

Thermochemical Basis of the Preparation of Well-Defined Transition Metal Carbide, Nitride and Carbonitride Reference Materials for Electron-Probe Microanalysis (EPMA)

Walter Lengauer¹, Marcel Bohn²

¹Vienna University of Technology, Getreidemarkt 9/164-CT, A-1060 Vienna, Austria

²CNRS, Microsonde Ouest, IFREMER, F-29280 Plouzané-Brest, France

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Abstract. A common and straightforward method for the standardisation in electron-probe microanalysis (EPMA) is the use of homogeneous reference materials prepared by various techniques such as by melting, sintering, high-temperature annealing and hot-pressing. The reference materials have to be analysed by independent methods accurately in order to define their “true” composition. For some compounds the preparation techniques are difficult because of their specific thermo-chemical properties (e.g. low diffusivities, high equilibrium nitrogen pressure, incongruent melting). In addition, many compounds show large homogeneity ranges with an a priori existing uncertainty in composition, contrary to what is generally preferred: to use compounds with a narrow homogeneity range (“line compounds”). For the latter, diffusional preparation techniques can be applied to yield diffusion layers instead of massive samples for standardisation. However, also single-phase samples with narrow homogeneity ranges can be prepared by diffusion, depending on the phase equilibria in the corresponding system.

The presentation summarises efforts that have been made in order to prepare various reference materials for carbon and nitrogen standardisation of EPMA by various techniques. The boundary conditions such as phase stabilities, phase compositions and diffusion kinetics, which are important for their preparation to obtain well-defined reference samples are discussed. These samples were applied to various WDS/EPMA-based studies of phase diagrams and diffusion kinetics by means of Cameca SX 50 and SX 100 microprobes.

1. Introduction

Accurate microanalysis is a very important precondition in the research and design of hard materials to which carbides, nitrides and carbonitrides belong. These compounds are used in a variety of high-tech applications such as tools for cutting, mining and abrasion, refractory interlayers in electronic devices and corrosive applications as well as for structural parts for thermally and mechanically highly-loaded materials. Fig.1 gives an impression of the diversity of geometry and fields of use of such parts.

2. Examples of Binary Phase Diagrams with Special Features

In the following compilation carbides, nitrides and carbonitrides of transition metals of groups 4 – 6 are considered, the other transition metal groups are of minor or no importance with respect to the application of carbides and nitrides, with the exemption of iron compounds which are very important for case-hardened parts.

2.1 Transition metal – carbon systems

In Fig.2 transition metal – carbon systems of group 5 and of Cr-C are shown, for other important systems such as Ti-C and W-C, the reader is referred to compilations on phase diagrams [1]. For the group 5 carbides so-called line compounds or at least compounds with a very narrow homogeneity range can be identified: the so-called ζ -phases. Hence, if such a phase is present in a sample, it can

be used as a standard because of its fixed composition, which is furthermore temperature-independent, i.e. the temperature of preparation does not influence the composition. For the Cr-C system this is true for all phases at temperatures lower than about 1500°C. It can also be identified that most of the compounds decompose peritectically, so they cannot be prepared by melting. Cr₇C₃ is an exemption but it shows a broader homogeneity range at high temperatures. Hence, melting is not appropriate for the preparation of these reference materials.

If phases with a broad homogeneity range should be used as a reference material (like the group 4 and 5 fcc carbides), the samples have to be single phased *and* homogeneous which is a difficult task upon preparation of such refractory compounds and needs high annealing temperatures due to low metal and carbon diffusivities.

2.2 Transition metal – nitride systems

As nitrogen is a gas, the nitrogen equilibrium pressure is very important in addition to the usual phase diagram information [2]. The group 4 transition metals will only release nitrogen upon melting, but group 5 and 6 transition metal nitrides require a high nitrogen partial pressure upon preparation. Also, some line compounds can be identified such as in the Ti-N, Hf-N, Ta-N and Cr-N systems (Fig.3), the importance of these is discussed below.

2.3 Choice of phases and measurement of the gross chemical composition

Due to the chemical shift encountered in EPMA spectra the best way of analysis is that the reference material and the sample to be analysed are of the same system. Another target for an EPMA reference material is the preparation of a homogeneous, single-phase material of high purity. If this condition is fulfilled, the micro-composition is identical to the bulk composition of the reference sample. The bulk reference sample is then appropriate for many gross chemical and physical analysis techniques of carbon and nitrogen which have limited or no spatial resolution. If the sample consists of a line compound (a compound with a very narrow homogeneity range) the composition of the sample is known *a priori* if the phase diagram information is correct. However, in several systems a line compound does not exist, or it is very difficult to prepare. Hence, chemical analysis must be applied for establishing the “true” composition of a reference material used in microprobe analysis.

The most versatile method of gross chemical analysis for carbon and nitrogen is carrier-gas hot-extraction in which the sample is decomposed by use of molten metals and the CO and N₂ are measured by thermal conductivity and IR spectroscopy. However, these techniques require reference materials themselves. Also techniques like Dumas analysis (volumetric analysis or gas-chromatography [9-11] of nitrogen) and combustion analysis together with conductivity measurements (absorption of CO₂ in NaOH) for carbon are employed. The calibration of these techniques is either not necessary or is conducted by compounds with a well-established composition such as pure carbon black or an organic compound. The pre-requisite is that the combustion or decomposition characteristics of sample and reference material does not influence the analysis. The accuracies of these methods are then on the order of lower than 1rel% of the non-metal content. Together with gravimetric metal analysis by combustion of the compounds in air or oxygen to form metal oxides, the composition of bulk samples so-obtained is sufficiently accurate for EPMA.

Only if a single-phase sample cannot be prepared the second choice is to prepare a diffusion couple containing layers of a compound which (1) has a narrow homogeneity range or is a *line compound* and (2) is well characterised for its composition, i.e. the corresponding phase diagram information has to be accurate.

Generally, there are several methods of choice for the preparation of bulk compounds: hot-pressing, diffusional preparation and arc melting. In addition, CVD could be used, if the constituents are gaseous or can be converted into gaseous compounds and if relatively thick layers can be prepared, which are then delaminated from the substrate for gross chemical analysis.

3. Experimental Preparation Techniques and Gross Analysis of Reference Materials

3.1 Hot-pressing

For hot-pressing the powders are filled in a graphite or boron nitride die and pressed at high temperature to almost full density. Fig.4 shows a scheme of the hot-pressing apparatus. Advantages of this technique are:

- relatively large samples can be prepared so that chemical analysis even of impurities can be performed accurately
- it is possible to prepare a variety of materials which are not accessible by other techniques, e.g. preparation of homogeneous ternary or quaternary compounds such as carbonitrides
- it is a fast technique.

However, there are also several pronounced disadvantages:

- a high impurity level because the powders are fine and have a high surface-to-volume ratio
- contamination with the die materials C (or B and N, respectively)
- in some cases porosity cannot be avoided
- unstable compounds such as the nitrides of group 5 and 6 transition metals cannot be hot-pressed because the samples become inhomogeneous (decomposition).

3.2 Diffusional preparation

The carbon and nitrogen diffusion into transition metals can produce very pure compounds because metal sheets can be used, almost free of contamination (e.g. metal sheets of > 99.99% Me are commercially available). Fig.5 shows a scheme of a vacuum induction furnace for establishing temperatures up to 1600°C and nitrogen pressures up to about 900 mbar. If higher pressures are needed, autoclaves have to be used. Fig.6 shows a scheme an autoclave for the preparation of carbides in graphite bed and nitrides upon use of high-pressure nitrogen for temperatures up to 2200°C and nitrogen pressures up to 40 bar. Such equipment is capable of keeping the conditions over many days or even weeks for equilibration and homogenisation of the reference materials. This is needed in high-melting compounds because of the low diffusion rate of C and N.

If pure nitrides are prepared, such an autoclave can be equipped without any graphite inserts, i.e. using a W heating tube and Mo heat shields. In case of carbide preparation, both parts are made of graphite.

Instead of a graphite bed, CH₄ can be used for carburisation of metal sheets. A furnace approaching very high temperatures of around 2500°C is shown in Fig.7. The sample is made of a metal strip and heated by high current.

The advantages of diffusional techniques are as follows:

- the impurity level can be very low (high purity metal foils are available)
- porosity can be mostly excluded
- compounds are accessible in form of diffusion layers.

The disadvantages of the diffusional preparation technique are:

- sometimes long reaction times are required if single-phase compounds are to be prepared
- generally, only binary compounds can be prepared because the diffusivities of two non-metals or two metals is generally different (with exceptions)
- a detailed data set of diffusional data and – for nitrides also nitrogen equilibrium pressure data – is necessary for the preparation of compounds.

3.3 Chemical vapour deposition (CVD)

If the constituents are gaseous or can be converted into gaseous compounds CVD can be applied to produce thick layers. The layers can be detached from the substrate and subjected to chemical analysis.

Advantages:

- the melting point of the metal does not play a role, because all metals have to be converted to volatile compounds, hence reference materials with a low-melting metal component can be prepared

The disadvantages of this method are:

- complicated apparatus and procedure (volatile compounds difficult to handle)
- the layers can show a gradient, hence delaminated layers had to be annealed to homogenise
- the chemical composition is not necessarily identical to the phase diagram information if thermodynamic equilibrium is not reached

From these pros and cons it is clear that CVD is preferred only for such cases where all other methods fail.

3.4. Arc-melting

Arc-melting is a very simple and effective technique for the preparation of bulk materials. A more complicated related technique which can even yield large single crystals is zone melting/annealing (e.g. [12]). These techniques serve well if a compound melts congruently and not e.g. in form of a peritectic reaction.

Advantages

- fast and easy-to-apply method
- produces dense and pore-free samples if the congruently melting compounds are stable, i.e. if no gas pores occur

The disadvantages of this method are:

- volatile constituents are liberated upon melting (e.g. nitrides decompose by formation of nitrogen)
- a multiphase microstructure is formed if incongruently melting/decomposing compounds are arc melted, which makes re-annealing necessary; depending on the decomposition temperature this re-annealing step can be time-consuming

Tab.1 gives an overview of accessible group 4 – 6 transition metal carbides and nitrides which are suited to serve as a reference material, together with appropriate preparation techniques. The subcarbides Me_2C of the group 5 transition metal carbides are not listed because they form compounds with a few mol% homogeneity range. A diffusion layer of these compounds group such as for the carbides Me_4C_3 is therefore inappropriate. They had to be prepared only by hot pressing powders which are not commercially available. On the other hand, group 5 subnitrides Me_2N – although showing a homogeneity range, too – can be annealed at appropriate nitrogen pressures to form homogeneous single-phase reference samples.

4. Results on the Preparation of Carbides, Nitrides and Carbonitrides for EPMA Use

Over the last three decades, a huge variety of samples have been prepared in our laboratory order to obtain well-characterised reference materials for EPMA. The EPMA studies were in turn used to investigate phase equilibria and diffusivities as well as for materials' characterisation (solid-state properties).

4.1 Carbides

By hot-pressing of fine powders carbides such as TiC, ZrC, HfC, Cr_3C_2 , WC, (Ti,Mo)C, (Ti,W)C (and also carbonitrides, see section 4.5) to disks between 10 – 50 mm in diameter and with 5 – 10mm thickness were prepared in our laboratory (Fig.8, bottom). In such specimens the porosity level is below 1%. For choosing appropriate hot-pressing conditions the phase diagram information

is necessary, e.g. the temperature for Cr_3C_2 must not exceed about 1800°C , otherwise it will decompose peritectically (compare Fig.2d).

In addition to hot-pressing, a large number of carbides was prepared by full carburisation of metal sheets upon diffusion of C. A full carburisation does not necessarily mean that the carbon content is 50 mol%, the carbides such as VC_{1-x} and Cr_3C_2 , for example, do not uptake such an amount of carbon. In addition, the in-diffusion of carbon can be stopped and the sample further annealed in inert atmosphere so that the sample is single-phase and homogeneous carbide MeC_{1-x} but does not contain 50 mol%C. Fig.8, top shows fully carburised metal sheets of V, Nb and Ta which were prepared in order to investigate the phase equilibria and carbon diffusivities in the various phases by means of diffusion couples such as shown in Fig.9 [3,4,13,14]. These diffusivities can be used to calculate the phase-boundary movement and to estimate the time when the sample is single-phase and, some time later, the diffusion profile is flat enough for taking such a sample as a homogenised reference material. In addition, to the plane-sheet samples wedge-type samples were especially suited for these calculations because they allow to show how fast the layer grows as a function of sheet thickness (see section 4.2.2).

The data points in Fig.2 were obtained by use of EPMA on diffusion couples prepared at different temperatures such as shown in Fig.9 by use of reference materials described in this study. Fig.10 gives EPMA line scans across such diffusion couples. It should be noted that for some systems, like Ta-C the discontinuities at the interfaces (due to two-phase fields) is on the order of tenth of wt%C. Together with accurate standardisation and measurement conditions within EPMA it is necessary to avoid relief effects. This is done by appropriate sample polishing or lapping procedures [15].

Some of the employed carbide reference samples were prepared by diffusion of carbon in metal sheets by means of the above-mentioned techniques, e.g. $\delta\text{-VC}_{1-x}$, $\delta\text{-NbC}_{1-x}$ and $\delta\text{-TaC}_{1-x}$, some by hot pressing (WC , Cr_3C_2), some by both techniques (Cr_3C_2 , $\delta\text{-TaC}_{1-x}$). The diffusivity of carbon in the various carbides decreases substantially from the first period of transition metals (Ti, V, Cr) to the last period (Hf, Ta, W), so that samples of TaC and WC can be prepared by C diffusion only if thin metal sheets are used as a starting material. Larger samples can of course be prepared by hot-pressing. Tab.2 gives an overview on experimental conditions and analysis results of reference samples prepared by C in-diffusion into metal sheet.

4.2 Nitrides

The preparation of well-characterised nitride specimens is the most difficult amongst the group of compounds studied here (compare discussion in [16] on pages 18-24). Upon inappropriate nitrogen equilibrium pressure and/or too low temperatures two-phase and inhomogeneous samples are obtained unsuitable to serve as a standard. Hence, most work in our laboratory was directed to this group of compounds for which studies on phase diagrams and diffusivities were indispensable.

4.2.1 Group 4 mononitrides

The preparation of “fully nitrated” (50mol%N) group 4 transition metal nitrides $\delta\text{-TiN}_{1-x}$, $\delta\text{-ZrN}_{1-x}$ and $\delta\text{-HfN}_{1-x}$ is relatively easy because their nitrogen equilibrium pressure is very low and hence these so-called fcc mononitrides can be obtained almost at any nitrogen equilibrium pressure usually established in a vacuum furnace or autoclave. The necessary pre-requisites are high-purity starting materials together with an apparatus with carbon- and oxygen-free conditions, i.e. heating elements and shields made out of refractory metals (W, Mo) rather than of graphite, together with the capability of keeping constant temperatures and pressures over several days (depending on the heating temperature). Fig.11 shows a photograph of reference samples with a nitrogen content very close to 50 mol%N obtained in an autoclave with a tungsten tube at temperatures of 1600°C and ambient nitrogen pressure.

4.2.2 Group 4 sub-nitrides

Sub-nitrides exist in the Ti-N and Hf-N systems, but not in the Zr-N system (compare Fig. 3). In the Ti-N system, the sub-nitrides η -Ti₃N_{2-x} and ζ -Ti₄N_{3-x} cannot be prepared in bulk form and exist only over a very narrow temperature range. The sub-nitride ε -Ti₂N has a decomposition temperature of around 1070°C but is stable down to room temperature and forms rapidly. Hence, in Ti/TiN powder mixtures arc-melted at much higher temperatures it is partially formed upon cooling whereas nitrogen loss upon melting has to be considered. It can be obtained in single-phase form by annealing these arc-melted samples with an overall nitrogen composition of 33 mol%N. Due to the fact that the nitrogen diffusivity is low the necessary annealing time just below the decomposition temperature is on the order of two weeks to obtain single-phase and homogeneous samples [17] such as shown in Fig.12, left. On the opposite, diffusion layers of ε -Ti₂N are easy to prepare (Fig. 12 right).

A very special situation exists in the Hf-N for the sub-nitrides η -Hf₃N_{2-x} and ζ -Hf₄N_{3-x}, isostructural to the respective phases in the Ti-N system. Due to the specific properties with respect to high-temperature stabilities and nitrogen diffusivities a diffusion-couple method has been worked out in our laboratory [18] to obtain bulk single-phase hafnium sub-nitrides from diffusion couples. First, wedge-type samples (Fig.13) were studied in order to investigate the influence of sheet thickness (total thickness of the wedge at a special position) on the diffusion layer thicknesses for a given temperature and diffusion time. It should be noted that the diffusion layer thicknesses increase as a function of decreasing sample thickness, hence by use of a wedge this behaviour can be studied in a single experiment at a given temperature [19-21]. From this information nitrogen diffusivities can be calculated to predict the appropriate temperature and diffusion time for the preparation of this phase out of the core of a nitrided, plane-parallel Hf metal sheet covering the desired sub-nitride phase. As seen from the wedge in Fig.13, this procedure can be employed for η -Hf₃N_{2-x} and ζ -Hf₄N_{3-x} by removal of two and one outer nitride phases, respectively. A plane-sheet sample for which this techniques was employed for obtaining a ζ -Hf₄N_{3-x} sample is shown in Fig. 14.

4.2.3 Group 5 fcc mononitrides

The fcc mono-nitrides of group 5 transition metals require much higher nitrogen equilibrium pressure than that of the 4th group. In Fig.3 the phase diagram of the Nb-N system is shown with isobars indicated for the δ -NbN_{1-x} phase and Fig.15 shows the equilibrium pressure of δ -VN_{1-x} and δ -NbN_{1-x} as a function of nitrogen content and temperature [22, 23]. No such complete data set is available for δ -Ta₂N_{3-x}, which is stable only above about 1800°C (Fig.3). From δ -VN_{1-x} to δ -Ta₂N_{3-x} there is a substantial decrease of nitrogen diffusivities. Hence, VN_{1-x} and NbN_{1-x} can be prepared relatively fast by in-diffusion of nitrogen at high temperature in the respective metal sheets, but the same procedure is not readily applicable to δ -Ta₂N_{3-x} because of the high nitrogen pressures needed (above 20 bar) and low diffusivities. The diffusional behaviour was again studied in detail by wedge-type samples. Fig.16 presents the microstructure of a wedge-type Ta-N sample showing the mono-nitride ε -Ta₂N_{3-x} as the outermost phase and δ -Ta₂N_{3-x} as the next one. This sequence is present for temperatures between 1800 and 1900°C, see Fig.3. Near the tip of the sample diffusion band of ε -Ta₂N_{3-x} is thickened due to the above-mentioned fact of geometry-driven thickness enhancement.

These samples – and the derived nitrogen diffusivities in tantalum nitride phases – give again a good insight of how long a plain-sheet sample of a certain thickness has to be annealed to contain single phase ε -Ta₂N_{3-x}. The latter phase has another advantage over other mono-nitrides: it is a line compound due to its crystal structure (non-Hägg compound), see EPMA scan across the two-phase tip of the wedge-type sample Fig.17. Hence, if such a phase is obtained in single-phase form the nitrogen composition is known *a priori*. This is not the case for fcc nitrides δ -VN_{1-x}, δ -NbN_{1-x} and δ -Ta₂N_{3-x} because of their homogeneity range (compare phase diagrams in Fig. 2). Fig.18 shows a ε -Ta₂N_{3-x} reference sample, the nitrogen content of which was measured by Dumas gas-

chromatography [11] and CGHE [24], the metal content by combustion to metal oxides and proved to contain exactly 50mol% N. Tab.3 gives information on experimental conditions of nitride reference materials prepared for EPMA. These samples are fully nitrated for a given nitrogen pressure.

4.2.4 Group 5 sub-nitrides

The sub-nitrides of group V transition metals β -V₂N, β -Nb₂N and β -Ta₂N show small but definite homogeneity ranges (Fig.3) and have lower nitrogen equilibrium pressures than the corresponding mononitrides [25,26]. If group 5 transition metal nitrides are desired but the furnace is not capable of high nitrogen pressure, annealing of sub-nitrides at pressures lower than 1 bar is a good alternative to mononitrides. However, because of the high equilibrium pressure of Ta₂N, the annealing temperature is rather low and hence the necessary time rather long.

4.3 Group 6 transition metal nitrides

This group requires the highest nitrogen equilibrium pressures. While two chromium nitrides (Cr₂N and CrN) and two molybdenum nitrides (Mo₂N in either modification, and fcc MoN_{1-x}) are accessible by nitrogen diffusion into metal sheet, δ -MoN is only at very high pressures and tungsten nitrides not accessible at all.

By annealing thin Cr sheet at T=1230°C at increased nitrogen pressure it was possible to obtain the line compound CrN with a composition of 50 mol%N (Tab.3). If the temperature is higher, this phase is no more a line compound and the homogeneity range widens substantially (compare with Fig.3). With the rise in temperature, the nitrogen equilibrium pressure increases, so that 50mol%N can only be established at increased N₂ pressures [4].

To increase the nitrogen potential for nitrating Mo, it is possible to use ammonia [27]. However, the use of ammonia is restricted to low temperature because of the fast decomposition of NH₃ (and hence reducing the nitridation potential to a N₂+H₂ mixture). At these low temperatures (<1000°C) the diffusivity of nitrogen is very low. Fig.19 shows an example of a wedge-type Mo-N sample obtained by ammonia nitridation showing mainly the fcc γ -MoN_{1-x} phase (the Mo₂N phase was absent). Due to the specific nitrogen diffusivities there is no thickness enhancement of diffusion layers [28]. The γ -MoN_{1-x} phase in such a diffusion couple has a large homogeneity range of about 10mol%N and is not suited for a reference material. In order to prepare such a homogeneous phase, long annealing of a plane-sheet sample has to be performed such as for group 4 and 5 mononitrides.

4.4 Ternary nitrides and carbonitrides

Diffusional preparation of ternary and higher higher-order nitrides and carbonitrides is a priori impossible due to different diffusivities of the various components leading to an inhomogeneous microstructure. Only if diffusion occurs along tie lines the interfaces of diffusion layers are planar [29]. An example is the nitridation of Ti/Zr alloys, in which a fcc phase δ -(Ti,Zr)N_{1-x} is formed on hcp α -(Ti,Zr)(N). In Fig.20, left a partly nitrated sample is shown in which the outermost phase δ -(Ti,Zr)N_{1-x} can be observed. The phase diagram for the Ti-Zr-N system at 1300°C is shown in Fig.20, right. During nitridation the Ti/Zr ratio in the fcc and hcp can be different if the tie lines are crossed by the diffusion path. Only in one case – if the diffusion path goes along the tie line, which is the case for a sample with a starting composition of 60mol%Ti+40mol%Zr – is the Ti/Zr ratio identical and constant in both phases (Fig.21, top). Hence, if such an alloy is fully nitrated a homogeneous sample can be obtained. In all other cases the Ti/Zr ratio is not constant even after full nitridation (Fig.21, bottom) and the necessary time is by far too long to homogenise the metals.

Similar is true if more than one non-metal is present, e.g. carbon and nitrogen. It is then more convenient to prepare such ternary and higher-order samples by hot pressing as it is shown in Fig.22 for group 4 transition metal carbonitrides [2]. Such samples proved to be homogeneous over the full range of carbon/nitrogen ratio by EPMA.

5. Conclusion

Due to the chemical shift encountered in EPMA high quality measurements need one or more reference materials out of the same system as the sample to be analysed. For the preparation of such reference materials the thermo-chemical boundary conditions are very important to obtain a homogeneous well-defined sample or – second choice – a well-defined diffusion layer. Therefore, a lot of information on stabilities, melting points, diffusivities and equilibrium pressures is necessary which was summarised in this study for a variety of group 4 - 6 transition carbides, nitrides and carbonitrides.

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Tables

Table 1. Features of the most important binary carbide and nitride phase for use as an EPMA reference material, compare also phase diagrams

a) Carbides

System	Phase	Features (phases, systems) + advantages, – disadvantages	Appropriate Techniques
Ti-C	δ -TiC _{1-x}	– broad homogeneity range – the only phase in Ti-C	DB, HP, AM
Zr-C	δ -ZrC _{1-x}	– broad homogeneity range – the only phase in Zr-C	DB, HP, AM
Hf-C	δ -HfC _{1-x}	– broad homogeneity range – the only phase in Hf-C	DB, HP, AM
V-C	δ -VC _{1-x}	– broad homogeneity range	DB, HP, AM
	ζ -V ₄ C _{3-x}	+ line compound – narrow DB	DL
Nb-C	δ -NbC _{1-x}	– broad homogeneity range	DB, HP, AM
	ζ -Nb ₄ C _{3-x}	+ line compound – narrow DL	DL
Ta-C	δ -TaC _{1-x}	– broad homogeneity range	DB, HP, AM
	ζ -Ta ₄ C _{3-x}	+ line compound – narrow DL	DL
Cr-C	Cr ₃ C ₂	+ narrow homogeneity range	DL, DB, HP
	Cr ₇ C ₃	+ narrow homogeneity range + broad DL	DB
Mo-C	Mo ₂ C	+ line compound	DL, DB, HP
W-C	WC	+ line compound – narrow DL	DB, DL, HP

DC: diffusion couple

Techniques: DB: diffusional preparation to end up with a bulk sample (long annealing)

DL: diffusional preparation to from a diffusion layer

HP: preparation by hot pressing

AM: preparation by arc-melting (and homogenization annealing)

b) Nitrides

System	Phase	Features (phases, systems) + advantages, – disadvantages	Appropriate Techniques
Ti-N	δ -TiN _{1-x}	– broad homogeneity range	DB, HP
	ϵ -Ti ₂ N	+ narrow homogeneity range + broad DL – long annealing at low if M	DL, HP, AM
Zr-N	δ -ZrN _{1-x}	– broad homogeneity range – the only phase in Zr-N	DB, HP
Hf-N	δ -HfN _{1-x}	– broad homogeneity range	DB, HP
	ζ -Hf ₄ N _{3-x}	+ narrow homogeneity range + broad DL in plane-sheet DC – grinding for DB sample	DB, DL
	η -Hf ₃ N _{2-x}	+ narrow homogeneity range + broad DL in plane-sheet DC – grinding for DB sample	DB, DL
V-N	δ -VN _{1-x}	– broad homogeneity range	DB
	β -V ₂ N _{1-x}	+ N ₂ pressure < 1bar	DB
Nb-N	δ -NbN _{1-x}	– broad homogeneity range	DB
	η -NbN	– long formation time (low T)	DL
	β -Nb ₂ N _{1-x}	+ N ₂ pressure < 1bar	DB
Ta-N	ϵ -TaN	+ narrow homogeneity range – p ≥ 30 bar N ₂ , T ≥ 1700°C – very thin if in form of a DL	DB, DL
	β -Ta ₂ N _{1-x}	– broad homog. range at highT	DB
Cr-N	δ -CrN	+ narrow homogeneity range – narrow only at low T	DB, DL
	β -Cr ₂ N	– broad homog. range at highT	DB
Mo-N	γ -MoN _{1-x}	– broad homogeneity range	DB
W-N	---	– no phase accessible by thermochemical techniques	---

Table 2. Data for the preparation of group 5 and 6 transition metal carbides as a reference material for EPMA. Starting material: high-purity metal sheets and industrial powders (hot-pressed samples)

Sample	Sheet thickness μm	Annealing temp. °C	Annealing time h	Composition wt%C +/- 0.5rel%
VC	290	1500	89	17.34
NbC	300	1830	51	11.29
TaC	240	2000	44	6.23
Cr ₃ C ₂	250	1590	62	13.30
WC	Hot-pressed disk	1950	1	6.128
Cr ₃ C ₂	Hot-pressed disk	1750	1	13.27

Table 3. Data for the preparation of group 4 - 6 transition metal nitrides as a reference material for EPMA. Starting material: high-purity metal sheets

Sample	Sheet thickness μm	Annealing T / $^{\circ}\text{C}$	Pressure / bar N_2	Annealing time h	Composition wt%N $\pm 0.5\text{rel}\%$
TiN	290	1500	1	170	22.58
HfN*	300	1800	3	51	7.25
VN**	1000	≤ 1650	≤ 40	≤ 233	see Fig.15
NbN**	500	≤ 1800	≤ 40	≤ 170	see Fig.15
TaN	100	1730	25	45	6.13
CrN	300	1230	31	263	21.18

*also sub-nitride samples were prepared (see text)

** series with more than 10 samples were prepared with different nitrogen content at different conditions, e.g. Fig.15 for NbN

Figures

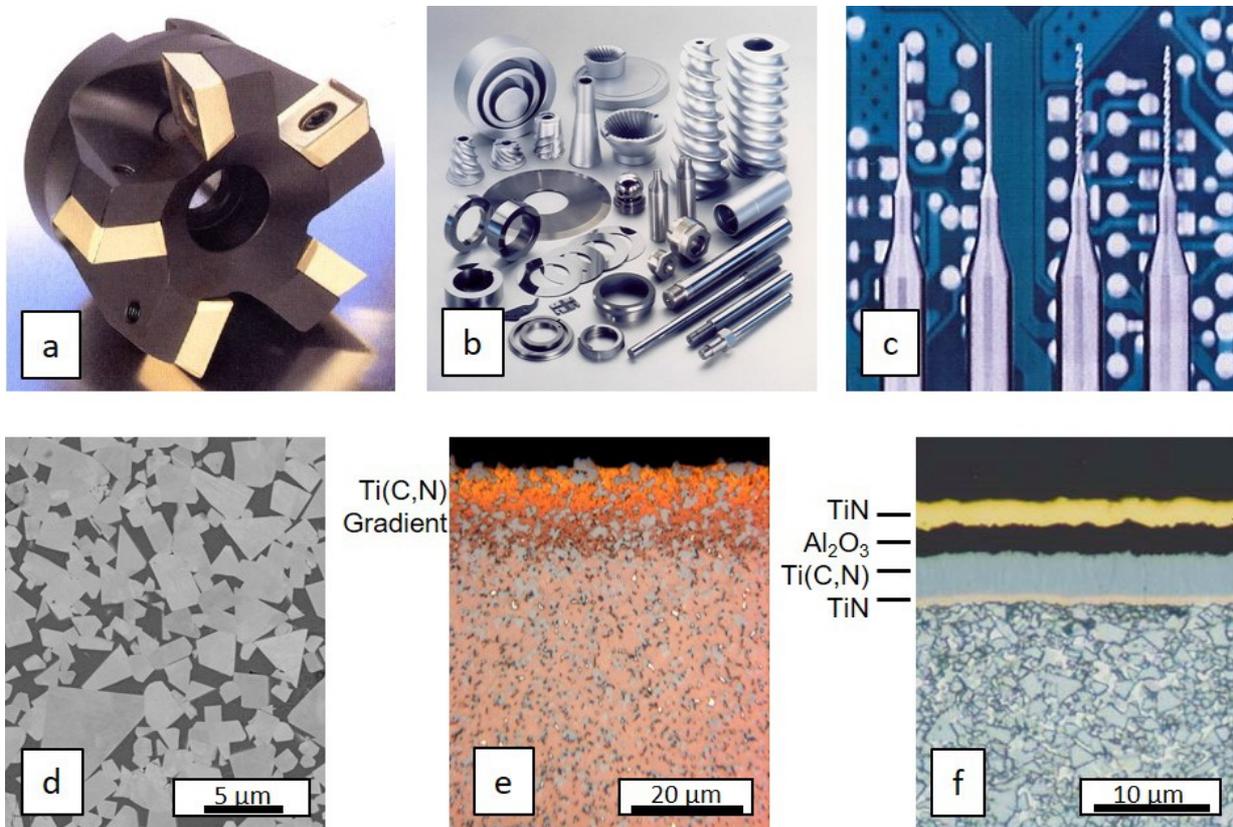


Figure 1. Examples of carbide-, nitride- and carbonitride containing parts used in a variety of applications. a) milling cutter with TiN-coated indexable hardmetal inserts, b) various tools composed of hardmetal (WC-Co), c) hardmetal drills for PCB drilling, d) microstructure of a coarse grained hardmetal for rock drilling, e) microstructure of the Ti(C,N)-enriched surface zone of a functionally-graded hardmetal, f) cross section of multilayer coating of a hardmetal

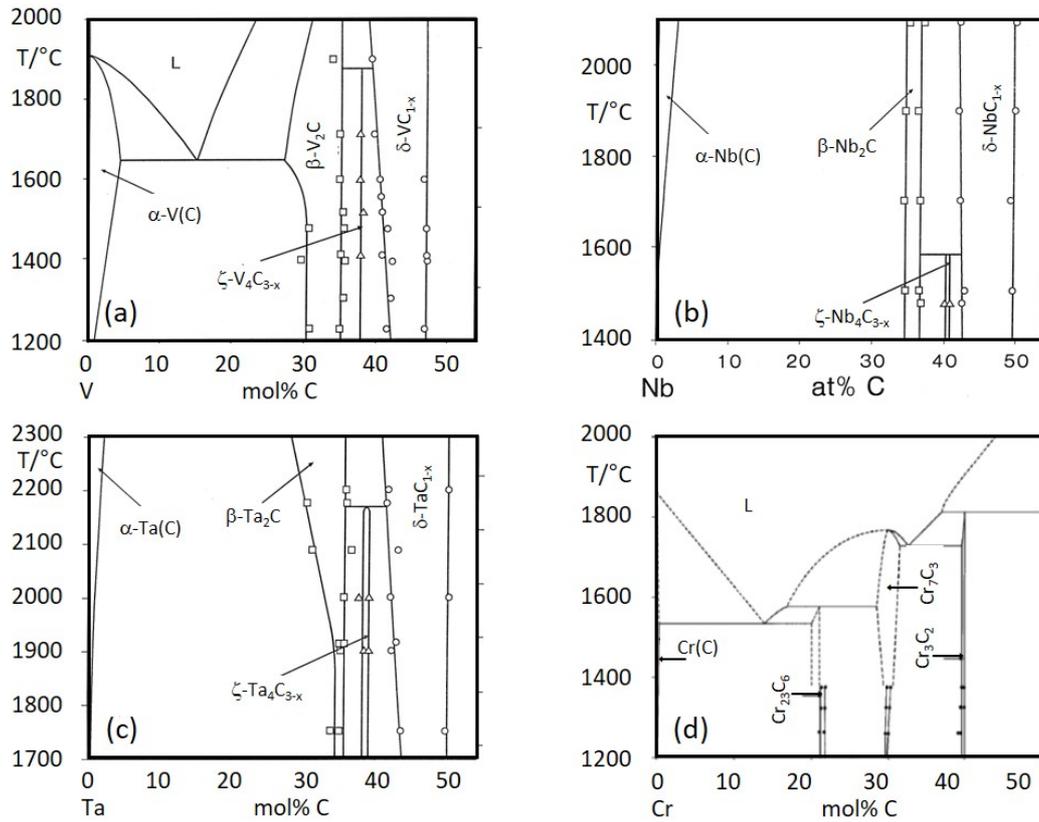


Figure 2. Re-investigated phase diagrams of various transition metal – carbon phase diagrams, a) V-C, b) Nb-C, c) Ta-C [3] and d) Cr-C systems [4]

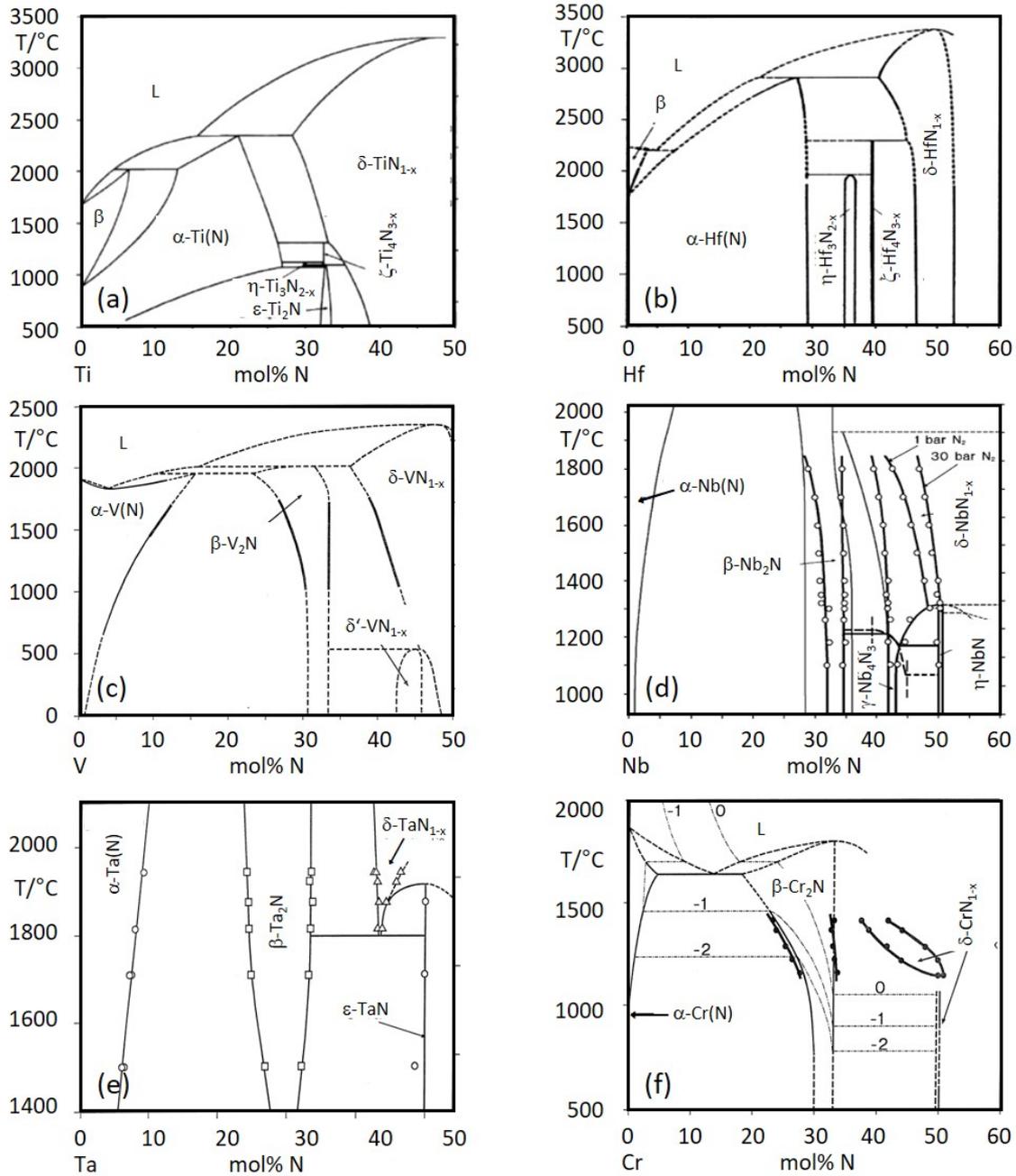


Figure 3. Phase diagrams of some group 4, 5 and 6 transition metal – nitrogen systems, a) Ti-N [5], b) Hf-N [6] c) V-N [7], d) Nb-N [8] e) Ta-N [3] and f) Cr-N [4]. In some phase diagrams the thin lines represent the phase fields before re-investigation, data points and bold lines: phase boundaries rearranged by EPMA, measurement conditions given in the cited references

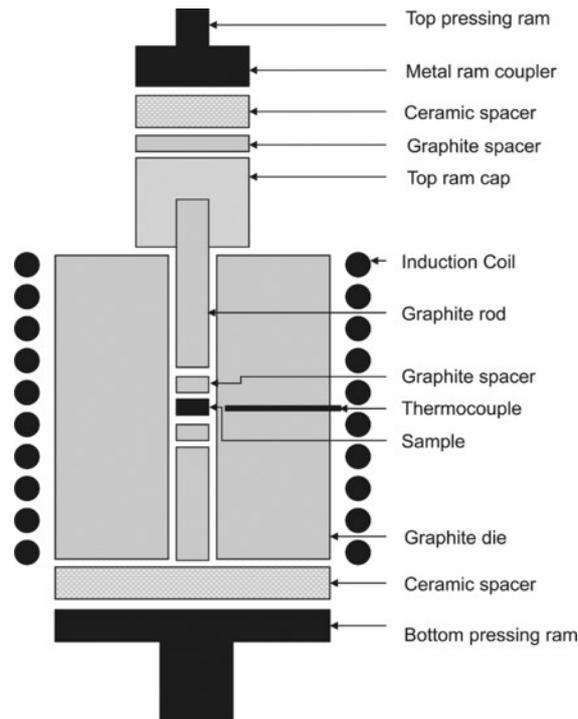


Figure 4. Scheme of the hot-pressing technique in which powdered compounds are uniaxially pressed at high temperatures in graphite or boron nitride dies

From: <https://authors.library.caltech.edu/23007/2/figure1.jpg>

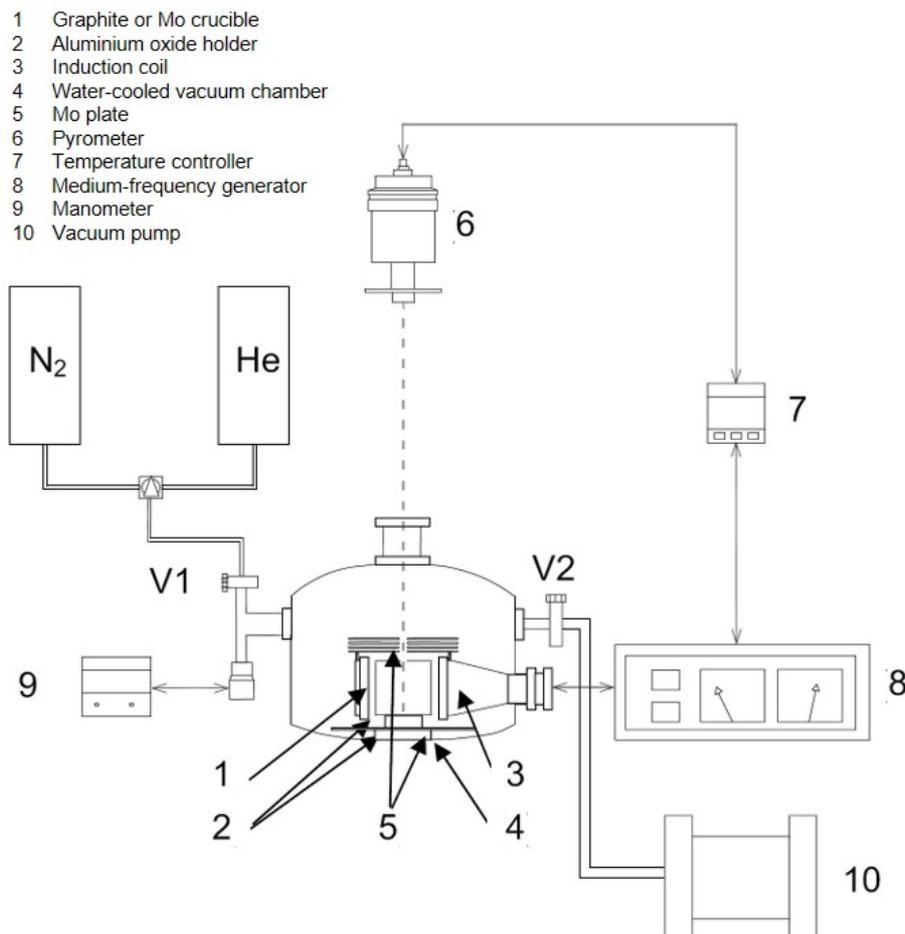


Figure 5. Scheme of a vacuum furnace used for reaction of metal sheets in nitrogen atmosphere (up to 900mbar) or graphite powder for T up to 1600°C. Carbon-free conditions can be established by using a Mo crucible which serves as a susceptor for inducing heating

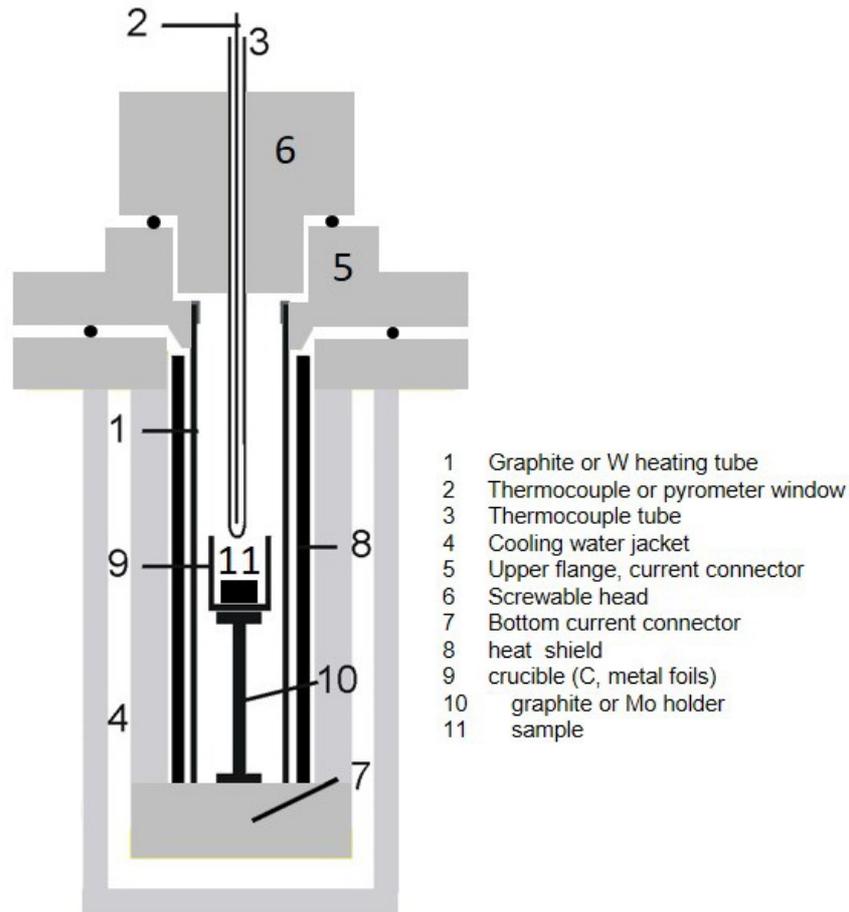


Figure 6. Scheme of a medium-pressure furnace (autoclave) for reaction of metal sheets in nitrogen atmosphere (up to 40 bar) or graphite powder up to 2200°C. Carbon-free conditions can be established by using a W heating tube and Mo sample holder

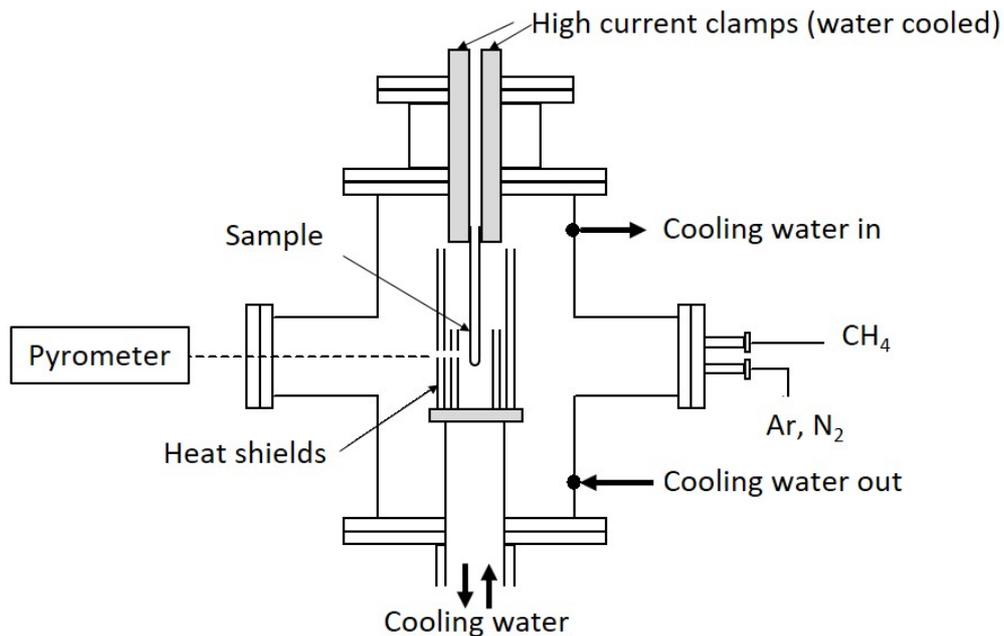


Figure 7. Scheme of a high-temperature furnace for reaction of CH_4 with metal sheet for carburisation. The metal sheet is a bent metal strip which is clamped between water-cooled electrodes. The temperature is measured by pyrometry, T is up to 2500°C

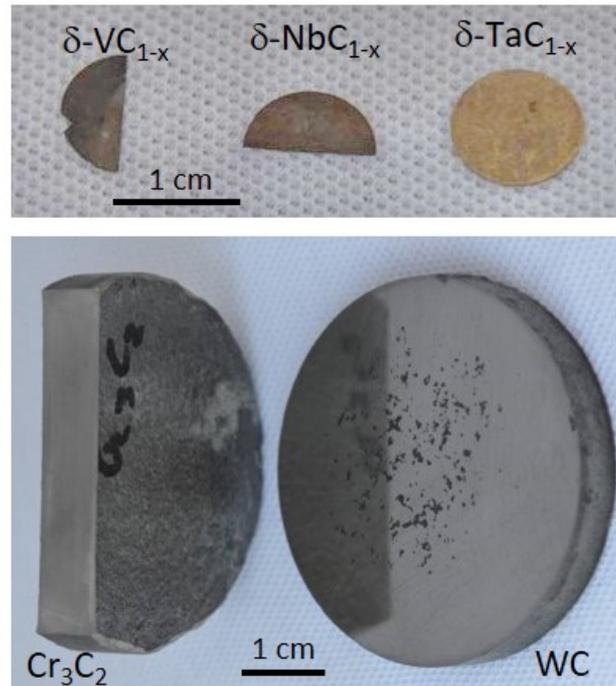


Figure 8. Carbide reference materials prepared by C diffusion or by hot-pressing powders. Top: VC_{1-x} (left) NbC_{1-x} (middle) and TaC_{1-x} (right) by C in-diffusion in metal sheet; bottom: Cr_3C_2 (left), WC (right) by hot pressing

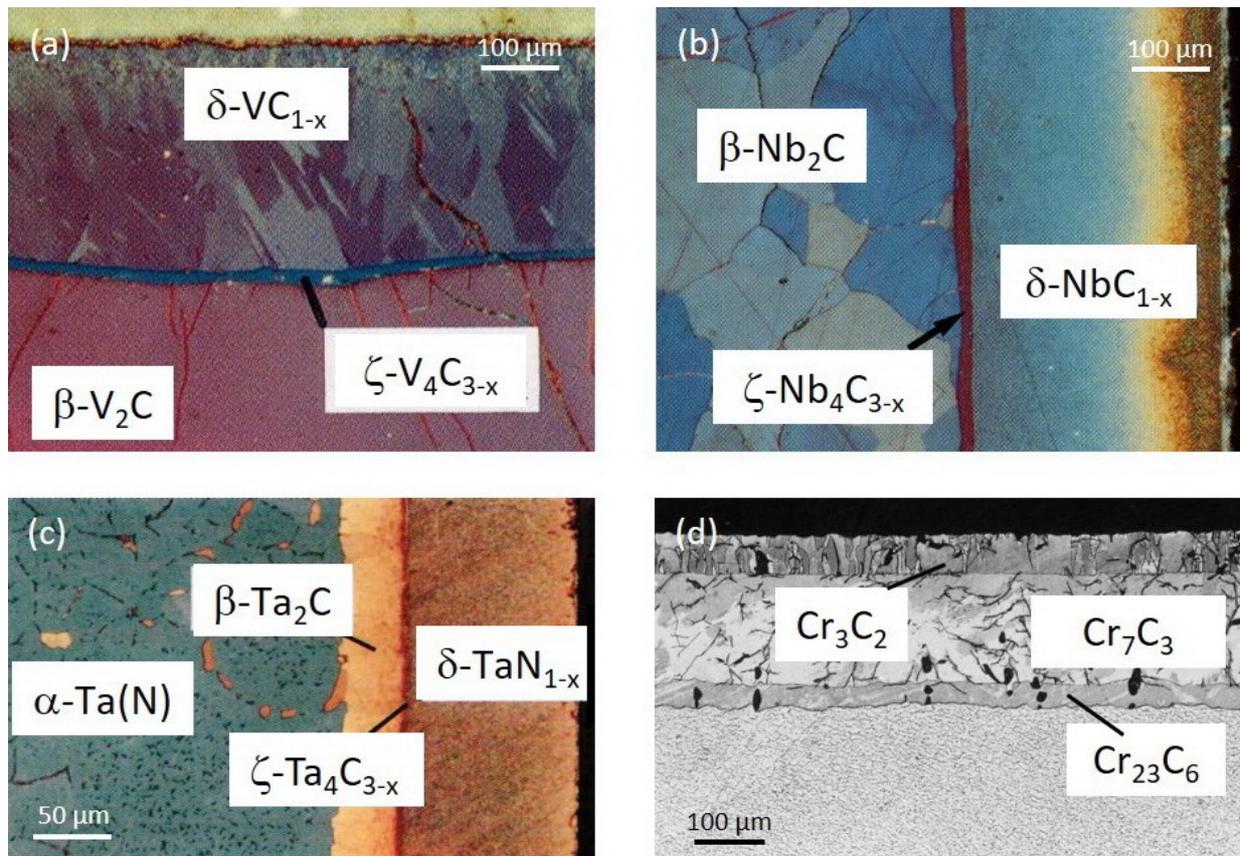


Figure 9. Microstructures of diffusion couples prepared by reaction of metal sheets or Me_2C phases with graphite in order to establish diffusion bands of ζ phases, a) V-C, b) Nb-C, c) Ta-C systems; or for studying layer-growth kinetics, d) Cr-C system. The ζ phases appear as a very narrow phase bands between δ - MeC and β - Me_2C phase bands and have a narrow homogeneity range, too. Compare with phase diagram presented in Fig.2 and EPMA line scans in Fig.10

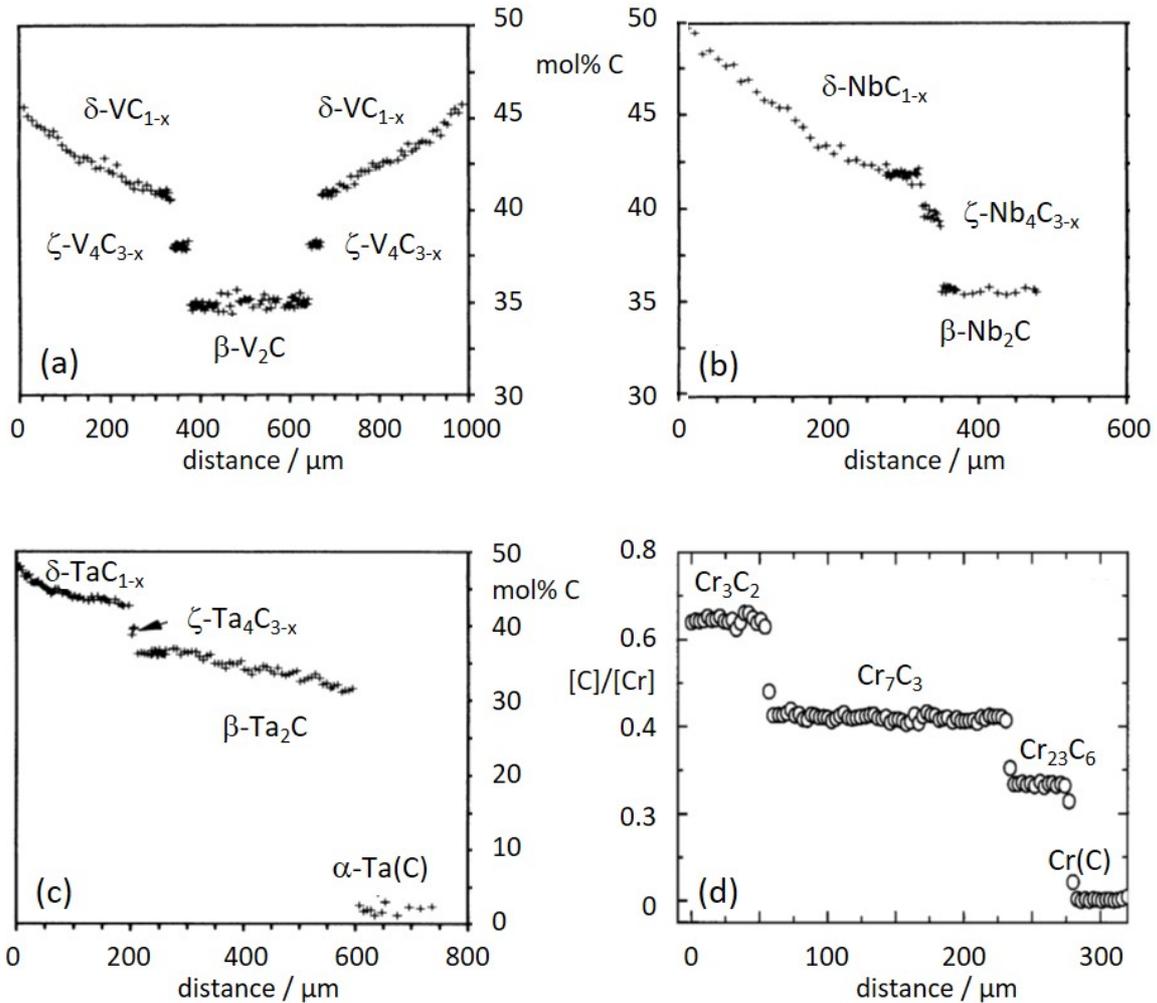


Figure 10. Line scans across diffusion couples (compare with Figure 9), a) across an entire diffusion couple for which a $\beta\text{-V}_2\text{C}$ sample was annealed in graphite powder, b) one half of a diffusion couple with starting from graphite – $\beta\text{-Nb}_2\text{C}$, c) across one half of a diffusion couple starting from graphite – Ta sheet and d) across the diffusion layers formed on Cr upon annealing of Cr sheet in graphite powder

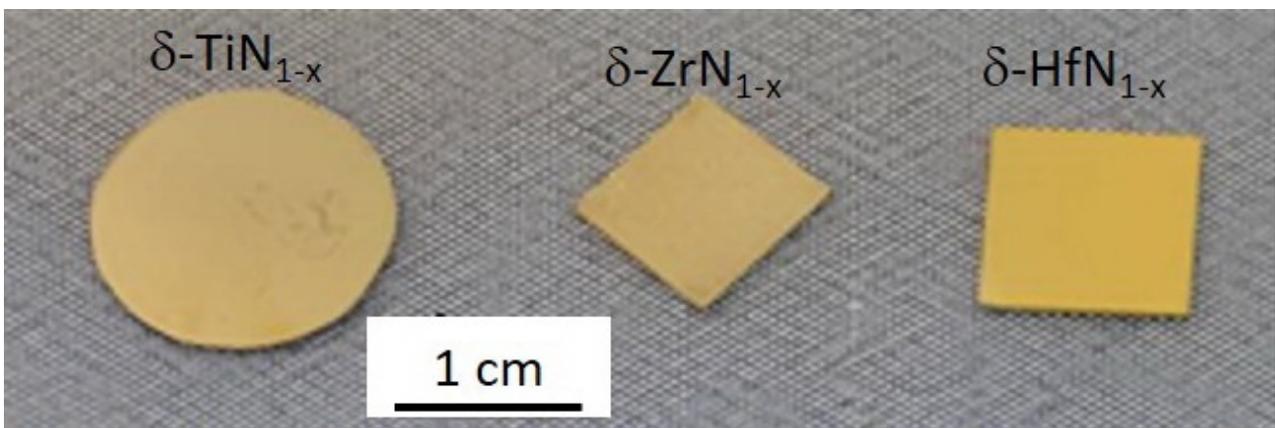


Figure 11. Nitride reference materials of group 4 mononitrides prepared by prolonged nitrogen diffusion into the respective metal sheets: $\delta\text{-TiN}_{1-x}$ (left), $\delta\text{-ZrN}_{1-x}$ (middle) and $\delta\text{-HfN}_{1-x}$ (right) reference samples; fully nitrated, with 50 mol% N

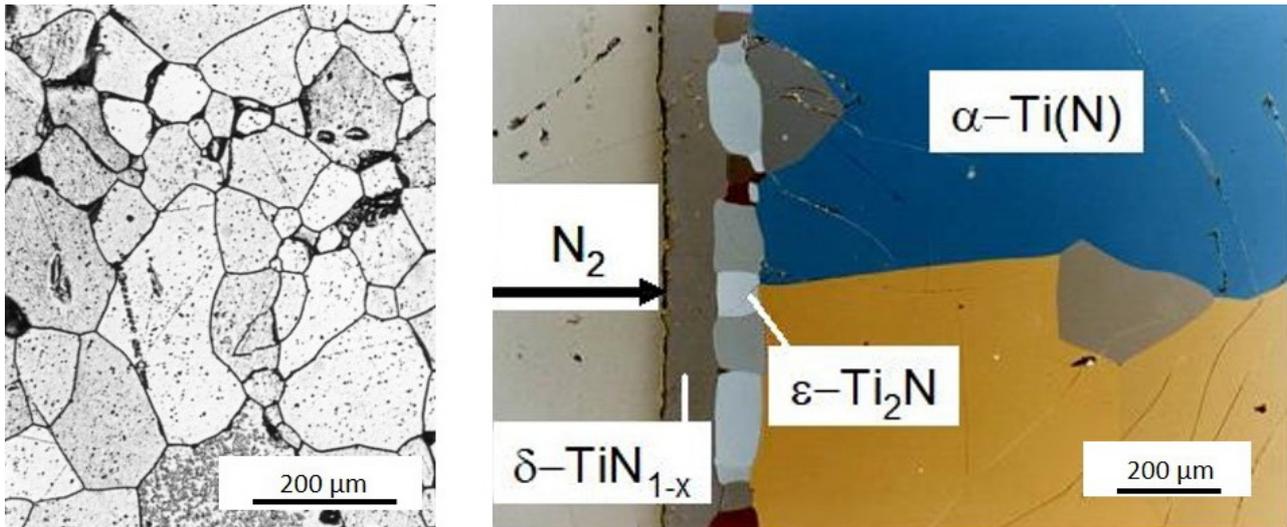


Figure 12. Subnitride reference material, left: microstructure of homogeneous ϵ - Ti_2N sample [17] prepared by arc-melting and extended annealing in a silica tube at 1000°C , due to etching with HF/HNO_3 (for identification of the grain boundaries) the sample shows etching pits, these can be removed by re-polishing with silica suspension; right: microstructure (in polarized light) of a $50\mu\text{m}$ thick diffusion layer of ϵ - Ti_2N between α - $\text{Ti}(\text{N})$ and δ - TiN_{1-x} , which is however not strictly homogeneous, but shows a very narrow homogeneity range

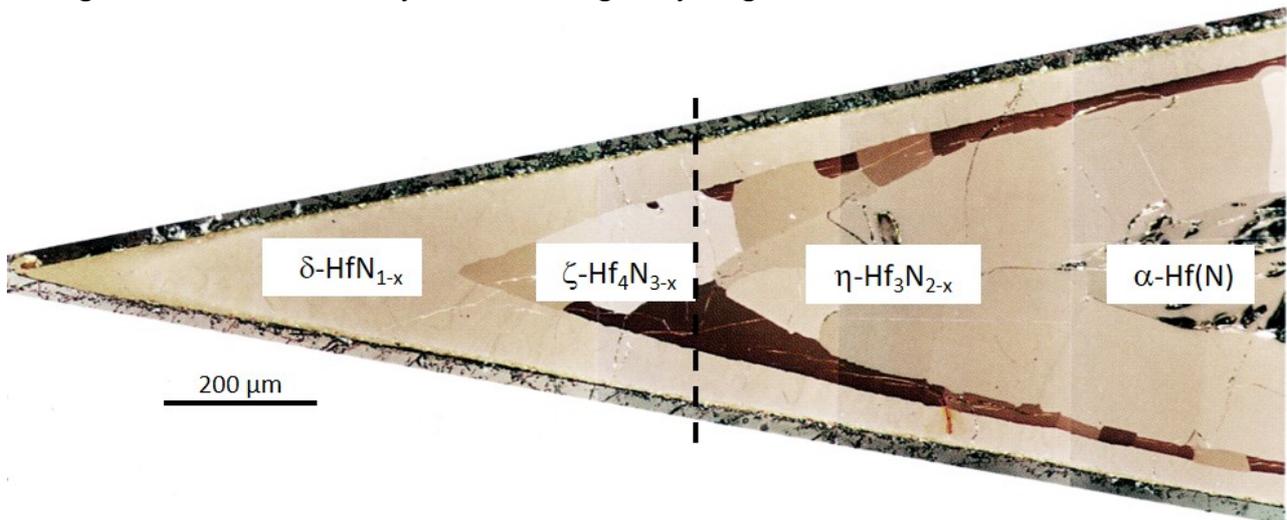


Figure 13. Wedge-type sample of Hf-N [18] showing an increase of diffusion layer thickness upon preparation of a single-phase sample out of the core of a plane-parallel diffusion couple. In first approximation the layer thickness enhancement is only due to the plane-sheet geometry, not to the effect of thickness enhancement near corners (deviation from plane diffusion geometry such as in spheres). The broken line corresponds to the phase sequence (δ - HfN_{1-x} - ζ - $\text{Hf}_4\text{N}_{3-x}$ - δ - HfN_{1-x}) in a plane sheet sample (Fig.14)

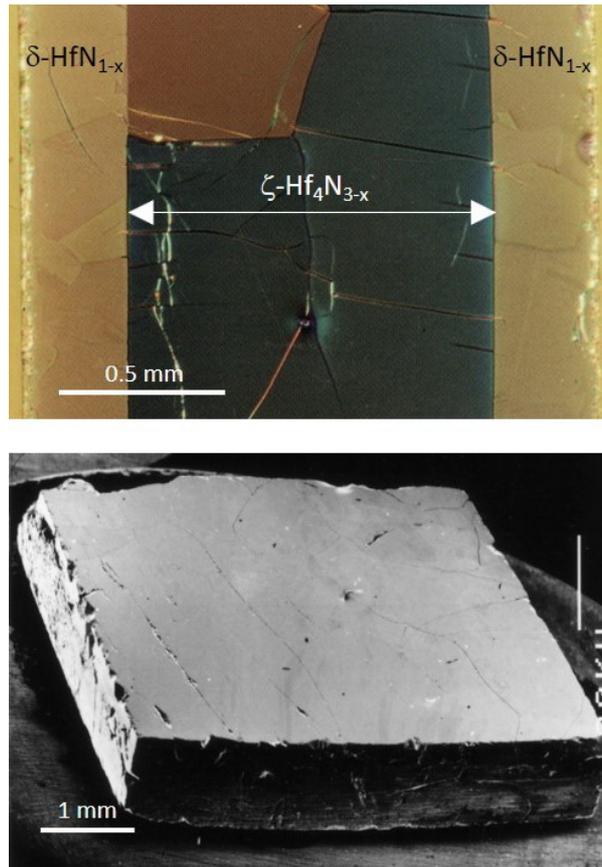


Figure 14. Top: plane sheet diffusion couple with $\zeta\text{-Hf}_4\text{N}_{3-x}$ in the core, corresponding with respect to layer sequence to the line across the wedge in Fig.13 [18], bottom: single-phase sample prepared from the core of the diffusion couple on top by grinding-off the outer $\delta\text{-HfN}_{1-x}$ layers of both sides. For obtaining a larger core, the sheet is thicker than the corresponding cross section indicated in Fig.13, the longer annealing time was calculated by using the diffusion data established from wedge-type samples [18]

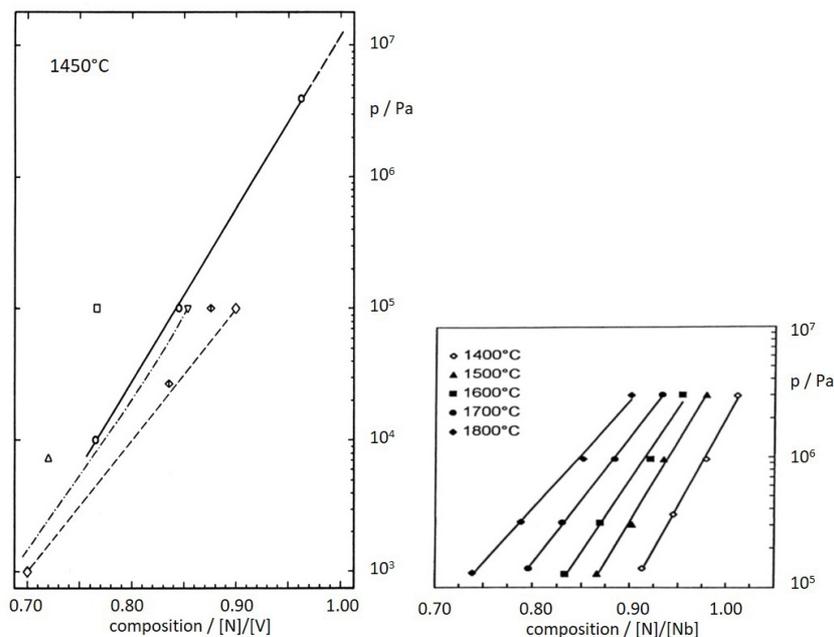


Figure 15. Nitrogen equilibrium pressures as a function of temperature and composition of $\delta\text{-VN}_{1-x}$ (left, literature compilation of [23]) and of $\delta\text{-NbN}_{1-x}$ (right [24]). Higher than ambient pressures are needed to establish a composition near 50 mol%N

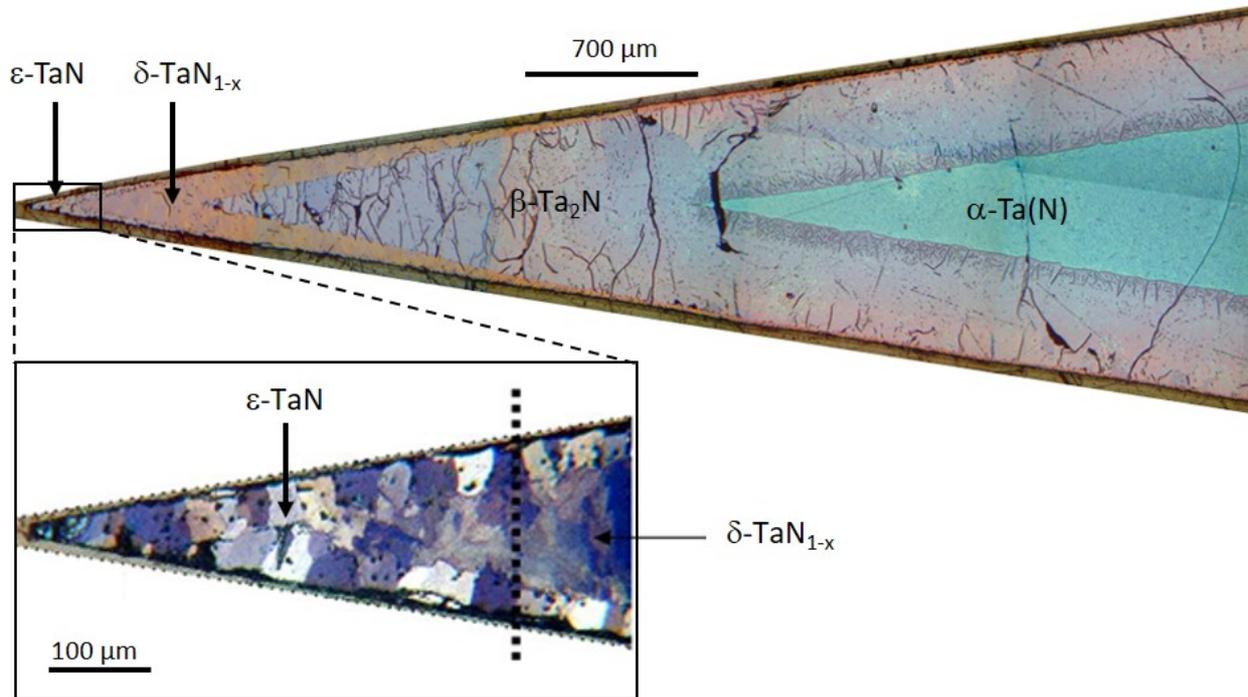


Figure 16. Polished cross section of a wedge-type Ta-N diffusion couple with magnified tip. The phase interesting for nitrogen calibration, because of its line-compound character (Fig.17). It forms in a thin diffusion band at the outermost position. Hence, upon using a thin Ta foil the time and temperature can be established when this phase grows from both sides and transforms the entire sample into a single-phase ϵ -TaN sample. Compare with Fig.18

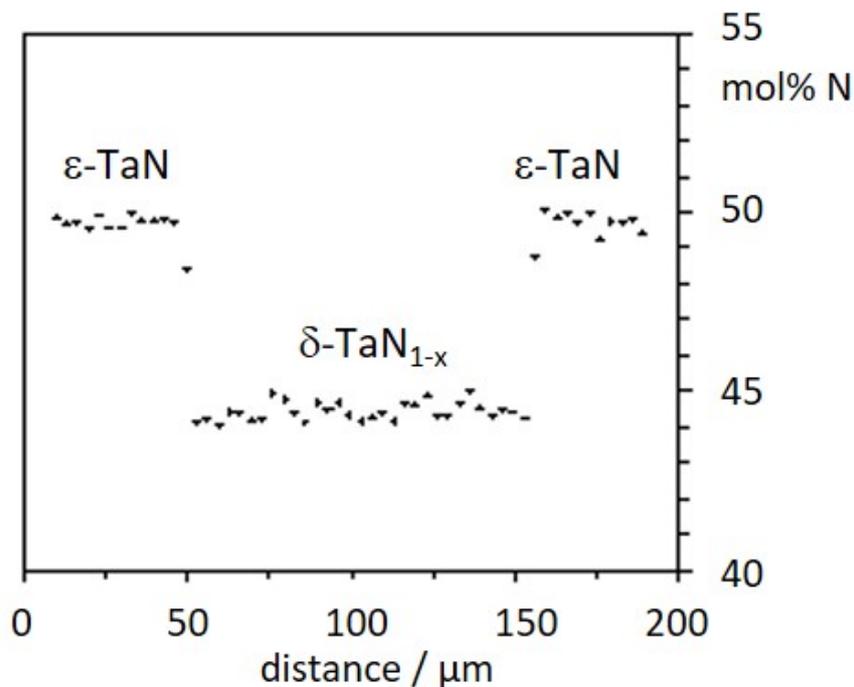


Figure 17. EPMA line scan across the tip of the wedge type diffusion couple indicated by the broken line at the bottom of Fig. 16. The line-compound character of ϵ -TaN was proved at a composition of 50mol% N [3,24]

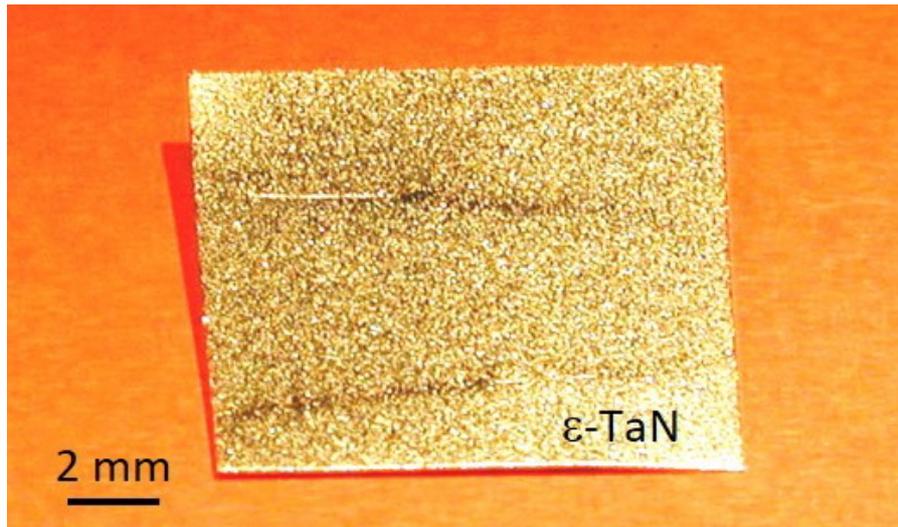


Figure 18. ϵ -TaN reference samples prepared by nitridation of metal sheets under the condition given in Tab.3, compare Fig 16 and 17

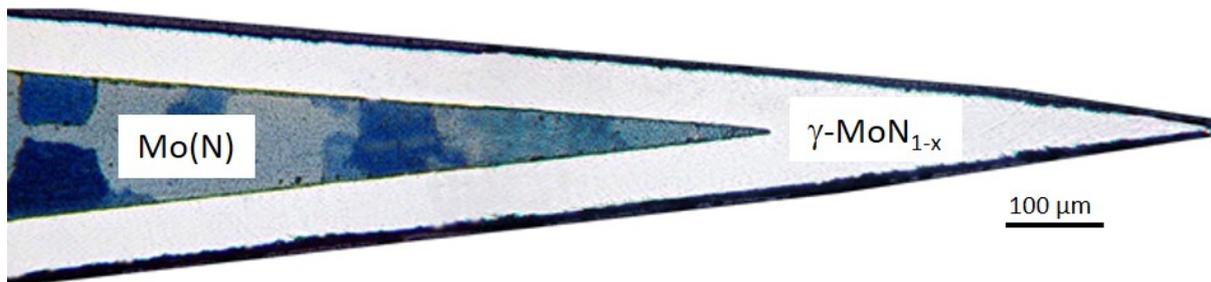


Figure 19. Wedge-type diffusion couple of the Mo-N system, prepared by use of NH_3 . No Mo_2N phase can be observed. The figure gives the boundary conditions for the preparation of a γ - MoN_{1-x} reference material starting from a Mo sheet

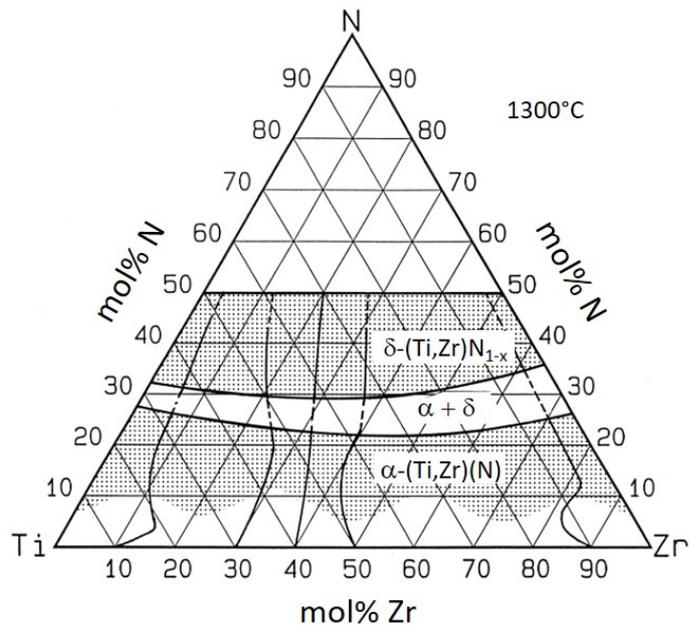
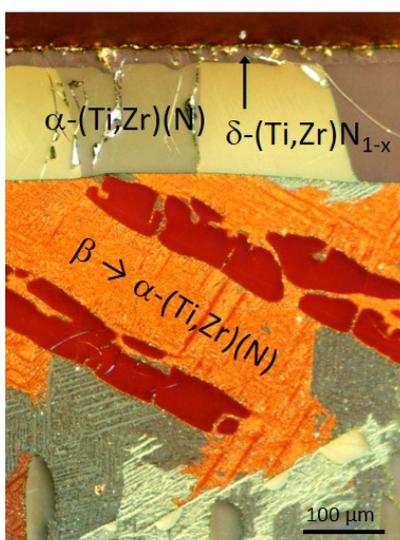


Figure 20. Left: partially nitrated Ti+Zr diffusion couple showing δ -(Ti,Zr) N_{1-x} on α -(Ti,Zr)(N) alloys (core: precipitated α -(Ti,Zr) N and transformed β -(Ti,Zr) N). Right: corresponding Ti-Zr-N phase diagram showing the diffusion paths of several Ti/Zr samples upon nitridation. Homogeneous δ -(Ti,Zr) N alloys can only be obtained from 60Ti40Zr alloys which show a linear diffusion path, see also Fig.21

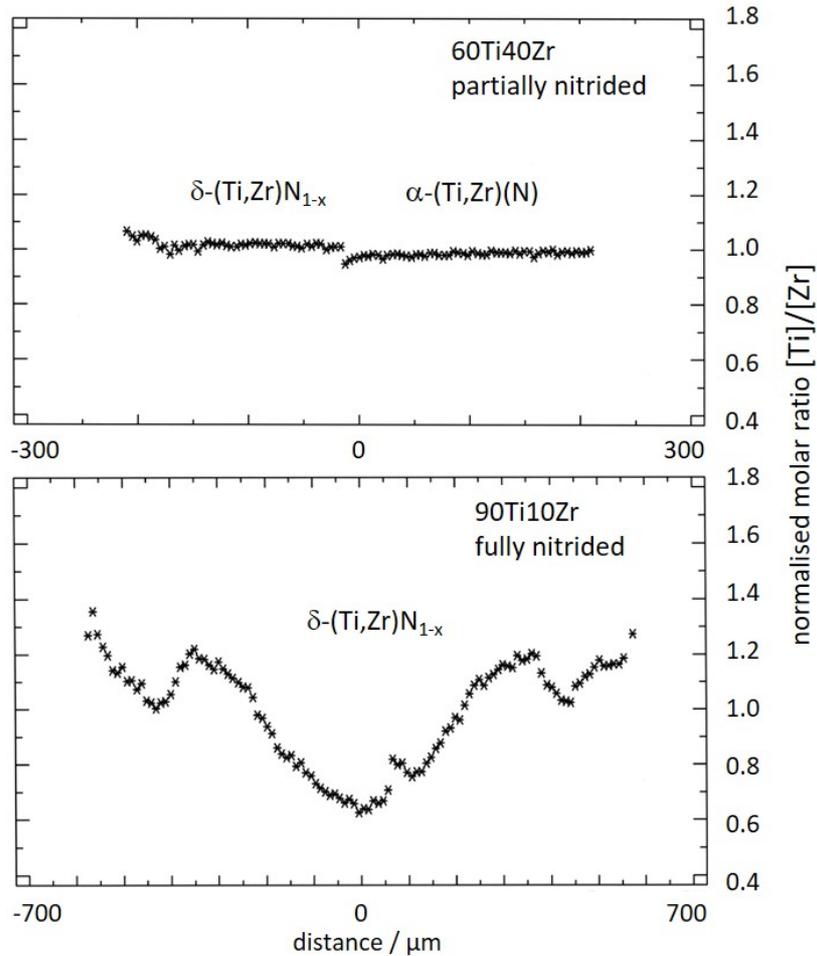


Figure 21. Top: EPMA line scans across a (Ti,Zr) sheet – N₂ diffusion couple. Only a sample with 60mol%Ti+40mol% Zr shows the same Ti and Zr content in both phases. Hence, upon full nitridation shows homogeneous Ti, Zr and N contents. If sample sheets with other than this Ti and Zr concentration is used, fully nitride samples with show an inhomogeneous Ti and Zr distribution (EPMA line scan at bottom). The Ti and Zr content was normalized to the starting composition for comparison

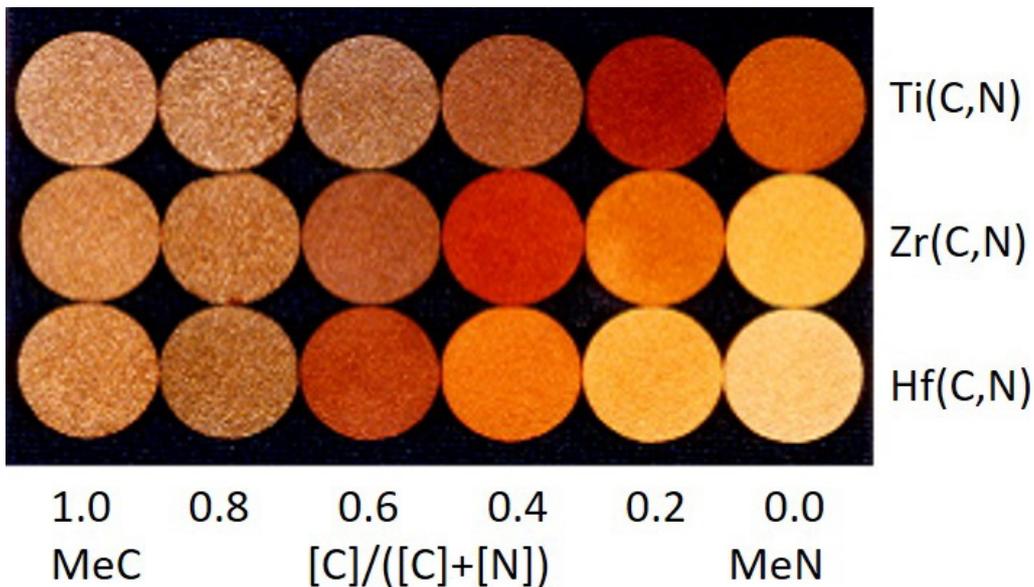


Figure 22. Group 4 transition metal carbonitrides (ground disks of 10mm diameter), carbides: left column, nitrides: right column, carbonitrides in between, prepared by hot-pressing

References

- [1] W. Lengauer, Carbides: Transition metal solid-state chemistry, in: Encyclopedia of Inorganic and Bioinorganic Chemistry, ed. R.A. Scott, John Wiley: Chichester. DOI: 10.1002/9781119951438.eibc0032.pub2 (2012).
- [2] W. Lengauer, Nitrides: Transition metal solid-state chemistry, in: Encyclopedia of Inorganic and Bioinorganic Chemistry, ed. R.A. Scott, John Wiley: Chichester. DOI: 10.1002/9781119951438.eibc0146.pub2 (2015).
- [3] H. Wiesenberger, W. Lengauer, P. Ettmayer, Reactive diffusion and phase equilibria in the V-C, Nb-C, Ta-C and Ta-N systems. *Acta Mater.*, 46(1998)651-66.
- [4] W. Mayr, W. Lengauer, P. Ettmayer, D. Rafaja, J. Bauer, M. Bohn, Phase equilibria and multiphase reaction diffusion in the Cr-C and Cr-N systems. *J. Phase Equilibria*, 20(1999)35-44.
- [5] W. Lengauer, The titanium-nitrogen system: A study of phase reactions in the subnitride region by means of diffusion couples. *Acta Metall. Mater.*, 39(1991)2985-2996.
- [6] W. Lengauer, D. Rafaja, G. Zehetner, P. Ettmayer, The hafnium-nitrogen system: Phase equilibria and nitrogen diffusivities obtained from diffusion couples. *Acta Mater.*, 44(1996)3331-3338.
- [7] C. Teichmann, W. Lengauer, P. Ettmayer, J. Bauer, M. Bohn, Reaction diffusion and phase equilibria in the V-N system. *Metallurg. Mater. Trans. A: Phys. Metallurgy Mater. Sci.*, 28A(1997)837-842.
- [8] W. Lengauer, M. Bohn, B. Wollein, K. Lisak, Phase reactions in the Nb-N system below 1400°C. *Acta Mater.*, 48(2000)2633-2638.
- [9] W. Kern, G. Brauer, Quantitative Stickstoffbestimmung bei Nitriden von Übergangsmetallen. *Talanta*, 11(1964)1177-1184.
- [10] W. Lengauer, On the application of the Dumas technique for the determination of nitrogen in refractory nitrides. *Talanta*, 38(1991)659-663.
- [11] R. Täubler, S. Binder, M. Groschner, W. Lengauer, P. Ettmayer P, Determination of nitrogen and carbon in refractory nitrides and carbonitrides by means of Dumas gas chromatography. *Mikrochim. Acta*, 107(1992)337-43.
- [12] A.N. Christensen, The crystal growth of the transition metal compounds TiC, TiN, and ZrN by a floating zone technique. *J. Cryst. Growth*, 33(1976)99-104.
- [13] D. Rafaja, W. Lengauer, H. Wiesenberger, Non-metal diffusion coefficients for the Ta-C and Ta-N systems. *Acta Mater.*, 46(1998)3477-3483.
- [14] D. Rafaja, W. Lengauer, H. Wiesenberger, M. Jøguet, Combined refinement of diffusion coefficients applied on the Nb-C and Nb-N systems. *Metallurg. Mater. Trans. A: Phys. Metallurgy Mater. Sci.*, 29A(1998)439-446.
- [15] W. Lengauer, J. Bauer, M. Bohn, H. Wiesenberger, P. Ettmayer, Electron probe microanalysis of light elements in multiphase diffusion couples. *Mikrochim. Acta*, 126(1997)279-288.
- [16] G.F. Bastin, H.J.M. Heijligers, Quantitative electron probe microanalysis of nitrogen. Eindhoven University of Technology (1988).
- [17] W. Lengauer, J. Bauer, A. Guillou, D. Ansel, J.-P. Bars, M. Bohn, E. Etchessahar, J. Debuigne, P. Ettmayer, WDS-EPMA nitrogen profile determination in titanium nitride/titanium diffusion couples using homotypic standard materials. *Mikrochim. Acta*, 107(1992)303-310.
- [18] W. Lengauer, D. Rafaja, R. Täubler, C. Kral, P. Ettmayer, Preparation of binary single-phase line compounds via diffusion couples: The subnitride phases η -Hf₃N_{2-x} and ζ -Hf₄N_{3-x}. *Acta Metall. Mater.*, 41(1993)3505-3514.
- [19] W. Lengauer, Multiphase reaction diffusion in transition metal-carbon and transition metal-nitrogen systems. *J. Alloys Compd.*, 229(1995)80-92.
- [20] D. Rafaja, W. Lengauer, P. Ettmayer, Multiphase layer growth kinetics in finite gas/solid diffusion couples. *Acta Mater.*, 44(1996)4835-4844.

- [21] M. Dopita, B. Wollein, D. Rafaja, W. Gruner, W. Lengauer, Layer-growth of tantalum nitrides by nitridation of Ta metal: the basis of the preparation of a well-characterised nitrogen standard material. Defect and Diffusion Forum, 194-199(2001)1613-1618.
- [22] W. Lengauer, P. Ettmayer, Physical and mechanical properties of cubic δ -VN_{1-x}. J. Less-Common Met., 109(1985)351-359.
- [23] M. Joguet, W. Lengauer, M. Bohn, J. Bauer, High-temperature reactive phase formation in the Nb-N system. J. Alloys Compd., 269(1998)233-237.
- [24] W. Gruner, B. Wollein, W. Lengauer, ϵ -TaN as a reference material for the determination of high nitrogen contents. Mikrochim. Acta, 146(2004)1-6.
- [25] N. Kieda, N. Mizutani, M. Kato, Non-stoichiometry and phase equilibria in beta-V₂N and delta-VN_{1-x}. J. Less-Common Met., 144(1984)293-299.
- [26] G. Brauer, W. Kern, Dissociation pressures and phase boundaries of niobium nitrides. Z. Allgem. Anorg. Chem., 507(1983)127-141 .
- [27] W. Lengauer, Formation of molybdenum nitrides by ammonia nitridation of MoCl₅ J. Cryst. Growth. 87(1988)295-98
- [28] V. Ucar, F. Chevire, F. Tessier, N. Krendelsberger, R. Marchand, W. Lengauer, Formation of molybdenum nitrides by ammonia nitridation of Mo powder and sheet. Defect and Diffusion Forum 194-199(2001)1607-1612.
- [29] F.J.J. van Loo, Multiphase diffusion in binary and ternary solid-state systems. Prog. Solid State Chem. 20(1990)47-99.