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Dilatometric study of low-alloy steels with silicon carbide addition

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Abstract Low-alloy steels produced via the traditional powder metallurgy process, using a die compaction, are currently widely used. Therefore, improving their properties is an issue that attracts much attention. The most common method of enhancing the properties of a given material is introducing additives, e.g., silicon to prealloyed low-alloy steels. It may be added through the mechanical alloying process. The article presents the results of research focused on an analysis of the influence of: (1) the mechanical alloying process, (2) various amounts of silicon carbide: 1, 2 or 3 mass% and carbon addition: 0.4 or 0.6 mass%, (3) different atmospheres, reducing or inert with 10 mass% of hydrogen and (4) the effect of annealing on phenomena occurring during the sintering of low-alloy steel. Moreover, changes in the sinters' microstructure and microhardness were also investigated. Based on the results, it was found that an increase in the amount of silicon in the material causes an increase in the shrinkage of the samples, prepared using mechanical alloying, during the sintering process. This observed effect was independent of the carbon content (0.4 or 0.6 mass%) in the samples as well as of the sintering atmosphere (reducing or inert with 10 mass% of hydrogen). The smallest porosity was observed for samples sintered directly after the mechanical alloying process. There is no need to use a hydrogen atmosphere during sintering—10 % of hydrogen added to an inert, e.g., helium atmosphere is enough to sinter the samples correctly.

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Introduction

Despite the fact that various novel materials, e.g., metal foams, shape memory alloys, nanomaterials or graphene are used more often nowadays, there is still necessity for applied materials that have been present for years. Similarly, new production technologies used for compaction and sintering are being developed and becoming increasingly more widespread, e.g., field-assisted sintering technique, metal injection molding and selective laser sintering [1–3]. However, the largest number of sintered parts is produced via die compaction. Low-alloy steels produced via the traditional powder metallurgy (PM) process are competitive materials due to the low costs of their production [4, 5]. At the same time, the additive of chromium and molybdenum improves mechanical properties of the steel [6]. Furthermore, sintered low-alloy steels are widely known as a cost-effective solution for high-volume structural components in the automotive or chemical industry, agriculture, construction equipment, the power tool industry, etc. [7]. Therefore, improving their properties is an issue that attracts much attention. The common method of enhancing the properties of the material is by introducing additives that will improve the mechanical properties of the produced elements, e.g., their creep resistance, hardness, yield strength and elasticity. This may be achieved by the addition of silicon, e.g., through mechanical alloying—MA, to prealloyed low-alloy steels [8, 9]. Silicon may also be introduced to the material in the form of silicon carbide (SiC) [10]. A further advantage of using this chemical

element as an alloy addition is its low cost, which raises the competitiveness of steel [8]. However, there are certain requirements that must be fulfilled in order to achieve the expected results while producing materials containing silicon, e.g., due to its high affinity for oxygen, it is important to use a very pure protective atmosphere during sintering [11]. On the other hand, if the sintering process is carried out improperly, the addition of silicon may decrease the material's properties.

The aim of the present work was to investigate the influence of the MA process and the amount of SiC and carbon addition on the thermal effects occurring during sintering of low-alloy steel, i.e., Astaloy CrL. In order to properly evaluate the differences between the produced materials, a dilatometer was used to register any dimensional changes and thermal effects; dilatometry is the most suitable method of observation of basic phenomena that are taking place during sintering low-alloy steels [12]. This technique was also successfully used for investigation of samples prepared from mechanically alloyed powders [13, 14]. Furthermore, the influence of powder annealing and atmosphere applied during the sintering process was investigated.

Materials and methods

Water-atomized iron powder prealloyed with the addition of 1.5 mass% of Cr and 0.2 mass% of Mo, commercial name—Astaloy CrL, manufactured and supplied by Höganäs AB, Sweden, was used as a base material. Silicon as an alloy additive was introduced as SiC (irregular particles with a size between 10 and 40 μm, supplied by Sigma-Aldrich) in the amount of 1, 2 or 3 mass%. Stearic acid, i.e., $CH_3(CH_2)_{16}COOH$, was added as the agent with the aim of controlling the MA process and, in principle, of preventing powder particle agglomeration. Then the powders were homogenized by MA. For MA, a highly energetic planetary mono ball mill, Fritsch Pulverisette 6 model, was used. The process was carried out in a tempered steel container equipped with grinding balls ∅ 10 mm, under a vacuum atmosphere. The ratio of powder mass to ball mass was at a level of 1:10. One cycle of milling time was 6 min, with a 30-min intermission period. The number of cycles was 200, and the rotary speed was 500 rot min^{-1}. The majority of particles obtained through this procedure had an average diameter around 20 μm, and they had a rounded shape. After the MA process, selected powder mixtures were annealed in vacuum atmosphere. They were heated at 10 °C s^{-1} to a temperature of 600 °C, held at that temperature for 60 min and then cooled in a furnace. This process did not affect in any way the shape and size of particles. Next, graphite, supplied by TIMCAL, was added to the powders mixtures—annealed ones as well as obtained directly after MA. The powders with added graphite, in the amount of 0.4 or 0.6 mass%, were mixed using Turbula equipment for 24 h. The obtained mixtures were used to prepare the samples compacted by one-sided pressing, under 600 MPa pressure. Each cylindrical sample had a diameter of 5 mm and height of 15 mm. Sintering behavior tests were carried out in a horizontal Netzsch 402 C dilatometer. The process was performed (1) in high-purity (99.9999) hydrogen and (2) in a mixture atmosphere of helium and hydrogen, i.e., 90 % He + 10 % H_2. The atmosphere flow rate for all measurements was 100 mL min^{-1}. The heating and cooling rates were 10 °C min^{-1}. The isothermal sintering temperature was 1120 °C. The holding time at the isothermal sintering temperature was 45 min. Two repetitions were measured. Data were analyzed with the use of Proteus software version 5.2.0 supplied by Netzsch.

Microstructure characterizations after etching with the use of Nital and microhardness HV0.025 of the samples after the sintering process were determined by using the microhardness, model Nexus 423A equipped with a Nexus Inv-1 set. At least ten measurements were taken.

Results and discussion

Figures 1–4 present the dimensional changes of the tested mixtures as a function of the applied temperature profile of the sintering process. The curves presented in Figs. 1 and 3 show the results obtained for mixtures containing 0.4 mass% of C and various amounts of SiC, i.e., 1, 2 or 3 mass%, sintered in hydrogen as well as in a mixed atmosphere containing 90 % He + 10 % H_2.

From the obtained results, it is possible to interpret the changes that take place in the samples during sintering depending on: (1) different amounts of introduced addition of SiC and (2) the sintering atmosphere that is used. Based on the results, it may be observed that an increased amount of SiC in the sample resulted in higher final shrinkage. This effect was independent of the applied atmosphere, i.e., reducing H_2 or the more inert 90 % He + 10 % H_2. Furthermore, the amount of carbon in the mixture did not affect the change in recorded shrinkage. The results for both samples with 0.4 mass% of C and samples with 0.6 mass% of C were very similar, Tables 1 and 2.

This result proves that the main effects intensifying the sintering process take place during the preparation of mixtures, i.e., during the MA process. In fact, during this process, the most significant changes or structural defects

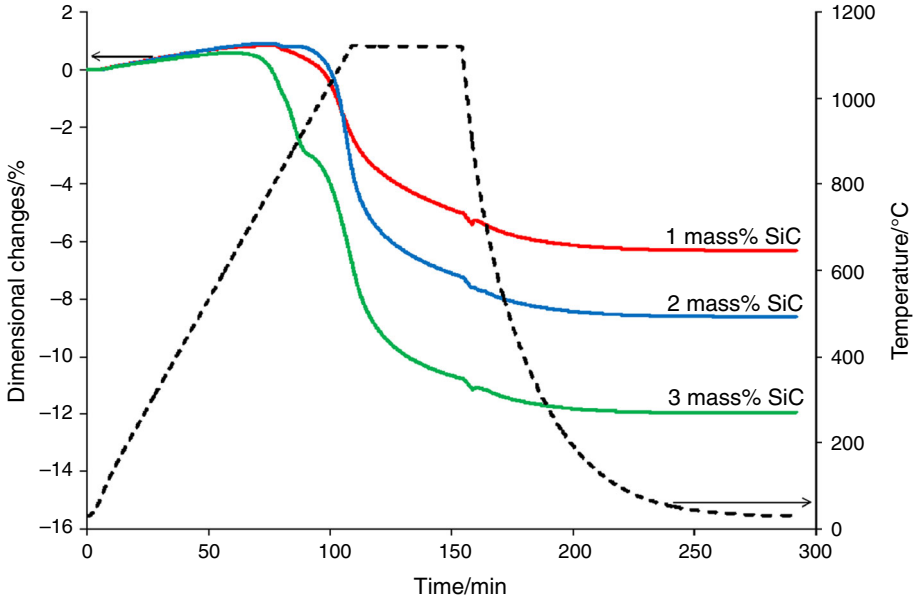

Fig. 1 Sintering of mechanically alloyed and annealed mixtures of Astaloy CrL powder; 1, 2 or 3 mass% of SiC and 0.4 mass% of C in pure hydrogen

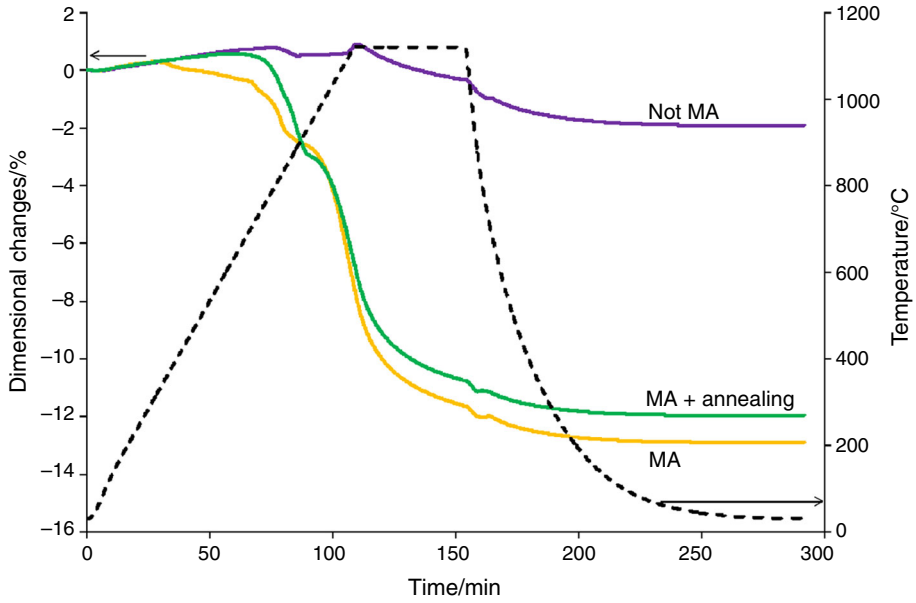

Fig. 2 Sintering of differently prepared mixtures of Astaloy CrL powder; 3 mass% of SiC and 0.4 mass% of C in pure hydrogen

of material occur, e.g., fragmentation, homogenization and particle hardening [11]. The above-mentioned effects greatly influence the subsequent sintering process of the produced mixtures that may also be observed in Figs. 2 and 4. Moreover, an increase in the SiC content causes faster hardening of mechanically alloyed particles as well as their higher fragmentation efficiency. Both of these features intensify the driving force of the sintering process. It was observed that the value of shrinkage for the MA mixtures, which occurred during heating, reached or even exceeded the dimensional changes that were taking place during isothermal sintering of the samples, Tables 1 and 2. The observed effects were independent of the type of applied atmosphere and the amount of carbon, i.e., 0.4 or 0.6 mass%.

The results presented in Figs. 2 and 4 allow us to observe the influence of the (1) MA process, (2) amount of carbon addition and (3) annealing of mechanically alloyed powder mixtures on phenomena occurring during the sintering process. The above-mentioned analyses were carried out for mixtures containing the highest amount of SiC, i.e., 3 mass%. The amount of carbon introduced just before the sintering process was, respectively, 0.4 or 0.6 mass%. The process was conducted under a hydrogen atmosphere or under a mixture atmosphere, i.e., 90 % He + 10 % H_2.

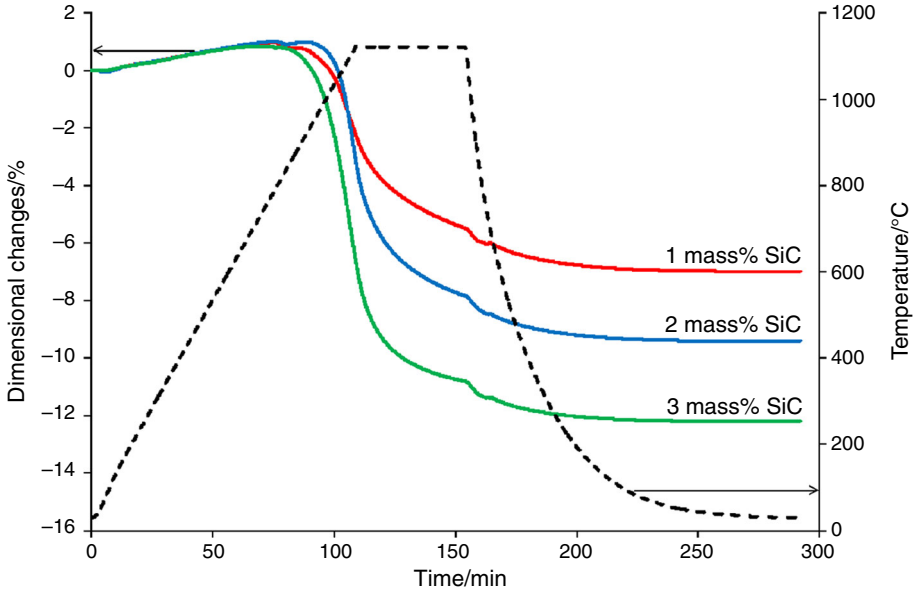

Fig. 3 Sintering of mechanically alloyed and annealed mixtures of Astaloy CrL powder; 1, 2 or 3 mass% of SiC and 0.4 mass% of C in helium atmosphere with 10 % of hydrogen

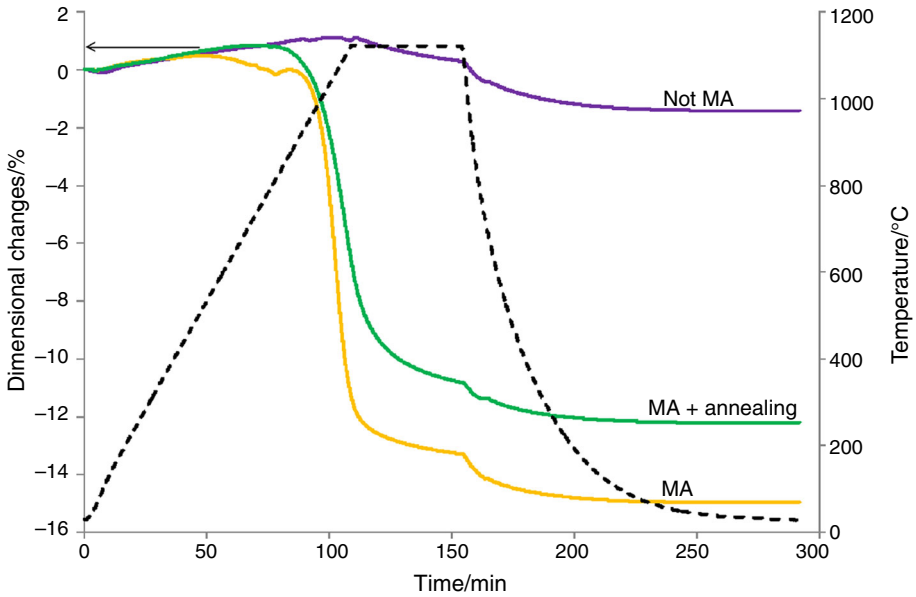

Fig. 4 Sintering of differently prepared mixtures of Astaloy CrL powder; 3 mass% of SiC and 0.4 mass% of C in helium atmosphere with 10 % of hydrogen

During heating to the isothermal sintering temperature of mixtures that were not mechanically alloyed on the dilatometric curves at about 900 °C, the αFe → γFe transformation was observed, Figs. 2 and 4. Different results were recorded for the samples after the MA process. The onset of the αFe → γFe transformation was shifted to the lower temperature range. This phenomenon was the consequence of the accumulated of large compressive strains during alloying as well as fragmentation of particles. Moreover, the intensity of registered peaks was also much smaller in comparison with not mechanically alloyed samples. These effects were independent of the applied atmosphere. Furthermore, the samples measured directly after MA process showed drastic shrinkage during heating, which started between 400 and 600 °C as a result of removal/evaporation of the organic agent from the specimen. This effect was not recorded for annealed samples. During cooling below 900 °C, the γFe → αFe transformation was registered. Green density of mixing powder was about 6.9 g cm^{-3}, while the density of the compacts after MA process was much lower, around 6.3 g cm^{-3}. The overall shrinkage of sinters produced from powders which were prepared only by mixing in a Turbula, as opposed to those that were obtained by MA in a highly energetic planetary mono ball mill, was usually about 1.5 %. Dimensional changes that were almost one order of

Table 1 Characteristic points of graphs for samples with 0.4 mass% of carbon addition

Atmosphere	SiC/mass%	Preparation	Start of the shrinking process		Shrinkage value at the start and end of the isothermal step		Overall shrinkage
			T/°C	Dimensional changes/%	Dimensional changes/%	Dimensional changes/%	Dimensional changes/%
H_2	1	MA + annealing	809	0.82	−2.37	−5.00	−6.32
	2	MA + annealing	804	0.89	−3.65	−7.23	−8.61
	3	MA + annealing	684	0.55	−6.75	−10.76	−11.95
	3	MA	350	0.27	−7.86	−11.64	−12.90
	3	Not MA	1120	0.90	0.90	−0.33	−1.92
He + 10 % H_2	1	MA + annealing	800	0.95	−2.32	−5.49	−6.99
	2	MA + annealing	804	0.98	−3.33	−7.85	−9.42
	3	MA + annealing	782	0.83	−6.61	−10.82	−12.22
	3	MA	593	0.43	−11.32	−13.29	−14.98
	3	Not MA	1120	1.14	1.14	0.29	−1.43

Table 2 Characteristic points of graphs for samples with 0.6 mass% of carbon addition

Atmosphere	SiC/mass%	Preparation	Start of the shrinking process		Shrinkage value at the start and end of the isothermal step		Overall shrinkage
			T/°C	Dimensional changes/%	Dimensional changes/%	Dimensional changes/%	Dimensional changes/%
H_2	1	MA + annealing	805	0.77	−2.68	−5.29	−6.68
	2	MA + annealing	902	0.83	−3.76	−7.35	−8.79
	3	MA + annealing	759	0.64	−6.12	−10.54	−11.76
	3	MA	363	0.29	−10.11	−13.96	−15.21
	3	Not MA	1120	1.06	1.06	0.13	−1.47
He + 10 % H_2	1	MA + annealing	882	0.78	−2.77	−6.20	−7.82
	2	MA + annealing	944	1.12	−2.60	−7.21	−8.76
	3	MA + annealing	844	0.89	−6.31	−10.02	−11.52
	3	MA	882	−0.04	−11.91	−14.14	−15.83
	3	Not MA	1120	1.33	1.33	0.38	−1.40

magnitude larger were observed for identical mixtures but sintered after MA, Figs. 2, 4 and Tables 1, 2. Conducting the annealing process of powders after MA, before consolidation, caused a decrease, in comparison with materials that were mechanically alloyed but not annealed, in the overall shrinkage (ca. 2–3 %) of the samples after sintering. The described results are independent of the various amounts of carbon in the prepared mixtures as well as of the atmospheres that were applied during sintering. Moreover, it was observed that, depending on the way the samples were prepared, the temperature of the beginning of the sintering process changed significantly. Mixtures investigated directly after the MA process showed a shifting of the beginning of the sintering processes to the lowest temperatures—about 500 °C, Tables 1 and 2. The initiation of shrinkage in the annealed samples was observed at a temperature of about 800 °C. On the other hand, sintering of mixtures that were not mechanically alloyed did not start before the sample reached a temperature of 1120 °C. On the basis of the obtained results, it could be concluded that the MA process had a strong influence on the sintering behavior of the investigated powder mixture. MA works as an activator which intensifies the driving forces of the sintering process. This phenomenon is correlated with the fragmentation of particles, accumulated energy during MA and the presence of lubricant additions, which can also be disintegrated in the course of the MA process [9]. Moreover, in high temperatures, above 1000 °C, the dominant mechanism for the reduction of oxides and the activation of the sintering

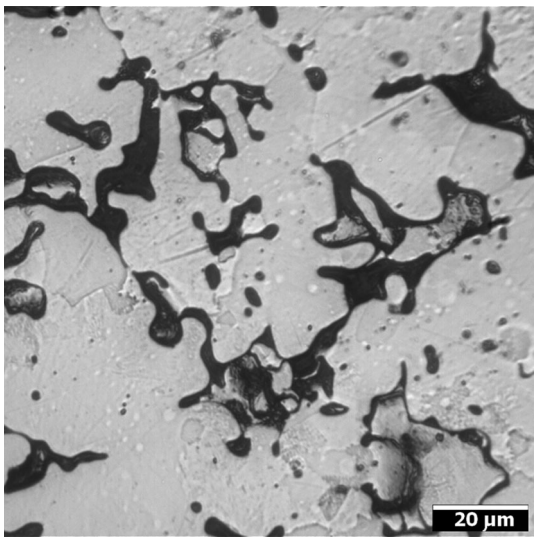

Fig. 5 Microstructure of a mixture of Astaloy CrL powder with the addition of 3 mass% of SiC and 0.4 mass% of C sintered in a hydrogen atmosphere

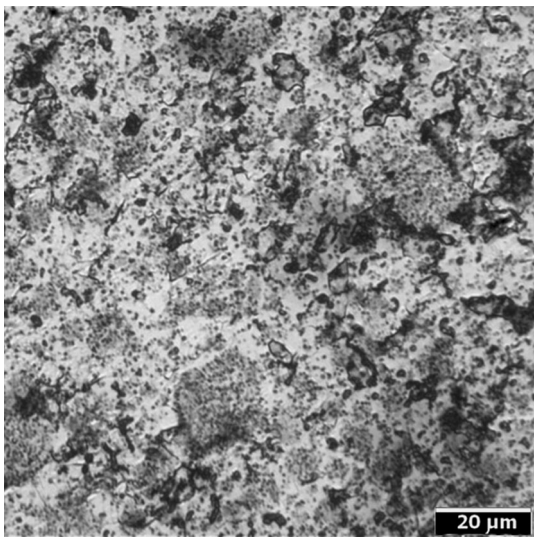

Fig. 7 Microstructure of a mixture of Astaloy CrL powder with the addition of 3 mass% of SiC and 0.4 mass% of C; mechanically alloyed and sintered in a hydrogen atmosphere

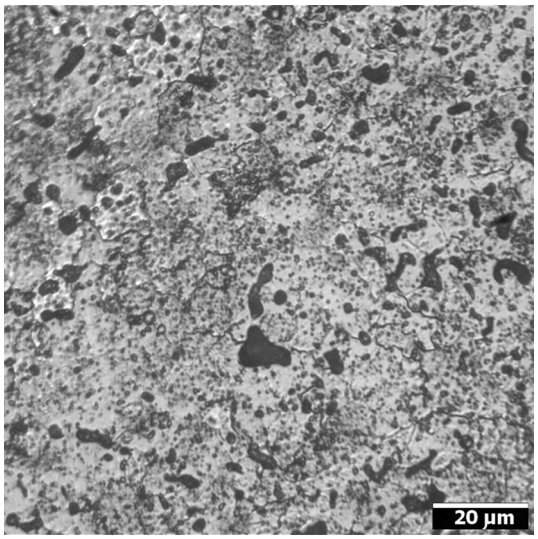

Fig. 6 Microstructure of a mixture of Astaloy CrL powder with the addition of 3 mass% of SiC and 0.4 mass% of C; mechanically alloyed, annealed and sintered in a hydrogen atmosphere

Table 3 Microhardness of samples with 0.4 mass% of C

SiC/mass%	Preparation	Atmosphere	
		H_2	He + 10 % H_2
1	MA + annealing	149 ± 34	202 ± 40
2	MA + annealing	230 ± 41	391 ± 74
3	MA + annealing	183 ± 44	389 ± 70
3	MA	259 ± 44	620 ± 222
3	Not MA	217 ± 66	374 ± 89

process is the carbothermal reaction. This effect has been described in another works [15–17].

Based on all of the obtained results, it may be observed that using an inert atmosphere with 10 % H_2 is enough to obtain the same results as after sintering in a reducing atmosphere of hydrogen. These observations are in accordance with results obtained in previous research [18].

Figures 5–7 present representative microstructures of the tested materials containing 3 mass% of SiC and 0.4 mass% of C. It was observed that the sinters of mixtures that were not mechanically alloyed had a greater amount of porosity, Fig. 5. Its shape was irregular, and the pores were often connected. On the other hand, sinters of mixtures that were annealed after MA revealed a significantly smaller amount of porosity in their structure. In Fig. 6, fine, spherical and individual pores may be observed. The highest densification was obtained for samples that were sintered directly after the MA process, Fig. 7. The above-mentioned dependences are in complete accordance with the dilatometric results that were presented before. They confirm that the driving force of the sintering process occurs most intensively for powders that were significantly deformed and fragmented during the MA process. Furthermore, it was observed that the increase in carbon addition up to 0.6 mass% did not significantly affect the modification of the samples' microstructures. Moreover, materials containing different amounts of introduced silicon had similar microstructures.

Table 4 Microhardness of samples with 0.6 mass% of C

SiC/mass%	Preparation	Atmosphere	
		H_2	He + 10 % H_2
1	MA + annealing	161 ± 23	316 ± 67
2	MA + annealing	195 ± 30	413 ± 61
3	MA + annealing	233 ± 34	466 ± 15
3	MA	260 ± 66	751 ± 524
3	Not MA	265 ± 94	526 ± 285

Microhardness tests were conducted for all samples. The obtained results are presented in Tables 3 and 4. Although the standard deviation of some measurements is significant due to the heterogeneity of microstructure, i.e., the matrix and precipitates, its medium value allows to make some observations about the differences between the samples. It was observed that the microhardness of the sinters increased along with an increase in the SiC addition from 1 to 3 mass%. This effect is even more visible for samples containing 0.6 mass% of C. Moreover, using an inert gas containing 10 % of hydrogen as a protective atmosphere allows to obtain higher hardness of the samples than in the case of sintering materials of an identical chemical composition, but in a hydrogen atmosphere. The described effect may be explained by the fact that the content of carbon in the material is decreased during sintering in hydrogen, which causes a drop in the microhardness values. Furthermore, microhardness of the final product decreases when annealing is performed before the sintering process. This phenomenon is associated with the sintering process and with the presence of porosity in the material structure. The highest value of microhardness was obtained for samples that were sintered directly after the MA process in a mixed atmosphere of 90 % He + 10 % H_2.

Conclusions

The MA process allowed to effectively introduce SiC–Astaloy CrL powder. Based on the results, it can be concluded that an increase in the amount of silicon in the material causes an increase in the shrinkage of the samples after MA during the sintering process. The observed effect was independent of the carbon content, i.e., 0.4 or 0.6 mass%, in the sample as well as of the sintering atmosphere—reducing or inert with 10 mass% of hydrogen. Annealing of the powder mixtures after the MA process allowed to obtain fine, spherical porosity in the structure of the material. The smallest porosity was observed for samples sintered directly after the MA process. There is no need to use hydrogen atmosphere during sintering, as 10 % of hydrogen added to an inert, e.g., helium atmosphere is enough to sinter the samples correctly. Higher values of microhardness were obtained for samples sintered in a mixed atmosphere, i.e., 90 % of helium with 10 % of hydrogen. These results were independent of the type of investigated mixtures.

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