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DIFFERENTIAL BAROTHERMAL ANALYSIS (DBA) OF Ni-BASE ALLOYS

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Abstract

The technique of differential barothermal analysis (DBA) combines the hot isostatic pressing technique and classical differential thermal analysis has been elaborated. This technique allows the study of the phase equilibria in the most of inorganic systems under pressure up to 200 MPa and temperatures up to 2000°C. The Ni-base alloy with the solidus, liquidus, γ'-phase and carbides dissolution temperatures of 1328, 1390, 1272 and 1255°C, accordingly, was chosen as a model material. By DBA technique the pressure coefficients of the above mentioned temperatures were established. The values of the obtained coefficients are 3–5 times larger than the melting point pressure coefficient for the pure Ni (the alloy base metal). The discussion of the data obtained is carried out.

Keywords: DTA, liquidus, Ni-base alloy, phase equilibria, pressure, solidus

Introduction

The study of the phase equilibria under high pressures and temperatures has been the subject of attention since the equipment permitting the application of external pressure on the objects under increased temperatures appeared both in laboratories and in industry. Since Dewar pioneer work [1] on ice melting point pressure dependence, investigations in this field have developed rapidly, and soon Parsons [2] published the data on carbon behavior under high pressures and temperatures. Further, phase equilibria studies were carried out by Tamman, Lussana, the Geophysics Laboratory in North America United States, and many others. For the purpose of the phase equlibria study under high pressures and temperatures the volumetric, conductivity and thermometric techniques were used. Bridgman [3, 4] did the prominent contribution to the high-pressure technique. He also studied P-V-T dependence for series of liquids and gases, solids press ability, melting phenomena under pressure, polymorph transitions in the series substances, series metals conductivity pressure dependencies and so on.

By the end of the last century a lot of experimental data on the phase equilibria under high pressures and temperatures were saved up. Most of them are cited in [5]. It

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should be noted, that all of these data are concerning with the individual substances and chemical compounds. The phase diagrams were built, and in many cases the high-pressure phases were identified with the crystal structure establishing. Such an approach is common for work in the field of high-pressure phase equilibria investigations. At the same time, if full phase diagrams at 0.1 MPa are applied, where much more phases exist including eutectics, solid solutions and others, it should be noted that experimental data in this field are quite limited.

For the goal of the high-pressure phase equilibria study, the series techniques are used, particularly tempering, X-ray methods, conductivity pressure dependence study, etc. In a number of such techniques the differential thermal analysis is widely used, with assistance of which not less than 20% of all the data on the high-pressure phase transformations were obtained.

It should be marked, that the accent appointed above to the hand of elements and chemical compounds narrows the common picture of the phenomena taking place under high pressure. Apparently, it is necessary to pay attention to the other parts of the high-pressure phase diagrams. One more thermodynamic parameter appearance, namely pressure, and establishing its effect on the phase transformations in all range of the components concentrations, it seems, it should be an object of the barothermal analysis (DBA) technique. To illustrate the suggested approach it should be noted, that practically all diversity of metal materials used now in practice are the multicomponent systems, and under its formation either static, or dynamic barothermal influence is used. In connection with the latter ones, the problems of the phase component formation in the multicomponent materials are topical.

At present the complex multicomponent Ni-base alloys occupies a leading place in manufacturing and intensity of their study. This circumstance determines by the applied value of Ni-base alloys, which are the bases producing the main parts of gas turbines. Contemporary Ni base alloys contain up to 12–15 main impurities, which are applied to improve corrosion resistance and mechanical properties under high temperatures.

Heatproof Ni-base alloys relate to the disperse-solidified metal materials [6]. In such alloys durability improving reaches mainly by the γ'-phase particles, based on Ni_3Al intermetallic compound. These particles form as a result of the spinodal disintegration of the γ-solid solution of Ni during alloy cooling. γ- and γ'-phases are isomorphic with the volume facet-centered lattice. Difference between them shows that γ-phase is the disordered solid solution of substitution, but γ'-phase is the ordered phase. Difference in the defect concentrations leads to the slight difference of the lattice parameters. Ni-base alloys contain the γ'-phase within 25–70 vol.%. For the purpose of alloy duration, doping with carbon and boron occurs leading to 1.5–2 vol.% of carbides and borides formation.

Thus, heatproof Ni-base alloy contains the complex-doped nickel solid solution, the γ'-phase particles, the metal-C carbides MC and, for some alloys, the metal-B borides MB [6]. As for the complexity of the content of Ni-base alloys, it is impossible to build the phase diagram taking into account all alloy components. For many applications, however, it is sufficient to know the solidus and liquidus temperatures, the

γ'-phase dissolution temperature, and the metal carbides formation temperature (T_S, T_L, $T_{\gamma'}$ and T_{MC}, accordingly). Knowledge of these temperature points permits at further thermal processing to achieve the optimum size and morphology of the γ'-phase and carbides particles. It should be noted the temperatures for all Ni-base alloys are known only at atmospheric pressure.

At present, for Ni-base alloys cast quality improving, particularly to heal the pores of various natures, the barothermal influence is widely used. In the last case the alloy is subjected to simultaneous high pressure and high temperature influence. This technique is known as the Hot Isostatic Pressing (HIP) [7, 8] that uses the compressed inert gas as a media that transfers the hydrostatic pressure in the range up to 200 MPa. The range of the pressures in the HIP technique is significantly lower (up to 10 times) than in the other methods allowing to reach pressures up to 10 GPa. The advantage, however, in the HIP, is the possibility to obtain sufficiently high pressures in large volumes, which is necessary for the wide application of the technique.

Thus, based on literature data, the goal of this study is elaborating the barothermal analysis method. The technique combines the achievements of the hot isostatic pressure and classical differential thermal analysis with further studies of special temperature points of Ni-base alloy (namely the solidus, liquidus, γ'-phase dissolution and the carbides formation temperatures) behavior as a function of external pressure.

Experimental

To elaborate the DBA technique one can use the hot isostatic press of ‘ABRA’ firm. In this plant (Fig. 1) there is the high-pressure vessel diameter of 400 mm and height of 1300 mm. In this volume the graphite resistance heater system (consisting of the wall and bottom heaters) is placed, which allows to reach the temperature up to 2000°C in the volume with the diameter of 250 mm and height of 750 mm. The wall and bottom heaters (each of them) provide with the WRe5-WRe26 thermocouples, which serve as sensors for the ‘Eurotherm’ electronic blocks of linear changing (heating or cooling) and keeping of the temperature. The starting argon pressure in the high-pressure vessel can be reached with the ‘Hydro-Pac’ compressor, and then the temperature scanning program can be launched. During heating the pressure was increased (Fig. 2) in according with the equation

$$PV=nRT \tag{1}$$

where P – pressure, V – volume, n – quantity of moles, R – Boltzmann’s constant, and T – temperature. The start pressure enabled to reach the pressure in the system up to 150–180 MPa at 1300–1400°C.

The measurement cell was presented by the molybdenum block of 50 mm height and a diameter of 50 mm, with the channel diameter of 20 mm for the WRe thermocouples and the samples placing. Differential and control signals went to PC where they were registered. The signal from differential thermocouple was measured with the sensitivity of $\pm 1\cdot 10^{-6}$ V, and frequency of the counts was 1 s^{-1}.

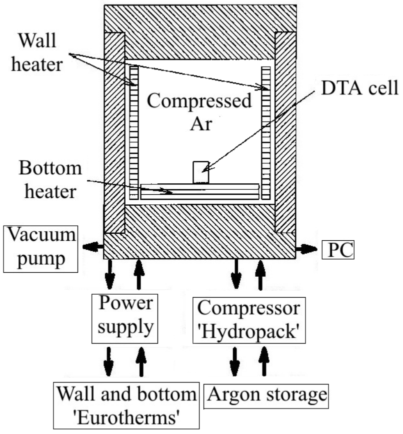

Fig. 1 DBA technique block scheme

To calibrate the control thermocouple, melting of Cu and Ni was carried out in the cell at 150 MPa. The obtained temperatures, T_m^{Cu} and T_m^{Ni} had the values of 1089±1 and 1462±2°C, accordingly. These data are in a good agreement with the literature ones [9, 10], which were obtained while studying the melting curves under pressure up to 2 GPa. The pressure coefficients of the melting points, dT_m/dP=(3.3; 4.0)°C/100 MPa for Cu and Ni, consequently, were established.

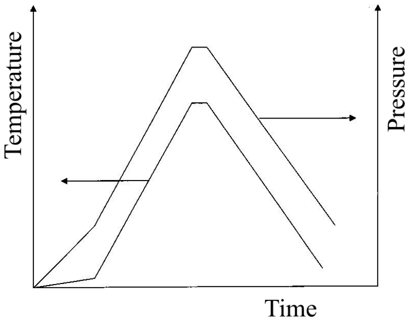

Fig. 2 Barothermal scanning cycle schematic view

The samples to study were cut from a known Ni-base alloy with the special temperatures at 0.1 MPa with the values as follows: 1272°C – the temperature of entire dissolution of γ′-phase $T_{\gamma'}$; 1328°C – the temperature of solidus T_S; 1355°C – the temperature of carbides dissolution T_{MC}; 1390°C – the temperature of liquidus T_L. The samples had a cylindrical shape with the diameter of 2 and height of (2–12) mm. As reference the molybdenum samples were used.

Results

DBA experiments can be carried out with masses of the samples of 400 mg (experiment 1), 1000 mg (experiment 2) and 1800 mg (experiment 3). In experiment 1 the heating rate was of 3°C min^{-1}, and the cooling rate was of 5°C min^{-1}. There were no thermal effects on the differential curve at heating. In the curve of cooling the exothermic peak was noted with the sharp maximum at the beginning of the transformation (at 1376°C) and the eroded end of transformation at 1306°C. The slope of the curve changed at 1348 and 1317°C.

In the second experiment the nickel alloy sample mass was increased to 1000 mg, and the cooling/heating rates were 10°C min^{-1} with the maximum scanning temperature of 1600°C and dwell time of 5 min. In the heating curve a clear complex endothermic peak can be observed and in according with it one can determine T_S=1345°C, T_L=1420°C, T_{MC}=1379°C, $T_{\gamma'}$=1315°C. At cooling, from the curve of the complex exothermic peak, the special temperatures were found, as follows: T_S=1320°C, T_L=1383°C, T_{MC}=1352°C, $T_{\gamma'}$=1313°C. Argon pressure in the region of the endothermic and exothermic peaks during first and second experiments was within 180±5 MPa.

In the third experiment the sample mass was of 1800 mg, and the heating/cooling rates were of 10°C min^{-1}. To increase the sensitivity of the experiment, a nickel alloy sample was placed immediately on the thermocouple, protected by ceramics. In this case it was possible to registrate the thermal effects, concerning the γ′-phase and carbides transformations, and the temperature of solidus. To determine the effect reproducibility, the measurement was carried out at ternary cycle of heating/cooling (Fig. 3). The first heating of the sample from room temperature up to 1400°C was carried out at the heating rate of 10°C min^{-1}. When the sample reached the temperature of 1400°C, there was the dwell time of 5 min, and further cooling was carried out at the rate of 10°C min^{-1}.

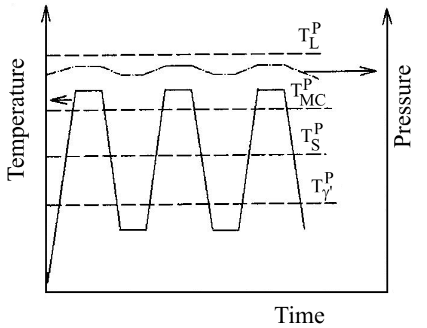

Fig. 3 Schematic view of the triple barothermal scanning

During the triple heating/cooling, as data on full melting experiments, the temperature did not exceed the temperature of liquidus under external argon pressure of 150 MPa. In the range of solidification, the alloy was in the plastic state, and deformed under gravity force. The shape change was observed visually at the end of the measurement cycle when the sample was removed from the cell. The reached magnitudes of the endothermic and exothermic peaks under these conditions were (25–30)·10^{-6} V. The common view of the peaks was reproducible well, with slight deviations of the special temperature points. The DBA data are collected in Tables 1 and 2.

Table 1 Differential barothermal analysis data on Ni-base alloy

Special temperatures	DTA data, P=0.1 MPa		DBA data at P_{2Ar}				DBA data at P_{1Ar}					
	T/°C		Exp. 1		Exp. 2		Exp. 3.1		Exp. 3.2		Exp. 3.3	
			T/°C									
	$V\uparrow$	$V\downarrow$	$V_1\uparrow$	$V_3\downarrow$	$V_2\uparrow$	$V_4\downarrow$	$V_2\uparrow$	$V_4\downarrow$	$V_2\uparrow$	$V_4\downarrow$	$V_2\uparrow$	$V_4\downarrow$
T_S	1328	–	–	1317	1345	1320	1347	1318	1347	1318	1343	1320
T_L	1390	1370	–	1376	1420	1383	–	–	–	–	–	–
$T_{\gamma'}$	1272	1272	–	1306	1315	1313	1313	1294	1310	1294	1297	1297
T_{MC}	1355	1355	–	1348	1379	1352	1353	1355	–	1353	1355	1357

P – pressure, $T_{\gamma'}$– phase entire dissolution temperature; T_S – temperature of solidus; T_L – temperature of liquidus; T_{MC} – temperature of carbides dissolution; $V\uparrow$ – heating; $V\downarrow$ – cooling; $V_1\uparrow$ – heating rate of 3°C min^{-1}; $V_2\uparrow$ – heating rate of 10°C min^{-1}; $V_3\downarrow$ – cooling rate of 5°C min^{-1}; $V_4\downarrow$ – cooling rate of 10°C min^{-1}; P_{1Ar} – argon pressure in the high pressure vessel of 180 MPa; P_{2Ar} – argon pressure in the high pressure vessel of 150 MPa

Table 2 Generalizing of the differential barothermal analysis data

Special temperature	Average data for 3.1–3.3 T/°C		$\mathrm{d}T_{1i}/\mathrm{d}P$/ °C(100 MPa)$^{-1}$		$\mathrm{d}T_{2i}/\mathrm{d}P$/ °C(100MPa)$^{-1}$	
	V↑	V↓	V↑	V↓	V↑	V↓
T_S	1346	1319	12	–6	9	–5
T_L	–	–	–	–	17	–12
$T_{\gamma'}$	1307	1295	23	15	28	27
T_{MC}	1355	1355	0	0	23	–3

$T_{\gamma'}$ – phase entire dissolution temperature; T_S – temperature of solidus; T_L – temperature of liquidus; T_{MC} – temperature of carbides dissolution; V↑ – heating; V↓ – cooling; $\mathrm{d}T_{1i}/\mathrm{d}P$ – pressure coefficients of the special temperatures per 100 MPa (i – S, L, MC, γ') to the samples heating to temperatures below the temperature of liquidus; $\mathrm{d}T_{2i}/\mathrm{d}P$ – pressure coefficients of the special temperatures per 100 MPa (i – S, L, MC, γ′) to samples heating to temperatures above the temperature of liquidus

Discussion

According to the DBA data (Tables 1, 2) the external argon pressure in the range of 150–180 MPa significantly rises the liquidus, solidus and γ′-phase dissolution temperatures. The temperature of carbides transformation stayed practically constant. To explain the observed phenomena, the existing models should be considered. For instance, from Klapeyron model, the phase transformation temperature modification in the single-component system depends on applied pressure taking place at the solid-liquid transformation, as a result of the difference of solid and liquid phases mole volumes. This describes the equation:

$$\frac{\mathrm{d}T}{\mathrm{d}P}=\frac{T_m\Delta V}{\Delta H} \qquad (2)$$

where T – temperature, P – pressure, T_M – melting point, ΔV – volumes difference, ΔH – latent heat of melting.

Let us consider the phase transformation temperatures modify under applied pressure. The main nickel alloy component is Ni, which has ΔV=0.45 cm^3 mol^{-1} [11], and the pressure coefficient of the melting temperature $\mathrm{d}T_m/\mathrm{d}P$=3.3 K/100 MPa [10] at latent heat of melting of 17.5 kJ mol^{-1} (at 0.1 MPa). For the alloy investigated the data on the latent heat are absent, but it is possible to suppose, that adding several additives in quantities usual for Ni-base alloys to the alloy studied should not significantly modify the values of the latent heat. Namely, the temperature of liquidus of the alloy is lower by 4.3% to compare with the pure Ni. This circumstance cannot significantly modify the pressure coefficient. At the same time, the pressure coefficient $\mathrm{d}T_L/\mathrm{d}P$=17 K/100 MPa observed in this study is five times over the value of the pure Ni. The value of solidus pressure coefficient is also significant, in average $\mathrm{d}T_S/\mathrm{d}P$=10 K/100 MPa, which is three times larger than the similar value for Ni.

If we suppose, that the main factor, which increases the solidus and liquidus temperature pressure coefficients of the alloy, is the mole volume difference appearing at external argon pressure of order of 150–180 MPa, the simple calculation shows, that mole volume difference under used pressure should be ΔV=1.35–2.25 cm^3 mol^{-1}. But, if we analyze these values, it follows, that at Ni mole volume, equal to 7.14 cm^3 mol^{-1}, estimation of ΔV=1.35–2.25 cm^3 mol^{-1} should lead to mole volume change by 18–30%, which, from the point of view of reason, is difficult to imagine. It seems Klapeyron's equation for the description of the phase transformations in the complex systems is invalid. Obtained for single-component systems, where the melting process occurs in a narrow temperature interval, as a result of far order disappearance, the Eq. (2) needs modification. In the last case the diffusion phenomena, the mutual components solubility, and the pressure dependencies of the processes should be taken into account.

The largest pressure coefficient was established for γ'-phase dissolution temperature. This phase transformation occurs in the solid state, and is determined mainly by the diffusion phenomena. It is evident, that in the compressed, plastic deformed body at high temperatures and pressures all diffusion mechanisms including grain boundary diffusion should modify the decreasing of mass transfer by diffusion, and process of the γ'-phase dissolution needs higher temperature.

The carbide dissolution temperature stays practically unchanged, and accords to the data at atmospheric pressure. The mechanism of this phenomenon has been established on the data of optical microscopy. In all the alloy samples, heated over the temperature of solidus, the pore presence is marked (Fig. 4). It is easy to understand the cause of its appearance if we take into account that at high pressures the gas diffusion coefficients and gas solubility in liquids sharply increase compared to the diffusion in solids. Argon at pressures of 150–180 MPa diffuses easily into melt (or into alloy at $T_S<T<T_L$) with no chemical interactions, and forms gas pores. These pores locate around the carbide particles, and their dissolution occurs in two stages. In the first one the atoms of the alloy components vaporize from the interface gas-liquid into gas pore, with the carbide particle within. In the second stage the diffusion from vapor phase into carbide takes place. Under cooling, the reverse process occurs.

In the case when the enrichment of the sample by argon is not so intensive, as in the second experiment, carbide dissolution occurs and this leads to the increase of carbide temperature dissolution.

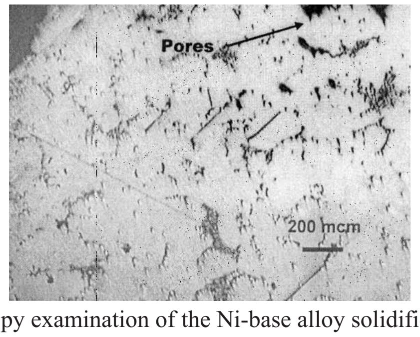

Fig. 4 Optic microscopy examination of the Ni-base alloy solidified at 150–180 MPa (the dark regions are the pores)

Conclusions

Thus technique of the phase equilibria under high pressure study has been elaborated. The technique combines the method of barothermal influence by using the hot isostatic press plant, and the classical technique of differential thermal analysis. Wide range of pressures (up to 200 MPa) and temperatures (up to 2000°C), heating/cooling rates of 15°C min^{-1} enabled to use this method for the phase equlibria study in the most known inorganic systems. It is possible to classify the elaborated technique as differential barothermal analysis.

The effect of hydrostatic pressure up to 180 MPa on the liquidus, solidus, dissolution of the γ'-phase and carbides temperatures have been studied. It was established that the γ'-phase dissolution, liquidus and solidus temperatures rise with the increase of the pressure. The pressure coefficients dT_i/dP are significantly higher than the Ni melting temperature arising under applied external pressure. The mechanism of the carbide transformation with the argon solubility participation needs a more detailed study.

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