Conf-901105--65

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DE91 006478

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October, 1990

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MASTER

To be presented at the Materials Research Society Fall Meeting, 11/26-12/1/90, Boston, MA

This work is supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences, under contract No. W-31-109-ENG-38.

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A SMALL ANGLE NEUTRON SCATTERING INVESTIGATION OF THE KINETICS OF PHASE SEPARATION IN AN Fe-27.5 AT.% Cr-5.6 AT.% Ni ALLOY

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ABSTRACT

The small angle neutron scattering has been investigated in situ at 450° and 500°C for a polycrystalline, duplex Fe-27.5 at.% Cr - 5.6 at.% Ni steel. A broad diffuse maximum in the scattering function is the signature of the α'- phase formation, and this maximum is superimposed on a strong, temperature-dependent component due to critical magnetic scattering. The time dependence of the shift in the peak intensity position to lower scattering vectors and the increase in peak intensity obey power law scaling behavior. Furthermore, the structure function exhibits dynamical scaling, after about three hours annealing. It is suggested that this behavior could be utilized to predict the microstructure, and hence some of the properties, after significantly longer annealing times.

INTRODUCTION

Because of the desirable properties imparted by the ferrite phase, cast duplex stainless steels have found wide usage in the nuclear, oil and chemical industries. Among the superior properties are high strength, improved weldability, high resistance to stress corrosion cracking and improved soundness of casting. However, not all effects associated with the presence of ferrite are beneficial. In addition to the major constituents, commercial steels invariably contain a range of minor constituents, and various carbides, sigma, chi and a bcc α'-phase are known to form. The σ-phase forms above about 650°C, the χ-phase in the range from 500 to 650°C and the α'-phase below approximately 500°C, as shown in Fig. 1 from Solomon and Devine [1]. In addition, a silicon containing G-phase forms below about 400°C. The general result is that, after long time aging in the range from about 300 - 500°C, the steels tend to become brittle, particularly with respect to shock loading [2]. The problem of characterizing the evolving microstructure and correlating it with the physical properties is exacerbated by the fact that many of the minor phases appear in minute volume fractions and may also be quite small and, hence, difficult to detect. A recent review of the current state of knowledge for commercial grade steels, has been given by Chung and Leax [3].

Small angle neutron scattering (SANS) permits a bulk measurement of particles with sizes in the range from approximately ten to a few hundred Angstroms. On the other hand, SANS samples the combined scattering from whatever particles are contained in the scattering volume, which for a neutron experiment is typically a few tenths of a cubic centimeter. In the present investigation, high purity starting materials were used as a means of avoiding possible confusion with the silicon containing G-phase and with carbide formation. The specific goal of this research was to investigate in situ at two suitably selected temperatures the kinetics of α'-phase formation in a high-purity, polycrystalline, duplex Fe-Cr-Ni alloy.

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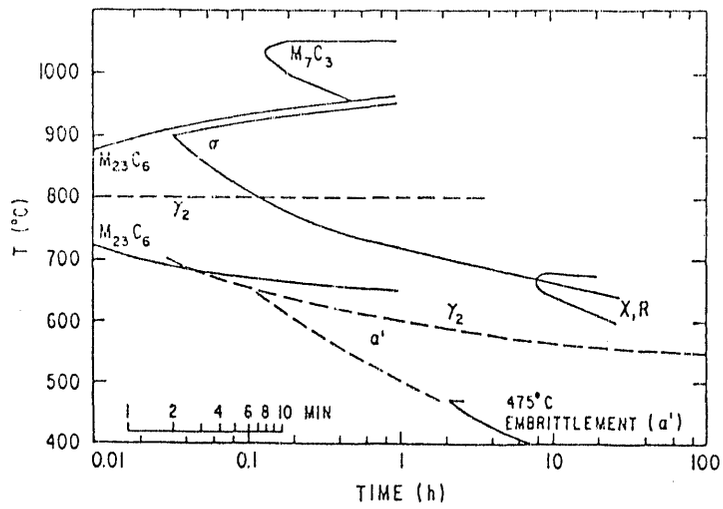

Figure 1
Time-temperature diagram for the formation of various phases at temperatures above 400°C in cast duplex stainless steels, after Solomon and Devine [1].

EXPERIMENTAL

Sample Preparation

An alloy of the composition Fe-27.5 at.% Cr- 5.6 at.% Ni was prepared from high purity starting materials; 99.999% Fe (Metalsmart), 99.996% Cr (Materials Research Corp.) and 99.999% Ni (Johnson Matthey). The constituent metals were melted and thoroughly mixed in an arc furnace equipped with a water-cooled hearth. The homogenized alloy was rolled in steps, with intermediate anneals, to plate stock 1-mm in thickness. Flat coupons 1.9 x 1.9 cm^2 were stamped from this stock.

The platelets were encapsulated in a quartz ampoule, backfilled with just under an atmosphere of helium, and given a homogenization anneal of 144 hrs at 1000°C. The samples were quenched by tossing the ampoule into an ice-brine solution and quickly breaking it, followed by vigorous stirring. In order to remove the oxide film produced in the quenching operation, the platelets were mechanically polished and then chemically etched for a few seconds in a solution consisting of 15 parts (by volume) HCl, 4 parts H_2O_2 (30%) and 10 parts H_2O.

Small Angle Scattering Measurements

The SANS measurements were carried out at the PLUTO reactor at Harwell. The small angle diffractometer [4] was located on a thermal neutron source, and the beam was passed through a cooled Be filter and a helical velocity selector. The velocity selector was set to pass 5Å neutrons in order to extend the momentum transfer range,

$$q = {}^{4\pi}/_{\lambda} \sin\theta, \qquad (1)$$

where λ in the neutron wavelength and θ is half the scattering angle. Collimation was achieved by use of two Cd apertures located 207 and 43 cm, respectively, before the sample. Scattered neutrons were counted by a two-dimensional (64 x 64 cm^2) LETI type detector filled with $^{10}BF_3$ gas and positioned 2.1 meters from the sample.

The sample, consisting of a stack of three of the 1-mm thick homogenized platelets described above, was positioned in a furnace and heated rapidly to the desired temperature. SANS data were collected for the times to be indicated later while the sample was maintained at the selected temperature. The SANS data were normalized to the same monitor count and corrected for empty

furnace background and for dark current. A 1-mm thick ordinary water sample was used as the intensity reference. Formally, the data were corrected as follows:

$$\frac{I_s(q)}{I_w(q)} = \frac{(S/M_s - Cd/M_{Cd}) - T_s(B/M_B - Cd/M_{Cd})}{(W/M_w - Cd/M_{Cd}) - T_w(C/M_C - Cd/M_{Cd})}, \tag{2}$$

where S, B, C, W and Cd refer to sample, sample background, empty quartz cell, water and cadmium blank scattering, respectively, and the M_i are the corresponding incident beam monitor counts. T_S and T_W refer to the transmission coefficients for the sample and water, respectively. These data were then converted to absolute cross sections (cm^{-1}, per unit steradian) by the relationship: [5,6]

$$S(q) = \frac{I_s(q)}{I_w(q)} \frac{1}{t_s T_s} \frac{(1-T_w)}{4\pi} g, \tag{3}$$

where t_S is the sample thickness and g is the inelasticity factor given by Jacrot [7] as

$$g = (1 - \exp(-0.6\sqrt{\lambda}))^{-1}. \tag{4}$$

RESULTS AND DISCUSSION

Composite plots, in ln ($S(q)$) vs ln q format, of the SANS measured at 450° and 500°C are shown in Fig. 2a and Fig. 2b, respectively. The broad diffuse maximum in the SANS profile is the scattering signature of the phase separation; i.e., α'-phase formation, and we shall return presently to it. The lower curve in Fig. 2b was measured for the homogenized sample before the

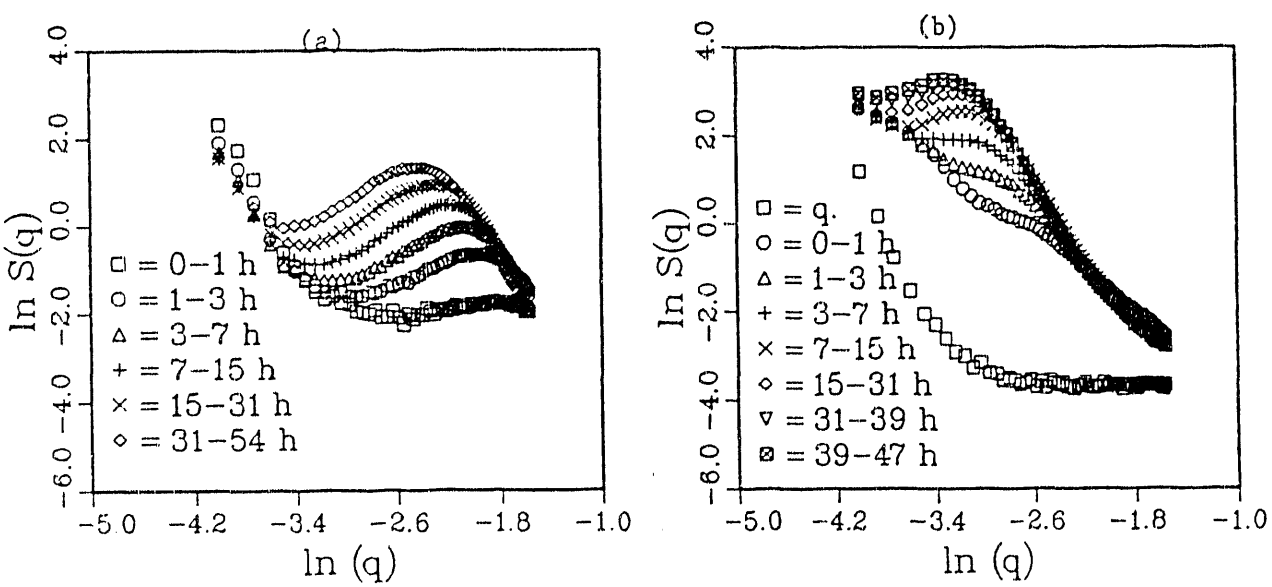

Figure 2
Absolute small angle neutron scattering from in situ measurements from Fe-27.5 at.% Cr-5.6 at.% Ni at: a) 450°C and b) 500°C. The in situ annealing times are indicated in the figures.

furnace was turned on. Similar scattering effects have been observed from high purity Fe-Cr samples [8] which had been fabricated and prepared in a similar manner. The low-q scattering

appears to remain nearly unchanged for the heat treatments investigated, and it is concluded that it doesn't interfere severely with our investigation of the α'- phase kinetics. Because of the purity of the starting materials and their absence in transmission electron micrographs (TEM) of these materials, it would appear as if carbides can be ruled out. Surface scattering effects [9,10] are possible, inasmuch as these samples were etched and not electropolished. Considered to be a more likely origin of this low-q scattering are some needles and platelets of yet unidentified structure and composition which have been observed [11] in a TEM study of an Fe-40 at.% Cr alloy, in the as-quenched and aged conditions.

Notice, also, in Fig. 2 that the diffuse maxima are positioned on a slowly varying scattering component which decreases monotonically with q and is temperature dependent. Based on more extensive investigations of a series of binary Fe-Cr alloys [12], this component of the SANS pattern can be attributed to critical magnetic scattering. The cleanest experimental way to remove the critical scattering component would be to make a short time SANS measurement immediately after reaching the decomposition temperature; i.e., before significant phase separation has taken place. Lacking such an experimental measurement, an effort to remove the critical scattering, along with the low-q component discussed above, was attempted by constructing a monotonically decreasing envelope upon which the phase separation diffuse maximum builds. In this construction, it was possible to use as a guide our experience with the binary Fe-Cr [12], since the scattering effects are similar and the kinetics of decomposition are slower. However, the <u>in situ</u> measurement mentioned above needs to be done.

Various kinetic models for alloy decomposition predict that the position of the diffuse maximum (q_m) and the intensity maximum ($S(q_m)$) should vary exponentially with decomposition time;

$$q_m \alpha t^{-a'} \tag{5}$$

and

$$S(q_m) \alpha t^{a''}. \tag{6}$$

Both relationships are well obeyed for the present system, over the time range investigated and indicated in Fig. 2a and 2b.

For the Fe-Cr-Ni duplex steel, we find (a', a") to be (0.153, 0.758) and (0.137, 0.913) for decomposition at 450° and 500°C, respectively. Chen and Epperson [13] have recently tabulated literature values of a' and a" for a number of systems exhibiting such interference maxima, and a wider range of experimental values was found than one would have expected from the extant theories. The values reported here are well within the range of those tabulated. The slowness of the reaction as indicated by the magnitude of a' is striking. Binder and Stauffer [14] point out that their cluster dynamics model depends on local conditions only and not on an average over the whole system. This may be particularly relevant if one considers the classical mean field concept of phase separation within a miscibility gap [15]. In the gap the coherent spinodal, the locus of points for which the second derivative of the free energy with respect to composition vanishes, separates the unstable region from the metastable regions. In the metastable regions, the system is unstable relative to localized, finite composition amplitude fluctuations, while below the spinodal line, the system is unstable against nonlocalized, infinitesimal composition fluctuations. Classical nucleation and growth takes place within the metastable regions, but the decomposition process is continuous below the spinodal line and may lead to an interconnected microstructure. An incubation period is associated with the former, but not the latter mode. Note, also, that for a given alloy the mode of decomposition is dependent on the decomposition temperature, relative to

the spinodal. Only systems with an infinite range of interaction will have this well behaved spinodal which separates the metastable and unstable regions [16,17]. Unfortunately, the range of interaction is presently not well understood. Grant, et al. [17] have shown theoretically that a first order perturbative correction substantially slows down spinodal decomposition, relative to that predicted by the Cahn-Hilliard-Cook theory [15,18].

The structure function is a fundamental measure of the nonequilibrium microstructure, and several dynamical theories [16] have attempted to treat the scaling as the system relaxes toward equilibrium. The basic idea is that, after some initial transient period, a time-dependent length scale is established which characterizes the system, i.e., the size of the ordered regions. Various choices of the length scale to use have been proposed. For example, Marro, Lebowitz and Kalos [19] (MLK) used the first moment of the scattering function,

$$q_1(t) = \sum_i q_i(t) S(q_i) / \sum_i S(q_i), \tag{7}$$

whereas Furukawa [20] used the reciprocal of the position of the peak in the scattering function, q_m^{-1}. According to the MLK hypothesis, the function

$$F(q / q_1, t) = q_1^3(t) S(q,t) / \sum_i q_i^2 S(q_i, t_i) \tag{8}$$

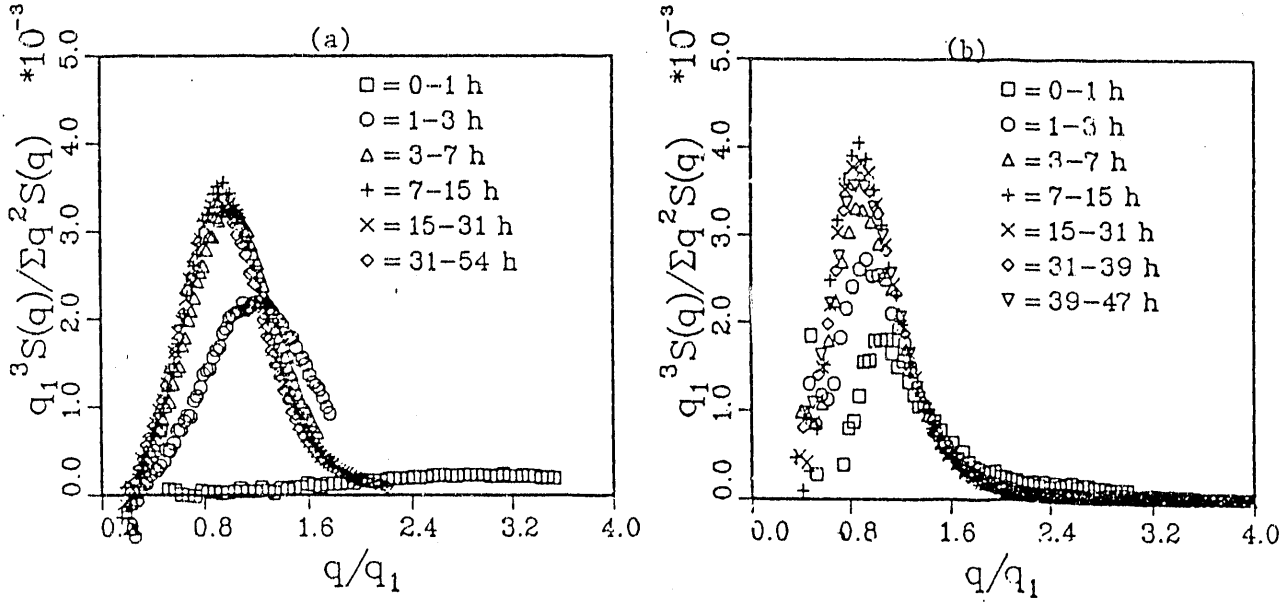

Figure 3
Test of the SANS data for Marro type dynamical scaling; a) 450°C, b) 500°C. The in situ annealing times are indicated in the figures.

should be independent of time. Figures 3a and 3b present this function for the Fe-Cr-Ni steel for 450° and 500°C aging, respectively. After approximately three hours aging at each of these temperatures, nearly time-independent MLK-type scaling of the structure function is observed. Given the approximate manner in which the scattering data were corrected for critical magnetic scattering, it would be unreasonable to expect a more constant result. Of course, dynamical scaling was not observed when the SANS data were not corrected for critical magnetic scattering. Forouhi [21] has correlated a change in microstructural morphology with a change in scaling behavior for an Al-Mg-Zn alloy; however, not enough such correlations have been carried out to

permit a general statement. An obvious possibility is that the transition period, such as seen for this steel, may be associated with the nucleation/growth stage, as opposed to coarsening or ripening, or with the interval in spinodal decomposition before discrete particles are discernible. More time resolved SANS measurements supplemented by higher resolution techniques, such as TEM or field ion microscopy, would be useful to elucidate this problem.

CONCLUSIONS

It has been shown that the kinetics of α'-phase formation in the duplex Fe-27.5 at.% Cr - 5.6 at.% Ni steel obey various scaling laws. Furthermore, the structure function exhibits dynamical scaling, after approximately three hours annealing. The implication is that, under carefully controlled conditions, these relationships may have utility in predicting the microstructure, and hence the mechanical properties, in a decomposing alloy after significantly longer aging times.

ACKNOWLEDGEMENTS

This work was sponsored by the U. S. Department of Energy, Basic Energy Sciences, Materials Science, under contract No. W-31-109-ENG-38.

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