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N. Matveeva, G. Demensky, L. Petrov, Yu. Kovneristyi, O. Teplov. CALORIMETRIC INVESTIGATION OF THE MARTENSITIC TRANSFORMATION IN NEAR STOICHIOMETRIC AND STOICHIOMETRIC Fe₃Pt AND SHAPE MEMORY EFFECT. Journal de Physique Colloques, 1982, 43 (C4), pp.C4-377-C4-382. 10.1051/jphyscol:1982455 . jpa-00222171

HAL Id: jpa-00222171

<https://hal.science/jpa-00222171>

Submitted on 1 Jan 1982

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CALORIMETRIC INVESTIGATION OF THE MARTENSITIC TRANSFORMATION IN NEAR STOICHIOMETRIC AND STOICHIOMETRIC Fe_3Pt AND SHAPE MEMORY EFFECT

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(Accepted 9 August 1982)

Abstract. - Heats and temperatures of the $\gamma \rightleftharpoons \alpha$ martensitic transformation in the Fe_3Pt alloy have been measured after quenching and annealing at 820 K. The results obtained are discussed in terms of heterogeneous atomic ordering $\text{Al} \rightarrow \text{Al}_2$ and eutectoid decomposition $\gamma \rightarrow \alpha + \text{Fe}_3\text{Pt}$, which occur during annealing and precede the martensitic transformation.

Introduction. - Alloys of the Fe-Pt system close to the Fe_3Pt composition undergo a $\gamma \rightleftharpoons \alpha$ martensitic transformation, being of particular interest, since properties of the martensite are governed by the other phase transformations, rival to the martensitic one. So the martensitic transformation of rapidly quenched alloys is not thermoelastic and is accompanied by a significant thermal hysteresis. When the martensitic transformation is preceded by the atomic ordering $\text{Al} \rightarrow \text{Al}_2$ it becomes a thermoelastic one and has a small thermal hysteresis. The alloys are capable of recovering their shape. The effect of atomic ordering on the martensitic transformation in the iron-base alloys with 23-27% Pt has been discussed often [1-7]. Various criteria were proposed to determine the thermoelasticity of transformation. According to [1] the major criterion is given by some level of the M_s point, depending on the degree of the long-range ordering, which should necessarily be below the Curie point. This level determines a small thermal hysteresis of transformation, certain tetragonality of the γ - and α -phases, enhancing crystallographic rearrangement, and small volume change during the $\gamma \rightleftharpoons \alpha$ transformation. One of the important properties of the thermoelastic transformation is its small driving force as compared to that of the non-thermoelastic one [8]. It can be expressed in terms of the heat effect and the transformation temperature [9-11]. The latent heat of the $\gamma \rightarrow \alpha$ transformation in Fe-24.5 Pt alloy is determined in one study [12]. It gives the value of $\Delta H_{\gamma \rightarrow \alpha}$ for the two ultimate conditions, disordered and annealed at 820 K for 120 hrs.

The present study is aimed at the calorimetric determination of the heat effects of the $\gamma \rightleftharpoons \alpha$ transformation in the quenched Fe-24 Pt and Fe-25 Pt alloys and at the process of atomic ordering at 820 K. The results obtained should be evaluated in connection with the processes occurring in alloys during annealing. The study also deals with the temperature dependence of deformation in order to establish the shape memory effect.

Experimental results. - The alloys were prepared by the method of levitation melting in helium and cast into a cylindrical mould. This

was followed by a solution treatment at 1373 K for 24 hrs and by water quenching from 1473 K. The ingots were cut into cylindrical specimens 5x8 mm for calorimetry and wire specimens 1 mm in ϕ for the study of deformation. Capability of alloys to the shape memory effect was determined on wires under torsion deformation. The phase composition was determined by X-Ray analysis. The Fe-24 Pt and Fe-25 Pt alloys consist of two phases $\alpha + \gamma$ after quenching, therefore before calorimetric study they were cooled down in liquid nitrogen in order to ascribe the heat effect to the full $\gamma \rightleftharpoons \alpha$ transformation. The heat effects were measured in a DSC-III Setaram calorimeter [3]. The error of the enthalpy determination was about 3%. The effect was separated from the zero line by the Berg method. The experiment was carried out as follows: the specimen was heated in the calorimeter up to 820 K, held at this temperature for some time and then cooled down to 150 K. Thereby one cycle included annealing-cooling-heating. A direct transformation proceeds rapidly, in time, being of the same order as the calorimeter constant ($\tau_c = 30$ s), therefore the M_s and M_f

points were taken at the beginning and maximum of the heat effect respectively. The reverse $\alpha \rightarrow \gamma$ transformation is delayed, its duration is more than τ_c , therefore the points A_s and A_f are taken at the

beginning and end of the peak respectively. Table I sums up the data on temperatures and heats of the $\gamma \rightleftharpoons \alpha$ transformation after several cycles of heating and cooling and short-time annealing at 820 K directly in the calorimeter. Fig.1 shows the heating curves of the Fe-25 Pt alloy for several cycles. The heating curves exhibit at least two effects for the reverse $\alpha \rightarrow \gamma$ transformation. Their values reduce, as is also the case for those of the $\gamma \rightarrow \alpha$ transformation. The A_s points of the first effect (I) reduce with the increase of the annealing duration, point A_s of the second effect (II) does not change

until the effect ceases after 6 hrs of annealing. The heat effects of the $\gamma \rightarrow \alpha$ transformation are individual and of sharp shape, corresponding to the high rate of the $\gamma \rightarrow \alpha$ transformation. After 11.5 hrs of annealing the heat effect of the $\alpha \rightarrow \gamma$ transformation is strongly smeared, it can hardly be separated from the zero line and precisely measured. The heat effect of the $\gamma \rightarrow \alpha$ transformation is small (about 150 J/mole) and it is proportional to the driving force of the thermoelastic martensitic transformation of this alloy. In the Fe-24 Pt alloy the heat effects of the $\alpha \rightarrow \gamma$ transformation divide into two after 2 hrs of annealing at 820 K, while sharp reduction of the ΔH value of the $\gamma \rightleftharpoons \alpha$ transformation also occurs in the first cycles at the constant points of transformation. After 5 hrs of annealing the heat effect II at 650 K disappears, while the first one (I) observed at lower temperatures is smeared. Fig.2 shows the time dependence of the temperatures and heats of the $\gamma \rightleftharpoons \alpha$ transformation. Fig.3 shows the temperature dependence of deformation for the Fe-24 Pt and Fe-25 Pt alloys after annealing at various temperatures and holding times. The quenched alloys do not exhibit any noticeable shape memory effect. The Fe-25 Pt alloy (Fig.3a), annealed for 4 hrs at 820 K, recovers the accumulated strain energy over a wide temperature range, the process being noticeably two-stage and incomplete. After annealing for 20 hrs this alloy (Fig.3b) does not undergo martensitic transformation down to 77 K. For Fe-24 Pt alloy (Fig.3c), annealed for 24 hrs, complete recovery is observed on heating over the range of 175-300 K. After annealing for 48 hrs at 873 K this range reduces down to 77-170 K. Degree of the long-range order in the Fe-24 Pt alloy is not high after heat-treatments described and is about 0,6 and 0,7 respectively.

Table I.

Cycle Nr	Time of an- neal- ing at 820 K, (hrs)	M _s ,K	M _f ,K	A _s , K	A _f , K	$\Delta H \quad \gamma \rightarrow \alpha$		$\Delta H \quad \alpha \rightarrow \gamma$	
						cal/g	J/mole	cal/g	J/mole
25 at % Pt									
I	Quen- ching from 1473 K	280	268	I 513	620	3,5	1328	I,4	531
				II 613	730			2,4	911
								3,8	1442
2	0,5	290	270	I 503	610	2,5	950	I,2	455
				II 613	730			I,8	683
								3,0	1138
3	1,5	280	270	I 450	570	1,9	720	I,5	683
				II 613	730			0,5	189
								2,0	872
4	3,5	260	230	I 430	540	1,3	490	I,1	417
				II 613	730			0,2	76
								I,3	493
5	6,5	213	200	I 344	465	0,8	300	I	379
				II -	-			-	-
6	11,5	193	187	I 328	-	0,4	150	smeared	
				II -	-			-	-
24 at % Pt									
I	Quen- ching from 1473 K	-	-	650	770	-	-	6,5	2428
2	0,5	332	316	655	760	4,8	1793	3,6	1345
3	1,0	310	291	650	755	2,0	747	1,9	710
4	10	250	240	I 300	smeared	1,4	522	smeared	
				II -	II -	-			

Fig.1. Heat effects of the $\gamma \rightarrow \alpha$ (a) and $\alpha \rightarrow \gamma$ (b) transformation in the Fe_3Pt alloy.

Fig.2. Dependence of the heats and temperatures of the $\gamma \rightleftharpoons \alpha$ transformation on holding time of the annealing at 820 K in the Fe_3Pt alloy.

Discussion

Analysis of the calorimetric data shows, that reduction of $\Delta H \gamma \rightleftharpoons \alpha$ depending on the annealing time (Fig.2a) at 820 K should be connected with, at least, two different processes. During the first annealing stages, when ΔH decreases rapidly and the temperature of the transformation start does not change (Fig.2b), one may assume, that only the amount of the phase transformed is decreased. Further for longer annealing time the change of the thermodynamic parameters of transformation is possible. This is confirmed by the change of the transformation temperature (Fig.2b). The dependence of ΔH on annealing time (Fig.2c) may be approximated by the equation as follows:

$$\Delta H_{\gamma \rightarrow \alpha} = K\sqrt{\tau} + \Delta H_{\tau=0}$$

A dependence of that kind may arise when the decrease of the amount of phase transformed is due to diffusion

Fig.3. Temperature dependence of the deformation, 0-1 elastic loading, 1-2 accumulation of the deformation on cooling, 2-3 unloading, 3-4 recovery of the deformation on heating.

a) Fe-25 Pt alloy annealed for 4 hrs at 820 K;
b) Fe-25 Pt alloy annealed for 20 hrs at 820 K;
c) Fe-24 Pt alloy annealed for 20 hrs at 820 K;
d) Fe-24 Pt alloy annealed for 48 hrs at 870 K.

processes. X-Ray data showed also the α -phase in the alloys, annealed at 820 K together with partially ordered austenite. This confirms the eutectoid decomposition: $\gamma \rightarrow \alpha +$

+ Fe₃Pt above 820 K, therefore the amount of the γ -phase decreases.

When annealing the quenched alloys, whose concentration of thermal vacancies is high, the initial rate of eutectoid γ -phase decomposition is also high, then on cooling the decomposition is interrupted by the martensitic transformation and finally frozen down. Further on annealing, an atomic ordering is prevailing, effecting the martensitic transformation, which follows. Decrease of the ΔH -value of the $\gamma \rightleftharpoons \alpha$ transformation is slowing down. After annealing for 10 hrs the ΔH of the Fe-24 Pt alloy decreased down to 522 J/mole; this is close to the value obtained in [13] (347 J/mole) for the alloy, annealed for 120 hrs.

During the isothermal annealing at 820 K a heterogeneous process of atomic ordering takes place. Ordered and disordered austenite are simultaneously present in the alloy. An amount of the ordered phase increases, but the heat effect of its martensitic transformation decreases. That is why up to the fifth cycle $\Delta H \alpha \rightarrow \gamma$ (I)-transformation slightly changes in time. The presence of two maxima (I and II) in the thermal effect of the transformation, with constant temperatures of one of them (II) and with decreasing temperatures for

the order (I), corresponds to the double bend in the curves of the temperature dependence of the electrical resistivity when heating the Fe_3Pt alloy, as in /1/. These phenomena are, apparently, of the same origin.

Finally, one should bear in mind that partially ordered alloys exhibit practically complete shape memory effect. This is in accordance with the assumption /3/ that high degree of the long-range order Li_2 is not a determinant criterion for shape memory. The idea about the inherited nuclei of martensite in austenite at the temperatures above A_s is not a speculative one for the Fe_3Pt alloy. These may be the local regions of the α -phase, produced by the eutectoid reaction.

Thus, isothermal annealing at 820 K, followed by heating and cooling over the interval of the $\gamma \rightleftharpoons \alpha$ transformation in the alloys close to the Fe_3Pt composition, results in the first cycles together with the atomic ordering $\text{Al} \rightarrow \text{Li}_2$ also in the eutectoid decomposition $\gamma \rightarrow \alpha + \text{Fe}_3\text{Pt}$. Decrease of the γ -phase amount causes sharp reduction of the heats of the $\gamma \rightleftharpoons \alpha$ transformation. On further cycles the martensitic transformation is mainly influenced by heterogeneous atomic ordering. Thereby, the transformation temperatures of the $\gamma \rightarrow \alpha$ -transformation also decrease. One should also take into account the rival phase transformations, since they may exert an effect on both the formation of the nucleus and on the character of the $\gamma \rightarrow \alpha$ martensitic transformation as well as on the final properties of the martensite.

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