Characterization of Nitinol Powder Produced by Reduction of Oxides by Calcium Hydride

T.A. Sviridova[a,*], A.V. Shuytcev[b], A.V. Kasimtcev[b,c] and G.V. Markova[b]

[a]National University of Science and Technology "MISIS", Leninsky prosp. 4, 119049 Moscow, Russia

[b]Tula State University, pr. Lenina 92, 300012, Tula, Russia

[c]"Metsintez" Ltd, Frunze 9, 300034, Tula, Russia

Several techniques were used to investigate the chemical and phase composition of four trial batches of nitinol powder produced by calciothermic reduction as well as their morphology and granulometric composition. Almost all powders produced by a similar procedure contained an allowable amount of impurities and were practically free of minor detrimental phases such as Ti_2Ni and Ni_3Ti. The powders under study have gamma or lognormal particle size distributions and spongy particles morphology typical of this production method. The tap density over 3 g/cm^3 was achieved at least in one case, which gives us an opportunity to successfully produce bulk articles by subsequent treatments such as sintering or hot isostatic pressing.

1. Introduction

Nitinol is a well-known intermetallic compound that has a lot of potential applications in biomedicine, aerospace, petroleum industries and instrumentation. Its most useful functional properties, such as shape-memory effect, superplasticity and very high ductility, are provided by reversible martensitic transformation $B2 \leftrightarrow B19'$ [1]. Unfortunately, NiTi has a relatively wide homogeneity region and its composition strongly influences the martensitic transformation temperatures [2], which greatly affects mechanical properties. It essentially restricts nitinol applicability because ingots produced by conventional metallurgical techniques exhibit perceptible fluctuations in chemical composition and additional heat treatment is required in order to obtain homogeneous bulk materials with desired characteristics.

Powder metallurgy is an alternative way of article production that enables to achieve chemical homogeneity [1]. The calciothermic reduction has proved to be a very perspective method of producing powder intermetallics including NiTi [3, 4]. The method has been known since the 1970s and at first was developed to extract Zr, Th, and U from oxide ores and later to obtain intermetallic compounds [5–8]. But having a potential military application, the method was kept secret until recently and is now coming into wide use [3, 9–11].

In the case of NiTi, the reaction of intermetallic formation can be written as

$$TiO_2 + Ni + 2CaH_2 \rightarrow TiNi + 2CaO + 2H_2 \uparrow . \quad (1)$$

It occurs in the temperature range of $1000 \div 1200\,°C$ and its mechanism was investigated in detail in [11]. The initial powder mixture of oxide, pure metal, and calcium

hydride heats up to about $820\,°C$. At this point, CaH_2 dissociates to hydrogen and calcium, which melts at the same time. The titanium reduction takes place at temperature about $900\,°C$ and both nickel and titanium dissolve in liquid calcium. Owing to a very fast diffusion in liquid medium, the metals gradually form a NiTi compound and practically pure intermetallic can be obtained by holding the mixture at $1150\,°C$ for 8 h. The resulting powder is cooled down for $10 \div 12$ h and after leaching, drying, and screening, the powder can be used to produce massive articles by some additional procedures such as sintering or hot isostatic pressing.

The main goal of this work is to characterize the powder NiTi intermetallic compound produced by calciothermic reduction. Several properties, which are crucial for massive article production, are taken into consideration. These properties are chemical and phase compositions, morphology, particle-size distribution, and bulk/tap densities.

2. Materials and methods

Four trial batches (I, II, III, and IV) of powdered nitinol, each with the mass of about 100 kg, were produced by calciothermic reduction at $1150\,°C$ for 8 h. Starting materials were Ni with purity $\geq 99.9\%$ and TiO_2-anatase ($\geq 98.0\%$). Commercially available CaH_2 powder ($\geq 93\%$) was used to prepare batches I and II; batches III and IV were prepared from purer CaH_2 compound ($\geq 96\%$) obtained by hydrogenation of metal calcium (grade KD, TU 5.176-90). All the powders were produced in a factory by a common procedure with the only difference that batches I and IV were subjected to additional grinding before leaching.

The inductively coupled plasma atomic emission spectroscopy with "Optima 4200DV" spectrometer was used to determine the chemical composition of the powders under study. A granulometric composition was obtained using ANALYSETTE 22 MicroTec plus equipment

───────

*corresponding author; e-mail: sviridova@misis.ru

(Fritsch) and software package STATGRAPHICS Plus for Windows. A procedure described in the Russian technical standard GOST 19440-74 was used to measure bulk and tap densities.

Phase composition was evaluated by means of an X-ray diffraction (XRD) analysis (Cu K_α radiation with graphite monochromator, room temperature) and software package [12] with a built-in Rietveld analysis. The powder morphology, microstructure and phase distribution within the powder particles were examined using scanning electron microscope (SEM) Hitachi S-3400 with energy-dispersive spectroscopy equipment.

3. Results and discussion

The chemical composition of the powders and a technical specification for an as-cast NiTi alloy of the most common brand TN1 are presented in Table I. These data show that apart from a relatively high nitrogen content, all the batches have compositions almost corresponding to the technical specification. Moreover, all powders show very stable composition with respect to basic elements, which is almost unattainable in metallurgical process. Besides, all powders contain Ca-impurity with its particularly high concentration in the batch I and the oxygen content of first pair of batches noticeably exceeds specification requirements. The relatively high amounts of oxygen can be explained by a higher impurities level in starting CaH$_2$, but a high concentration of gas-forming elements (O, N, H) does not seem to be critical, because the following high-temperature treatment proceeds in fine vacuum, which facilitates the volatilization. The influence of calcium on the terminal properties is presently unexplored.

TABLE I

Chemical composition of TN1 as-cast alloy according to technical specification TU 1-609-394-84 and four batches of the NiTi powder.

Material	Chemical composition [wt.%]							
	Primary elements		Impurities					
	Ni	Ti	C	Ca	Fe	Si	N	O
as-cast alloy TN1	base	$42.7 \div 45.7$	≤ 0.1	–	≤ 0.3	≤ 0.15	≤ 0.05	≤ 0.2
batch 1	base	45.61	0.08	0.34	0.14	0.04	0.11	0.74
batch 2	base	44.3	0.06	0.09	0.12	0.07	0.08	0.62
batch 3	base	44.42	0.058	0.11	0.10	0.08	0.12	0.13
batch 4	base	44.25	0.077	0.23	0.34	0.05	0.08	0.14

Figure 1 shows XRD patterns and a quantitative phase composition of the powders under study. The picture demonstrates that at least batches III and IV consist of only cubic $B2$ and monoclinic $B19'$ phases and seem to be free of Ti$_2$Ni and TiNi$_3$ detrimental phases usually contained in as-cast alloys [13]. In the first two batches, XRD reveals several admixtures: Ni$_3$Ti, Ni, α-Ti solid solution, and in the case of batch I, even some traces of CaTiO$_3$ phase, which correlates with a higher amount of Ca and oxygen in this particular powder (Table I). It is worth noting that a lower level of impurities in CaH$_2$ reagent prevents the formation of both foreign compounds and minor detrimental phases of the Ni–Ti system. Therefore, the purification of CaH$_2$ results in more homogeneous materials with practically only two — $B2$ and $B19'$ — modifications of the NiTi compound.

It should be noted that a small quantity of minor phases can be undetectable by XRD analysis especially in this case of diffraction patterns with wide reflections of martensitic phase. And indeed, SEM investigation of the powder cross-sections reveals traces of Ti$_2$Ni phase (Fig. 2) in batches II, III, and IV along with several other phases: Ti(N,C) in batch I, Ti$_2$Si in batch II, and Ti-based solid solution in batch IV.

An almost biphasic composition of all the powders indicates that a martensitic transformation starts above and finishes below room temperature. As it follows from XRD quantitative phase analysis, various powders differ in the ratio of the monoclinic $B19'$ and cubic $B2$ modifications: the amount of $B19'$ phase is higher in the first pair of batches. It suggests that the powders have different start and finish temperatures of martensitic transformation, namely, the first pair of the powders has higher transformation temperatures. At first glance, the amount of high-temperature $B2$ phase correlates with the purity of CaH$_2$ reagent and may be explained by a higher amount of oxygen in batches I and II (Table I). But in Ref. [14], it was revealed that O-doped as-cast NiTi alloys, on the contrary, have lower temperatures of martensitic transformation and therefore there should be other reasons explaining the difference in the ratio of $B19'$ and $B2$ phases.

Figure 3 shows the morphology of the TiNi powder of different batches and demonstrates that all powder particles have a spongy branchy surface and mostly a nonequiaxial form, which is quite typical for powders produced by calciothermic reduction. It is clearly seen (Fig. 3) that the powder particles of various batches differ
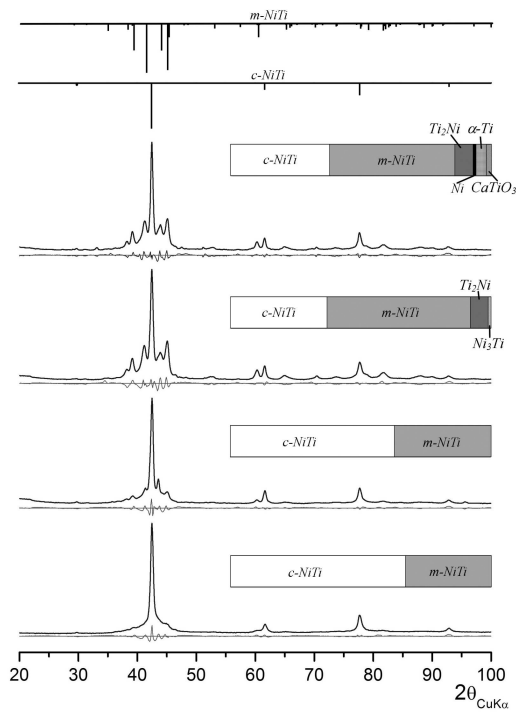
Fig. 1. XRD patterns and quantitative phase composition of I ÷ IV powder batches (top-down). c-NiTi and m-NiTi denote cubic ($B2$) and monoclinic ($B19'$) modifications of NiTi, the difference curves obtained by the Rietveld analysis are shown below each diffraction pattern.
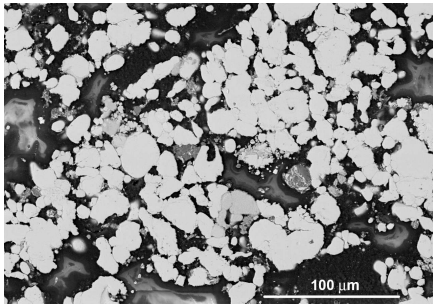

Fig. 2. The SEM image of powder cross-section for batch IV.

in size and the coarsest powder has been produced in batches II and III. The obvious reason of that is the additional grinding of the powders of I and IV batches before the leaching procedure.

Figure 4 demonstrates a granulometric composition of the powders under study. The average size of the powders as well as their bulk and tap densities are presented in Table II. Batch I and IV seem to be the finest powders produced and, according to statistical analysis, have a gamma particle size distribution. Batch II shows bimodal distribution as well as batch III, where the main greatsize mode has an almost normal particle size distribution. Batches I and IV, having similar distributions, differ in the average size. It suggests that the higher impurities
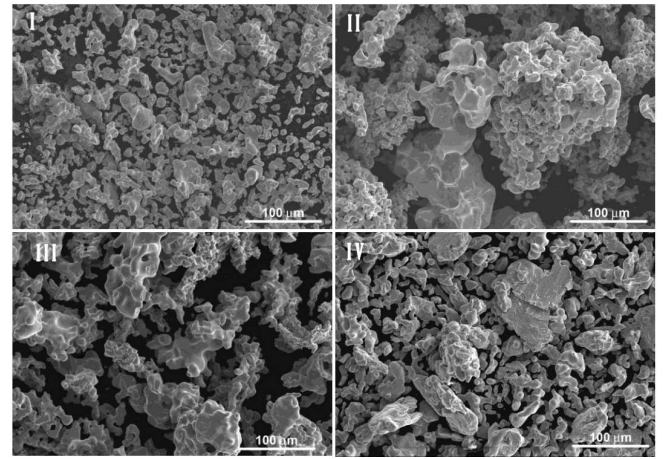

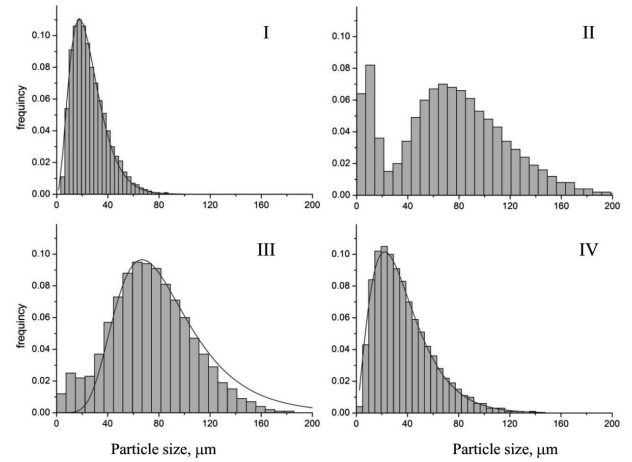Fig. 3. SEM images of powders of I, II, III, and IV batches.

Fig. 4. A granulometric composition of powders of I, II, III, and IV batches. Solid lines show bestfit curves for gamma (batches I and IV) and normal (batch III) distributions.

level provides finer powders, which is also confirmed by comparison of coarse batch III with batch II, containing a noticeable amount of fine fraction.

TABLE II

Bulk and tap densities of various batches of the Ni–Ti powder.

Batches of Ni–Ti powder	Bulk density [g/cm^3]	Tap density [g/cm^3]	Average size [μm]	Standard deviation [μm]
I	2.25	2.88	26	13
II	1.39	1.75	72	43
III	1.54	2.02	74	32
IV	2.38	3.18	37	22

Making a comparison of Fig. 4 and Table II, one can conclude that finer powders (batch I and IV) provide a higher density and an additional gain can be achieved for the powder with a wider size distribution (batch IV).

According to technical specification, a minimum residual porosity of the bulk articles can be attained if the tap density of the NiTi powder is not less than 3 g/cm^3 and only one powder — batch IV — complies with this requirement. Therefore, this powder is likely to be a good candidate for the following sintering or hot isostatic pressing (the details are seen in [15]). The other batches can also be used in the fabrication of special materials with a controllable open and closed porosity.

4. Conclusion

A comprehensive study of the NiTi powders produced by calciothermic reduction was carried out. The comparison of the chemical composition's data of the resulting powders and the standard composition of the as-cast NiTi alloy shows that the calciothermic reduction provides a stable composition with respect to the basic elements — titanium and nickel — whereas the nitrogen content slightly exceeds the specification requirement.

An X-ray diffraction analysis combined with the SEM investigation detected two main NiTi phases with cubic ($B2$) and monoclinic ($B19'$) crystal structures as well as traces of several minor phases whose amount depends on the purity of CaH$_2$ reagent. It seems that the quality of starting CaH$_2$ affects other important properties. Among them the values of martensitic transformation temperatures influence the ratio of the monoclinic $B19'$ and cubic $B2$ modifications and may result in mechanical properties of final bulk articles. Another property depending on the purity of CaH$_2$ reagent is average particle size: a high impurity content provides a finer powder.

The additional grinding used before a leaching procedure gives rise to a finer powder with a gamma distribution of particle sizes that permits to achieve the promising tap density 3.18 g/cm^3 suitable for the following bulk article manufacturing. Batches with lower tap density can be used in the fabrication of products with a controllable porosity.

References

[1] M.H. Elahinia, M. Hashemi, M. Tabesh, S.B. Bhaduri, *Progr. Mater. Sci.* **57**, 911 (2012).

[2] K. Otsuka, X. Ren, *Progr. Mater. Sci.* **50**, 511 (2005).

[3] A.V. Kasimtsev, T.A. Sviridova, *Russ. Metall. (Metally)* **2012**, 435 (2012).

[4] A.V. Kasimtsev, N.P. Reutova, L.M. Mnasina, N.P. Zubkov, T.A. Sviridova, Yu.A. Turutin, *Russ. J. Non-Ferrous Metals* **52**, 519 (2011).

[5] R.E. Cech, *J. Metals* **26**, 32 (1974).

[6] R.E. Cech, N.Y. Scotia, Patent US3625779.

[7] R.O. Suzuki, T. Ueki, M. Ikezawa, T.H. Okabe, T. Oishi, K. Ono, *Mater. Trans. JIM* **32**, 272 (1991).

[8] T.H. Okabe, K. Fujiwara, T. Oishi, K. Ono, *Metall. Trans. B* **23**, 415 (1992).

[9] M. Ilayaraja, L.J. Berchmans, S.R. Sankaranarayanan, *Metall. Mater. Eng.* **20**, 35 (2014).

[10] O. Bayat, A.R. Khavandi, R. Ghasemzadeh, *J. Alloys Comp.* **520**, 164 (2012).

[11] A.V. Kasimtsev, V.V. Zhigunov, *Russ. J. Non-Ferrous Metals* **51**, 150 (2010).

[12] E.V. Shelekhov, T.A. Sviridova, *Met. Sci. Heat Treat.* **42**, 309 (2000).

[13] M.Yu. Kollerov, A.V. Gusev, A.A. Sharonov, *Light Alloys Technol.* No. 2, 87 (2012) (in Russian).

[14] J. Otubo, O.D. Rigo, A.A. Coelho, C.M. Neto, P.R. Mei, *Mater. Sci. Eng. A* **481–482**, 639 (2008).

[15] A.V. Kasimtsev, G.V. Markova, A.V. Shuitsev, Yu.V. Levinskii, T.A. Sviridova, A.V. Alpatov, *Metallurgist* **58**, 1038 (2015).