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THERMAL EXPANSION OF CHROMIUM-RICH IRON-BASED OR IRON/NICKEL-BASED ALLOYS REINFORCED BY TANTALUM CARBIDES

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Six alloys reinforced by TaC carbides based on iron (ferritic) or both iron and nickel (austenitic) were studied in thermal expansion between 100 and 1200°C for two microstructure orientations. The heating, isothermal and cooling parts of the dilatometry curves were characterized. The thermal expansion of the ferritic alloys is less important than for the austenitic alloys. A compressive deformation of matrix subjected to stresses applied by the carbides network was observed. The importance of this phenomenon seems depending more on the matrix nature than on the microstructure orientation.

Keywords: *thermal expansion, chromium-rich iron based alloy, tantalum carbides.*

An increase in temperature induces a geometrical expansion for most materials, especially for the metallic alloys, with as consequences the possible development of internal stresses when they are not free to deform or when the whole considered piece is not homogeneous in temperature. This is particularly true for refractory alloys and superalloys the temperature of which can vary between room temperature and more than 1000°C [1] in service. To minimize such stresses appearing when temperature varies significantly, one usually looks for lowering the Young's modulus or the average thermal expansion coefficient of materials. Several parameters can influence the thermal expansion of an alloy: its chemical composition, the natures and volume fractions of the phases present in its microstructure (if their thermal expansion behaviours are different from one another), and possibly the local microstructure orientation in the case of foundry alloys.

The aim of this work is to study the possible effects of these three parameters on the thermal expansion of selected metallic alloys which are especially refractory and which can be candidates for uses at high temperatures in corrosive environments.

Materials and methods. Three iron-based alloys and three {iron+nickel}-based alloys, all containing about 30 wt.%Cr but various amounts of Ta and C, were elaborated by High Frequency induction foundry (around 100 g for each ingot), from pure elements. Their obtained chemical compositions are given in Table 1 (obtained contents, measured by Energy Dispersion Spectrometry), while their microstructures are illustrated by several micrographs and X-Ray Diffraction patterns in Figs. 1 and 2 (Scanning Electron Microscope Philips XL30, Back Scattered Electrons mode, accelerating voltage of 20kV; Bruker XPERT-Pro Diffractometer). These are composed of a bcc-ferritic (respectively fcc-austenitic) matrix of Fe (resp. Fe+Ni) containing the other elements in solid solution (almost all Cr and a part of Ta and of C), and of carbides. These ones are almost exclusively TaC carbides in the FeTa1, FeTa3, FeNiTa1 and FeNiTa3 alloys, while chromium carbides are also present (in very small quantities) in the FeTa2 and FeNiTa2 alloys, in addition to the TaC. The TaC carbides are the most present in all alloys, essentially in the interdendritic spaces where they constitute a network, continuous in some of the alloys. Such alloys were previously studied from the thermodynamic point of view in earlier works [2, 3].

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Table 1. Chemical compositions of the studied cast alloys
(EDS* measurements, average $\pm 1\sigma$; 3** to 6*** locations at $\times 250$)

Alloys	weight %	Fe	Ni	Cr	C	Ta
Based on Fe**	FeTa1	bal.	/	29.8 ± 0.7	0.2	2.1 ± 0.5
	FeTa2	bal.	/	29.5 ± 2.7	0.4	2.4 ± 0.4
	FeTa3	bal.	/	29.2 ± 1.6	0.4	6.2 ± 1.1
Based on Fe and Ni***	FeNiTa1	bal.	34.2 ± 0.5	29.6 ± 0.3	0.2	2.9 ± 0.3
	FeNiTa2	bal.	34.0 ± 0.4	30.0 ± 0.3	0.4	2.8 ± 0.4
	FeNiTa3	bal.	32.5 ± 0.2	29.5 ± 0.3	0.4	6.4 ± 0.3

* EDS: Energy dispersion spectrometry.

Fig. 1. Microstructures of the three alloys based on Fe (SEM* in BSE** mode, XRD*** patterns).
(* SEM: Scanning electron microscope; ** BSE: Back scattered electrons; *** XRD: X-Ray diffraction): ■ – bcc (matrix); ● – fcc (matrix); △ – TaC; ◇ – Ta₂C.

The samples, parallelepipeds of about $4 \text{ mm} \times 4 \text{ mm} \times 2.5 \text{ mm}$ (*: direction of the measured dilatation), were cut in the ingot following two procedures. These ones allowed studying the thermal expansion in the direction of the thermal gradient existing during solidification, or in the direction perpendicular to this thermal gradient under solidification (Fig. 3), as is to say globally in directions respectively parallel and perpendicular to the primary dendritic arms [4]. The thermal expansion was measured

using a Setaram TMA 92-16.18 apparatus during heating at room temperature up to 1200°C (rate of $10 \text{ K} \times \text{min}^{-1}$), at the 10 minutes-isothermal stage at 1200°C and during cooling (rate of $-20 \text{ K} \times \text{min}^{-1}$). Only the parts of the curves above 100°C were considered since the thermal equilibrium of the apparatus was achieved only after heating over this temperature.

Fig. 2. Microstructures of the three alloys based on both Fe and Ni (SEM in BSE mode, XRD patterns): ● – fcc (matrix); △ – TaC.

Fig. 3. The two cutting modes used to obtain samples for the study of thermal expansion following the two orientations to the thermal gradient during solidification. *a* – parallel; *b* – perpendicular.

Results and discussion. The obtained dilatometry curves are presented in Fig. 4. The heating parts are distinguished from the cooling parts while the isothermal parts, not represented, are simply vertical lines joining the extremities of the two latter ones, in each case.

One can first notice that the thickness of all samples effectively increases with temperature (at least on the greatest part of the curves), without any discontinuities, according to the absence of any crystallographic change for the matrix over this temperature range. Indeed the FeTa alloys are initially and remain ferritic and the FeNiTa alloys – austenitic [2, 3]. Secondly, except for the FeNiTa1 alloy (parallel and perpendicular) and for the FeNiTa3 alloy (parallel), and also maybe at the FeNiTa2 alloy (perpendicular), there is generally a deceleration of the elongation for the highest temperatures. In some cases a beginning of contraction can appear before reaching 1200°C (e.g. FeTa3 for the two orientations), which goes on at the isothermal stage. This leads to both a cooling-part of the dilatometry curve which is clearly below the heating part and a final contraction of the sample after return to 100°C and to room temperature. Indeed, except for the alloys FeNiTa1, FeNiTa2 (perpendicular only) and FeNiTa3 (parallel only), all the thicknesses at 100°C are lower after dilatometry experiment than before (negative deformations).

Fig. 4. Thermal expansion of the six alloys for the two microstructure orientations.
 I' – heating; $2'$ – cooling (parallel);
 I'' – heating; $2''$ – cooling (perpendicular).

and the thermal contraction between 100 and 1200°C are almost equal for each alloy, without real effect of the orientation. In contrast the isothermal negative deformation at 1200°C tends to be more severe for the perpendicular case than for the parallel case (except for only FeNiTa2), which can be logically found again with the average rates

of isothermal contraction given in Table 3. There is also a global difference in total thermal expansion or contraction between all the ferritic alloys and all the austenitic alloys: the first ones generally display slow thermal expansion or contraction and high isothermal negative deformation or contraction rates by comparison with the latter alloys.

Table 2. Deformations during heating, at the isothermal stage and during cooling

Alloy	//	$\Delta\epsilon_{100 \rightarrow 1200}$ (%)	$\Delta\epsilon_{T=1200}$ (%)
		$\Delta\epsilon_{1200 \rightarrow 1000}$ (%)	
	+	$\Delta\epsilon_{100 \rightarrow 1200}$ (%)	$\Delta\epsilon_{T=1200}$ (%)
		$\Delta\epsilon_{1200 \rightarrow 1000}$ (%)	
FeTa1	//	0.71	-0.132
		-1.47	
	+	1.42	-0.137
		-1.48	
FeTa2	//	1.55	-0.072
		-1.60	
	+	1.41	-0.094
		-1.57	
FeTa3	//	1.29	-0.103
		-1.48	
	+	1.27	-0.125
		-1.53	
FeNiTa1	//	2.24	-0.019
		-1.86	
	+	2.40	-0.036
		-2.10	
FeNiTa2	//	1.82	-0.123
		-1.90	
	+	2.15	-0.032
		-2.09	
FeNiTa3	//	2.22	-0.029
		-2.03	
	+	1.87	-0.066
		-2.05	

Concerning the average coefficients of thermal expansion or contraction (Table 3), it can be noticed that the coefficient is higher for heating than for cooling, but there is no real effect of the microstructure orientation. The main difference of coefficient is between the ferritic alloys (10 to $14 \times 10^{-6} \text{ K}^{-1}$) and the austenitic alloys (14 to $21 \times 10^{-6} \text{ K}^{-1}$).

The fast expansion observed for the austenitic alloys of this study in comparison with the ferritic alloys is in accordance with previous measurements, for example on pure iron [5] (for of course distinct temperature ranges). The presence of more or less high fractions in tantalum carbides, the thermal expansion of which is much lower than

the matrixes ones (coefficient of only $6.3 \times 10^{-6} \text{ K}^{-1}$ for TaC [6]) and even lower than for chromium carbides (10.1 to $10.6 \times 10^{-6} \text{ K}^{-1}$ for Cr_xC_y [6]), leads to a progressive deformation in compression of the matrix by the more or less connected interdendritic carbides when this matrix is mechanically weakened by the temperature become very high at the end of heating. This visco-plastic compression of the matrix accompanies the release of the tensile-stress affecting progressively the carbides during the first part of heating (induced by the increasing matrix-carbides interaction), previously observed for ternary alloys containing chromium carbides [7]. This goes on at the isothermal stage and results in a negative deformation of the sample after return to the room temperature. This deformation, which seemed being not really dependent on the microstructure orientation, was here enhanced in the case of the ferritic alloys, the bcc $\rightleftharpoons$ matrix of which is mechanically less resistant than the more compact fcc $\rightleftharpoons$ matrix.

Table 3. Deformations during heating, at the isothermal stage and during cooling

Alloy	//	average $\alpha_{250 \rightarrow 750} (\times 10^{-6} \text{ } ^\circ\text{C}^{-1})$	average $\Delta\epsilon/\Delta t$ at 1200°C (% / min)
		average $\alpha_{750 \rightarrow 250} (\times 10^{-6} \text{ } ^\circ\text{C}^{-1})$	
	+	average $\alpha_{250 \rightarrow 750} (\times 10^{-6} \text{ } ^\circ\text{C}^{-1})$	average $\Delta\epsilon/\Delta t$ at 1200°C (% / min)
		average $\alpha_{750 \rightarrow 250} (\times 10^{-6} \text{ } ^\circ\text{C}^{-1})$	
FeTa1	//	10.5	-0.013
		10.5	
	+	14.0	-0.014
		10.5	
FeTa2	//	12.9	-0.007
		11.1	
	+	13.2	-0.009
		11.1	
FeTa3	//	10.7	-0.010
		10.4	
	+	13.2	-0.013
		10.6	
FeNiTa1	//	21.2	-0.002
		14.3	
	+	20.9	-0.004
		18.2	
FeNiTa2	//	20.8	-0.012
		16.0	
	+	20.2	-0.003
		17.1	
FeNiTa3	//	19.5	-0.003
		17.3	
	+	20.0	-0.007
		16.4	

CONCLUSIONS

Carbides in general and tantalum carbides in particular which are among the most stable at high temperature, are very useful for strengthening refractory alloys used at high temperature. However they can induce irreversibility for the thermal dimensional variations when temperature varies, which is furthermore obviously not isotropic although no clear dependence on the microstructure orientation was demonstrated. Phenomena similar to ones earlier observed for simple alloys reinforced with chromium carbides, were found here in the case of ferritic and austenitic iron-based alloys. They can be source of permanent dimensional changes after temperature cycles, and maybe of deterioration of the alloys at the microscopic scale.

РЕЗЮМЕ. В статті розглянуто шість сплавів, що базуються на залізі (феритні) та на нікелі та залізі (аустенітні), зміцнених карбідами TaC та їх термічне розширення між 100 та 1200°C для двох мікроструктурних орієнтацій. Представлені та обговорені нагрівання, ізотермічна та охолоджувальна ділянки на дилатометричних кривих. Термічне розширення феритних сплавів є менш вираженим ніж аустенітних. Стискальні деформації матриці призводять до напружень які поширюються на колонії карбідів. Важливість цього явища вбачається у впливі фази матриці на мікроструктурні особливості сплаву в цілому.

РЕЗЮМЕ. В статье рассмотрено шесть сплавов, которые базируются на железе (ферритные) и на никеле и железе (аустенитные), упрочненных карбидами TaC и их термическое расширение между 100 и 1200°C для двоих микроструктурных ориентаций. Представлены и обсуждены нагревание, изотермический и охлаждающий участки на дилатометрических кривых. Термическое расширение ферритных сплавов есть менее выраженным, чем аустенитных. Сжимающие деформации матриц приводят к напряжениям, которые расширяются на колонии карбидов. Важность этого явления состоит во влиянии матричной фазы на микроструктурные особенности сплава в целом.

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