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Study of the spinodal decomposition of an Fe–28Cr–2Mo–4Ni–Nb alloy by small-angle neutron scattering

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Superferritic stainless steels become embrittled when aged in a temperature interval around 475° C. This phenomenon has been studied in the alloy Fe–28Cr–2Mo–4Ni–Nb by measuring the decrease in the energy absorbed in the impact test as a function of ageing time at 475° C. The change which occurs in the microstructure has been studied by small-angle neutron scattering. It is shown that ageing at 475° C produces the decomposition of the alloy in zones rich in chromium via spinodal decomposition. The high rate of embrittlement observed, compared with that which occurs in Fe–Cr binary alloys of similar chromium content, is related to a faster development of the spinodal decomposition in the steel studied.

1. Introduction

Some of the problems associated with the traditional ferritic stainless steels of high chromium content have been overcome during the last decade in the development of the so-called superferritic stainless steels. These are ferritic stainless steels of high chromium content, alloyed with molybdenum and sometimes nickel and with very low interstitial content. They show an increased ductility and a higher pitting and crevice corrosion resistance in sea water than the traditional ferritic stainless steels [1, 2].

However, the superferritic stainless steels become embrittled when exposed in a temperature interval around 475° C, a fact which in the past has received much attention in Fe–Cr alloys [3–5] and which has been very difficult to relate to changes in the microstructure.

Now, it is widely accepted that the 475° C embrittlement is caused, at least in Fe–Cr alloys with enough chromium content, by the decomposition of the ferrite, which can be either by the nucleation and growth of α' precipitates, or via the development of spinodal decomposition in small zones rich in chromium inside the unstable regime of the miscibility gap. The embrittlement which occurs in superferritic stainless steels, as measured by the reduction in the energy absorbed in the impact test, is more severe than in Fe–Cr alloys with similar amounts of chromium. Therefore, it seems that the additional elements present in the superferritic stainless steels affect the velocity of the spinodal decomposition in a way not very well known at present.

The detection of the initial stages of the spinodal decomposition is very difficult using the traditional techniques of electron microscopy and X-ray diffraction. The reason is that the atomic sizes and the X-ray diffraction powers of the iron and chromium atoms are very similar. In the present study, small-angle neutron scattering has been used in order to follow the evolution with time of the phase separation in the superferritic stainless steel Fe–28Cr–2Mo–4Ni–Nb when aged at 475° C. Because the difference in the scattered amplitudes of iron and chromium is rather large for neutron scattering, this technique has a much higher sensitivity than that using X-rays.

Evolution of the embrittlement of the alloy was also studied by measuring the energy absorbed by Charpy specimens in the impact test as a function of the ageing time at 475° C.

2. Experimental procedure

The composition of the alloy studied is given in Table I. The steel was produced by the VOD method. The small amount of niobium is added in order to form carbonitrides so that the amount of interstitial elements in solution is reduced to very low levels. The alloy was kindly supplied by Thyssen Edelstahlwerke AG in the annealed condition in the shape of plates 13 mm thick. The average grain size was 80 μm as measured by the mean linear intercept. At half-depth of the plates, flat grains of much larger size than average were found.

Charpy specimens of 10 mm × 10 mm square section were machined with different orientations with respect to the rolling direction. The orientation is

TABLE I Composition (wt %) of the alloy studied

Cr	Mo	Ni	C	N	P	Mn	Si	Nb	Fe
28.8	2.40	3.88	0.005	0.04	0.019	0.28	0.36	0.43	bal.

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described by a code of two letters: the first indicates the orientation of the normal to the plane of fracture and the second one indicates the direction of crack propagation, where L and T indicate longitudinal and transversal directions, respectively, and S indicates the direction perpendicular to the surface of the plates.

The specimens used for small-angle neutron scattering were machined in 10 mm side square plates and of about 1.5 mm thick which, after exposure at 475° C, were reduced to 1 mm by mechanical polishing to a specular finish.

The neutron scattering experiments were carried out in the D-17 diffractometer at the high-flux reactor of the Institut Laue-Langevin at Grenoble. The neutron wavelength used was 1.2 nm in order to avoid the complications of multiple Bragg scattering. The diffraction patterns were corrected for absorption and detector efficiency and put on absolute scale using the incoherent scattering of water. A 64 × 64 cm^2 (4000 cells) BF_3 multidetector, together with computer facilities to average counting at different $\boldsymbol{q}$ values with the same $|\boldsymbol{q}|$ was used. The data treatment allowed separation of the nuclear and magnetic contributions to the pattern taken with an applied magnetic field. All experiments were made at room temperature.

As the Curie temperature of the steel studied is higher than room temperature, the small-angle neutron scattering spectra of the samples may have a magnetic contribution. Other studies carried out in the Fe–Cr system have claimed proportionality between nuclear and magnetic contributions to the angular averaged diffraction pattern (see, for example, LaSalle and Schwartz [6]). However, it should be noticed that when the samples receive different thermomechanical treatments, the magnetic properties and, therefore, the magnetic contribution to neutron diffraction might have changed. In the present experiments the field produced by an electromagnet was used in order to identify the magnetic contribution.

3. Results and discussion

In the present experiments it was found that for a given sample, the angular averaged diffraction pattern obtained without magnetic field and with a 5 kOe magnetic field (which is sufficient to magnetically saturate the sample) are different (see Fig. 1). However, the patterns are proportional except at low scattering vectors, $\boldsymbol{q}$ ($q \approx 0.005$ nm, where $q = 4\pi \sin\theta/\lambda$), presumably because of the influence of the magnetic domain structure. The patterns associated with only nuclear and with nuclear plus oriented magnetic diffraction show that the angular averaged pattern obtained with applied magnetic field corresponds to the average of the magnetic oriented contribution. But the pattern obtained without magnetic field (Fig. 1) corresponds to an average direction of the sample magnetic moments making an angle different from zero with the plane of the flat specimen, against the magnetic softness of the material. On the other hand, the ratio of the peak height of the nuclear contribution to the peak height of the total averaged contribution (obtained with applied magnetic field) is 0.63(2). This shows that the nuclear and angular averaged diffraction patterns obtained with applied magnetic field are proportional in the range of interest.

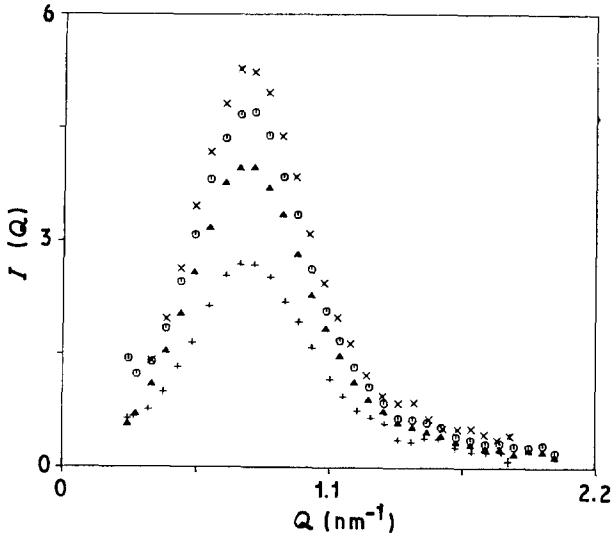

Figure 1 Effect of a 5 kOe magnetic field on the diffraction pattern of the steel aged at 475° C for 50 h. Averaged control: (⊙) with $B = 0$, (▲) with $B = 5$ kOe. (+) Nuclear control, (x) nuclear and magnetic orientation with $B = 5$ kOe.

The phase separation which takes place inside the miscibility gap was studied at 475° C for the following ageing times: 0, 4, 22. 50 and 135 h. The neutron diffraction patterns are shown in Fig. 2. The peak positions, q_m, and the peak heights, I_m, change with time according to the following relationships

$$q_m(t) \propto t^{-a} \quad (1)$$

$$I_m(t) \propto t^{a'} \quad (2)$$

where a and a' were obtained from a least squares fit and are equal to 0.24 and 1.1, respectively. The same values are obtained by considering only the nuclear contribution or the nuclear plus oriented averaged magnetic contribution. These parameters were determined by other authors in an Fe–32Cr alloy and the values reported are between 0.12 and 0.2 for a, and between 0.48 and 1.0 for a'. This indicates that in the steel studied here, the phase separation occurs more rapidly than in the Fe–32Cr alloy. However, it should

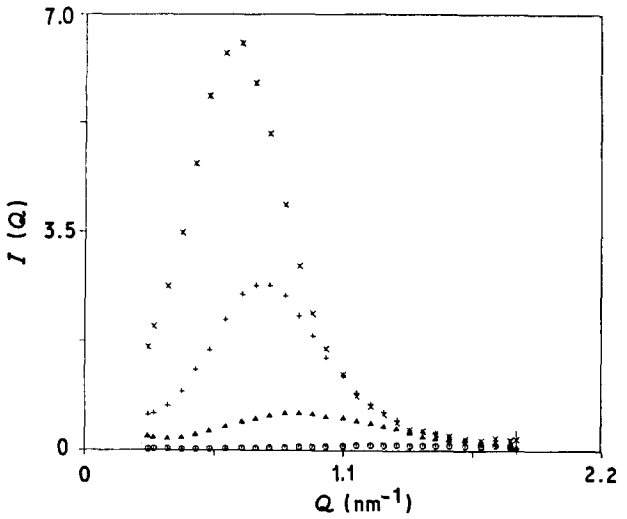

Figure 2 Diffraction patterns of the steel aged at 475° C for (⊙) 4 h, (▲) 22 h, (+) 50 h, (x) 135 h.

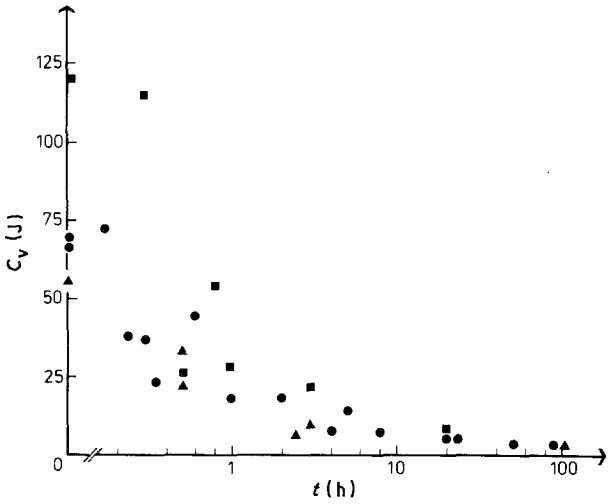

Figure 3 Energy absorbed in the impact test of Charpy specimens in the (●) T–L, (■) L–S and (▲) L–T orientations plotted against ageing time at 475° C.

be noticed that the values mentioned above for a and a' are sensitive to the solution treatment [6], although the origin of this effect is not well understood.

On the other hand, the results of the impact tests of Charpy specimens with different orientations and aged for different times are shown in Fig. 3. It may be noticed that severe embrittlement takes place after very short times of exposure at 475° C and that after about 7 h ageing the energy absorbed drops to a nearly constant value of about 5 J which is independent of the specimen orientation. Fig. 4 shows the fracture surface appearance of Charpy specimens in the unaged condition and after ageing for 20 h. It can be noticed that there is a complete change in the type of fracture from mainly ductile to completely cleavage fracture.

The embrittlement was accompanied by an increase in the yield stress and the presence of deformation by twinning. The alloy studied in the unaged condition also deformed partly by twinning in the temperature interval between 230 and 400° C as reported elsewhere [7]. In order to elucidate whether the appearance of twinning in this temperature interval could be related to the beginning of the spinodal decomposition of the alloy, one specimen was treated at 360° C for 42 h and studied by neutron scattering. The pattern obtained was either "the same", or "very similar" to that corresponding to unaged specimens. Therefore, it seems quite likely that the twinning observed in the above temperature interval is not related to the spinodal decompositon. It should be noticed that high-temperature twinning takes place after very short times of exposure at the test temperature (the time of heating up the specimens and stabilizing the temperature, which was about 1 h in these tests at high temperature).

The embrittlement observed in the steel studied here occurs more rapidly than in other ferritic stainless steels of lower chromium content [8]. This is in agreement with the fact that in Fe–Cr alloys of about 30% Cr content, the rate of embrittlement at 475° C increases with the amount of chromium [9]. Nichol *et al.* [10] have compared the impact behaviour of several ferritic stainless steels and they have shown that the embrittlement in the alloy Fe–26Cr–1Mo occurs much more slowly than in the alloy Fe–29Cr–4Mo–2Ni. In addition, chromium, nickel and molybdenum may have an influence on the embrittlement observed. In fact, by using Mössbauer spectroscopy it has been shown [11] that nickel accelerates the spinodal decomposition in the ferritic phase of a duplex stainless steel. Therefore, the fact that the value of a' for the alloy studied here is higher than the corresponding value for the Fe–32Cr alloys studied by other authors, is in agreement with the higher rate of embrittlement observed.

In the theories of the spinodal decomposition of Hilliard, Cahn and Cook [12–14] and of Langer *et al.* [15], the equation which describes the evolution of the small-angle scattering when the lattice strain energy is neglected (see, for example, [6]) has a solution for $q > |G''/2\Gamma|$ which decays to the Ornstein–Zernicke relationship

$$S(q) = kT/(G'' + 2\Gamma q^2) \quad (3)$$

where G'' is the second derivative of the free energy, $S(q, t)$ is the autocorrelation function which is proportional to the scattered intensity, Γ is the gradient energy coefficient, k is the Boltzmann constant and T is the absolute temperature. It should be noticed that in the derivation of Equation 3 the lattice strain energy is neglected.

Therefore, a plot of $1/S$ against q^2 should give a straight line with a slope equal to $2\Gamma/kT$ and the intercept with the $q = 0$ axis should be equal to

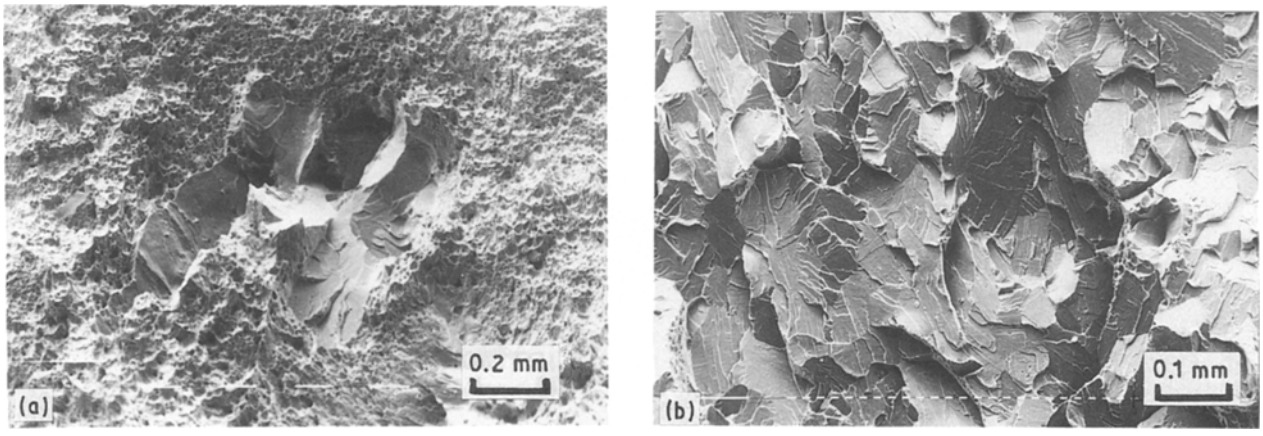

Figure 4 Fracture surfaces of Charpy specimens with an L–T orientation: (a) annealed, (b) aged at 475° C for 20 h.

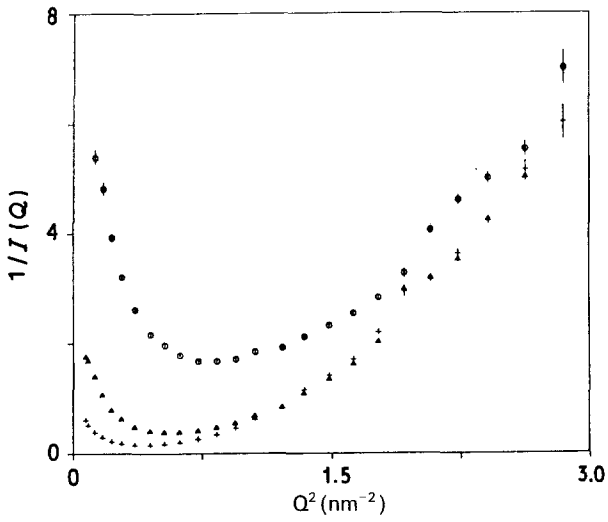

Figure 5 Plot of the inverse of the intensity against q^2 for samples aged for (⊙) 22 h, (▲) 50 h and (+) 135 h, at 475° C.

(G''/kT). This plot is shown in Fig. 5 where it can be seen that a straight line represents reasonably well the behaviour of the alloy at high q. The values obtained for G'' and Γ are -2.0×10^8 erg cm^{-3} and 9.5×10^{-10} erg cm^{-1}, respectively, taking into consideration only the nuclear diffraction. The calculation based in the total contribution is less accurate because the magnetic moments of the atoms in the crystal are not very well known. This may explain the different results obtained by different authors. The value of G'' is much smaller than that found in Fe–32Cr by Nishizawa *et al.* [16] for ageing at 500° C (about 10^{10} erg cm^{-3}), but it is of the same order as the value of -5.0×10^8 erg cm^{-3} estimated by LaSalle and Schwartz [6] in the same alloy.

It should be noticed that the experimental set-up generally used in small-angle neutron scattering does not take into account the magnetic state of the sample. Therefore, the magnetic contribution to the diffraction patterns might be strongly dependent on the sample history, and this can explain the very different values for G'' and Γ found in the literature [6, 16]. However, our values should not be considered to be much better than the existing ones, because of the limitations in the q-range available, due to the presence of the electromagnet close to the multidetector.

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