

## MECHANICAL PROPERTIES OF COMPOSITES WITH TITANIUM DIBORIDE FABRICATED BY SPARK PLASMA SINTERING

Microstructure and mechanical properties of the 316L steel composite reinforced with TiB<sub>2</sub> phase were examined. The test materials were obtained by SPS technique from powders. From testing of the mechanical properties it follows that the optimum temperature for the fabrication of 316L steel-TiB<sub>2</sub> composites by SPS is 1100°C. Studies have also proved that the critical content of TiB<sub>2</sub> phase in steel matrix should not exceed 6vol%. Above this level, the plastic properties of the composite become unstable and strongly dependent on the time of sintering.

*Keywords:* Composite, Spark Plasma Sintering (SPS), Mechanical properties

### 1. Introduction

By the technology of powder metallurgy, materials difficult to obtain by other methods are produced. The development of SPS and HP-HT methods has significantly expanded the possibilities for controlled synthesis of new materials. The high sintering pressure applied in powder metallurgy is an effective tool for the control of diffusion process. New opportunities emerge along with the introduction of SPS technology based on high-current heating process. The specific character of current heating allows for the accumulation of energy and intense heating of contact points between the powder particles touching each other. The result is rapid formation of intergranular bridges, which serve as a path for the spreading diffusion process. The additional effect of compaction pressure is densification of processed material and increased area of intergranular bonds [1-5].

An important feature of the SPS method is that it allows preserving the original grain size of powder components and avoids the excessive grain growth. Materials obtained by the SPS technique are characterized by high structural homogeneity produced within the entire volume of a sample. The method also offers high speed, precise selection of the sintering parameters and energy efficiency. The disadvantages include the need to work with high direct current and relatively small size of the resulting end product [6-8]. In recent years, the SPS method has been widely used in the manufacture of composite materials based on copper [9,10], nickel [11,12], and aluminium [13-15], or iron [16-18]. Studies have mostly focused on optimization of the sintering process and achieving satisfactory physical, mechani-

cal, electrical and tribological properties. However, accurate determination of mechanical properties of the sintered composite materials based on ferro-alloys, particularly the determination of the yield strength and tensile strength  $R_m$ , has some limitations, which are mostly due to the dimensions of sinters obtained by the method of SPS. The composite sinters discussed in this study, processed by SPS, had a diameter of 20 mm and thickness comprised in the range of 7-8 mm. In view of the dimensions so small, it was necessary to develop own genuine methods for testing of the mechanical properties. It was decided to implement the tensile test, as characterized by high repeatability of results and accuracy in the determination of different mechanical parameters. The developed method enabled the tensile test to be carried out at elevated temperatures of up to 1000°C. The option of cutting out eight tensile specimens from one sinter has created the possibility of working on samples manufactured under the same conditions, and therefore giving the same reproducibility of results for each type of the sintered material tested. For example, Liu et al. [19] conducted tensile tests at room temperature on the superaustenitic stainless steel reinforced with 10-30vol% TiN. The composites were obtained by hot-isostatic pressing. Tensile tests were carried out on cylindrical specimens with threaded ends. Compared to the matrix without reinforcement, the composites were characterized by high yield strength (UTS), but low tensile strength and elongation. The best results in terms of UTS and elongation were obtained on composites containing 10vol% TiN. Increasing the content of reinforcement to 30vol% has resulted in a significant drop of both the tensile strength and elongation.

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The main aim of the studies described in this article was testing the mechanical properties of 316L steel-TiB<sub>2</sub> composites, especially their behaviour at elevated temperatures. The results are continuation of the research discussed in [16,20], where other methods of consolidation of powders based on Fe and TiB<sub>2</sub> were described along with their impact on physical and mechanical properties of the sintered composite materials. The present research is focused on the composites containing TiB<sub>2</sub> in an amount from 2 to 8 vol%. This content of the reinforcement produces materials with a wide range of properties. The 316L steel-TiB<sub>2</sub> composites are materials dedicated primarily for high temperature applications as a cheaper alternative to composites used currently [21-25]. Therefore, in the studies, particular emphasis was put on the determination of mechanical properties at elevated temperatures.

## 2. Experimental procedure

For the manufacture of composites by SPS, powders of AISI316L austenitic commercial steel (25 μm in diameter, KAMB Import-Export) and TiB<sub>2</sub> (99.9 wt.% purity, 2.5-3.5 μm in diameter, H.C. Starck) were used. Powder compositions were prepared by mixing appropriate components in TURBULA for 8 hours.

Four variants of composites reinforced with 2-8 vol% TiB<sub>2</sub> were fabricated. The tested materials were sintered by SPS in an FCT HPD5 device (Germany). Pressing of powder mixtures took place in a graphite die at a maximum pressure of 35 MPa in a vacuum environment. The compaction under a pressure so low does not affect the melting point of the material [26]. The vacuum and long-time of pressing were used to vent the mixture charged into the die. Then, a protective gas (argon) was introduced into the sintering chamber. Sintering was conducted at 1000°C and 1100°C. The time of sintering was 5 and 30 minutes. The heating rate was 200°C/min. The sintered specimens were 7-8 mm high and had a 20 mm diameter.

Microstructure of the 316L steel-TiB<sub>2</sub> composite was examined by SEM using a high-resolution scanning electron

microscope (Hitachi SU-70) equipped with a field emission gun and a set of Thermo detectors. Chemical analysis of the sintered materials was done by WDS.

Microhardness was tested under a load of 2.94 N with FM-7 Vickers hardness tester (Future-Tech Corp.). Ten microhardness measurements were taken on each sample, and then the average value was calculated. The standard deviation of HV0.3 was less than 4% of the average value. As a next step in the studies, from each sintered composite (h = 7-8 mm, φ = 20 mm), the tensile specimens were prepared by electrospark method. From each sinter, 7-8 specimens with dimensions of 0.5 mm×0.5 mm were cut out (Fig. 1a). One of the cut out specimens is shown as an example in Figure 1b. Testing of mechanical properties was carried out on specimens with a 5 mm base deformed at a rate of  $6 \times 10^{-4} \text{ s}^{-1}$ . Tensile tests were performed at temperatures ranging from 20°C to 950°C. Studies involved the use of a testing machine equipped with a furnace for high temperature testing (up to 1000°C). A jaw of the design adapted to stretching of micro specimens cut out by the method described in literature [20] was used.

## 3. Results and discussion

Figure 2 compares the microstructure of a composite based on 316L stainless steel with different content of TiB<sub>2</sub> (2-8 vol%). A uniform distribution of the reinforcing phase in a steel matrix is visible accompanied by the presence of small precipitates distributed at the TiB<sub>2</sub> phase boundary and in the matrix (Figs. 2,3). The size of the precipitates ranges from a few up to several microns. Chemical analysis (WDS) of these small precipitates has indicated the presence of boron and chromium. They were formed during the sintering process by SPS. In the same composite but sintered under high pressure, phases containing chromium and boron were not observed to occur [26,27].

Figure 4 shows the results of microhardness measurements. Based on these results it was concluded that microhardness depends on the content of reinforcing phase in the composite matrix and on the sintering conditions (time and temperature).

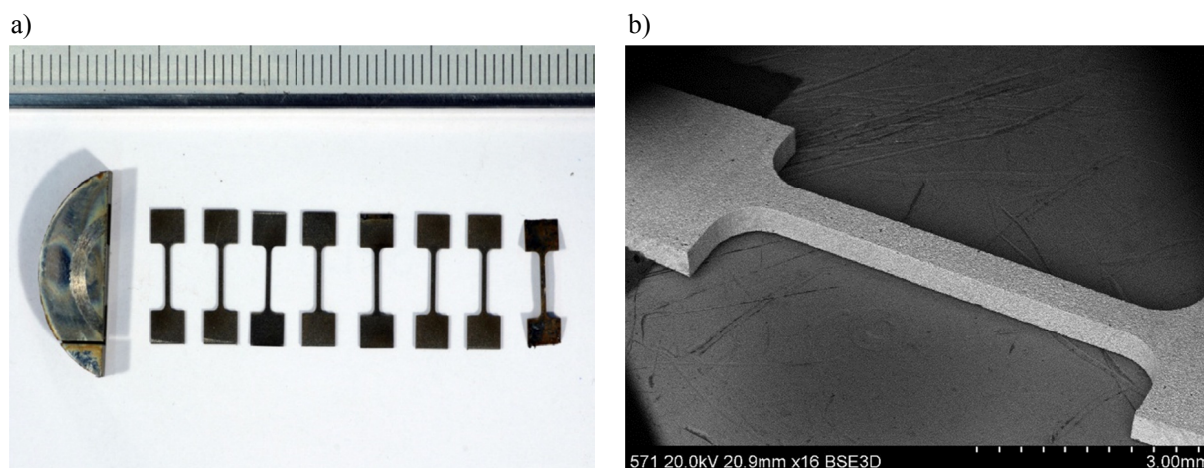


Fig. 1. a) A set of specimens, and b) example of a tensile specimen cut out by the electrospark process (316L steel-8vol% TiB<sub>2</sub> composite)

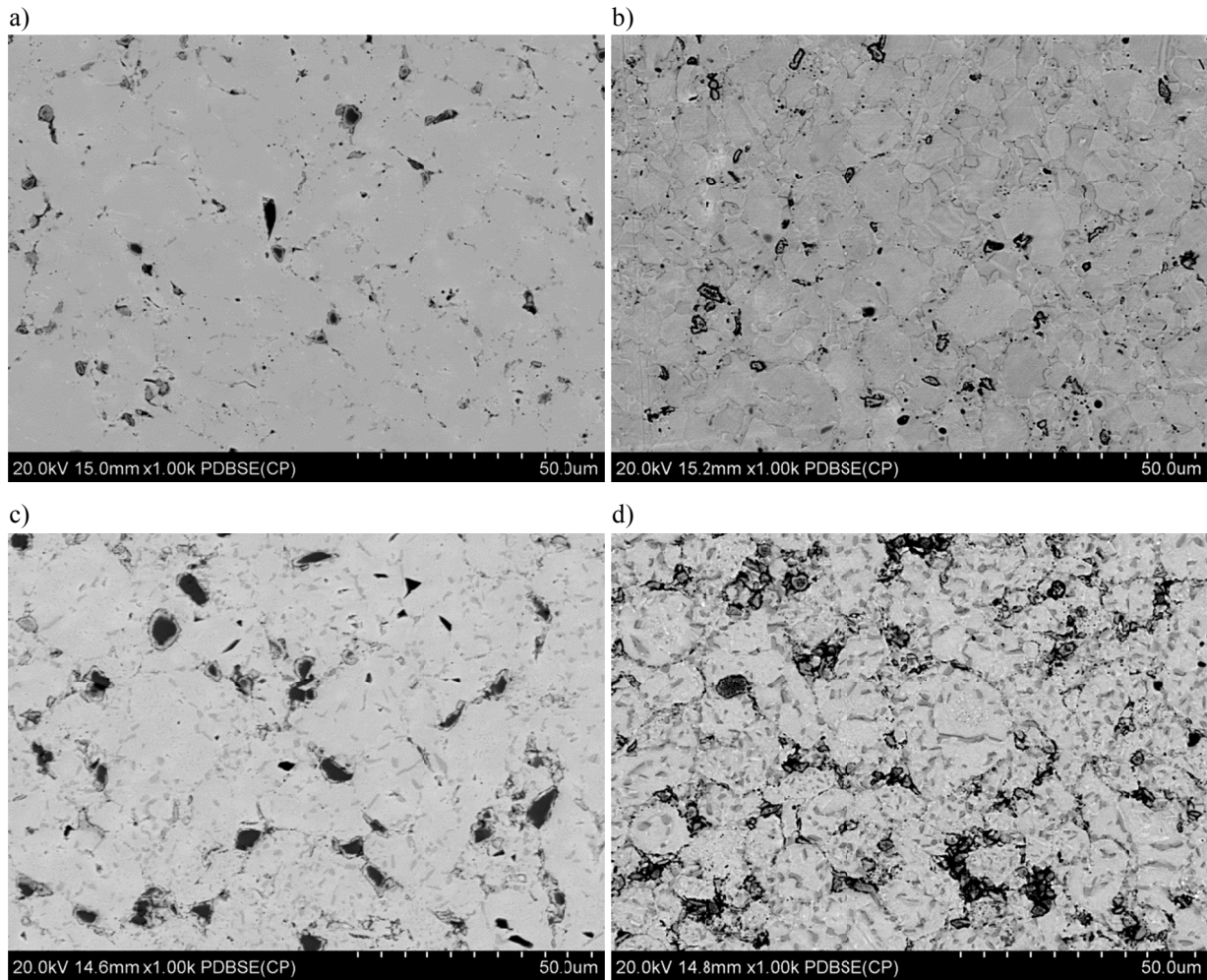


Fig. 2. Microstructure (SEM) of composites sintered at 1100°C for 5 minutes: a) 2vol% TiB<sub>2</sub>, b) 4vol% TiB<sub>2</sub>, c) 6vol% TiB<sub>2</sub> and d) 8vol% TiB<sub>2</sub>

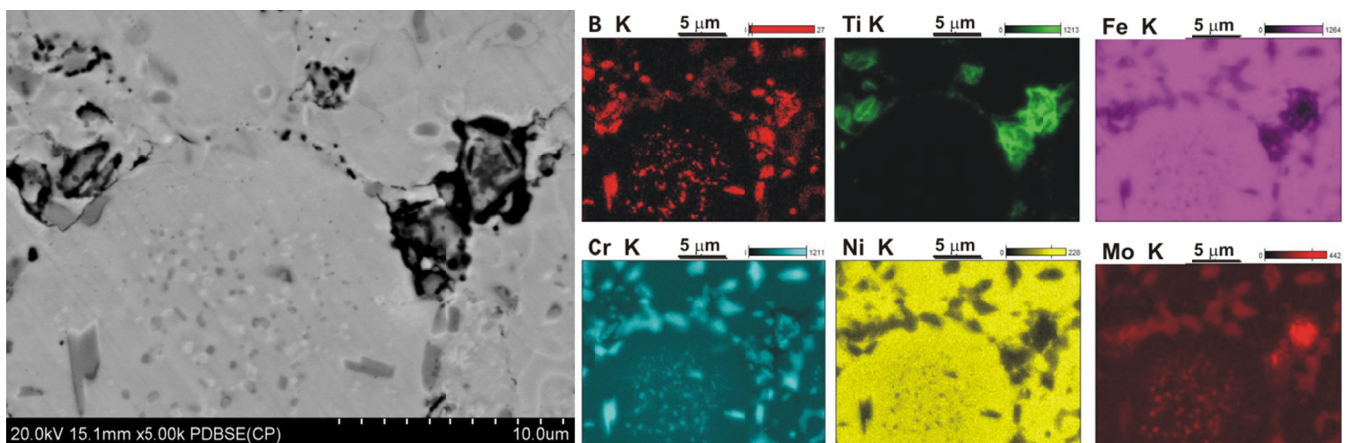


Fig. 3. Microstructure (SEM) and surface analysis (WDS) of the 316L steel-8vol% TiB<sub>2</sub> composite (sintered at 1100°C for 5 minutes)

Microhardness gradually increases with the TiB<sub>2</sub> content increasing in the matrix. It is low in the range of 175-235 HV0.3 for the sintering temperature of 1000°C and the time of 5 and 30 minutes, but increasing the temperature by 100°C definitely improves the microhardness raising it by 60-80%. Microhardness of the 316Lsteel-TiB<sub>2</sub> composite was in the range of 330-415 HV0.3 for the sintering temperature of 1100°C and time of 30 minutes.

Tensile tests were performed on specimens obtained in four time-and-temperature variants of the SPS process. Two sintering temperatures were applied, i.e. 1000°C and 1100°C, and the sintering time of 5 and 30 minutes. Comparing the results of mechanical tests obtained for different variants of the sintering process (Figs. 5-8) has demonstrated that of critical importance for the specimens obtained within a given range of the SPS parameters is the sintering temperature. The temperature of the

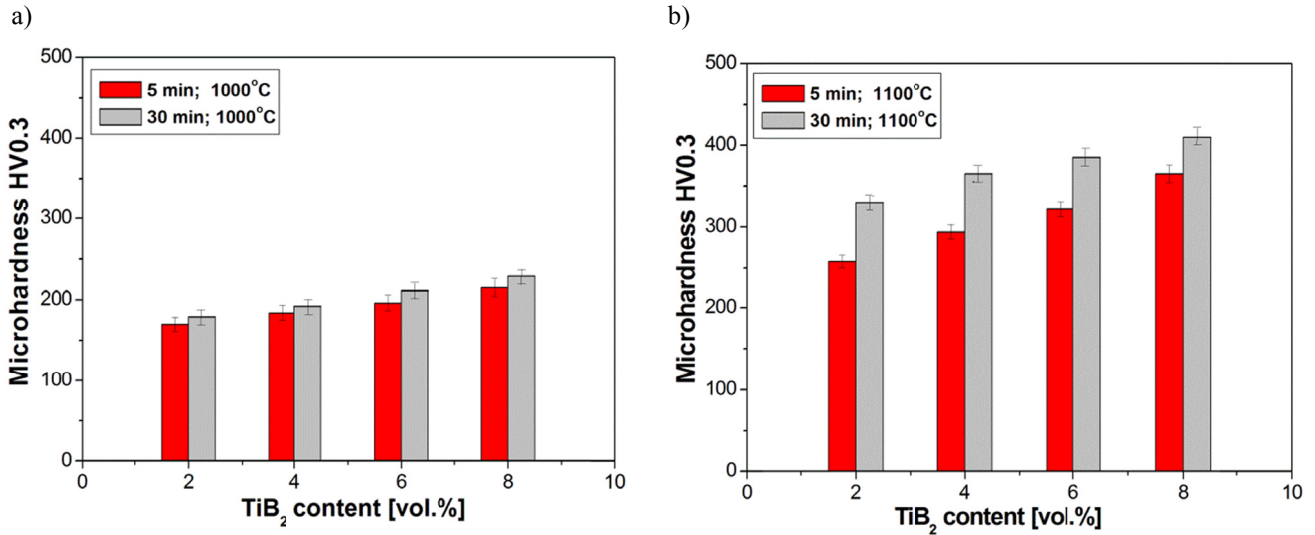


Fig. 4. Microhardness of the 316L steel-TiB<sub>2</sub> composite sintered by SPS at: (a) 1000°C and (b) 1100°C

sintering process was selected basing on previous experience with sintering the 316L austenitic stainless steel powder and on thermodynamic predictions regarding the diffusion process taking place in an Fe-TiB<sub>2</sub> system. The obtained results showed that the temperature of 1000°C can not provide the consolidation of composite components at a level of the intermolecular diffusion. The measured after-sintering density of the composite

has reached the level of 82-85% of the theoretical density, while porosity was in the range of 6-18% [16]. This proves absence of the liquid or semi-liquid phase during the consolidation process, which should be reflected in the results of mechanical tests shown in Figures 5-8. The best mechanical properties at the sintering temperature of 1000°C were obtained for the variant with 6vol% TiB<sub>2</sub>, where the following values of the mechanical properties

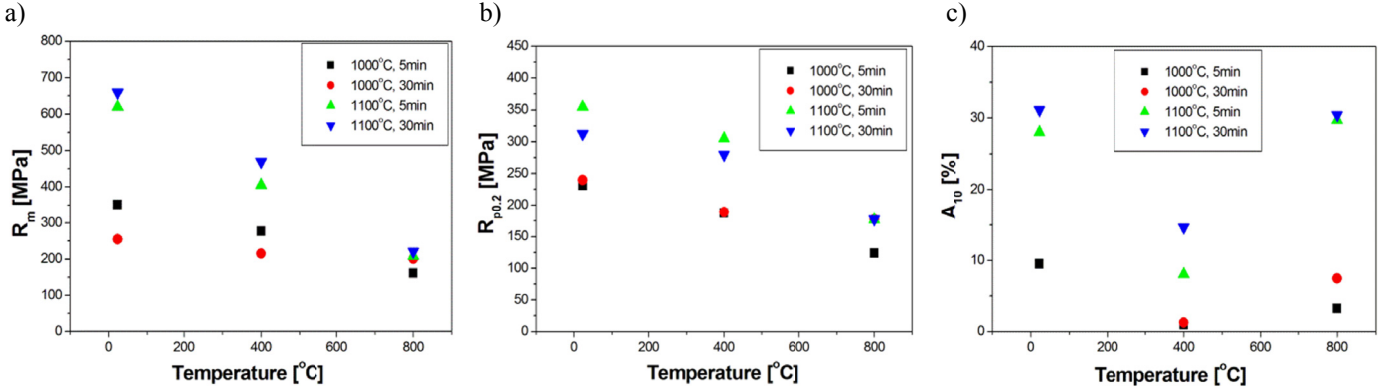


Fig. 5. The obtained mechanical properties: (a) tensile strength ( $R_m$ ), (b) yield strength ( $R_{p0.2}$ ), (c) elongation ( $A_{10}$ ) determined during the tensile test of 316L steel-2vol% TiB<sub>2</sub> composite

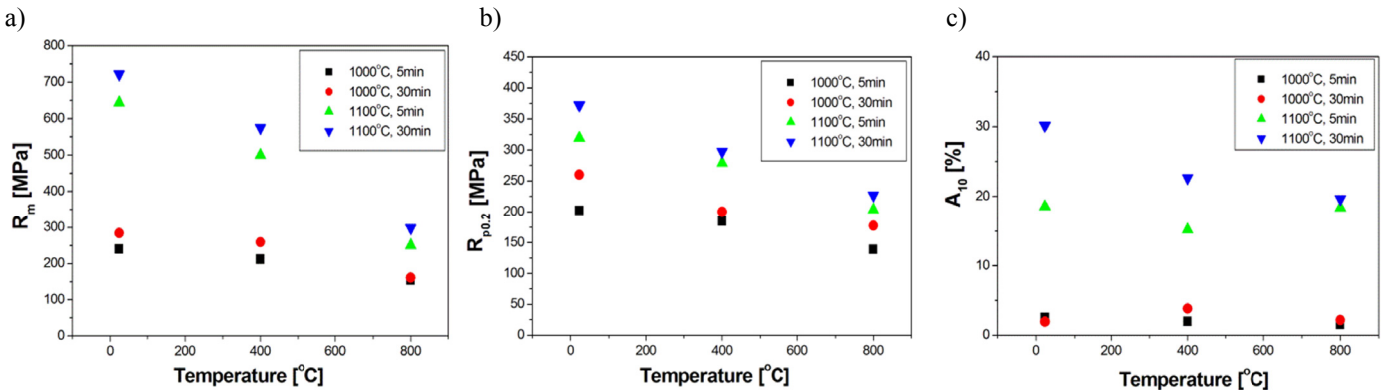


Fig. 6. The obtained mechanical properties: (a) tensile strength ( $R_m$ ), (b) yield strength ( $R_{p0.2}$ ), (c) elongation ( $A_{10}$ ) determined during the tensile test of 316L steel-4vol% TiB<sub>2</sub> composite

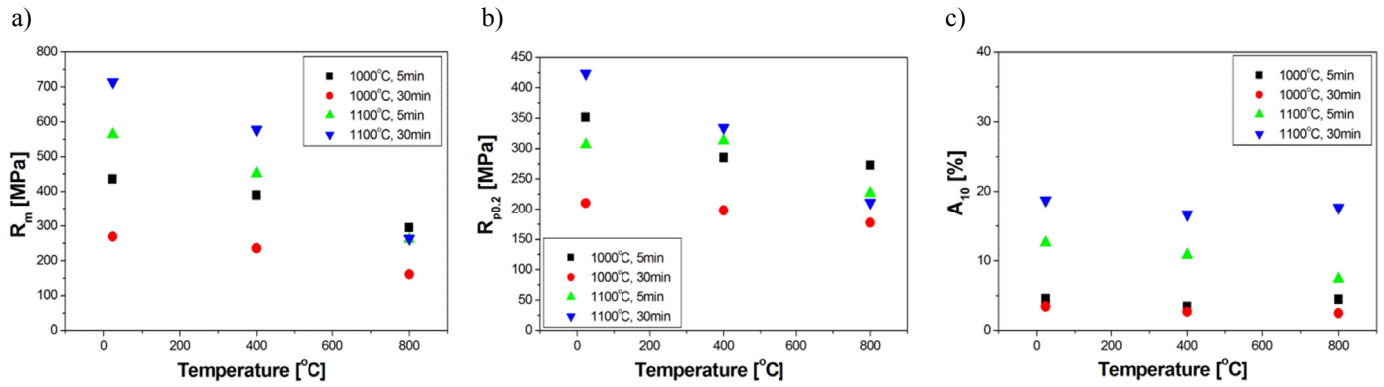


Fig. 7. The obtained mechanical properties: (a) tensile strength ( $R_m$ ), (b) yield strength ( $R_{p0.2}$ ), (c) elongation ( $A_{10}$ ) determined during the tensile test of 316L steel-6vol% TiB<sub>2</sub> composite

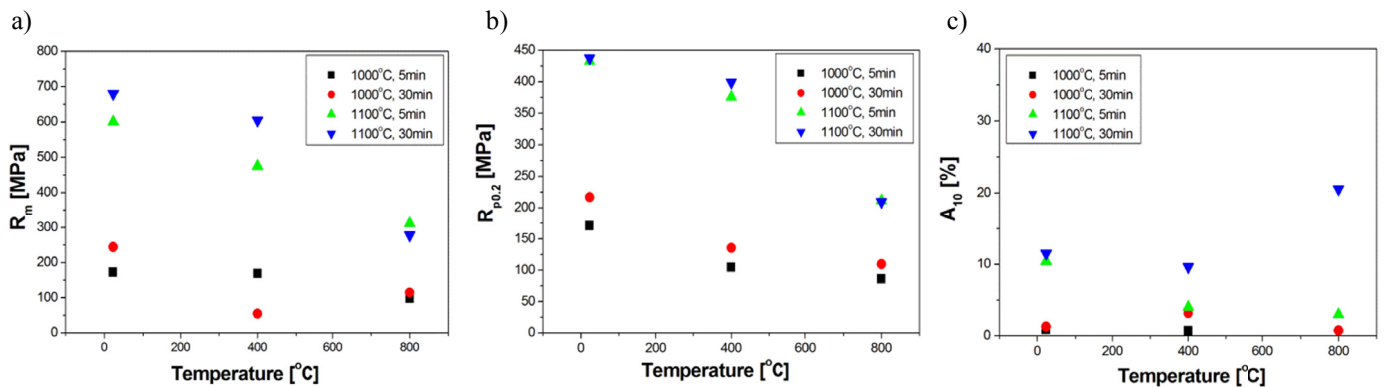


Fig. 8. The obtained mechanical properties: (a) tensile strength ( $R_m$ ), (b) yield strength ( $R_{p0.2}$ ), (c) elongation ( $A_{10}$ ) determined during the tensile test of 316L steel-8vol% TiB<sub>2</sub> composite

were obtained for the 1000°C-5min specimen:  $R_m = 450$  MPa,  $R_{p0.2} = 350$  MPa,  $A_{10} = 4\%$ . Analysis of the effect of sintering time (5 and 30 minutes) on the properties obtained in samples sintered at 1000°C gave inconclusive results. This may suggest balancing on the edge of conditions which provide the consolidation of powder at the diffusion border with the participation of semi-liquid phase. Increasing the sintering temperature to 1100°C produced material with much better mechanical properties. Figure 2 shows the microstructure of non-deformed samples containing different amounts of TiB<sub>2</sub>, i.e. from 2vol% to 8vol%. The samples were obtained by sintering at 1100°C for 5 minutes. It was a variant of the sintering temperature which provided the best mechanical properties, i.e. strength and ductility, in all samples tested (Figs. 5a-8a). In all cases examined in this variant (the content of the reinforcing phase from 2vol% to 8% TiB<sub>2</sub>, the sintering temperature of 1100°C), high values of the tensile strength  $R_m$ , i.e. exceeding 600MPa, were obtained at room temperature. The yield strength  $R_{p0.2}$  showed similar favourable characteristics. Increasing the deformation temperature in a sequence of 20-400-800°C resulted in a decrease of mechanical properties following a non-linear course of changes (Figs. 5b-8b), where the rate of decrease was increasing with the increase of temperature.

In the case of elongation  $A_{10}$ , a strong ductility-limiting factor was the content of the reinforcing TiB<sub>2</sub> phase. Exceeding the 6vol% TiB<sub>2</sub> content in steel matrix brought sharp decline of ductility (Figs. 5c-8c). This was particularly true in the case

of samples sintered for 5 minutes. A characteristic feature of samples obtained by SPS at 1100°C was the occurrence of a minimum ductility at the temperature of 400°C. This was particularly evident in the case of samples with the lowest and highest content of TiB<sub>2</sub>, i.e. 2vol% and 8vol%, respectively.

Analysis of the results has indicated that mechanical properties of the resulting sintered composites are strongly influenced by the time of sintering. The optimum sintering temperature at a level of 1100°C enabled obtaining fast bond between the particles of powder and the degree of consolidation exceeding in all variants 97% [16]. This proves the appearance of a liquid phase and efficient diffusion-based exchange of components. Even the sintering time as short as 5 minutes was sufficient to produce the material with satisfactory mechanical properties. In all the cases examined, increasing the sintering time to 30 minutes has resulted in an improvement of the mechanical and plastic properties. A particularly advantageous increase of elongation was observed in the samples with 8vol% TiB<sub>2</sub>. These samples after a long time of sintering showed the increase of ductility proportional to the increase of deformation temperature (Fig. 8c  $A_{10}$  for steel-8vol%TiB<sub>2</sub> composite, 1100°C-30 min). A similar, although less pronounced, relationship was observed in samples with the lower content of TiB<sub>2</sub>. In these samples, the sintering time of 5 minutes was sufficient to provide the required ductility. In contrast, samples sintered at 1100°C for 5 minutes and deformed at 800°C showed the ductility drop to 2vol%. The

reason was the difference in the structure of phase boundaries caused by the sintering time. The shorter time of 5 minutes was sufficient to effect a reaction involving the liquid phase and to obtain a high level of consolidation of the individual particles with small thickness of the resulting boundary. As a consequence, the structure with locally varying chemical composition was formed, in which the deformable phase was mixed with the precipitates of hard phases. The longer time of sintering, i.e. 30 minutes, has brought structure homogenization advantageous for the plastic phases. Additionally, as observed in other studies [20], in the process of deformation at elevated temperature, the structure was consolidated and its ductility reduced due to the dynamic precipitation. Longer time of sintering produces (30 minutes) the structure more stable thermodynamically. Then the dynamic precipitation proceeds with less intensity than it does in the structure obtained as a result of the short time of sintering (5 minutes). Under such conditions, the main process accompanying the high temperature deformation is sliding along the grain boundaries not hindered by precipitation. The occurrence of this phenomenon is also encouraged by a large volume of material with the homogeneous structure and high ductility within the grain boundaries. This is visible in the composite microstructure examined on fractures of the specimens stretched at high temperatures (Figs. 9,10). A high level of homogeneity was observed on the entire cross-sectional area of sample with gently rounded structure components indicating the plastic flow of material.

#### 4. Conclusions

Testing of mechanical properties has proved that the optimum temperature for the fabrication of 316L steel-TiB<sub>2</sub> composites by SPS is 1100°C. The use of lower temperature can not produce stable and fast intermolecular bonds that benefit from the appearance of a liquid phase. Important is also the time of sintering, as it affects the degree of reaction between different components of the system, and thus the homogeneity of resulting microstructure. This is particularly well visible during deformation carried out at high temperature of 800°C, when the mechanical properties of the examined material are affected by the additional processes, which do not occur at room temperature. These include, among others, the dynamic precipitation and sliding along grain boundaries. Detailed examinations of the properties of the obtained sinters show that the TiB<sub>2</sub> phase content in a steel matrix should not exceed 6vol%. When this level is exceeded, the plastic properties become unstable and strongly dependent on the sintering time. The maximum tensile strength  $R_m$  assumes its lowest values when the content of TiB<sub>2</sub> in the composite is 2vol%, while in the range of 4-8vol% TiB<sub>2</sub> a constant high level of  $R_m$  is obtained. Considering the data obtained it can be concluded that the optimum content of TiB<sub>2</sub> in the tested composites based on a 316L steel matrix is 4vol%. This composite material obtained by SPS has the highest tensile strength and satisfactory yield strength and is suitable for use in a wide range of temperatures.

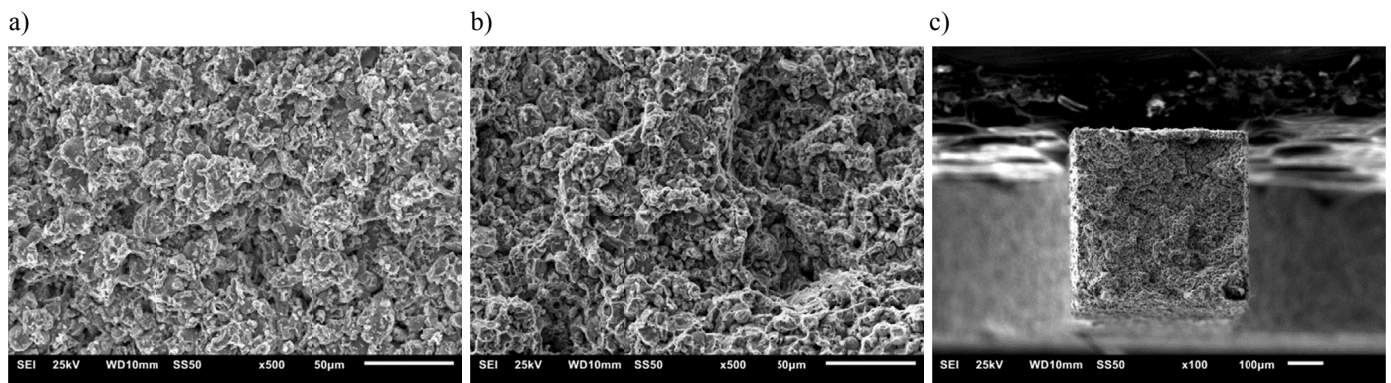


Fig. 9. Selected specimen fracture showing the microstructure of composite with 2vol% TiB<sub>2</sub> sintered by SPS (1100°C-30 min) after the tensile test carried out at: a) 400°C b) and c) 800°C

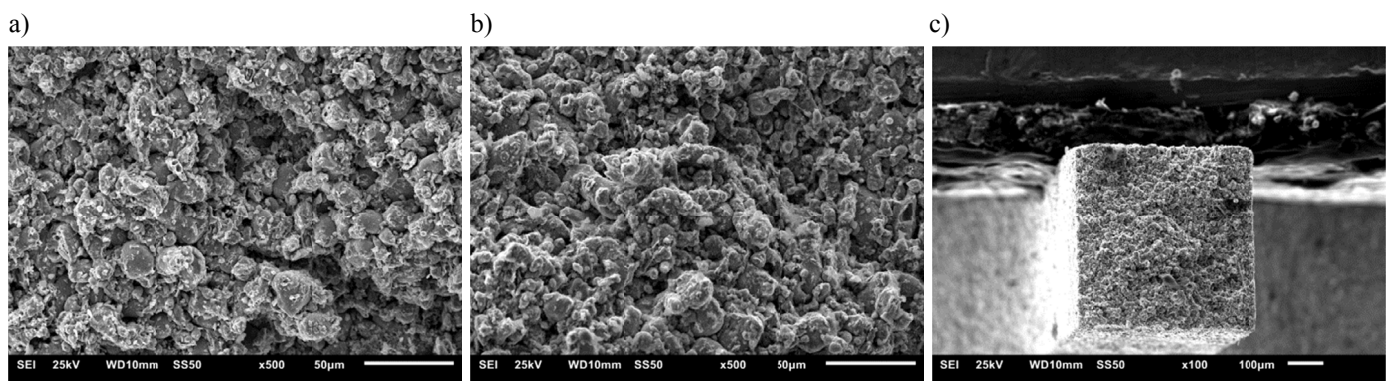


Fig. 10. Selected specimen fracture showing the microstructure of composite with 8vol% TiB<sub>2</sub> sintered by SPS (1100°C-30 min) after the tensile test carried out at: a) 400°C b) and c) 800°C

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