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DTA INVESTIGATION DURING HIGH GAS PRESSURE MOLYBDENUM NITRIDIZATION*

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Abstract

Differential thermal analysis shows many interesting properties that allow for prompt finding the place (*p,T*) and characteristics (endothermic, exothermic) of a phase transition or chemical reaction. In application to reactive sintering under active gas atmosphere at high pressure despite of numerous technical problems encountered during DTA measurements we found its unique possibilities. That allows for quantitative estimation of nitrogen involved in reaction of phase transition from the hexagonal phase to the cubic phase of MoN, and vice versa, in high gas pressure condition. DTA high gas pressure measurement system has the maximum operate temperature 2000°C at pressure 2 GPa.

Keywords: high pressure high temperature DTA and DPA, molybdenum nitride, phase diagram, phase transition

Introduction

The main incomparable advantages of the differential thermal analysis (DTA) are: easy to identify the phase transitions or chemical reaction according to pressure and temperature (*p,T*) co-ordinates and their character of the transition (exothermic or endothermic) In application to reactive annealing under high active gas pressure i.e. nitrogen, a lot of technical problems accompanying their realizations have to be solved. We found unique possibilities of applications of DTA and differential pressure analysis (DPA) [1, 2]. High pressure measurements allowed to quantity estimations of the nitrogen incorporated into the Mo and latter MoN sample during phase transition from cubic to hexagonal phase at high pressure high temperature conditions (HPHT).

Experimental

The way of carrying out DTA investigations under high pressure in general is the same as the typical low pressure measurement, except for kinetic conditions and the activity factor of substrates [3, 4].

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Below in Fig. 1 the sets for DTA and DPA under high gas pressure up to 2 GPa of nitrogen and at temperature up to 2000°C are presented.

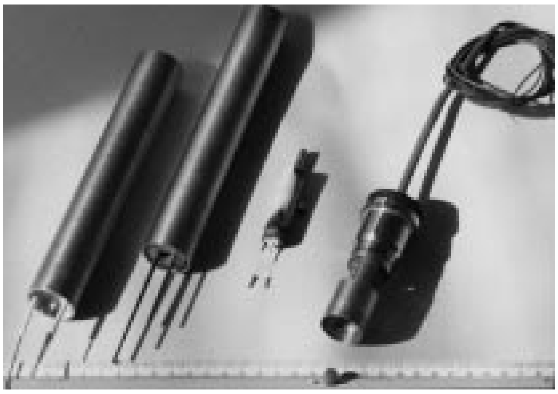

Fig. 1 The high pressure insert to the high pressure chamber for DTA analyses

On the left side in Fig. 1 two furnaces are seen, the left one made of the kanthal wire is destined for experiments performed at lower temperatures, on the right side the tungsten furnace for temperature up to 1850°C. On the side the measuring head made of the hexagonal BN with thermocouples and the high pressure plug with fit-through for electric signals are shown.

The characteristic feature of the system is the three zone furnace, enabling to retain the long and appropriate temperature plateau, and the cylindrical measuring head made of the hexagonal boron nitride. This material has excellent heat conductivity and very good chemical resistance, that ensures chemical immunity to the sample, here molybdenum and later molybdenum nitride. As the reference material, standard Al_2O_3 powder was used. In both vessels of the head the PtRh6/30% thermocouples were used. Additionally in the system three other PtRh6/30% thermocouples were used to control the furnace zones. Temperature was precisely controlled by Eurotherm regulators with the accuracy of the stability better than ±0.5°C from 600 up to 1850°C.

Because of the very low time constants of the system, it was possible to apply very steep characteristics of temperature rise and decrease, which increased the sensitivity of the differential temperature and pressure measurements significantly, and effected the precision of measurement of the phase transitions temperature.

The pressure variations in the closed chamber system were measured and recorded by means of the bridge method with using manganin coil, typically 78 Ohms, with the sensitivity better than 0.1 bar. The registration of all data was performed by a quick computerized system with Keithley 199 DMM/Scanner, allowing to record up to 30 measurements per second.

The especially characteristic measurement performed for the first time in such a high pressure in the phase relation investigations were coincidental measurements of the pressure change and its directions (evidently approved the concentration of the nitrogen change in the sample – direct quantitative measurement) accomplished by the temperature change in the system. It gave direct indications on the kinetic rate in the investigated system occurred during the high gas pressure annealing at especially high activity of the gas component (N_2 or O_2).

Results and discussions

The figures show the typical records of the phase transitions for molybdenum nitride at several pressures from 0.3 up to 1.8 GPa and temperature from 1000 up to 1720°C. The observations were performed in the conditions as follows:

- changes of the sample temperature *vs*. time
- change of the differential temperature of the sample and reference *vs*. time
- change of the differential temperature of the sample *vs*. reference temperature
- and change of the gas pressure in the closed chamber *vs*. time and reference temperature.

In Table 1 presented below the characteristic points of phase transitions and accomplished pressure change (dP) connected with the sample stoichiometry are shown.

Table 1 Characteristic points of phase transitions and accomplished pressure change

Transition from the ‘gamma’ to the ‘delta’ MoN phase Exothermic reaction				Transition from the ‘delta’ to the ‘gamma’ MoN_x phase Endothermic reaction			
P/bar	*T*/°C	N/Mo ratio	dP-pressure/bar	*P*/bar	*T*/°C	N/Mo ratio	dP-pressure/bar
3000	1105	72	190	3080	1115	72	160
5200	1200	73	120	5000	1210	73	100
9300	1360	75	50	9450	1350	74	40
10180	1440	78	110	10100	1430	77	90
10200	1450	79	120	10200	1440	78	100
13000	1540	83	100	13500	1536	82	80
13600	1570	86	100	13530	1600	85	70
16000	1680	92	80	16500	1690	91	60
18000	1710	94	70	18200	1720	93	50
9400 $\gamma\to\delta$	1350	76	30	9400	1350	76	20
9100 $\delta\to\beta+\gamma$	980	–	40	9200	1160	–	90

The typical run of the reference temperature stabilized by Eurotherm is shown in Fig. 2, the real time is scaled in seconds. The y-axis shows the reference temperature on Al_2O_3 – the temperature run ideally follows the temperature program of Eurotherm.

The points indicated in Fig. 3 represent the symmetric jumps of pressure caused by the phase transformations in the molybdenum nitride. In this case we observe the secondary run of nitridization, the first one is presented in the end of this chapter.

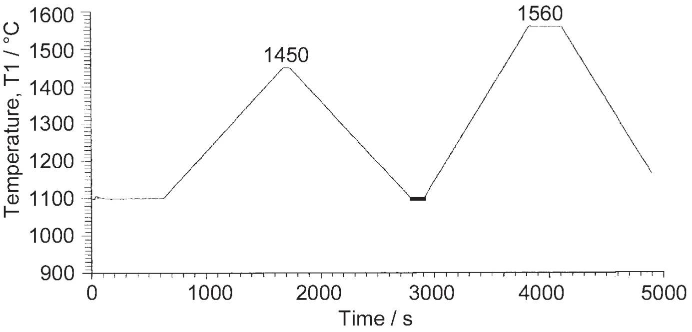

Fig. 2 The curve of the reference temperature measured inside the Al_2O_3 powder

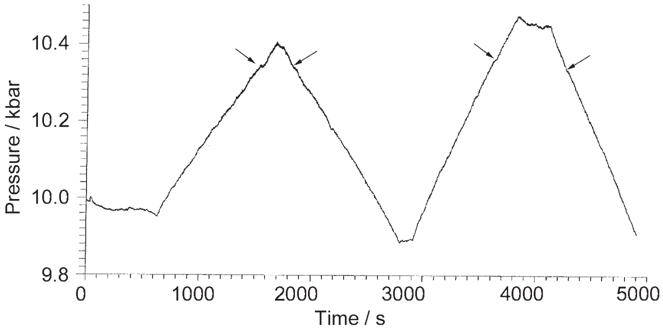

Fig. 3 Compared to Fig. 2 curve of the pressure variations in the closed system with the MoN sample examined by DTA method

The characteristic run of phase transition from δ to γ phase as a function of reference temperature (Al_2O_3) taking place at 1.35 GPa of nitrogen can be seen in Fig. 4. The endothermic transition firstly caused the decrease of the pressure followed by the desorption of nitrogen during δ to γ phase transition. Therefore, the final increase +dP in the gas system is seen in the figure.

In Fig. 5 an exothermic run of DPA measurement in which the effect of the pressure rise (+dP) caused by the temperature increase in the sample region is clearly seen and then followed by the general decrease of pressure in the system caused by the phase transformations from cubic non stoichiometric phase to the hexagonal stoichiometric one is shown. The final (–dP) is indicated by the arrow marker.

The variation of the pressure here observed consists of two components: the first one effected by the gas nitrogen absorption or emission from the sample during the phase transitions, the second one caused by the exothermic or endothermic reaction and the heat change prompting the pressure rise or decrease.

For the presented results of molybdenum nitride phase transition from phase γ to δ and reversely, we observe – in the case of δ to γ phase transition – an endothermic effect which is characteristic of a very rapid lowering pressure in the beginning

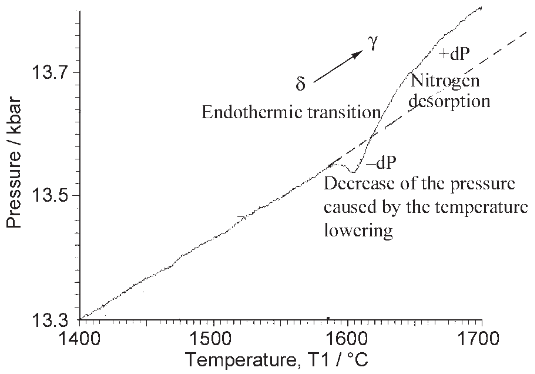

Fig. 4 The characteristic run of endothermic phase transition from δ to γ phase observed at nitrogen pressure 1.355 GPa and temperature 1600°C

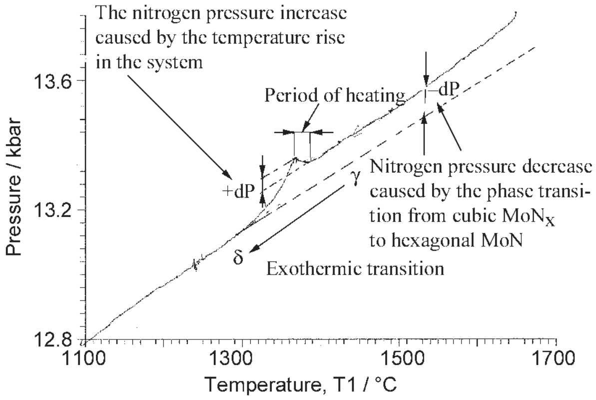

Fig. 5 An exothermic run of DPA measurement in which the effect of the pressure rise (+dP) caused by the temperature increase in the sample region is evidently seen

caused by decreasing the temperature in the sample region with following desorption of nitrogen resulting in an increase of the total pressure in the high pressure system.

How big is this effect we can observe in Fig. 4 which is directly taken from the registration system. We can see the character and kinetic of phase transition running under high gas pressure. Total free volume of the high gas system is 300 to 350 ccm and typical sample mass is 8 to 15 g.

The pressure fall in Fig. 4 is caused by an endothermic reaction and the final increase of the pressure in the system by 7–8 MPa is caused by the phase transition from the stoichiometric phase δ to the nonstoichiometry γ phase.

In Fig. 5 DPA results obtained at high pressure made in the function of reference temperature are shown. While the exothermic reaction occurs during the system cooling ramp, the rapid peak of the sample temperature, accompanied with the pressure rise is observed. Then it is followed by a final pressure decrease by magnitude of several Mpa, caused by the absorption of the nitrogen from the closed place of the high pressure system. These phenomena are accomplished by the phase transition from the understoichiometric γ cubic phase to the δ hexagonal stoichiometric one.

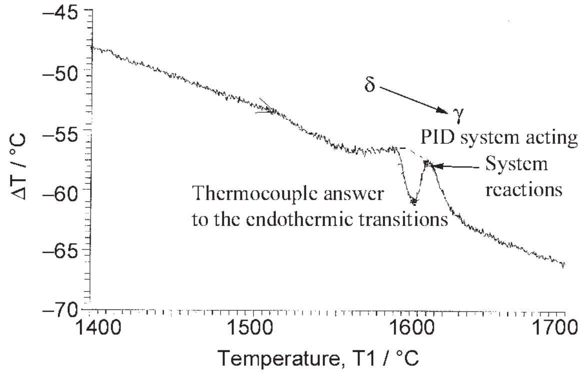

Fig. 6 The relations between T_2–T_1 in the function of the reference temperature T_1 for the phase transition at 1600°C (1873 K) and pressure 1.35 GPa

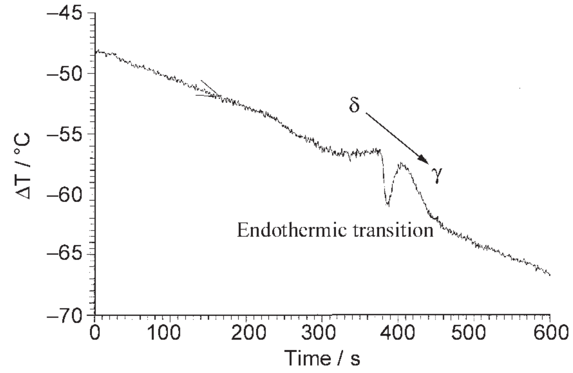

Fig. 7 DTA of the phase transition δ to the γ-MoN_x with nitrogen desorption and PID heating furnace system answer in the function of time

In Figs 6 and 7 we can see the characteristic DTA curve accompanying such endothermic reactions in the Mo–N system. The same effect as in Fig. 6 is presented in Fig. 7 but as a function of time. This presentation gives an explanation for the time aspects and kinetic relations in the high pressure high temperature system. In Fig. 7 it is seen that total time of transformation in the presented (*p, T*) conditions, from the hexagonal δ phase to the cubic γ, encloses in 80 to 100 s, when the time constant of our furnaces is about 20 to 30 s.

In Fig. 8 both endo- and exothermic phase transitions made by DPA analysis for two slightly different pressures are plastically presented as a function of reference temperature. *p, T* conditions of transitions are pointed.

The temperature of the phase transitions from δ to γ phase for the molybdenum nitride and reversible directions from γ to the δ phase take place in the same range of

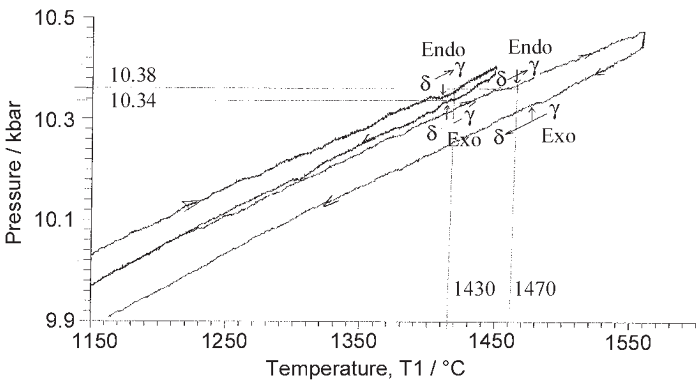

Fig. 8 The dependence of the pressure at high pressure system as a function of temperature shown at low magnifications

±10°C, which demonstrated negligible hysteresis of the transition and equilibrium nitrogen content conditions around the sample, i.e. sufficient nitrogen to complete such rapid reactions. As it is seen from this direct curve of DPA a very little pressure shift caused a considerable shift of the temperature of transition in Mo–N system observed by DTA. It resembled to the high inclination of the isobars on the phase diagram of Mo–N, proposed for this region of p,T conditions [5, 6, 7].

The low magnifications enables to observe at the same draw two phases transitions effected in reverse directions for very close high pressures of nitrogen in the system [6].

Conclusions

High pressure differential thermal analyses (HP-DTA) is an important component of the *in situ* phase transformation detection of the new phases obtained only under high pressure.

For the new materials – mainly oxides and nitrides (in which one component is a gas) – a very effective high pressure differential pressure analysis (HP-DPA) gives additionally the possibility for precise quantity analysis during the phase transition under various experimental pressure conditions.

New phase diagrams can easily be established by using both DTA and DPA measurements under high pressure.

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