INFLUENCE OF NICKEL ON 475°C EMBRITTLEMENT OF Fe-Cr-Ni ALLOYS: MÖSSBAUER EFFECT STUDY

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The phenomenon of "475°C embrittlement" of Fe-Cr-Ni alloys with Fe/Cr ratios of 2.7 and 1.05, containing 0, 2 and 4 at.% Ni, has been investigated using the Mössbauer effect and hardness measurements. The results show that the addition of nickel to Fe-xCr alloys ($x = 25$ and 45 at.%) increases the transformation rate notoriously in the first hours of aging, the effect of this element being more important for alloys with Fe/Cr = 1.05.

1. Introduction

Ferritic high-chromium steels and duplex stainless steels (Fe-Cr based alloys) are very used as substitutes for expensive nickel alloys and austenitic stainless steels, because of their lower cost and similar stress corrosion resistance. However, they are susceptible to an age hardening process when exposed to temperatures from 400°C to 550°C. This phenomenon, called "475°C embrittlement" is characterized by a considerable increase in hardness accompanied by a loss in ductility. Several theories have been proposed to explain this phenomenon. Nowadays, the generally and most accepted theory is that 475°C embrittlement is due to a coherent precipitation within the miscibility gap of the Fe-Cr system that gives rise to a separation of the original phase α into a chromium-rich (α') and a chromium-depleted phase (α). The existence of a miscibility gap in the Fe-Cr system was first suggested by Williams and Paxton [1] and confirmed by Chandra and Schwartz [2].

The magnitude of the embrittlement depends on the composition of the phase α. It is known that the early formation of the phase α' is promoted by the presence of vanadium [3], and nitrogen [4]. Other elements as nickel and copper seem also to influence the phase separation of Fe-Cr alloys [5]. This paper describes a systematic microhardness and Mössbauer effect study concerning the influence of nickel on the decomposition of Fe-Cr bcc solid solutions with Fe/Cr ratios of 2.7 and 1.05.

2. Experimental details

Fe, Cr and Ni were melted together under argon atmosphere in a plasma furnace.

Table 1
Chemical analysis of the alloys

Alloy	Fe	Cr	Ni	Fe/Cr
Fe-25Cr	73.0	27.0	–	2.70
Fe-25Cr-2Ni	71.6	26.6	1.8	2.70
Fe-25Cr-4Ni	70.6	25.4	4.0	2.70
Fe-45Cr	51.4	48.6	–	1.05
Fe-45Cr-2Ni	50.7	47.8	1.5	1.05
Fe-45Cr-4Ni	49.9	47.2	3.9	1.05

The chemical composition of the resulting ingots was established by Energy Dispersive X-Ray Spectroscopy (EDS), the results of which are listed in table 1. After quenching treatment at 1100°C, in vacuum, the samples were aged at 475°C for periods up to 500 hr (1.8×10^6 s), followed by quenching into cold water.

The microhardness was measured with a Vickers indenter, under a load of 50 g. Each hardness value is the mean of 10 measurements.

Mössbauer spectra were obtained at room temperature using a transmission configuration. Velocity calibration was performed with an α iron thin foil. Probability curves of the internal field distribution (hereafter $P(H)$ curves) were calculated by using the numerical method of Hesse and Rubartsch [6].

3. Results and discussion

The variation of hardness with aging time at 475°C is shown at fig. 1. The shape of these curves is similar to the obtained in iron-chromium based alloys by other authors [4,7,8]. For the quenched state there is a systematic increase in hardness with increasing chromium and nickel contents. This is attributed to the bcc matrix distortion, provoked by the presence of the substitution elements Cr and Ni. The hardening processes of these Fe-Cr and Fe-Cr-Ni alloys take place without an apparent incubation period. In fact, in the first few minutes of aging there is a rapid rate of hardening followed by a decreasing rate with aging time up to 500 hr for all the studied alloys.

Fig. 2 shows the room temperature Mössbauer spectra and data fits for some Fe-Cr-xNi studied alloys in the as-quenched state and after 500 hr of aging. For the as-quenched state, all the Mössbauer spectra present a sextet of peaks, characteristic of a ferromagnetic phase. However, for the Fe-25Cr-4Ni alloy a 7th peak close to the zero velocity is identified, which is the result of the austenitic phase (γ) stabilization induced by the nickel. The evolution of the Mössbauer parameters of this alloy with aging time has not been considered in this work
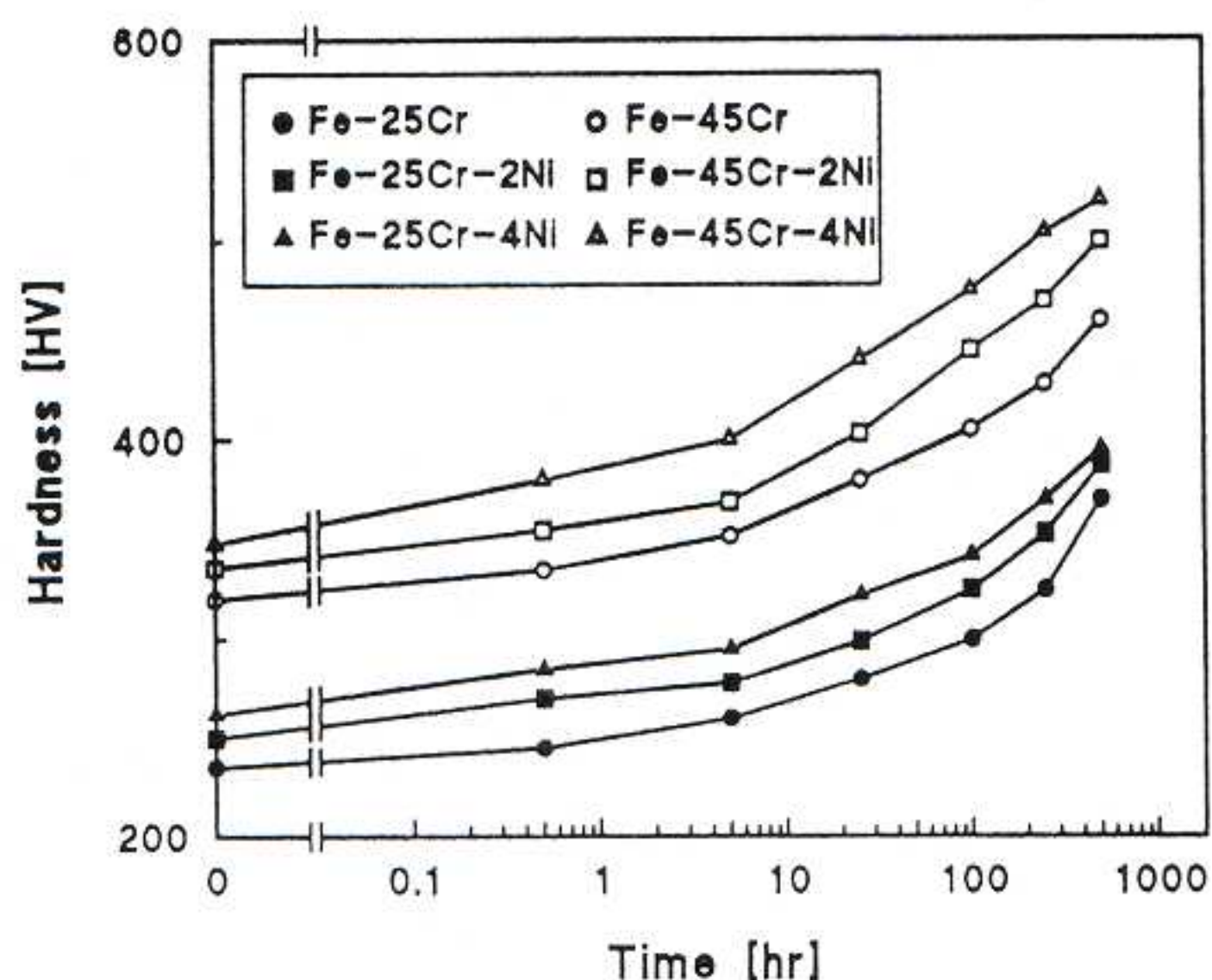
Fig. 1. Variation of hardness with aging time for the Fe-Cr-Ni studied alloys.

since the existence of the paramagnetic phase (γ) did not allow the analysis of the evolution of the phase α'.

By visual analysis the definition of the peaks is only dependent on the percentage of chromium; in the as-quenched state, spectra of alloys with Fe/Cr = 1.05 are not so clearly resolved as those for Fe/Cr = 2.7, as a consequence of the hyperfine field (H) decrease provoked by chromium.

The values of the hyperfine field obtained for the Fe-Cr and Fe-Cr-Ni alloys in the quenched state and after aging are indicated in table 2. For the quenched state the values of the hyperfine field of the Fe-25Cr and Fe-45Cr alloys are in very good agreement with the obtained from the extrapolation of these compositions on the curve $H = 344 - 3.10x\%Cr$ (eq. (1)) proposed by Vilar [9], and with the results of other authors [5,10-12].

The addition of 2% Ni to both Fe-Cr alloys with Fe/Cr = 2.7 and Fe/Cr = 1.05 slightly decreases the values of the internal field of such alloys in the quenched condition. Considering the values of the internal field for the Fe-Cr-Ni quenched alloys with a nickel content of 2% and assuming that the internal field of these alloys has a linear composition dependence, as in the case of the Fe-Cr alloys, it is reasonable to accept that the empirical equation $H = 342 - 3.15x\%$ Cr (eq. (2)) holds for the Fe-Cr-Ni ferromagnetic decomposed alloys. However, it should be pointed out that this equation has been constructed using only 2 points, and so, more data will be important to confirm its validity.

For both families of alloys there is an increase of the hyperfine field between the quenched state and 0.5 hr of aging time, which is so much important the higher are the contents of chromium and nickel in the alloys. After 500 hr of
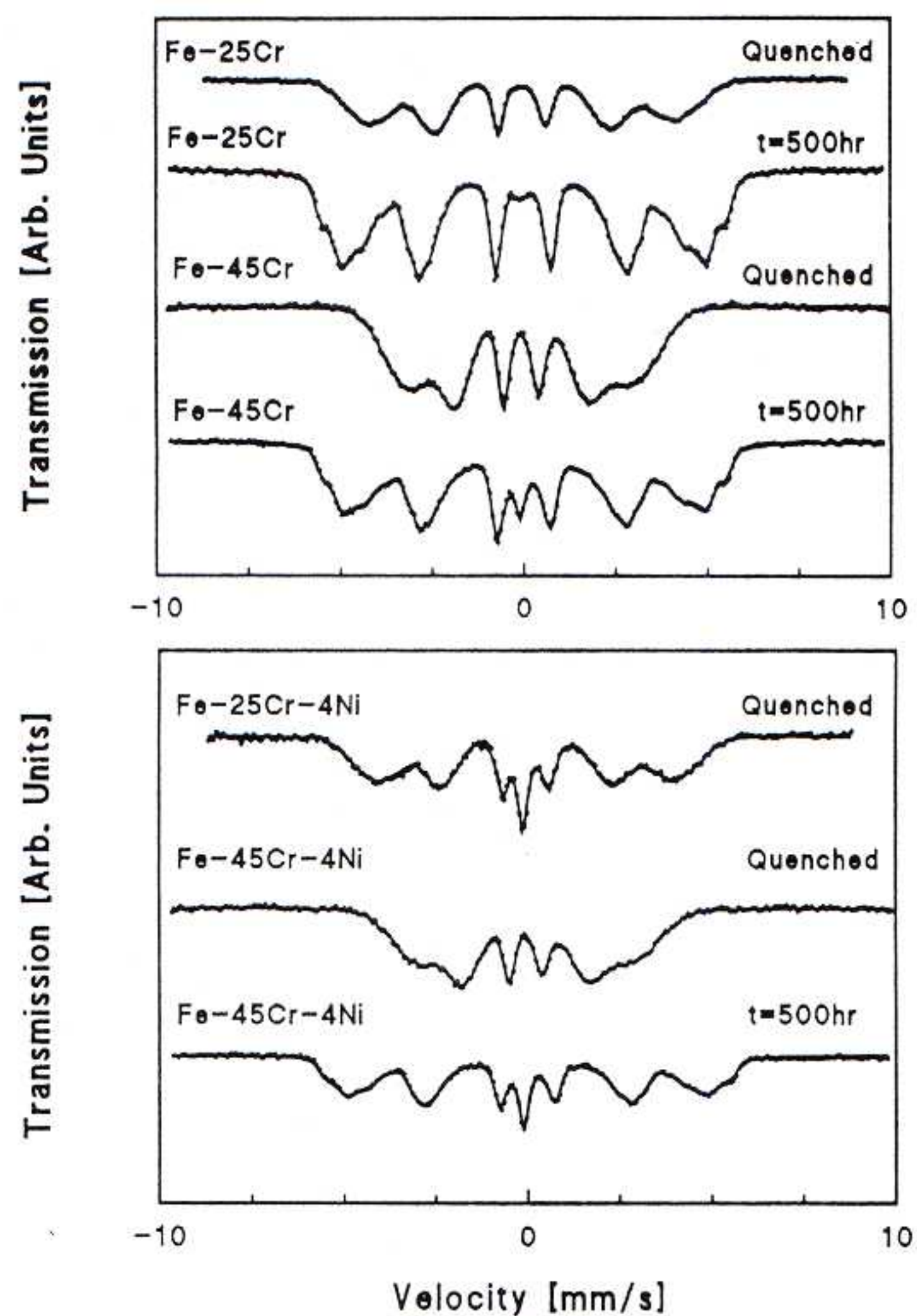
Fig. 2. Mössbauer spectra of some Fe-Cr and Fe-Cr-Ni alloys.

aging, alloys with Ni present more pronounced paramagnetic peaks than those without Ni, corresponding to a later stage of decomposition. This observation is in agreement with the values of chemical composition estimated for the matrices

Table 2
Chromium content in the various 500 hr aged matrices

Alloy	H (kOe)			
	Quenched	0.5 hr	25 hr	500 hr
Fe-25Cr	260	263	280	299
Fe-25Cr-2Ni	258	263	285	301
Fe-45Cr	194	206	255	296
Fe-45Cr-2Ni	191	208	276	298
Fe-45Cr-4Ni	187	218	283	301

Table 3
Hyperfine field of the Fe-Cr and Fe-Cr-Ni alloys

Alloy	H (kOe)	Equation	%Cr
Fe-25Cr	299	(1)	14.5
Fe-25Cr-2Ni	301	(2)	13
Fe-45Cr	296	(1)	15
Fe-45Cr-2Ni	298	(2)	13

of the Fe-Cr-xNi ($x = 0$ and 2%) alloys after 500 hr of aging (table 3), since alloys with Ni present after this period of time, matrices poorer in Cr than those without Ni.

It is known that the decomposition of the Fe-Cr solid solutions causes the appearance of zones with different compositions. Two models have been proposed for the mechanism of the phase decomposition of the Fe-Cr based alloys. In the first one, the decomposition of the initial α solid solution causes nucleation and growth of germs rich in chromium, with the equilibrium composition, dispersed in a chromium-depleted matrix. Hirata and Kirwood [13] showed that if the aging process takes place with a great density of small germs, the matrix must impoverish in chromium, remaining however homogeneous. Thus, in accordance with this model of decomposition the evolution of the $P(H)$ curves during the aging process is characterized by a displacement of these curves to higher values of the hyperfine field without broadening of the $P(H)$ distributions. This is accompanied by the development of a central paramagnetic peak, with $H = 0$ kOe, in the Mössbauer spectra, which amplitude increases during the aging process.

The second model of decomposition is based on the classical spinodal theory [14,15], in which the kinetics of spinodal decomposition is described by a nonlinear diffusion equation. To overcame the impossibility of solving this equation, the linearized equation [14] has been used. According to this equation the structure of an alloy during the aging is described by the overlap of sinusoidal fluctuations of composition. Thus, the evolution of the $P(H)$ curves with aging time is characterized by a more or less constant value of the mean hyperfine field and a very important broadening of the distributions. Moreover, the amplitude of the contribution corresponding to $H = 0$ kOe must be small.

The decomposition mode of the Fe-Cr based alloys has been the subject of several papers. In a recent work, Kuwano [16] claimed that nucleation and growth process play a dominant role in the phase decomposition of Fe-Cr alloys in the concentration range from 21% to 36.3% Cr whilst spinodal decomposition becomes predominant in the concentration range from 42% to 60% Cr. According to this author the decomposition mode show a gradual transition from the nucleation and growth to spinodal decomposition with increasing Cr content, in

disagreement with the spinodal theory in which there is a well-defined spinodal line between the two modes of decomposition. Different results were obtained by Vilar [9]. This author showed that for Fe-Cr alloys with 30% to 45% Cr the early stages of decomposition can not be well described neither by the nucleation and growth model nor by the classical spinodal theory based on the linearized equation of Cahn's model.

In the present work the aging of Fe-Cr alloys with Fe/Cr = 2.7 does not provoke significant broadening of the $P(H)$ curves meaning that they decompose forming precipitates with sharp interfaces with the matrix, by a nucleation and growth like process, in accordance to previous results on the Fe-Cr alloys [9,16]. The aging of the alloys with Fe/Cr = 1.05 is rather different from those with Fe/Cr = 2.7 since it is accompanied by a significant broadening of the $P(H)$ distributions and a progressive increase of the internal field, fig. 3, in particular
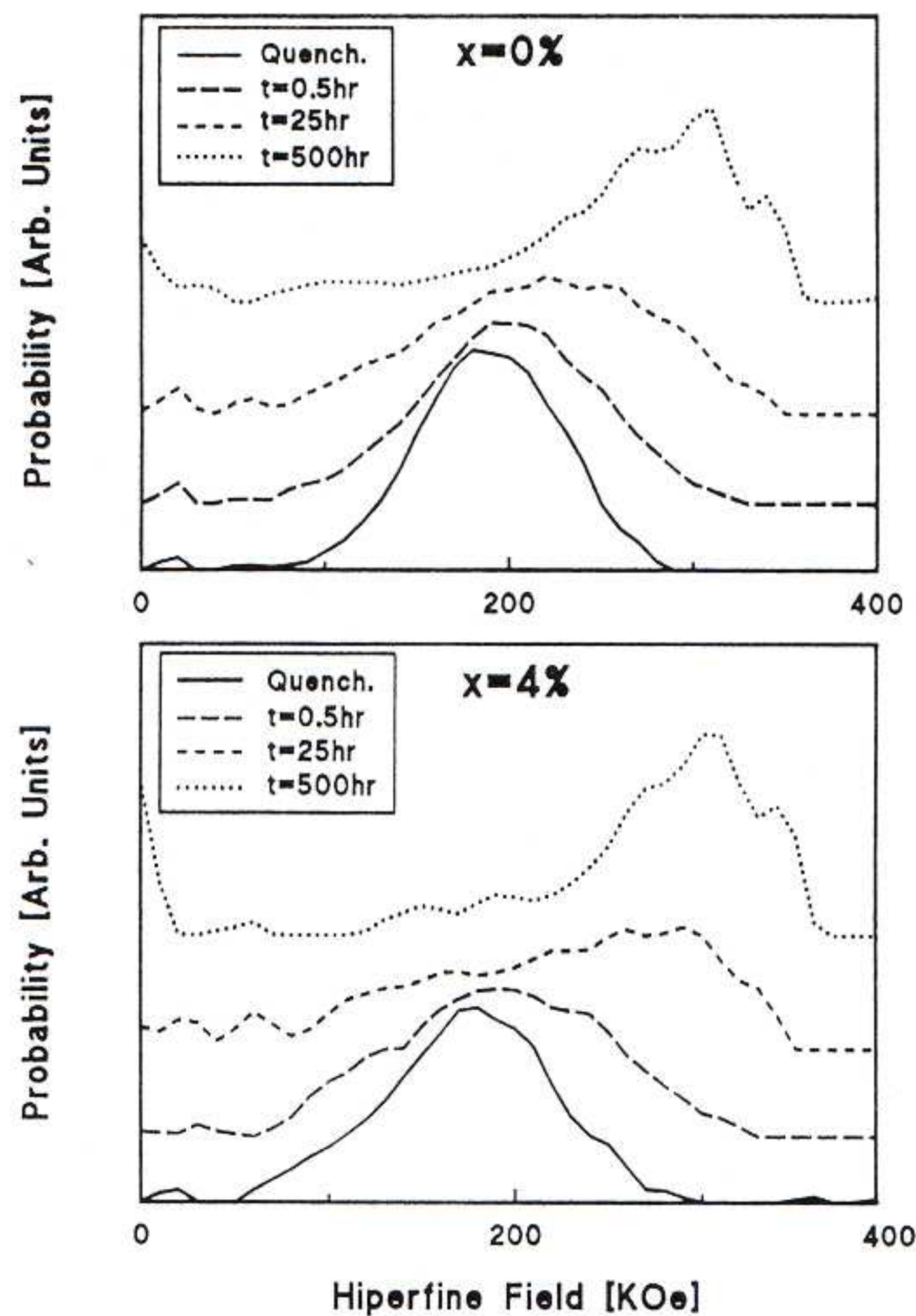

Fig. 3. $P(H)$ curves of the Fe-45Cr-xNi alloys with $x = 0$ and 4 at.% Ni, for various states of aging.

for the first hours of aging. This means that the decomposition of these alloys occurs with deviation from the compositional homogeneity. Moreover, it leads to the conclusion that none of the models, nucleation and growth and classical spinodal decomposition, are able to describe correctly the aging of the Fe-Cr-Ni alloys with Fe/Cr = 1.05, which is in agreement with the results of Vilar [9].

The analysis of the results shows that nickel influences the decomposition of Fe-Cr alloys with Fe/Cr = 2.7 and 1.05, promoting a more rapid rate of decomposition in the first hours of aging. This is clearly seen by the kinetics of transformation of the studied alloys, fig. 4.

There are essentially two ways in which Ni can influence the decomposition process. Firstly, Ni can widen the miscibility gap of Fe-Cr system and thus increase the thermodynamic driving force for phase separation at 475°C [5]. This hypothesis seems to be a probable explanation for the results now obtained since, for the maximum aging time, matrices richer in iron were estimated for alloys with higher chromium and nickel contents. However, aging time higher than 500 hr would be required to confirm this hypothesis. Secondly, since the decomposition rate of ternary alloys is controlled by the interdiffusion coefficient [17], Ni can play an important role on Fe-Cr interdiffusion. To test this hypothesis, diffusivity data of Cr in α-(Fe) and in α-(Fe-Ni) phases would be necessary but unfortunately, at our knowledge, there is no available literature indicating Fe, Cr and Ni diffusivity in the bcc region of the Fe-Cr-Ni system.
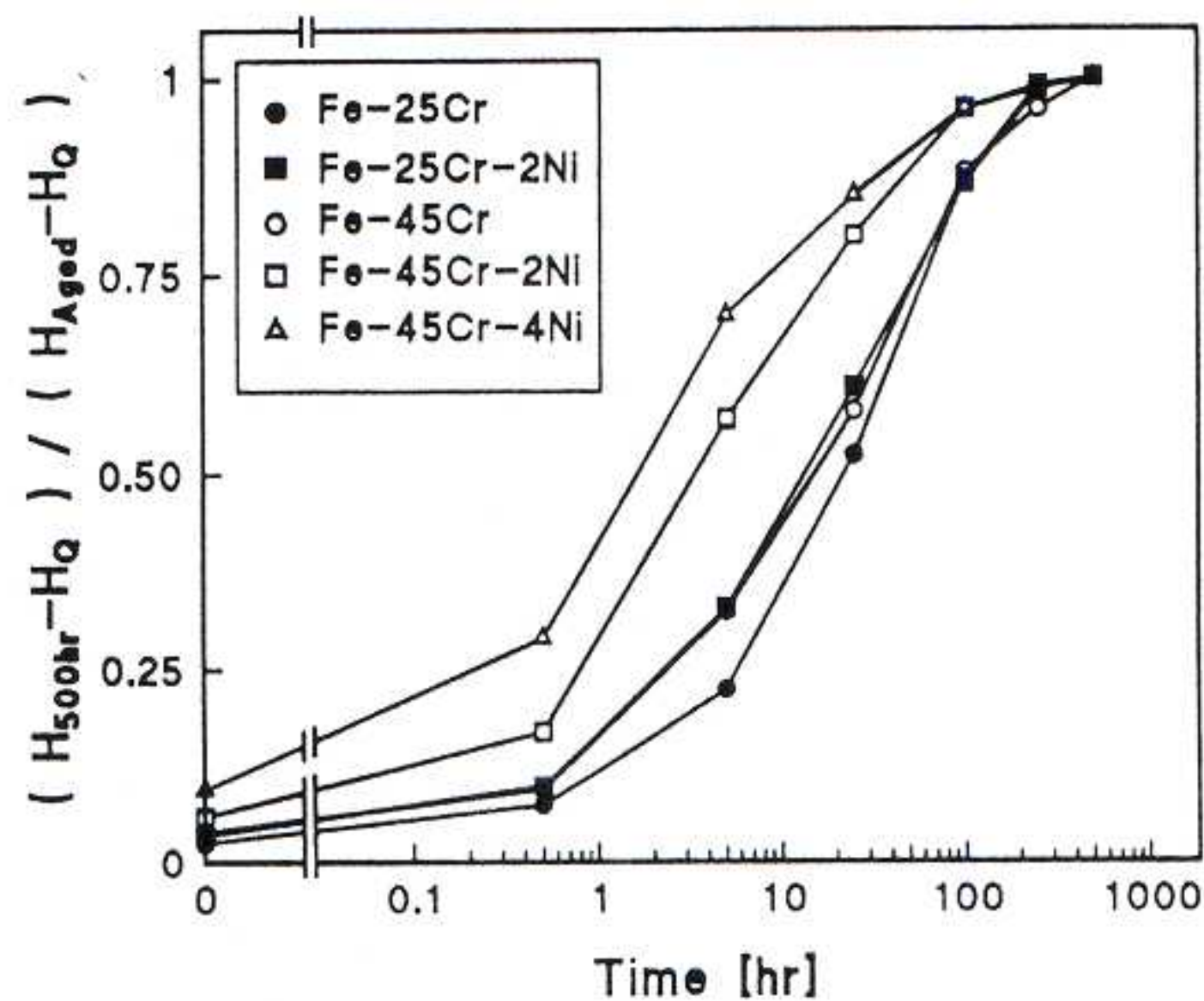

Fig. 4. Kinetics of transformation of the Fe-Cr-Ni alloys.

4. Conclusions

(1) Nickel promotes the decomposition of Fe-Cr alloys at 475°C, the influence of this element being more important for the alloys with $Fe/Cr = 1.05$.

(2) The decomposition of Fe-25Cr-xNi ($x = 0$ and 2%) alloys induces formation of precipitates with sharp interfaces with the matrix, and takes place without an apparent incubation period.

(3) Aging of Fe-45Cr-xNi ($x = 0$, 2 and 4%) alloys begins without an apparent incubation time and develops with a significant broadening of the hyperfine distributions. This means that the decomposition process must occur with compositional fluctuations.

Acknowledgments

References

[1] R.O. Williams and H.W. Paxton, J. Iron Steel Inst. 185 (1957) 358.
[2] D. Chandra and L.H. Schwartz, Metallurg. Trans. 2 (1971) 511.
[3] P. Koutaniemi, V. Heikkinen and A. Saarinen, Met. Sci. 18 (1974) 94.
[4] A. Hendry, Z.F. Mazur and K.H. Jack, Metal. Sci. 23 (1979) 482.
[5] H.D. Solomon and L.M. Levinson, Acta Met. 26 (1978) 429.
[6] J. Hesse and A. Rubartsch, J. Phys. E. Sci. Instrum. 7 (1974) 526.
[7] M.J. Blackburn and J. Nutting, J. Iron Steel Inst. 202 (1964) 610.
[8] R. Lagnerborg, Trans. A.S.M. 60 (1967) 67.
[9] R. Vilar, PhD Thesis, Université de Paris-Sud, Centre d'Orsay, France, 1983.
[10] H. Yamamoto, Jap. J. Appl. Phys. 3 (1964) 745.
[11] R.B. Roy and B. Solly, Scand. J. Metall. 2 (1973) 243.
[12] C.E. Johnson, M.S. Riidout and T.E. Cranshan, Proc. Phys. Soc. 81 (1963) 1079.
[13] T. Hirata and D.H. Kirkwood, Acta Metall. 25 (1977) 1425.
[14] J.W. Cahn, Acta Metall. 9 (1961) 795.
[15] J.W. Cahn, Acta Metall. 14 (1966) 1685.
[16] H. Kuwano, Trans. Jap. Inst. Metals, Vol. 26, 7 (1985) 482.
[17] J.E. Morral and J.W. Cahn, Acta Met. 19 (1971) 1037.