Journal of the European Ceramic Society 17 (1997) 447–451

0955-2219/97/$17.00
PII: S0955-2219(96)00208-7

SHS Extrusion of Long Sized Articles from Metalloceramic Materials

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(Received 15 September 1995; revised version received 1 October 1996; accepted 4 October 1996)

Abstract

The linking of Self-propagating High-temperature Synthesis (SHS) with extrusion in the SHS extrusion process, including equipment, production conditions, and product quality is presented. The succeptibility of different composite refractory materials to plastic deformation is found to be important. Examples of practical applications of the method are given. © 1996 Published by Elsevier Science Limited

1 Introduction

A new SHS extrusion method is being used to obtain long articles from brittle, not easily deformable, refractory materials. The method is designed for shaping of synthesized combustion products by extruding them through a forming die. The structure results from high-temperature deformation. It is this peculiarity of the method which makes it suitable not only as an effective refractory material processing technique but also as a process in which plastic deformation at high temperatures and at relatively low pressures ($P < 500$ Ma), a property that has been inadequately studied, is exhibited.

In this study, much attention is given to aspects of the process. An attempt is made to explain the feasibility of extruding different objects at extrusion temperatures of about 1000°C (this temperature is only determined by the operation conditions of the press equipment). The feasibility of plastic deformation has been shown in particular cases. A large number of different SHS-extruded materials and articles has been obtained.

2 Experimental Results

One of the main problems in the development of a method is the choice of the object of the investigation. Can all SHS materials be extruded and what are their suitability criteria? On the basis of the available experimental data, the main condition of material extrusibility was found. At the extrusion temperature, the materials should contain a sufficient amount of a phase capable of providing for plastic deformation of the whole material volume. The necessary amount of the phase may be different for different materials.

As is known, plasticity is a function of many parameters, among which pressure and temperature are the most important.[1] Therefore, to ensure that, after synthesis, the material remains in a plastic state, its temperature must be sufficiently high. The most common candidates for SHS extrusion are synthetic hard tool materials (SHTM),[2] containing a wear-resistant component (TiC, Cr_3C_2, TaC, TiB) and a binding metal or alloy (Ni, Co, Ti, steel). It is the binder which provides for the plasticity of such materials. At sufficiently high temperatures, the binder serves as a lubricant, facilitating the slip of hard particles. The material can be deformed as a viscous plastic body, and articles can be formed from it. Studies show that the succeptibility of composites to plastic deformation appears at temperatures of up to 0·7–0·9 T_m of the metal components (but not of the hard base).

This may be illustrated by experimental results from extrusion of Ti–Ni materials. Figure 1 shows the dependence of the extrusion completeness (which reflects the material plasticity) on the nickel content. As a criterion characterizing the product output it is convenient to take the extrusion completeness defined as the ratio of the extruded shaped material to the charge blank mass: $K_M = m/m_0$. At a low content (20%), the material plasticity is low despite a high combustion temperature. The extrusion completeness did not exceed 10%. A binder content of 20% may be considered as a conventional limit above which material extrusion can take place. It should be noted, however, that under different extrusion

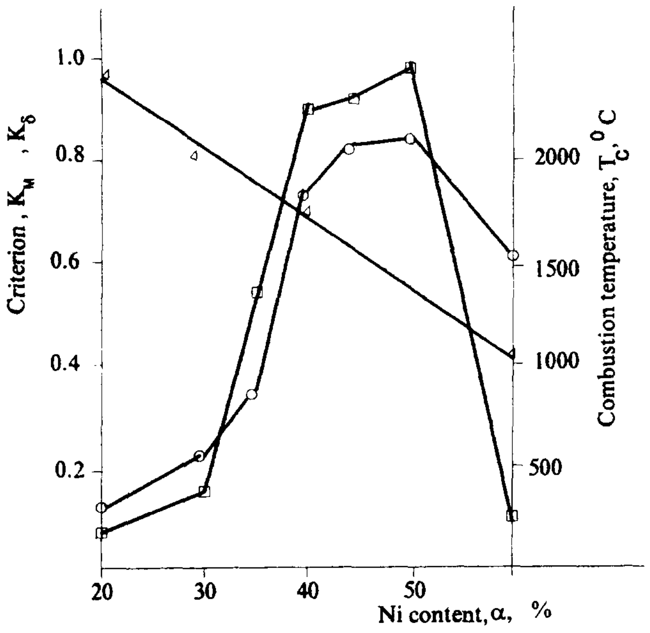

Fig. 1. Plot of the extrusion completeness (K_M, ○), surface quality criterion (K_δ, □) and the combustion temperature of compositions (T_c, ◁) versus the Ni content.

conditions (higher initial temperature of the blank, heating of the compaction equipment), the compositions with a 10% binder content may be extruded.

As the binder content increases from 20 to 50%, there is a continuous increase of the extrusion completeness. As it rises further (to 60%), there is an abrupt decrease in the combustion temperature and consequent underreacting of the components. The surface quality criterion K_δ, which also reflects the material plasticity, behaves in a similar way. As a measure of the surface condition the flow layer dimension δ, equal to twice the surface crack depth, may be taken. However, since the relative defective flow layer dimension is more significant than the absolute one, the corresponding criterion may be defined as $K_\delta = (d - \delta)^2/d^2$, where d is the rod diameter. That the material plasticity rises substantially for binder content between 30 and 40% is remarkable.

There are some differences in the SHS extrusion of hard-alloy materials containing intermetallic compounds (TiNi, NiAl, Ni_3Al) as a binder. The deformation still occurs due to the binder plasticity (for instance, in the intermetallic compound NiAl, the brittle–ductile transition is observed at 700°C). However, in the synthesis of intermetallic phases in the combustion mode a sufficient amount of heat is released to obtain pure, single-phase materials, which is impossible with an inert binder.

Let us consider the peculiarities of the extrusion of such materials using the TiC–TiNi system as an example (Fig. 2). At a low TiNi content (<10%) the extrusion is unfeasible because of insufficient

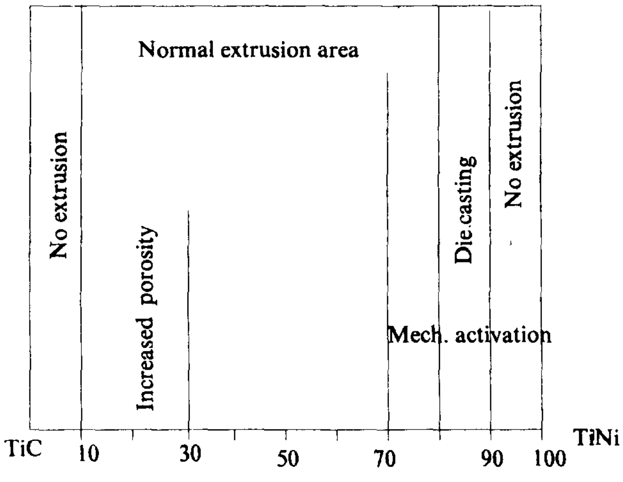

Fig. 2. SHS extrusion modes of TiC–TiNi, %.

material plasticity. At 10–80% TiNi, the extrusion is normal, i.e. the product is rod-shaped. At a content of 10–30%, a higher porosity is observed, which may be explained by the low material plasticity. At 85% TiNi, the material after synthesis becomes a low-viscosity liquid. When even a low pressure is applied, the product flows out of the die and solidifies on the gauge walls as a tube. At >80% TiNi in the material and without applied heating, synthesis is only possible with preliminary mechanical activation of the charge. As the TiNi content increase up to 100%, the extrusion ceases because the reaction-induced temperature fails to reach the brittle–ductile transition temperature of the intermetalloid (T_c = 630°C for the Ti + Ni composition the time of mechanoactivation was 10 min). Thus, the use of a reacting binder substantially increases the useful range of its content in the material.

A different picture is observed in the SHS extrusion of tungsten-based cast alloys. The alloys consist of tungsten crystallites surrounded by a solid Ni–Fe–W solution. Both phases (the grain and binder) are metal systems, and their plasticity is sufficient. Therefore, in the extrusion of such compounds, plastic deformation of the tungsten grains, whose shape becomes an extended oval and which are oriented in the extrusion direction, is observed.[3] Thus, the high plasticity of all the alloy phases results in a clear deformation texture in the articles.

A more complicated situation takes place during the production of heating elements based on molybdenum disilicide. The main difference is the absence of the fusible metal binders which are needed for deformation of the SHTM group. Moreover, the assortment of additives capable of improving the properties of silicide systems is rather limited. The silicon activity in molybdenum disilicide is as high as that of metallic silicon.

Therefore it is very difficult to obtain cermet type materials based on silicides. As binder metals for such materials, only 15 fusible transitional metals may be used, including gold and silver, which do not react with molybdenum silicides to form a eutectic system with silicon.[4] However, because of the low performance of the systems formed and the high cost of the reactants, their use is limited. Nevertheless, at the Institute for the Structural Macrokinetics, Russian Academy of Sciences, a group of materials based on molybdenum disilicide and a method of producing heating elements from them have been developed. The work was a success mainly due to the use of mullite, as a filling agent and dielectric component of the system. Though molybdenum disilicide and mullite have approximately the same melting temperatures (2050 and 1950°C, respectively), the brittle–ductile transitions are substantially different (between 1950 and 2050°C[5] and between 1650 and 1950°C, respectively). Since extrusion occurs at temperatures of 1700–1900°C, it is clear that at the moment of moulding only the mullite is in the viscoplastic state. This is confirmed by the appearance of the oxide phase as drops and rolls on the rod surface.[6]

Furthermore, the microstructures of transverse and longitudinal sections were identical, with no grain deformation in the silicide phase. There is a continuous three-dimensional frame of molybdenum disilicide particles with the volume filled with the oxide phase.

3 Process Parameters

Let us consider now the influence of process parameter. One of the most important factors is the delay time, the interval between combustion initiation and the initial pressure application. It is the time interval needed for the rheological properties to attain the optimal level for shear deformation under the compaction and extrusion conditions.

Numerical studies of the SHS extrusion process based on a thermal model[7] showed that the die configuration largely determined the heat-transfer and shear deformation processes during extrusion. Therefore, experiments with dies of different configurations can estimate the extent to which the article characteristics are affected by these processes. From the parameters for die configuration, the conical part angle γ and the die parallel length L were selected.

The $m(\tau_d)$ curves for dies with different γ are presented in Fig. 3. The nonmonotonic shape of these curves is characteristic of a wide class of SHS materials and may be explained by the following considerations. Let us introduce some characteristic times: reaction time τ_r, material structure formation time τ_f, material plasticity loss time (survivability time) τ_s. The times τ_r and τ_f are essentially the effective parameters of the chemical reaction process (the final product development and the structure formation process (the compact material formation), and the time τ_s characterizes the rheological factors. Depending on the relation between the delay time τ_d and the characteristic times τ_r, τ_f, τ_s, different limiting cases of SHS extrusion are realized.

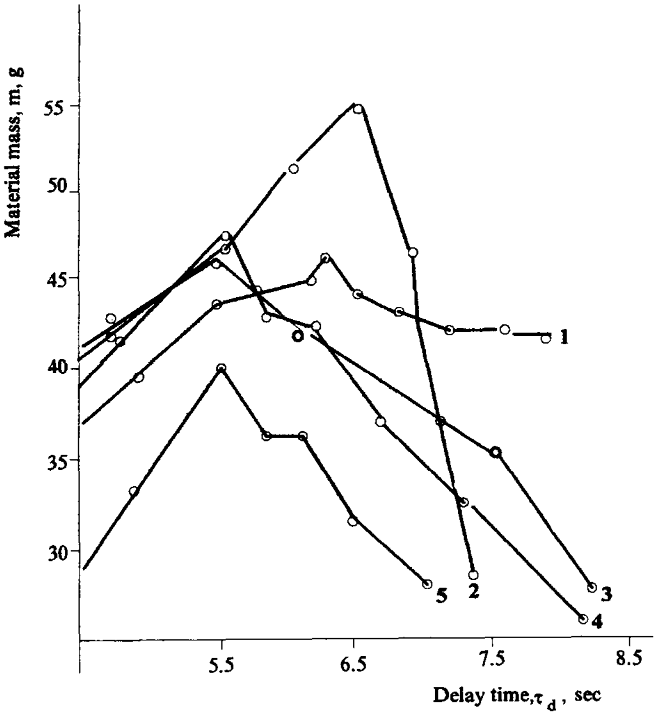

Fig. 3. Plot of moulded material mass versus delay time for dies with different angle of the conical die part: 1–180, 2–150, 3–120, 4–90, 5–60.

At small delay times, the material is extruded as a base powder and initial components which did not react. This is accompanied by extruding under load drops of the metallic binder. All this takes place at $\tau_d < \tau_r$ because the final product formation reaction in the whole volume is not completed, the alloy structure is not formed, and the binder is in a liquid state. As the delay time (the rising branch of the curves) exceeds τ_r, fragments of the formed compound start to appear; however, a part of the material is extruded as a hard base powder. This specimen region is characterized by an inhomogeneous temperature field, and three-dimensional zones with the formed structure or with the liquid binder. As τ_d and τ_f get closer, the formed material proportion increases (the extrusion completeness rises accordingly) and reaches a maximum at $\tau_d = \tau_f$. Thus, τ_f may be conventionally evaluated from the $m(\tau_d)$ curve extremum. As the delay time increases further, the extrusion completeness decreases gradually (the descending branch of the curves), because cooling of the formed material results in an increase in the three-dimensional specimen zones which have lost their deforming ability. Finally, at $\tau_d > \tau_s$, the output die section is completely clogged. As a consequence, τ_s can be found experimentally for real conditions. Thus, the four cases of the SHS extrusion process may be distinguished, and their time ranges be experimentally determined in each case.

As can be seen from Fig. 3, the cone angle of the conical part of the die determines the location of curves 1–5, having no effect on their general shape. The nonmonotonic behaviour of K_M (γ) (Fig. 4) may be explained by the fact that the influence of the variable γ is complex. On the one hand, γ determines the material flow behaviour, and with this in mind, a smaller angle is useful because it provides a smoother variation of the profile and a lower extrusion resistance. On the other hand, the conical die part is an intensive heat-transfer surface where the material cools quickly especially at acute angles, which results in clogging of the die. This interaction of hydrodynamic and thermal factors gives rise to the extremum in the curve K_M (γ) and, consequently, to an optimal region of γ values. The optimal angle value of the conical part of the die depends on the chemical, thermophysical, and rheodynamic properties of the material. For TiC/30–40% Ni, γ_{opt} is 150°, which is in good agreement with the results of Stelmakh.[7]

The die parallel length L has a substantial effect on the mechanical stability of the material flow in the article during extrusion and shaping. At L = 0–2 mm, the material flow is extremely unstable and the article cannot be moulded. Moreover, the effect of elastic "swelling" of the rods is observed (the final article diameter is larger than the die opening diameter). The experiment reproducibility is low. As the die parallel length increases, the extrusion instability decreases gradually, and the surface quality and reproducibility are improved. After a certain optimal value is achieved a further increase of L has no substantial effect. Completeness of the material extrusion in the studied range of L = 0–35 mm was nearly constant. No effects associated with die clogging were observed, perhaps as a consequence of the sufficiently high speed of the material passing though the shaping opening at which the heat removal is not significant.

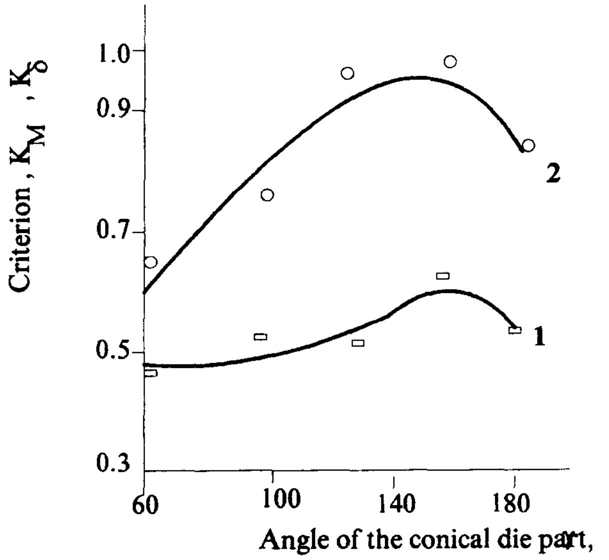

Fig. 4. Plot of the extrusion completeness (1) and surface quality criterion (2) versus the angle of the conical die part at delay time = 6·3 s.

4 Applications

SHS extrusion is used to produce slender articles ($h/d \gg 1$) which cannot be obtained by other compaction methods. As examples of practical applications of the method, only those articles have been selected whose production process is already being implemented, whose operation characteristics have been investigated and where experience of their usage has been gained.

One of the promising and quick-developing methods to harden metal surfaces is electro-spark alloying based on the principle of material transfer onto a cathode in electric discharge. The main advantages of the process are: low consumption of hardening electrode, absence of any tool mechanical working after its hardening, simplicity of equipment and flexibility of coating composition and thickness over a wide range.

It should be pointed out that in spite of the many installations for electro-spark alloying in our country and abroad, hardening electrodes are not industrially produced, in part owing to difficulties for their manufacture, especially for electrodes of small diameter (1–2 mm). Development of the SHS-extrusion method resulted in a highly productive technological process for a wide range of tungsten-free hard alloys and electrodes suitable for industrial output in the desired quantities.

Multiple tests of SHS-electrodes and coatings have been realized. Technological conditions for producing electrodes which provide stability of density, hardness, and specific resistance have been identified.

In another example, the production of heaters designed for long operation in a corrosive medium at temperatures above 1600°C is very urgent. Most of the studies are based on molybdenum disilicide because of its stable thermal, electrophysical, and operational characteristics. The industrial method of producing these heaters includes more than 50 operations; it is complicated, power- and time-consuming. Furthermore, additives such as bentonite clay and other plasticizers, needed at the cold nozzle extrusion and sintering stages, decrease substantially the heater working temperature and bring about high-temperature creep.

Application of SHS extrusion to obtain the heating elements is promising because of its ability to perform the material synthesis from the initial component powders in tens of seconds (instead of hours) and to mould articles of a given size and shape.[8] Moreover, its use substantially simplifies the heater production process, decreases the energy consumption and eliminates the use of complex and expensive equipment. In addition, no plasticizer (bentonite clay) is required and the working temperature can be increased substantially.

Tests of heaters showed their serviceability up to a temperature of 1830°C, where no higher temperature creep was observed; the specimen size and shape remained practically unchanged in short-term heating up to the melting temperature of the components (2000°C). Extremely severe operation tests (fast thermal cycling with heating up to the limiting working temperature) showed a higher durability of SHS heaters in comparison with conventional specimens. During the tests, the electrophysical characteristics were measured. The specific electrical resistances obtained in the temperature range of 20–1500°C exceeded the values of conventional heaters. Among other applications of SHS extrusion we may distinguish the production of hard-alloy electrodes for facing, of the screw blanks for cutting tools (drills, cutters), of tools for the treatment of stone, and of microrolls. Microcutters for glass engraving were produced with a resistance not lower than that of conventional diamond cutters. Bars of magnetic abrasive materials were produced which may be successfully used as grains in roughing tools. The grains may be oriented in the grinding wheel by applying a magnetic field which increases the tool output.

5 Conclusions

The advantages of SHS extrusion as a method of producing slender articles from refractory materials are reviewed. However, apart from the purely technological advantages, this article has revealed the strengths of SHS extrusion as a method for investigating the synthesis, structure formation, and high-temperature plastic deformation of the materials involved. At present it is difficult to forecast all the promise of SHS extrusion as a research tool; it is clear that a combination of theoretical and experimental methods will be required.

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