


Figure 5. Thermal conductivity and Young modulus graph of (a) WC_{0.6}-Co-Ti, (b) WC_{0.7}-Co-Ti, (c) WC_{0.8}-Co-Ti composite sample.

R² value of fit line in Figure 5.c is lower than the others. It is caused by Young modulus values of WC_{0.8}+Co_{0.1}+Ti_{0.1} and WC_{0.8}+Co_{0.05}+Ti_{0.15} compositions, being very close to each other for both ultrasound methods. When SEM images are examined, considering that WC ceramic particles form a strong bond after sintering, grain growth is observed in Figures 5.a and 5.b and is a

homogeneous structure. It can be seen that the structure includes two types of pores, small and large. In Figure 5.c, particle boundaries can be seen and the pores are very small and circular in shape.

4. Conclusions

In this study, two different ultrasonic non-destructive techniques were employed to measure the mechanical wave velocity in WC-Co-Ti composites and the relationship between thermal and elastic properties of WC-Co-Ti ceramic-metal composites was investigated. Two different methods (pulse-echo and immersion) have been used for ultrasonic velocity measurements and obtained values are consistent with each other. The main objective of this work was to study efficiency and ability of the pulse-echo ultrasonic in comparison with immersion technique to evaluate some physical properties in WC-Co-Ti composites. The variation of WC and Co/Ti content was clearly identified by the use of both considered techniques. Furthermore, pulse-echo proved to be a suitable method for the investigation of such materials, but it was also less time-consuming than the second considered ultrasonic technique. The described difficulties that can be expected using immersion technique suggest that in the cases where two sides of the composite are accessible, pulse-echo technique is recommended.

A good agreement between the results presented in this study, indicates that both ultrasonic techniques can be considered as a quantitative non-destructive assessment tools. It is therefore concluded that these methods can be used in the evaluation of physical properties in ceramic metal matrix composites, producing interpretable results. As the amount of porosity in the structure increases, the ultrasonic wave velocity propagation decreases (SEM images).

References

- Ashraf, A. A., 2014. Measurement of thermal conductivity and diffusivity of different materials by the transient plane source method using hot disk thermal constants analyzer, 1–7.
- BiliciÖzkan, V., Sarpün, İ. H. and Kılıçkaya, M. S., 2018, Evaluation of the Elastic and Thermal Properties of WC/Fe-Ti Ceramic-Metal Composites Fabricated by Powder Metallurgy, *International Journal of Scientific & Engineering Research*, 9(8), 10-14.
- Bouda, A. B., Halimi, R., Benchaalaa, A. and Lebaili, S., 2003. Ultrasonic NDE of materials grain size and hardness, WCU, Paris.
- Castellano, A., Foti, P., Fraddosio, A., Marzano, S. and Piccioni, M.D., 2014. Mechanical Characterization of CFRP Composites by Ultrasonic Immersion Tests: Experimental and Numerical Approaches, *Composites Part B: Engineering*, Vol. 66, 299-310.
- Castellano, A., Foti, P., Fraddosio, A., Marzano, S. and Piccioni, M. D., 2016. The ultrasonic C-Scan technique for damage evaluation of GFRP composite materials, *International Journal of Mechanics*, Vol. 10, 206-212.
- Ekroth, M., Frykholm, R., Lindholm, M., Andrén, H. O. and Ågren, J., 2000. Gradient zones in WC–Ti(C,N)–Co-based cemented carbides: experimental study and computer simulations, *Acta Materialia*, 48, 2177–2185.
- Fernandes, C. M., Senos, A. M. R., Vieira, M. T., Antunes, J. M., 2008. Mechanical characterization of composites prepared from WC powders coated with Ni rich binders, *International Journal of Refractory Metals and Hard Materials*, 26, 491.
- Fernandes, C. M., Senos, A. M. R., 2011. Cemented carbide phase diagrams: A review, *International Journal of Refractory Metals and Hard Materials*, 29, 405 – 418.
- Gaoa, Y., Luoa, B. H., Heb, K. J., Zhanga, W. W. and Baia, Z. H., 2018. Effect of Fe/Ni ratio on the microstructure and properties of WC-Fe-Ni-Co cemented carbides, *Ceramics International*, 44, 2030 – 2041.
- Genga, R. M., Cornish, L. A. and Akdoğan, G., 2013. Effect of Mo₂C additions on the properties of SPS manufactured WC–TiC–Ni cemented carbides, *International Journal of Refractory Metals and Hard Materials*, 41, 12-21.
- Guo, Z., Xiong, J., Yang, M., Song, X. and Jiang, C., 2008. Effect of Mo₂C on the microstructure and properties of WC–TiC–Ni cemented carbide, *International Journal of Refractory Metals and Hard Materials*, 26, 601-605.
- Gu, D. D. and Shen, Y. F., 2007. Influence of reinforcement weight fraction on microstructure and properties of submicron WC-Co-p/Cu bulk MMCs prepared by direct laser sintering, *Journal of Alloys and Compounds*, 431, 112 – 120.
- Hong, S., Wu, Y. P., Zhang, J. F., Zheng, Y. G., Zheng, Y. and Lin, J. R., 2016, Synergistic effect of ultrasonic cavitation erosion and corrosion of WC-CoCr and FeCrSiBMn coatings prepared by HVOF spraying, *Ultrasonics Sonochemistry*, 31, 563 – 569.
- Hongsheng, C., Keqin, F., Ji, X., Jianjun, L., Zhixing, G. and Hui, W., 2012. Characterization and forming process of a functionally graded WC–Co/Ni composite, *International Journal of Refractory Metals and Hard Materials*, 35, 306-310.
- Konyashin, I., Lachmann, F., Ries, B., Mazilkin, A. A., Straumal, B. B., Kübel, C., Llanes, L. and Baretzky, B., 2014, Strengthening zones in the Co matrix of WC–Co cemented carbides, *Scripta Materialia*, 83, 17 – 20.
- Krautkramer, J. H., 1977. *Ultrasonic Testing of Materials*, Springer–Verlag, Berlin.

- Krishnaveni, K., Sankara, N. and Seshadri, S. K., 2006. Electrodeposited Ni-B coatings: Formation and evaluation of hardness and wear resistance, *Materials Chemistry and Physics*, 99 (2-3), 300-308.
- Kursawe, S., Pott, P., Sockel, H. G., Heinrich, W., Wolf, M., 2001. On the influence of binder content and binder composition on the mechanical properties of hardmetals. *International Journal of Refractory Metals and Hard Materials*, 19, 335-40.
- Lekatou, A., Karantzalis, A. E., Evangelou, A., Gousia, V., Kaptay, G., Gacsi, Z., Baumli, P. and Simon, A., 2015. Aluminium reinforced by WC and TiC nanoparticles (exsitu) and aluminide particles (in-situ): Microstructure, wear and corrosion behavior, *Materials & Design*, 65, 1121 – 1135.
- Markham, M. F., 1957. Measurement of elastic constants by the ultrasonic pulse method, *British Journal of Applied Physics*, 6, 56 – 63.
- Mohammadzadeh, H., Rezaie, H., Samim, H., Barati, M. and Razavizadeh, H., 2014. Synthesis of WC-Ni composite powders by thermochemical processing method based on co-precipitation, *Materials Chemistry and Physics*, 1-11.
- Shon, I-J., Jeong, I-K., Ko, I-Y., Doh, J-M. and Woo, K-D., 2009. Sintering behavior and mechanical properties of WC-10Co, WC-10Ni and WC-10Fe hard materials produced by high-frequency induction heated sintering, *Ceramic International*, 35, 339-344.
- Tarrago, J. M., Roa, J. J., Valle, V., Marshall, J. M. and Llanes, L., 2015. Fracture and fatigue behavior of WC-Co and WC-CoNi cemented carbides, *International Journal of Refractory Metals and Hard Materials*, 49, 184 – 191.
- Voitovich, V. B., Sverdel, V. V., Voitovich, R. F. and Golovko, E. I., 1996. Oxidation of WC-Co, WC-Ni and WC-Co-Ni hard metals in the temperature range 500-800°C, *International Journal of Refractory Metals and Hard Materials*, 14, 289-295.
- Yi, He, 2005. Rapid thermal conductivity measurement with a hot disk sensor Part 1. Theoretical considerations, *Thermochimica Acta*, 436, 122 -129.
- Zhang, Z. Q., Wang, H. D., Xu, B. S. and Zhang, G. S., 2015. Investigation on influence of WC-Ni addition on rolling contact fatigue behavior of plasma sprayed Ni-based alloy coating, *Tribology International*, 90, 509 – 518.
- Zhong, Y. and Shaw, L. L., 2011. Growth mechanisms of WC in WC-5.75wt %Co, *Ceramics International*, 37, 3591 – 3597.
- Zhong, L. S., Zhang, X., Wang, X., Xu, Y. H., Wu, H. and Fu, Y. H., 2016. Growth kinetics of WC-Fe layer formed at the surface iron during solid-phase diffusion, *Ceramics International*, 42, 16941-16947.
- Xu, P. Q., 2011. Dissimilar welding of WC-Co cemented carbide to Ni₄₂Fe_{50.9}C_{0.6} Mn_{3.5}Nb₃ invar alloy by laser-tungsten inert gas hybrid welding, *Materials and Design*, 32, 229-237.