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Process parameter optimization of pulsed electric current sintering of recycled WC-8Co powder

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Abstract. The WC-8Co powder, crushed and milled from recycled hard metals, was compacted with the pulsed electric current sintering method. The smallest particles were of the size about 0.4 μm and agglomerates 1–7 μm. Effect of the sintering temperature and heating rate were studied. Hard metal was sintered to a density of 98.3% at 1613 K within 3.5 min under 16 MPa pressure. Density and hardness were highest for the slowest heating regime, 98.1% and HV1 1981 kg/mm^2, respectively. Heating speed 100 K/min was used for fabrication of fully densed samples, sintered under pressure of 100 MPa, at 1593 K in 3 min.

Key words: pulsed electric current sintering, WC-Co, microstructure, density, hardness.

1. INTRODUCTION

The cemented carbide hard materials, namely WC-Co, consist of hard tungsten carbide particles, embedded into metallic binder phase. They have the combination of high hardness, good wear resistance and toughness, which make WC-Co an attractive material for machining, cutting, drilling and metal injection applications [1–4]. Powder metallurgy is the main route for processing and manufacturing of bulk cemented carbides, such as cutting tools, drill tips, machining elements or dies. Conventional and pressure-assisted sintering methods like hot pressing and HIPing, as well as relatively new sintering methods such as pulsed

electric current sintering, high-frequency induction heating sintering and microwave sintering are techniques for manufacturing of tungsten carbide based materials and other hard materials [2,3]. These materials are also used in the form of protective surface layers; thermal spray processing is the most common fabrication technique for this purpose [2]. As WC-Co has been widely applied in industry, the recycling of this material is relevant. For this purpose, especially powder metallurgy can be applied [5].

Pulsed electric current sintering process (PECS) is a relatively new method for sintering of a wide variety of materials. This technology has attracted a lot of attention in materials research in the last decade, evidenced by sevenfold increase in the number of publications about electric current assisted sintering of various materials [6]. There are still different types of classifications among electric current sintering techniques, and yet the name of this process has many variations [6]. In this paper pulsed electric current sintering or PECS will be used. This consolidation technology uses Joule heating, provided by passing electric current through two electrodes and powders in graphite moulds between them [6,7]. This technology is fast and requires lower sintering temperatures. Thus the process is less sensitive to the characteristics of the powders [6], which is a benefit while working with recycled powders. In this method the powder or a pre-compact is placed into a graphite mould and a force is applied for compacting the powder, enhancing the sintering behaviour and to provide a continuous contact between two electrodes. Higher pressures can be applied depending on the equipment configuration during or before the sintering. The heating rates are higher as compared to conventional methods, and sintering durations are also considerably shorter, typically less than 10 min [6–8].

Another factor, affecting the process parameters of PECS application, is related to the electrical conductivity of the powder to be sintered [8]. The amount of Co, size distribution of both the powder to be compacted as well as its constitutive powder components and morphology of the WC-Co powders are the major influencing factors that must be taken into account [2,6,7]. The better the Co powder is distributed around the WC particles, since the Co powder has smaller size than WC, the more effective the electric current flows through the material. This may be one of the reasons why this method is mostly applied to the nano- and microsized powders. Another motivation for using PECS method is that the small particle size of the starting material can be preserved in the final compact. Examples from literature of last five years are collected in Table 1, and they are compared by process parameters and final material properties. The published studies on consolidation of WC-Co materials by PECS are carried out with commercial powders or they are produced in laboratory scale. However, information about compacting recycled powders is not available.

In this study, WC-8Co recycled powder has been compacted to its full density by the PECS process. Dependence of densification and hardness behaviour of the material on the process parameters has been studied. Microstructure examination and grain size analysis were conducted for the sintered pieces.

Table 1. Some WC-Co powders, compacted with the spark plasma sintering, described in [7–17]

WC-Co powder wt%Co Particle sizes, nm	Sintering parameters Temperature, K; time, min; heating speed, K/min; pressure, MPa	Compact Hardness, HV; relative density, %; grain size, nm	Reference
6Co, 200	1553, 2, 100, 60	2180 HV10, 97, 650	[8]
6Co, 300	–, –, –, –	2024, 98.73, 650	[9]
6.29Co, 30	1373, 10, –, 50	94 HRA, 99.1, 350	[10]
7Co	1273, –, –, –	92.1 HRA, 95.4, WC190	[11]
	1323, –, –, –	93.8 HRA, 98.8, WC213	
	1373, –, –, –	94.1 HRA, 99.9, WC253	
	1423, –, –, –	94 HRA, 99.9, WC320	
7Co, nano	1373, –, –, –	2093, 99.96, WC220	[12]
8Co, 150	1423, 5, –, –	–, 99.9, 350	[13]
8Co, 33	1150, 5, 100, 10 kN	2030, –, 200	[2,14]
10Co, 100	1173–1373, 10, 100, 50/100	1600, 95, 350	[14]
10Co, WC 200 + Co 28, WC 200 + Co 450	1323–1473, 10, 60, –	2030 [2] < 90 HRA, 99, 180 94.5 HRA, 99.98, 200	[7]
11Co, WC 80 + Co 60	1373, 5, 200, 25	92.8 HRA, 98, 770	[15]
12Co	1273, –, –, –	1472 HV30, 1557 HV0.5, 97.93, –	[16]
	1323, –, –, –	1512 HV30, 1613 HV0.5, 99.35, WC 700 ± 70, Co 290 ± 50	
	1373, –, –, –	1450 HV30, 1579 HV0.5, 99.89, WC 800 ± 40, Co 250 ± 60	
12Co, 40–250	1373, 10, 150, 60	1450, 99.89, 800	[2,17]

2. MATERIALS AND TEST PROCEDURES

The recycled hard metal WC-8Co powder, manufactured by Tikomet Oy Jyväskylä, was used in the tests. Before the processing, the powders were crushed and milled. The particle size distribution of the powder was studied with the laser diffractometer Lecotrac LT100. For the tests, the powders were dispersed in ethanol. The morphology of the powders as well as the structure of the compacts was studied with Hitachi 4700-S FEG-SEM and their chemical compositions were confirmed with the EDS analysis. Compactions of the material were carried out with the PECS equipment of FCT System Type HPD25/I. The powders were compacted and then sintered in moulds (ISO-63 type graphite). Graphite foil was used for protecting the inner surface of the mould and for improving the contact between the punches and the powder. In order to maintain a better thermal insulation, the 10 mm carbon felt was used. The diameters of the final compacts were 20 mm; 18.4 g of WC-Co powder was used in every experiment in order to achieve a final compact with an average thickness of approximately 4 mm. The schematic of equipment configuration and outline of the study is shown in Fig. 1.

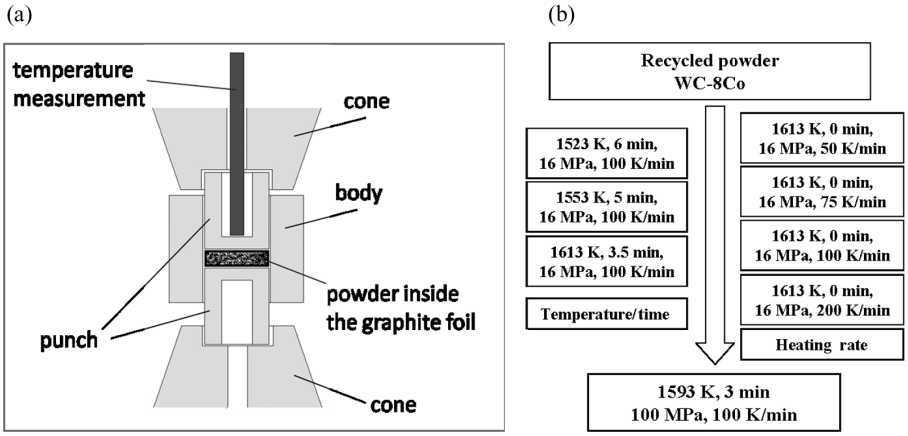

Fig. 1. Process schematic (a) and steps of sintering of WC-Co powders (b).

WC-8Co powders were sintered at temperatures of 1523–1613 K for 0–10 min under a vacuum of 7 Pa. The temperature measurement during process was made by an optical pyrometer in vertical direction from upper graphite punch, through a central hole; the wall thickness between the hole and the powder was 5 mm. The applied pressure was varied between the minimum for the equipment (about 16 MPa) and 100 MPa in the last test. The current was applied with pulse duration of 10 ms, the pause between pulses being 5 ms. Different heating rates were used in the range 50–200 K/min. After compaction of the WC-Co material, the graphite foil was removed from the surface of the compacts by sandblasting. The samples were ground with the diamond abrasive disks, polished to 1 μm finish and finally mechano-chemically polished by colloidal silica (0.06 μm).

The densities were measured by the Archimedes method using water for the measurements. The theoretical densities of the compacts were calculated by comparing the measured values with the theoretical density of the system $\rho_{WC\text{-}8Co}$ = 14.74 g/cm^3. The Vickers hardness numbers with 1 and 10 kg load were determined with the Zwick & Co Z323 apparatus. The XRDs were measured with Philips PW 1701 diffractometer applying the CuK_α radiation. The micro-structure evaluations as well as grain size analysis were made from secondary electron images, obtained by a scanning electron microscope. The average WC particle size in compacted bodies was determined from SEM images by using Image-J software. These analyses were made from four different SEM images of each sample at ×10 000 and ×5000 magnifications. Images were processed to similar contrast levels, thresholding and unit scaling were performed. During measurements the grains were converted into ellipses, for which the average size of grains was calculated.

3. RESULTS AND DISCUSSIONS

3.1. Powder characteristics

According to the X-ray diffraction pattern (Fig. 2), the recycled WC-8Co powder contains only WC and Co phases. Its particle size distribution (Fig. 3) after milling is $d_{0.1}$ = 0.852 μm, $d_{0.5}$ = 4.81 μm, and $d_{0.9}$ = 19.96 μm. In Fig. 3 there are three peaks in the particle size distribution, the smallest being close to 0.4 μm, the second one near to 1 μm and the highest one at 7 μm. The SEM study (Fig. 4) revealed the powder to consist of larger particles with rounded

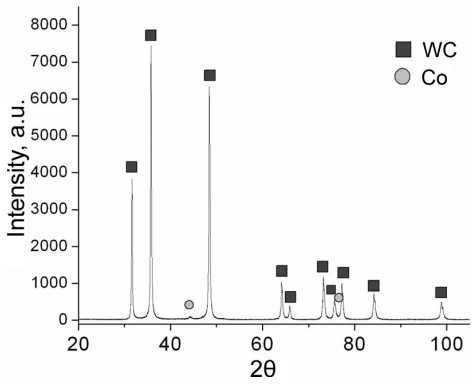

Fig. 2. X-ray diffraction patterns of the studied recycled WC-8Co powder.

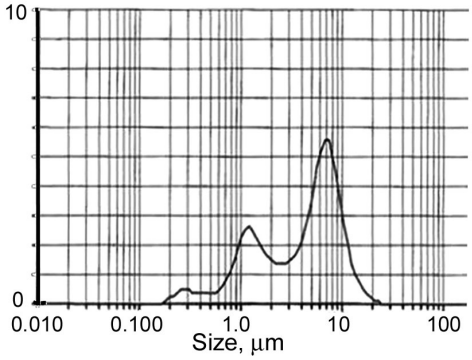

Fig. 3. Particle size distribution of WC-8Co powders in the laser diffractometer study.

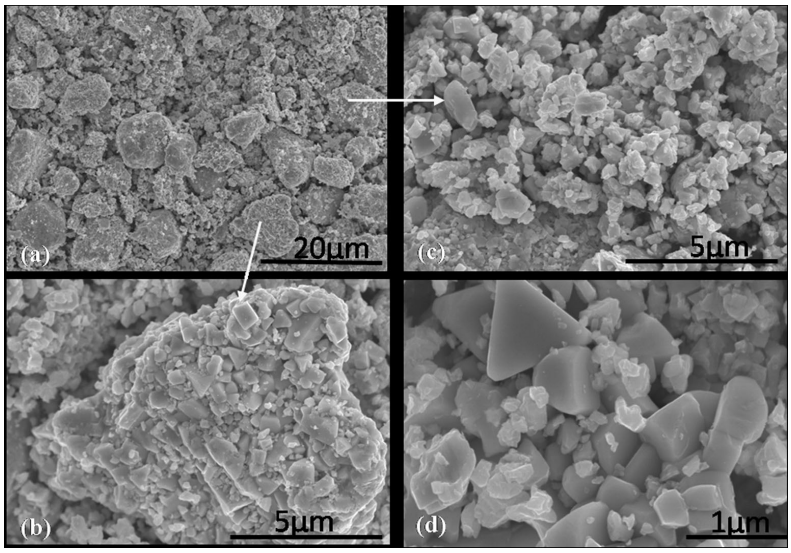

Fig. 4. Recycled WC-8Co powder composed of agglomerate-like large particles (a and b) evenly distributed within smaller WC and Co particles (c and d).

corners, mainly related to the particle size, corresponding to the highest peak, and of the small sized particles, corresponding to the second peak and close to the $d_{0.1}$ value. The agglomerate-like bigger particles were observed to be formed by "originally" small WC particles, which have not been crushed or ground to a smaller size, but remained as big particle-like dense structures of round and irregular shape (Fig. 4a, b). Smaller WC particles had angular shape with sharp edges similar to new powders (Fig. 4c, d).

3.2. Optimizing the PECS process parameters

The optimization of the PECS processing temperature was based on the values found in literature. In [13], the applied temperature is higher than 1423 K for WC-8Co, having particle size of 150 nm. The recycled powder, used in this study, had particle size of over 400 nm, thus an increase in the processing temperature was expected. In Table 1 the WC-6Co has a sintering temperature as high as 1523 K [8] and, therefore, it was suggested that the recycled powder may require such processing temperature. The applied PECS process parameters and the properties of the compacts achieved are given in Table 2. The average grain sizes of sintered compacts were between 0.490–0.540 μm, and grains corresponding to the large agglomerates and particles of the starting powder were observed in microstructure. Increase of the processing temperature or pressure did not influence markedly the final average grain size.

The first experiments were carried out in order to optimize the processing temperature, and also to find the time when the shrinkage, e.g. displacement of the piston, ends. Since with sintering for 6 min at a temperature of 1523 K the theoretical density was only 87.1%, the temperature was gradually increased to 1553 K (5 min) and to 1613 K (3.5 min). Heating rate and pressure were kept constant (100 K/min and 16 Mpa, respectively). At 1613 K, a dense microstructure was acquired and the theoretical density was approximately 98.3%.

Table 2. PECS compacting parameters together with the hardness and density of the compacts

Sample	PECS process parameters				Properties of the compact				
	Temperature, K	Time, min	Heating rate, K/min	Pressure, MPa	Hardness, HV1	Hardness, HV10	Density, g/cm^3	Relative density*, %	WC av. size, μm
R1	1523	6	100	16	1957 ± 73	1741 ± 26	12.95 ± 0.10	87.1	0.492
R2	1553	5	100	16	2076 ± 58	1935 ± 33	13.83 ± 0.08	93.2	0.490
R3	1613	3.5	100	16	2177 ± 84	2034 ± 31	14.55 ± 0.06	98.3	0.524
R4	1613	0	50	16	1981 ± 29	2072 ± 36	14.53 ± 0.07	98.1	0.486
R5	1613	0	75	16	1896 ± 93	1758 ± 29	14.33 ± 0.09	96.5	0.476
R6	1613	0	100	16	1858 ± 50	1836 ± 41	14.29 ± 0.07	96.5	0.539
R7	1613	0	200	16	1703 ± 36	1718 ± 30	13.87 ± 0.01	94.0	0.506
R8	1593	3	100	100	2222 ± 86	2055 ± 22	14.78 ± 0.02	100.0	0.504

* Theoretical density of WC-8Co was regarded as 14.74 g/cm^3 in the calculations.

Thus the following tests were carried out with varying heating rates up to a sintering temperature of 1613 K. In order to neglect the effect of pressure and time, the applied force was at the minimum and sintering time was 0 min. The applied heating rates were 50, 75, 100 and 200 K/min. When comparing the different holding times at 1613 K, the density after 0 min was only 96.5%, hardness being 1858±50 HV1, while after 3.5 min these values were 98.3% and 2177±84 HV1, respectively.

Accordingly, the processing time in the last, high pressure compression, was chosen to be 3 min. In order to obtain fully dense compact, the pressure was increased to 100 MPa. Since increasing the pressure allows lower processing temperatures [6], it was decreased to 1593 K, also to avoid squeezing of Co. The heating rate of 100 K/min was chosen during sintering, to benefit from the significantly short processing time of the PCES method. Comparison of surface and cross-section hardness of the compacts is given in Fig. 5. The surface hardness of R1 is rather high and close to R3 even though there is a big difference between density values of the two compacts, which may be related to the difference in their cross-section hardness.

The structures of the compacts with lighter carbide particles on the dark cobalt matrix are shown in Fig. 6. Larger pores and loose stacking of WC particles were observed in the low temperature samples R1 and R2 (Figs. 6a and b), while the pore sizes in sample R3, compacted at 1613 K, were smaller (Fig. 6c). The compacts, sintered by the slow heating rate of 50 K/min, had a dense microstructure, which had bonded WC particles with neck formation, resulting in the density of 98.1% and hardness of 1981±29 HV1 (Fig. 6d). On the other hand, the sample R7, sintered with the fastest heating rate of 200 K/min, had poorly bonded WC particles and a skeleton with loose formation (Fig. 6g), which corresponds to the low values of density (94.0%) and hardness (1703±36 HV1). As shown in Table 2, lower density and hardness values were achieved for higher heating rates in correspondence with the results given in

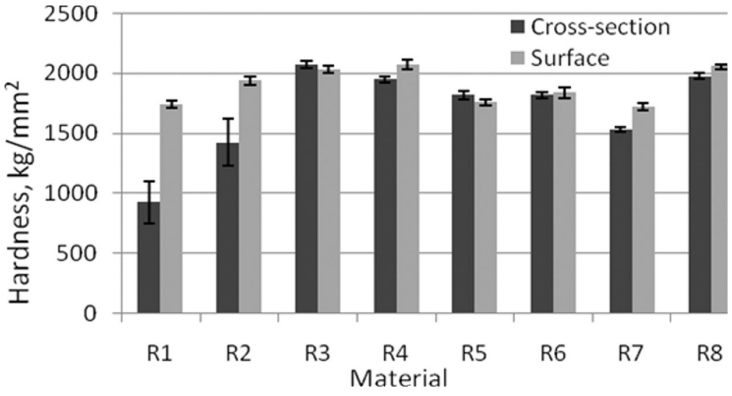

Fig. 5. Comparison of HV10 values from cross-section and surface for all samples.

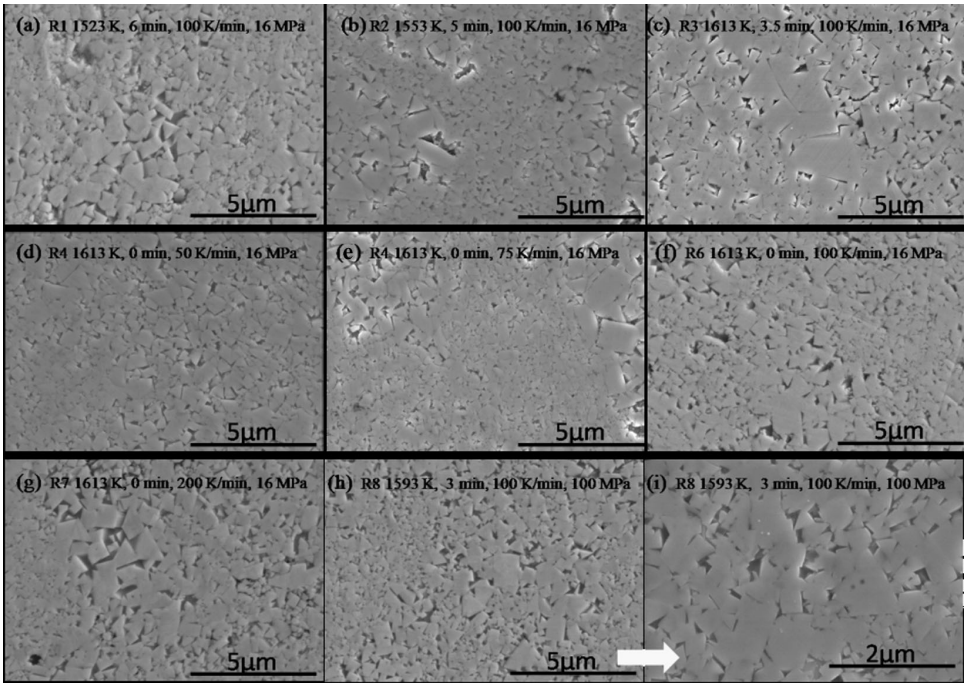

Fig. 6. The structures of the compacts (a) R1, (b) R2, (c) R3, (d) R4, (e) R5, (f) R6, (g) R7, (h) and (i) R8.

literature [6]. With slower heating, both the longer time at process temperature region and longer effective time of the high pressure have an influence on the densification. In the sample R8, fully dense (100% T.D.) structure with hardness of 2222±86 HV1 was achieved. The microstructures after sintering are given in Fig. 6h, i. The compacts have a pore-free microstructure; the gaps between WC particles are Co-rich regions. There is no evident grain growth after sintering according to the microstructure images. The size of large WC particles is consistent with particle size of agglomerates and particles, which are not crushed during recycling in the powder. Therefore the applied process parameters in the last experiment could be considered as the optimum condition for sintering similar powders.

The XRD pattern of the fully dense compact is given in Fig. 7. The W_2C phase was observed in the compacted material. It may be due to the presence of the oxide layer on the surface of the WC particles, causing reduction of carbon and formation of the W_2C phase [18].

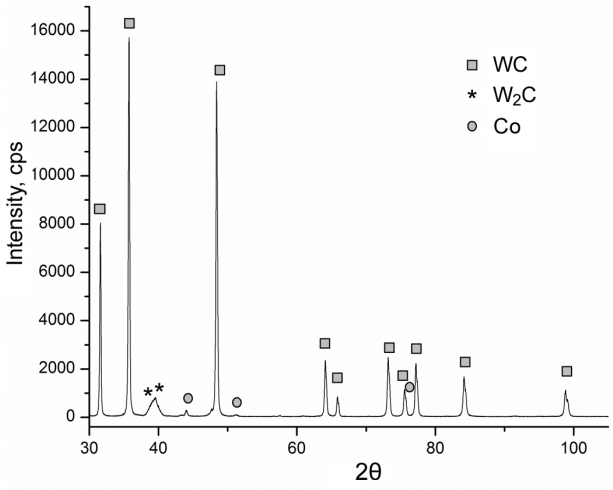

Fig. 7. X-ray diffraction patterns of the full dense compact of R8.

4. CONCLUSIONS

Recycled WC-Co powder was consolidated by the pulsed electric current sintering method. The ideal sintering temperature for this material was found to be around 1613 K, if applying compacting pressure was low and sintering time was 3.5 min. Under pressure of 100 Mpa, the fully dense structure with hardness of 2222 HV1 was obtained at 1593 K in 3 min, which is comparable with literature. Fast heating rate (200 K/min) resulted in a porous structure (T.D. 94.3%), while with the slow heating rate (50 K/min) the structure was clearly denser (T.D. 98.5%). Density values were similar (about 97%) for heating rates of 75 and 100 K/min, therefore the optimized heating rate was accepted as 100 K/min to benefit the rapid processing of the PECS technique. In the experiments no significant grain growth was observed.

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Taaskasutatava WC-8Co-pulbri elektriimpulsspaagutusprotsessi parameetrite optimeerimine

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Taaskasutatava kõvasulami purustamisel ja jahvatamisel saadud WC-8Co-pulber tihendati, kasutades elektriimpulsspaagutust (PECS-protsess). Saadud kõvasulamipulbris olid väikseimad osakesed suurusega ~0,4 μm ja pulbriosakeste aglomeraadid suurusega 1–7 μm. Uuriti paagutustemperatuuri ja kuumutamise kiiruse mõju paagutatud materjali omadustele. Paagutuse käigus tõusis pressise tihedus 98,3%-ni, kui temperatuur 1613 K saavutati 3,5 min jooksul rõhul 16 MPa. Suurim materjali tihedus ja kõvadus saadi aeglaseimat kuumutusrežiimi kasutades, vastavalt 98,1% ja 1981 HV1. Täieliku pressise tihenemiseni jõuti kuumutamise kiirusel 100 K/min temperatuurini 1593 K kolme minuti pikkuse kuumutamisega, kasutades rõhku 100 MPa. Suurem kuumutamise kiirus (200 K/min) tõi kaasa olulise poorsuse tõusu pressises.