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Synthesis of TiN Powders Using Dynamic CRN Method

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Abstract

Dynamic carbothermal reduction-nitridation (DCRN) is a new approach developed to produce more effective ceramic powder production than classical static system of carbothermal reduction-nitridation (CRN) method. In this new technique of DCRN, powder is produced in a moving system and production takes place at relatively lower temperatures and/or shorter times than CRN method. This study examines production of TiN powder by the DCRN method. The granules were prepared using TiO_2 and carbon black powders in the stoichiometric ratio ($C/TiO_2=2$). TiN powders of sub-micron were obtained in a graphite reactor from the prepared granules under N_2 gas flow. The effects of various test parameters were investigated for TiN synthesis, such as temperatures of reaction (1350-1450°C), reaction time (0.5-3 h), N_2 gas flow rate (60-120 L/h) and reactor rotation speed (2-6 rpm). The phases and microstructures of the powders were characterized by XRD, SEM and FESEM analyses.

Keywords: Titanium nitride, Titanium dioxide, Powder synthesis, Dynamic carbothermal reduction

1. INTRODUCTION

Titanium nitride (TiN) is used in many applications due to its high hardness, good electrical conductivity, high melting point (2927°C), relatively low specific gravity, high wear resistance, chemical inertness and high corrosion resistance [1,2]. Examples of application areas are cermets, cutting tools, decorative applications, refractory and cover layer for metals and alloys, biocompatible materials and coatings, structural elements at high temperatures, etc. [3, 4]. In addition, suitable electrical conductivity makes it an important electrically conducting ceramic for use in an electrode for biomedical applications [5].

TiN powders can be synthesized by various methods such as carbothermal reduction [6,7], chemical vapour deposition (CVD) [8], molten salt synthesis (MSS) [9], plasma spray [10], self-propagating high temperature synthesis (SHS) [1], low-temperature solvent-free synthesis [11], solid state chemical techniques [5], sol-gel method [12].

The carbothermal reduction and nitridation of titania (TiO_2) to produce TiN proceeds according to the reaction:

$$TiO_2 + 2C + 1/2N_{2(g)} \rightarrow TiN + 2CO_{(g)} \qquad (1)$$

Several parameters such as raw materials, reaction temperature and time influence the process [13]. TiN does not appear to form in one step reaction. Experimentally, the reaction sequence involving the formation of various titanium-rich phases, such as Ti_3O_5 and Ti_4O_7 were observed. The combination of excess C and using high temperature always led to the formation of TiC [14] as a secondary phase besides TiN main phase.

In this work, TiN powder production was carried out following to the modified form of

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carbothermal-reduction and nitridation (CRN) method. In this new approach, the reaction was carried out in a dynamic media by rotated furnace and the system is called dynamic carbothermal-reduction and nitridation (DCRN). We aimed to produce TiN in shorter time and at lower temperature compared to CRN method using such new technique of DCRN. The objective of this study is to characterize the influence of the parameters on the dynamic carbothermal synthesis of TiN from TiO_2. Process variables were temperatures (1350-1450°C), reaction time (0.5-3 h), N_2 gas flow rate 60-120 L/h) and reactor rotation speed (2-6 rpm).

2. EXPERIMENTAL

In this work, TiO_2 (Alfa Aeser, 99.9%), carbon black (Körfez Petrokimya, 99.9%) and N_2 gas (ARTOK, 99.9%) were used as the reactants. The flow diagram of the experimental work is shown in the Figure 1.

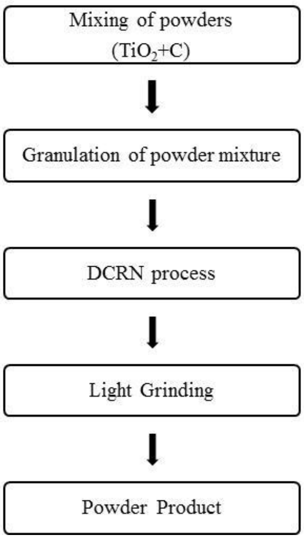


Figure 1. The flow diagram of experimental work for DCRN method in synthesising TiN powders.

TiN synthesis using TiO_2 and C following to the Reaction 1, requires C/TiO_2 ratio of 2. In the current study this ratio was taken into account when preparing the powder mixture. The dry powder mixture of TiO_2 and C was prepared in a polypropylene container using 5 mm zirconia balls. Granulation was carried out in a container with the help of a binder (5 % glycerol-alcohol solution in volume) and obtained granules were sieved in the range of 1-3 mm. Then the granules were put into a graphite reactor, which was placed in the middle of the alumina tube in an atmosphere-controlled horizontal type furnace for DCRN process. The synthesis was carried out at different temperature range under various flow rates of nitrogen gas and at different reactor rotation speeds (2-6 rpm). Schematic presentation of the DCRN process is given in the Figure 2.

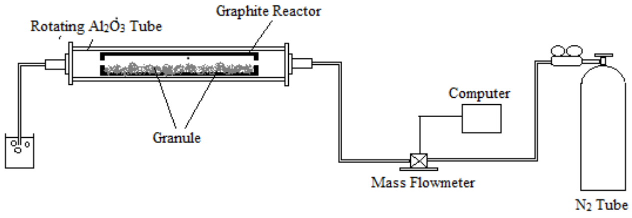


Figure 2. Schematic presentation of the DCRN process

The N_2 flow rate was kept constant for all tests unless otherwise stated. After charging the furnace with granules N_2 flow was set to 60 L/h for 30 minutes. Then the gas flow rate was lowered to 30 L/h and kept to this level until the furnace reacted to 1000°C. When the furnace temperature reached to 1000 ^oC the N_2 flow was set to 60 L/h and kept to this level throughout the reaction until cooling where furnace reached to 1000 ^oC. On cooling between 1000 ^oC and 300 ^oC N_2 flow rate was set to 30 L/h. After 300 ^oC until room temperature N_2 flow was adjusted to 1.2 L/h. This gas flow program was constant for all the tests carried out.

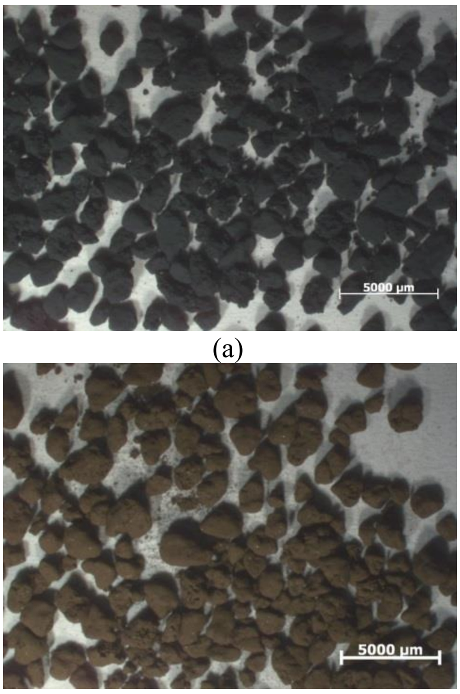
Alumina tube starts rotating right at the beginning of the DRCN process. However after completing reactions and on cooling where temperature reached to 1000^{o}C rotation was stopped. This is to avoid any contamination from graphite reactor due to wear of the reactor. After DCRN process, the products were lightly grinded in an agate mortar with pestle. The powdered products then were characterized by various techniques.

The microstructure, size and morphology of synthesized TiN powders were characterized by scanning electron microscopy (SEM) (Joel 6060 LV) and also energy dispersion spectroscopy (EDS) used for the elemental analysis. The formed phases were determined by XRD analysis (Rigaku Ultima). Stereomicroscope of Zeiss (Discovery V12) was used for surface images. Some of the products exhibiting sub-micron in powders were analysed using FESEM.

3. RESULTS AND DISCUSSION

The aim of the granulation was to prevent powder loss during the DCRN process, otherwise both N_2

flow and rotating of the reactor can make easy powder motion (lost) out of the system. Granules made large enough to stay in to the reactor were shown in Figure 3. It was observed that after the reaction granules stayed in their initial form, i.e., in their size and shape during the DCRN process. However, it is seen that the black colour of the granules before the reaction turned into dark brown colour of TiN powder after the reaction.



(a)

(b)

Figure 3. Stereomicroscope images of the granules (a) before (TiO_2+C mixture) and (b) after the DCRN process (TiN)

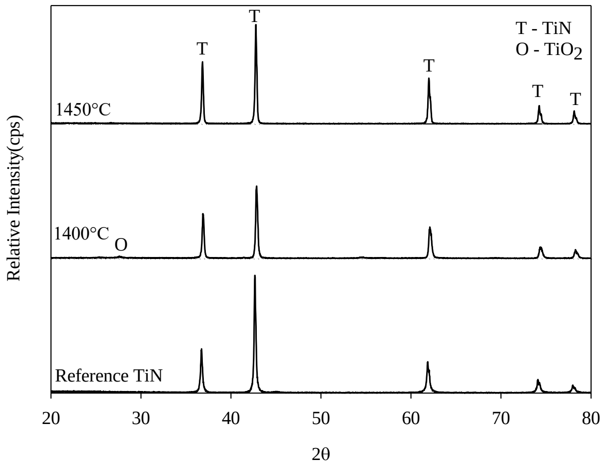


Figure 4. XRD analysis of obtained powders after 0.5 h DCRN process at different temperatures. JCPDS for TiN powder is 01087-0633 and TiO_2 is 00-021-1272 antase.

Figure 4 shows results of the DCRN process carried out for 0.5 hour at different temperatures. A full conversion from TiO_2 to TiN was achieved at 1450 °C for 30 minutes. However, small amount of TiO_2 was found in the product produced at 1400 °C.

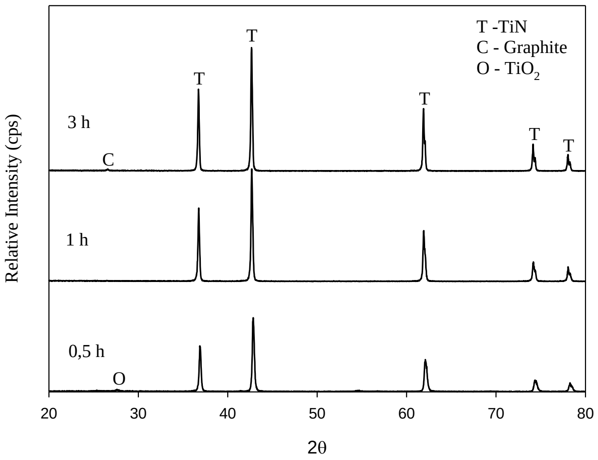


Figure 5. XRD analysis of obtained powders by DCRN process at 1400°C for different times

XRD analysis of synthesized powders by DCRN process for different time (0.5h, 1h and 3h) at 1400°C and at a rotation rate of 4 rpm was given in Figure 5. Here, the 0.5 h period was not sufficient for full TiN production since small amount of TiO_2 was observed. Increasing reaction duration to 1 h resulted in full conversion to TiN. Further increase in the time of the process has no effect of TiN formation but resulted in a C peak observation. The reason for this is thought to be caused by the abrasion of the graphite reactor due to the formed very hard TiN particles.

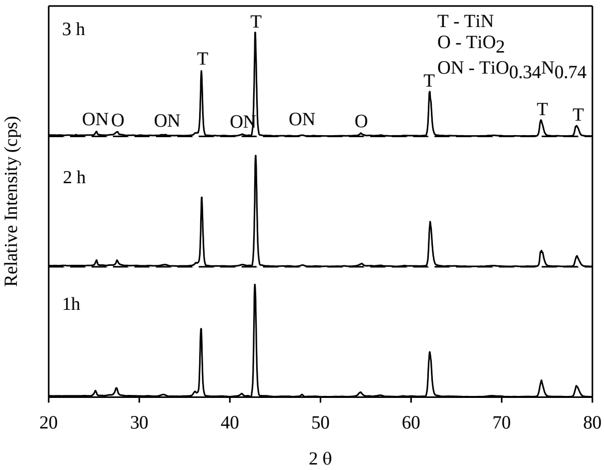


Figure 6. XRD analysis of obtained powders by DCRN process at 1350°C for different times

Figure 6 shows the XRD analysis of synthesized powders by DCRN process for different time (1h, 2h and 3h) at 1350°C and at a rotation rate of 4 rpm. Besides excessive amount of TiN phase, TiO_2 and $TiO_{0.34}N_{0.74}$ phases were also observed after DCRN process. Therefore, 1350°C was insufficient for the synthesis of TiN by the DCRN method even for 3 hours reaction duration.

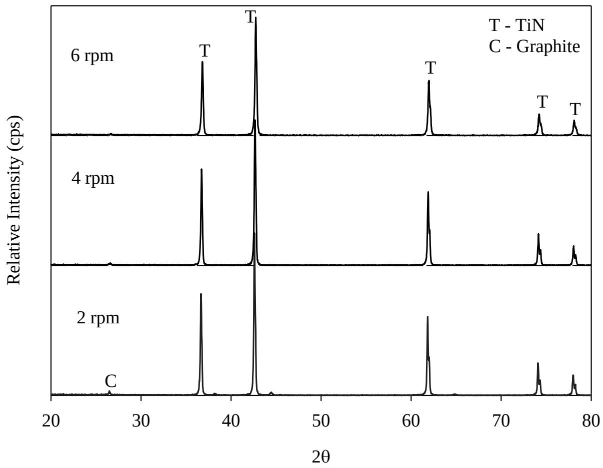


Figure 7. XRD analysis of obtained powders by DCRN process in the different rotation rates at 1400°C for 1h

Figure 7 shows the XRD analyses of the synthesized powders by DCRN process for different rotation rates (2, 4 and 6 rpm) at 1400°C for 1 hour. Except small amount of C in the test of 2 rpm, they all showed full TiN conversion with products of very high crystallinity. Therefore, test with 4 rpm can be selected as an optimal rotation rate for TiN synthesis by DCRN process at 1400°C for 1h.

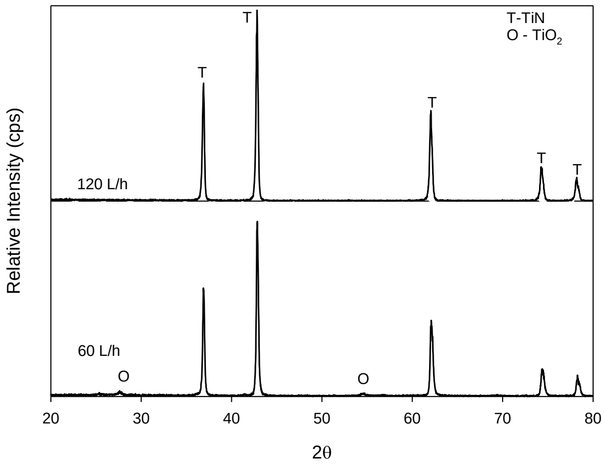
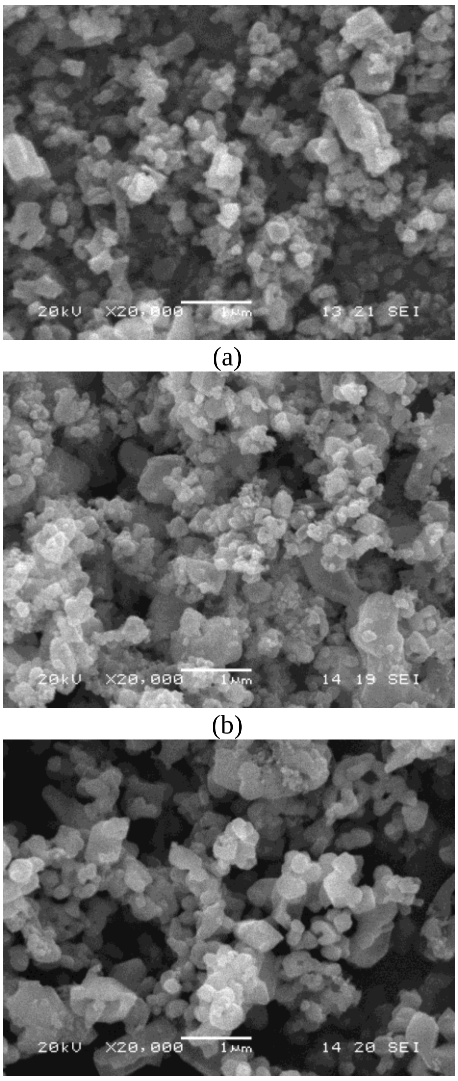


Figure 8. XRD analysis of obtained powders by DCRN process in different N_2 gas flows at 1400°C for 0.5h

Increasing in gas flow rate was performed in order to achieve shorter reaction duration at 1400°C. XRD analyses of the produced powders by DCRN process for different N_2 gas flow (60 L/h and 120 L/h) at 1400°C for 0.5 hour and 4 rpm rotation rate were shown in Figure 8. Reaction product after DCRN at 1400°C for half an hour at 60 L/h N_2 gas flow showed some amount of TiO_2 phase. By increasing the gas flow to 120 L/h, TiN conversion has been fully realized. Therefore, in order to shorten the reaction duration gas flow rate should be increased. 120 L/h can be selected optimal for N_2 gas flow for TiN synthesis by DCRN process at 1400°C for 0.5h. If the DCRN process occurs at 1400°C and 60 L/h gas flow, the TiN conversion takes place in 1h (Figure 5). Thus, if someone to decide in producing TiN using DCRN process they should make a decision choose between long duration (1 h) or high gas flow rate (120 L/h).



(a)

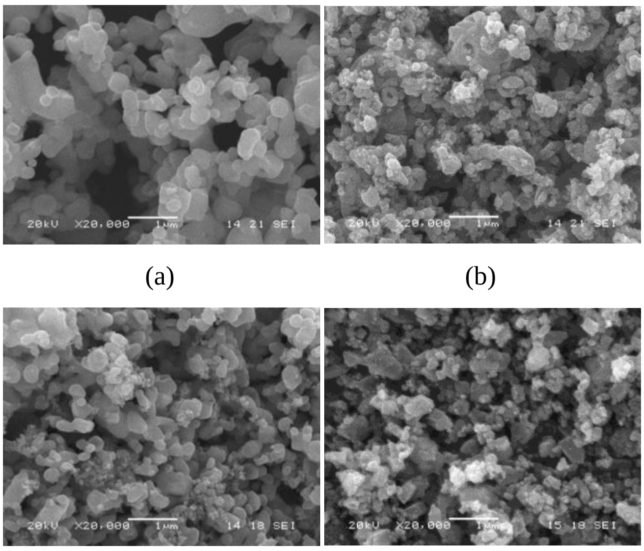
(b)

(c)

Figure 9. SEM micrographs of the synthesized TiN at 1400°C (a) 0.5h, (b) 1h and (c) 3h

Figure 9 shows the SEM micrographs of the synthesized powders by DCRN process for different reaction time (0.5h, 1h and 3h) at 1400°C. In general, the product powders reveal homogeneous narrow size distribution of equiax submicron particles. As seen here, the particle size of powders increased with an increase in reaction time.

It was shown in the earlier work [15] that an excessive amount of C addition to the TiO_2+C mixture has no better effect on the TiN formation by the DCRN method. It was reported that when C/TiO_2 ratio was 2.5 the TiN powders are produced at 1400 °C for 4 hours with reactor rotating speed of 1.38 rpm and 72 L/h N_2-gas flow rate [15]. Therefore, in our work of study the optimum temperature was confirmed as 1400°C and reaction duration at this temperature was 1 hour with 60 L/h N_2 gas flow rate and provided that stoichiometric ratio of C/TiO_2 mixture and reactor rotation speed of 4 rpm were used.



(a) (b)

(c) (d)

Figure 10. SEM micrographs of the synthesized TiN by DCRN at 1400°C for 1h (b) 2 rpm, (c) 4 rpm and (d) 6 rpm. Image in (a) is from static CRN run at 1400°C for 3h.

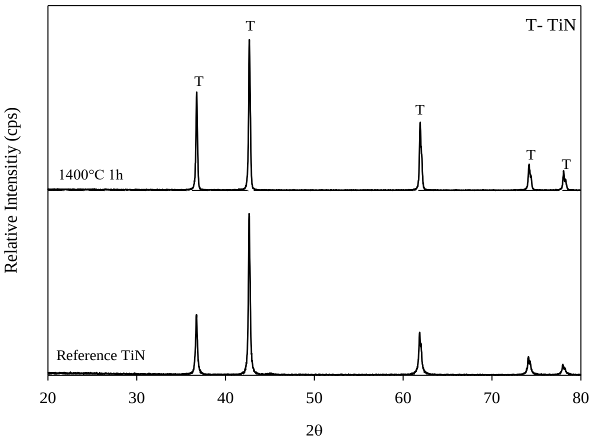
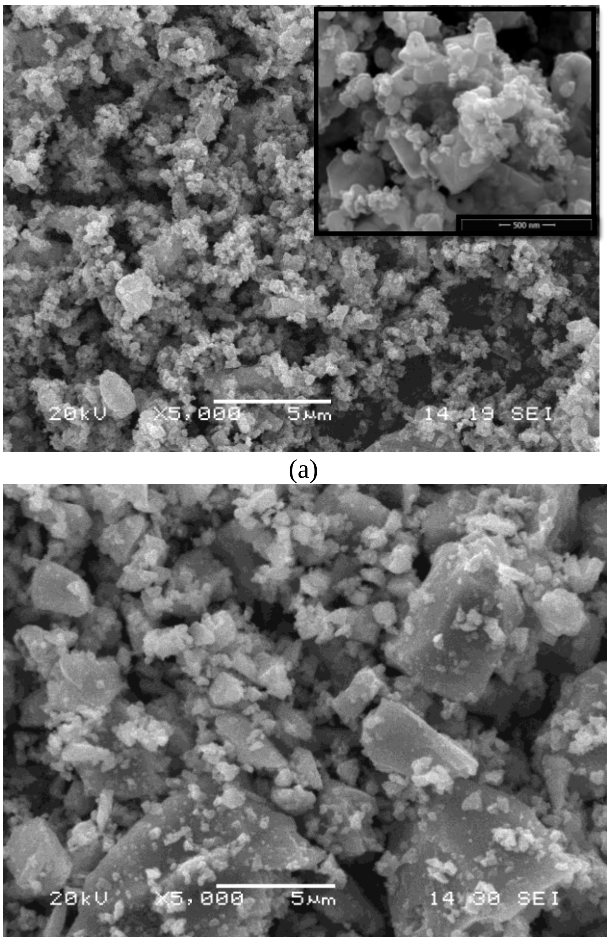


Figure 11. XRD results of reference powder and as-produced TiN powders from DCRN at 1400°C 1 h, 4 rpm.

In Figure 10, SEM micrographs of produced powders with static system (no rotation of the reactor) and different rotation rates (2 rpm, 4 rpm and 6 rpm). The produced powder by CRN process in static system has a larger grain size compared to others obtained in dynamic system of DRCN. In addition, with the increasing rotation rate was considerably reduced the grain size but caused some sort of agglomerate as well. It can be said that the increase in rotation speed also affects the particle size and the best result is obtained at the rotation rate of 4 rpm. All SEM images were taken after very light hand grinding of the granules in an agate mortar and pastel.

As shown in Figure 12 that TiN powders produced at 1400°C for 1h using 4 rpm reactor speed and 60 L/h N_2 gas flow using DCRN are very much smaller than the commercial TiN powders. Produced TiN powders are more rounded and more homogeneously and narrow size particle distribution than the reference powders. Scale bar is 500 nm on the small image on the corner of (a) showing nanosize range particles. TiN powders produced in this work in shorter time and lower temperature with single stage process of the DCRN method compared to two step processes of the carbothermal reduction of a combustion synthesized precursors [2]. The DCRN method has also advantages over the mechanical activation and subsequent carbothermal reduction – nitridation reaction, where nano crystalline Ti(C,N) powders could be produced only [7].



(a)

(b)

Figure 12. SEM micrographs of (a) synthesized TiN powder with a magnified FESEM image on the corner of the same sample and (b) commercial TiN powder from Alfa Aeser. Scale bar on the small image is 500 nm.

4. CONCLUSIONS

TiN powders were successfully synthesised by dynamic carbothermal reduction – nitridation (DCRN) process using TiO_2 and carbon black mixed in stoichiometric ratio. Reactor speed along with gas flow rate were effective in determining optimum temperature and time for the full conversion of TiO_2 to TiN. This method considerably lowers the time (up to 30 min) to complete the reaction and yields near nanosize submicron equax and narrow size distribution of very fine powders. It is therefore an economical and energy saving method. Near nanosize powders of TiN in the range of 100-150 nm was obtained at 1400°C for only 1 h using 60 L/h N_2 flow rate and 4 rpm reactor speed without using additives. It is possible further to lower duration to 30 min by increasing N_2 flow rate up to 120 L/h.

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