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Thermodynamic calculations for knowing local very high temperatures in service in refractory nickel alloys

Patrice Berthod

Laboratoire de Chimie du Solide Minéral (UMR 7555), Faculté des Sciences et Techniques,
UHP Nancy 1, Nancy-Université, B.P. 239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)
E-mail : patrice.berthod@lcsm.uhp-nancy.fr

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ABSTRACT

Three alloys based on Ni-30wt.%Cr and containing carbides were cast and heated for several hours at targeted temperatures chosen between 1250^{0}C and 1340^{0}C. Fractions of carbides or molten areas were measured by image analysis. Comparison between measured carbides fractions and results of thermodynamic calculations were consistent for 1250 and 1300^{0}C. For the highest targeted temperatures mismatches were noticed. Thermodynamic calculations performed to reach measured values of carbide fraction allowed an accurate determination of the real temperature. Comparison between metallography and calculations were never so good concerning molten areas. Thermodynamic calculations are able for determining real temperatures for mushy states but several conditions need to be respected.

KEYWORDS

High temperature;
Refractory alloys;
Carbides;
Molten zones;
Thermodynamic calculations;
Metallography.

INTRODUCTION

Transport or industrial applications involving very high temperatures can sometimes lead to local hot spots. Temperatures as high as 1250^{0}C or more can be locally obtained in some places which cannot be accessible for a direct measurement of temperature. Fortunately, if the time of exposure to heat is long enough, materials can be very close to their thermodynamic equilibrium and, if cooling is fast enough, the characterization of their microstructure and following thermodynamic calculations, may give some indications about the level of temperature which was locally known by the piece.

The aim of this work is to study this possibility by performing high temperature exposures in furnace on some alloys, and by examining if the microstructure changes really allow deducing the levels of temperature. These alloys were simple ternary nickel-based cast alloys containing chromium carbides, which are composed of phases which can be easily distinguished from one another and quantified in terms of surface fractions.

EXPERIMENTAL

Synthesis of the alloys and exposures to high temperatures

The three studied alloys are all based on nickel (almost 70 wt.%), as many superalloys destined to high temperature applications[1]. They contain 30 ±1 wt.% of chromium, to achieve sufficient resistance against hot corrosion[2], 0.2, 0.4 or 0.8 wt.% of carbon to obtain carbides which are among the possible particles used for improving creep-resistance[3]. They can be considered as simple versions of real industrial carbides-strengthened nickel-based superalloys.

These alloys were synthesized by foundry, using a high frequency induction furnace (CELES), in an inert atmosphere of 300mbar Ar. Pure elements, nickel and chromium (Alfa Aesar, purity of more than 99%) and carbon (graphite), were melted together and thereafter solidified in a copper crucible cooled by water circulation. The three obtained ingots were cut in order to obtain four almost cubic samples of about $0.25 cm^3$ for each alloy. They were exposed to air at high temperature in a tubular furnace (Carbolite), with the following operating conditions:

- 15 hours at 1250^{0}C (targeted temperature), then water quenching, or
- 15 hours at 1300^{0}C (targeted temperature), then water quenching, or
- 5 hours at 1320^{0}C (targeted temperature), then water quenching, or
- 5 hours at 1340^{0}C (targeted temperature), then water quenching.

Microstructure characterization and thermo dynamic calculations

Thereafter the twelve heat-treated samples were all cut into two equal parts, embedded in cold resin, ground with SiC paper from 250 to 1200 grit, and polished with 1μm alumina particles in order to obtain a mirror-like surface state. The general microstructures of the mounted samples were examined using a Scanning Electron Microscope (SEM, Philips XL30). Five micrographs were taken per sample in Back Scattered Electrons mode (BSE), at several magnifications (×125 to ×500) depending on the microstructure coarseness obtained. Micrographs were analyzed using Adobe Photoshop in order to determine the surface fractions of the different phases seen in microstructure, by image analysis. Some Wavelength Dispersion Spectrometry (WDS) measurements were performed using a Cameca SX100 microprobe to determine the chemical compositions in some areas in microstructure.

The Thermo-Calc software[4], working with a database containing the descriptions of the Ni-Cr-C system and of its sub-systems[5-8] was used in order to compare real microstructures to the calculated ones. When mismatches were noted Thermo-Calc was used again in order to deduce the temperatures to which the observed microstructures correspond.

RESULTS AND DISCUSSION

Evolution of the alloys with temperature predicted by thermodynamic calculations

The theoretical metallurgical state of the alloys at all the four high temperatures is qualitatively given in figure 1 by the section at 30 wt.%Cr of the ternary Ni-Cr-C phase diagram computed with Thermo-Calc. At 1250 and 1300^{0}C the three alloys are still wholly solid, with a microstructure composed of a FCC Ni-based matrix and chromium carbides of the M_7C_3 type. At the highest temperature (1340^{0}C) all alloys are partially molten, while at the fourth temperature, 1320^{0}C, all alloys are very close to the eutectic valley.

The calculated microstructures at stable state are more precisely described in figure 2, with one graph per alloy, in which several curves show the evolutions of the mass fractions of the three phases which can exist depending on temperature: the FCC Ni matrix (containing some Cr and C in solid solution), the M_7C_3 carbide and the liquid. During heating from 1250^{0}C, the mass fraction of carbide slowly decreases until entering in the neighbourhood of the solidus temperature when it rapidly decreases to become zero just before

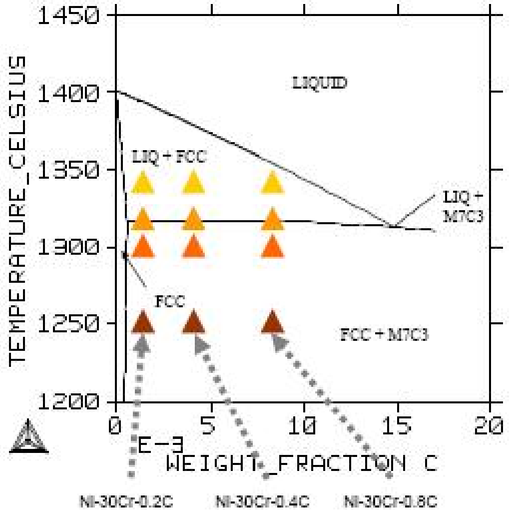

Figure 1: Section at 30 wt.% Cr of the Ni-Cr-C phase diagram calculated by Thermo-Calc

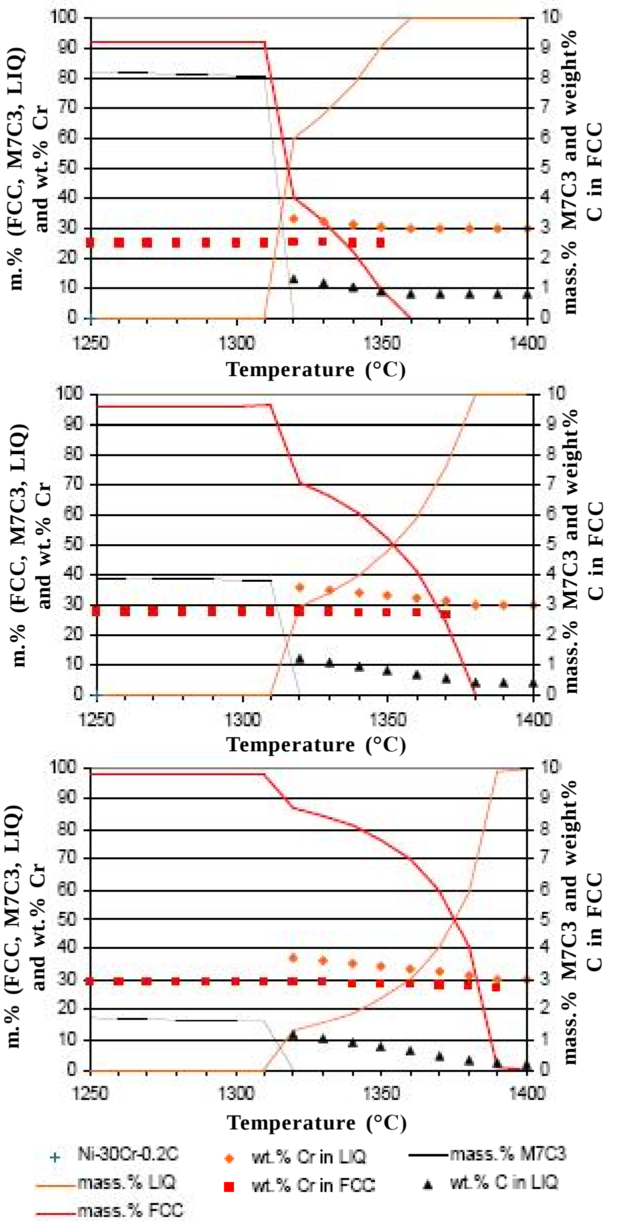

Figure 2: Evolutions of the mass fractions of all phases and of their Cr and C weight contents versus temperature according to Thermo-Calc

matrix begins to melt. The temperature of fusion's beginning is almost the same for the three alloys, while, in contrast, fusion finishes at a temperature which depends on carbon content. The higher the carbon content is, the lower the liquidus temperature is. Concerning the chemical compositions of matrix and of liquid, the Cr content remains almost constant in matrix while the forming liquid contains more chromium than matrix at the temperatures at which these two phases exist together.

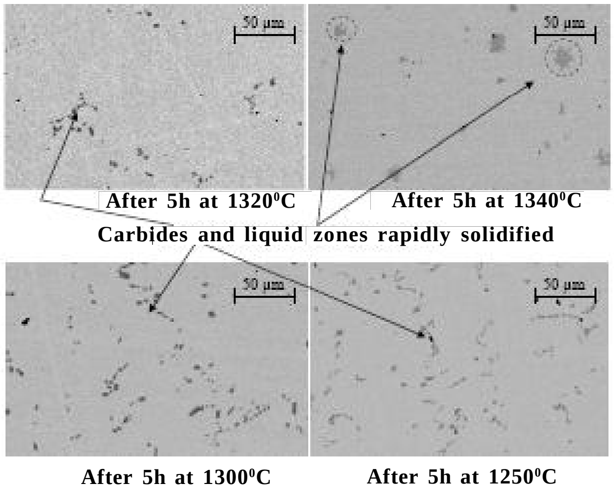

Figure 3: Microstructures of the Ni-30Cr-0.2C alloy obtained after water quenching from high temperature (SEM, BSE mode)

In contrast, for the same temperatures, carbon is significantly more present in liquid than in matrix (e.g. 1wt.%C in liquid for the Ni-30Cr-0.2C alloy near 1330°C, to compare with about 0.05 wt.% in matrix). Indeed, at such temperature, the carbon content in liquid is near the eutectic value (figure 1).

This high carbon concentration in liquid when it exist (alloy in a partially molten state) will help to sufficiently distinguish, with the SEM in BSE mode, the volumes of alloys which were in the liquid state just before water-quenching.

Microstructures of the quenched alloys

The microstructures of all samples are illustrated by SEM/BSE micrographs in figures 3-5 for respectively the Ni-30Cr-0.2C, Ni-30Cr0.4C and Ni-30Cr-0.8C alloys. The alloys heat treated at a temperature among 1250, 1300 and 1320^{0}C display classical microstructures composed of a dendritic matrix and interdendritic carbides, which are more or less coarse or numerous, depending on both the carbon content in alloy and the exposure temperature. Their microstructure are of the same type as what can be observed for similar alloys after cooling from lower temperatures (1200^{0}C and less) or in as - cast conditions[9].

In contrast, the alloys quenched from 1340^{0}C are very different. The Ni-30Cr-0.2C contains dark particles, with often a "star"-like shape, instead of the initial carbides. WDS pinpoint microanalysis shows that

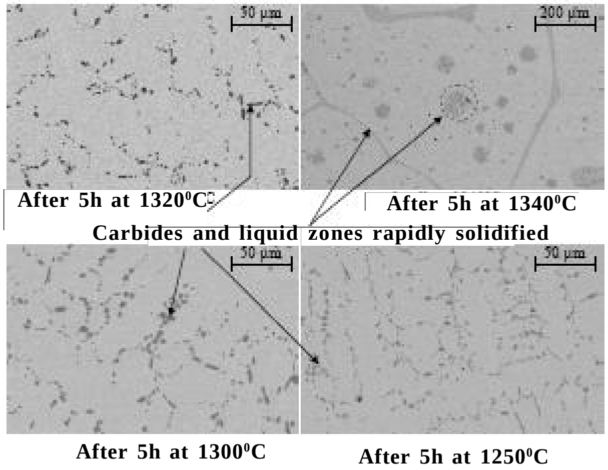

Figure 4: Microstructures of the Ni-30Cr-0.4C alloy obtained after water quenching from high temperature (SEM, BSE mode)

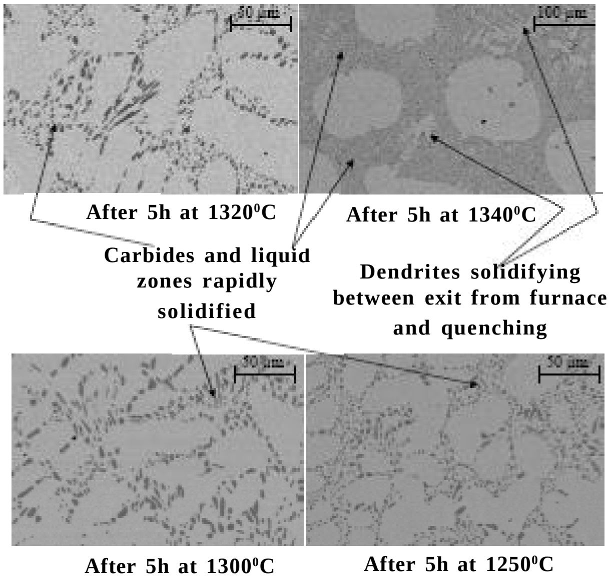

Figure 5: Microstructures of the Ni-30Cr-0.8C alloy obtained after water quenching from high temperature (SEM, BSE mode)

TABLE 1: Comparison between the calculated micro structures and the observed ones after water quenching (case of Ni-30Cr-0.2C alloy)

Ni-30Cr-0.2C Targeted temperature Deduced temperature	Thermo -Calc *	Calculated vol.% *	Measured surf.%	Real experiments
Targeted: 1340°C Deduced: ?	LIQ	19.2	not meas.	quench. liq.
	FCC	80.8	not meas.	matrix
	M7C3	/	/	carbides
Targeted: 1320°C	LIQ	13.3	/	quench. liq.
Deduced: ≈1316°C	FCC	86.8	≈ 99	matrix
**	M7C3	/	0.58 ±0.21	carbides
Targeted: 1300°C	LIQ	/	/	quench. liq.
Deduced: ≈1300°C	FCC	98.1	about 98	matrix
**	M7C3	1.9	1.94 ±0.23	carbides
Targeted: 1250°C	LIQ	/	/	quench. liq.
Deduced: ≈1250°C	FCC	98.0	about 98	matrix
**	M7C3	2.01	1.85 ±0.61	carbides

*Calculations performed for T = targeted temperature; ** Value of T which allows reaching the measured values of carbides (or molten areas) fractions by thermodynamic calculations

TABLE 2: Comparison between the calculated micro structures and the observed ones after water quenching (case of Ni-30Cr-0.4C alloy)

Ni-30Cr-0.4C Targeted temperature Deduced temperature	Thermo -Calc *	Calculated vol.% *	Measured surf.%	Real experiments
Targeted: 1340°C Deduced: ?	LIQ	40.3	> 7.7	quench. liq.
	FCC	59.7	about 92	matrix
	M7C3	/	/	carbides
Targeted: 1320°C Deduced: ≈1317°C **	LIQ	29.8	/	quench. liq.
	FCC	70.2	about 97	matrix
	M7C3	/	2.80 ±0.21	carbides
Targeted: 1300°C Deduced: ≈1300°C **	LIQ	/	/	quench. liq.
	FCC	95.6	about 96	matrix
	M7C3	4.42	4.34 ±0.66	carbides
Targeted: 1250°C Deduced: ≈1250°C **	LIQ	/	/	quench. liq.
	FCC	95.5	about 95	matrix
	M7C3	4.53	5.01 ±1.24	carbides

*Calculations performed for T = targeted temperature; ** Value of T which allows reaching the measured values of carbides (or molten areas) fractions by thermodynamic calculations

they contain almost ten atomic percent of carbon, which explains their dark colour when observed with the SEM in BSE mode. In the cases of the Ni-30Cr-0.4C and Ni-30Cr-0.8C alloys quenched from 1340°C, curious microstructures can also be seen. In the Ni-30Cr-0.4C alloy one can notice the existence of elongated and interconnected dark zones (shape analogous to the grain boundaries in classical cast alloys) and spherical zones (similar to the star-like particles in the Ni-30Cr-0.2C alloy but here clearly mixed with matrix inside the round area. WDS measurements performed with not-focalized electrons beam showed that these areas are especially rich in carbon: 0.92±0.36 wt.%C (and 37.49±2.60 wt.%Cr) in the spherical dark zones (partially mixed with matrix), 1.13±0.08 wt.%C (and 40.54±1.38 wt.%Cr) in the elongated dark zones (average value from three results ± standard deviation). In the Ni-30Cr-0.8C alloy quenched from 1340°C, the

TABLE 3: Comparison between the calculated micro structures and the observed ones after water quenching (case of Ni-30Cr-0.8C alloy)

Ni-30Cr-0.8C Targeted temperature Deduced temperature	Thermo -Calc *	Calculated vol.% *	Measured surf.%	Real experiments
Targeted: 1340°C Deduced: ?	LIQ	77.9	53.2 ±14.3	quench. liq.
	FCC	22.1	about 47	matrix
	M7C3	/	/	carbides
Targeted: 1320°C Deduced: ≈1316°C **	LIQ	60.3	/	quench. liq.
	FCC	39.7	about 91	matrix
	M7C3	/	8.71 ±0.92	carbides
Targeted: 1300°C Deduced: ≈1300°C **	LIQ	/	/	quench. liq.
	FCC	90.7	about 88	matrix
	M7C3	9.34	11.78 ±0.62	carbides
Targeted: 1250°C Deduced: ≈1250°C **	LIQ	/	/	quench. liq.
	FCC	90.5	about 89	matrix
	M7C3	9.47	10.95 ±1.06	carbides

*Calculations performed for T = targeted temperature; **Value of T which allows reaching the measured values of carbides (or molten areas) fractions by thermodynamic calculations

dark zones are considerably more developed since they seemingly fill interdendritic spaces. In these zones WDS measurements gave 1.40±0.08 wt.%C (and 38.01 ±0.18 wt.%Cr). Here and there additional very small matrix dendrites can be noted. They are connected to matrix areas and seem having grown towards the interdendritic dark zones.

Volume fractions of the different phases according to metallography and calculations

For each sample, i.e. each alloy and each exposure temperature, five SEM/BSE micrographs were taken, generally at ×500 but sometimes at lower magnifications (×125) for the samples in which zones of quenched liquid obviously existed). For the samples obtained by quenching from 1250, 1300 or 1320^{0}C, with microstructures seemingly composed of matrix (white) and chromium carbides (dark), image analysis allowed specifying the surface fractions of carbides. For the three alloys and the two lowest temperatures, results displayed in TABLES 1-3, show a very good agreement with values predicted using Thermo-Calc, for the samples exposed to 1250^{0}C and 1300^{0}C. These comparisons were done after conversion of the calculated mass fractions into volume fractions by using 8.12 g cm^{-3} for matrix and 6.941 g cm^{-3} for carbides[10] by assuming that they are of the M$_7$C$_3$-type as predicted by Thermo-Calc (WDS pinpoint analysis was not possible since these carbides were too small).

In contrast, for the two highest temperatures, calculated results and metallography observations and/or surface fractions measurements show significant mismatches. Indeed, for 1320^{0}C thermodynamic calculations led to the existence of liquid while no zones of quenched liquid were seen in samples which obviously still contained carbides in interdendritic spaces (with fractions significantly lower than at 1300 and 1250^{0}C). For 1340^{0}C a better agreement is qualitatively found between calculations and experiments. Indeed, one can reasonably think that, after quenching from 1340^{0}C, the star-like dark particles seen in Ni-30Cr-0.2C, the grey boundaries and bi-phased spherical domains existing inside matrix for Ni-30Cr-0.4C, and the dark interdendritic continuous areas in Ni-30Cr-0.8C, probably all correspond to liquid areas at 1340^{0}C (predicted by Thermo-Calc) before quenching. However, surface fractions measured by image analysis (after having made a mask to take the small dendrites formed before quenching as belonging to liquid at 1340^{0}C in the case of the Ni-30Cr-0.8C alloy) are very different from the calculated ones. Calculated fractions of liquid are significantly greater than fractions measured by metallography way.

General commentaries

Even at very high temperatures, carbides still exist in the studied alloys, but with logically volume fractions significantly lower than for temperatures such as 1000 and even 1200^{0}C[9]. Nevertheless these carbides are still present enough to allow measuring their surface fraction by image analysis. This allowed, in a first time, verifying that there was a good agreement between the real measured surface fractions and the ones deduced from the mass fraction issued from Thermo-Calc calculations, for the three alloys and at the two lowest temperatures in this study, 1250^{0}C and 1300^{0}C (TABLE 1 to TABLE 3). In contrast, first mismatches were noticed for 1320^{0}C, since the three alloys were partially melted according to Thermo-Calc while no molten (then rapidly solidified) area was seen in the microstructures of the corresponding samples. For 1340^{0}C, all alloys are partially molten, according to both calculations and experiments (obvious for the Ni-30Cr-0.8C and Ni-30Cr-0.4 alloy, and probable for the Ni-30Cr-0.2C). However, the quantities of liquid were significantly different between calculations (high fractions of liquid) and experiments (lower fraction for the Ni-30Cr-0.8C alloy, the sole alloy for which a metallo graphic assessment was possible with a sufficient precision).

These mismatches can be explained either by a real temperature which was perhaps slightly lower than the targeted one (case of the alloys exposed to 1320^{0}C) or to a lack of precision of the database with which Thermo-Calc worked. In the first case, the three surface fractions measured by image analysis can be supposed to be close of the corresponding volume fractions and converted into mass fractions by using the densities given above. Thereafter, Thermo-Calc can be used to look for the temperatures which allow obtaining the real mass fractions. Thus, for the Ni-30Cr-0.2C, Ni-30Cr-0.4C and Ni-30Cr-0.8C alloys, the values of carbide surface (or volume) fractions (respectively 0.58, 2.80 and 8.71 vol.%), converted into mass fractions (resp. 0.50, 2.40 and 7.54 mass.%), lead to the temperatures to which the three alloys were really exposed (resp. 1316, 1317 and 1316^{0}C) that are slightly lower than the targeted one (1320^{0}C). This proves the possibility or efficiency of post-mortem determination of real temperatures by using both phase fraction metallographic measurements and thermodynamic calculations.

The same procedure, applied to the Ni-30Cr-0.8C exposed to 1340^{0}C (53.2 vol.% then 53.2 mass.% if the-unknown- density of the frozen liquid alloy is assumed as being close to the matrix one) would lead to a temperature which is also close to 1317^{0}C. This result, obviously false since the real temperature was probably between 1320 and 1340^{0}C, can be due to several possible reasons: a lack of precision of the measured value of the frozen liquid surface fraction, a possible difference between the densities of matrix and frozen liquid, or a lack of precision of the used database. Concerning the first possible reasons, it is true that the standard deviation calculated from the five measured values, is especially high (14.3%). If one considers the sum of the average temperature added with the standard deviation (67.5 vol.% then 67.5 mass.% since densities of matrix and frozen liquid are supposed being equal), thermodynamic calculations would lead to 1328^{0}C, which is a more acceptable value. Thus, the dispersion of measured values of the surface fraction of liquid may explain the mismatch between metallography and calculations. But, it is also true that a not very good conversion of surface fraction into mass fractions, due to a not true equivalence between surface and volume fractions or to the unknown densities, can lead to this mismatch. A lack of precision of the used database can be also a third cause of the mismatch, since it was earlier found that the description of the liquid phase was not efficient enough[9] and notably that it led to liquidus temperatures which were too low (then probably liquid fractions too high in the mushy state) when compared to Differential Thermal Analysis results obtained for ternary Ni-Cr-C alloys.

CONCLUSION

The post-mortem determination of real temperatures to which some parts of industrial refractory pieces were locally exposed in service, can be done by coupling metallographic image analysis and thermodynamic calculations, with good precision in some cases. This method is analogous to the one used for a previous work[11] in which it was the carbon content in alloy which played the role of equation's unknown value instead of temperature here.

It appeared in the present work that the method accuracy was better for alloys which were still solid than when temperature was high enough to partially melt them. In addition, in the latter case, a fast cooling would be necessary to distinguish at ambient temperature the areas which were molten. This method also supposes that the temperature map of the studied piece remained constant on long times for stabilizing the microstructures of the concerned alloys and that these microstructures allow clear separation of one phase from the others, as here carbide from matrix. It is also important that the database used in thermodynamic calculations is efficient enough in the temperature range of consideration. If these conditions are all respected, real temperatures can be deduced by this way with good accuracy for inaccessible locations in service, even in case of partial fusion.

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