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Study of equilibrium and non-equilibrium intergranular segregations of sulphur in nickel by high resolution microprints and electrochemical testing

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Two non-destructive tests are used to characterize the intergranular segregation of sulphur in polycrystalline nickel. According to the thermal treatment, two mechanisms can be considered: (a) After quenching and tempering an equilibrium mechanism applies. Using the McLean model, the intergranular segregation energy of sulphur in nickel was estimated and a value of $-98\,\mathrm{kJ\,mol^{-1}}$ obtained. (b) A non-equilibrium mechanism explains the results obtained after recrystallization treatments.

1. Introduction

The ability of sulphur to segregate on several different sites in polycrystalline nickel (dislocations, grain boundaries, surfaces) is a well-known phenomenon since it manifests itself both in changes in the mechanical properties and in the resistance to corrosion of the material [1–11]. Nevertheless, only surface segregations or embrittling intergranular segregations can be directly analysed by Auger electron spectrometry (AES).

We have recently demonstrated [12] that the intergranular surfaces of samples which do not exhibit intergranular failure in a conventional mechanical test may be exposed for subsequent AES analysis by utilizing a hydrogen-assisted cracking mechanism. It was shown [12] that the presence of hydrogen does not modify the nature or quantity of the elements segregated at the grain boundaries.

In this paper, the results obtained using two other complementary methods are described, both of which allowed rapid detection, on a material surface, of the presence or absence of intergranular sulphur segregation.

The first technique, described in detail by Beaunier and Froment [13, 14], consists of a potentiostatic etch carried out in 2N H_2SO_4 in the transpassive zone. After a transition period, the dihedral angle at the grain boundaries thus exposed is independent of the attack time [13, 14]. The angle is a function only of the crystallographic characteristics of the boundary and its chemical composition. It has been established that, for a given alloy, the most acute angles in the equilibrium profile are observed in alloys with the greatest intergranular segregation. This correlation is accepted in the case of Si intergranular segregations in nickel–silicon alloys [15, 16].

Preliminary tests conducted on samples of commercial nickel tempered at 625° C showed that a tempering time of 1 to 5 days was sufficient for the sulphur segregation to promote intergranular embrittlement and the correlation between etch groove topography and segregation was shown [5].

The second technique used identifies more specifically sulphur, or any sulphur compound giving off H_2S gas in the presence of acid. This method [17, 18] incorporates the specificity of the Baumann reaction (formerly used for the detection of sulphide microprecipitates) with the increased resolution offered by modern autoradiographic techniques. Since silver sulphide, Ag_2S, forms on

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the sites laden with sulphur, it is possible to locate sulphur on the solid surface studied. The "map" of the distribution of sulphur in the material which is thus obtained is easily explored with a scanning electron microscope equipped with an X-ray spectrometer. For example, in the case of sulphur intergranular segregation, and in the absence of all sulphur compounds, the sulphur segregated is indirectly detected when the Ag_2S precipitates are observed on grain boundaries of the technical nickel [19].

The results obtained using these two methods were compared with those obtained by AES for a commercial nickel sample containing 20 ppm of sulphur. Using the results, an attempt was made to improve our comprehension of the various mechanisms of sulphur intergranular segregations, since the many causes of sulphur intergranular segregation cannot be described by a single mechanism of equilibrium segregation, such as was proposed by McLean [20].

2. Materials

The five grades labelled 1 to 5 which were used contained from 99.3 to 99.98 wt % nickel.

Grade 1 (99.3 wt % Ni) served as the reference, in the form of an ingot of analytical-grade nickel analysed in a laboratory of IRSID. This grade was chosen because its composition is similar to that used by Wache [6–9] and Henry *et al.* [21] and also because its purity is comparable with that most commonly used by industry (INCO nickel 200).

The commercial Grade 2 (57 ppm of sulphur) is available in the form of bars and Grade 3 (7 ppm of sulphur) is sold as sheet metal.

Finally, two high-purity grades were used in order to determine, among other things, the role of third elements: the first was obtained from Johnson-Matthey (Grade 4) in the form of sheet metal; the second, the INCO 270 nickel quality (Grade 5), was procured in the form of sheet metal.

Analytical tests were carried out on these materials in order to detect the presence and quantity of more than forty elements. The amounts of the principal impurities, which were determined by several methods, such as spark mass spectrometry, optical emission spectrometry, atomic absorption spectrometry, are outlined in Table I.

3. Experimental techniques

3.1. Sample preparation

The nickel samples studied were either in the form of small cylinders of 10 mm of diameter or in the form of sheet metal 1 mm thick. The samples were annealed either in sealed quartz capsules or in pure nickel crucible filled with corundum (compare with Section 3.2.) under a dynamic primary vacuum. After annealing all observations were carried out only after removing approximately 0.1 mm of the surface, in order to avoid taking into account phenomena due to surface effects. The surfaces were then mechanically polished with a 1 μm diamond paste.

3.2. Heat treatments

Two types of thermal treatments were carried out:

(a) annealing of homogeneous samples which causes intergranular segregation controlled by an equilibrium kinetics; and

(b) short primary recrystallization annealings

TABLE I Materials used and their principal impurities

Grade	Purity	Origin (form)	Impurity content (ppm)										
			S	C	Si	Ca	Mg	Mn	Co	Al	Ti	Mo	Fe
1	99.3	IRSID (Ingot)	20	600	250	80	12	15	No data	1000	1500	1000	1000
2	99.4	INCO Nickel 200 (Bar)	57	740	450	20	500	1500	600	150	400	8	800
3	99.6	INCO Nickel 200 (sheet)	7	600	250	50	350	1600	300	200	30	0.5	550
4	99.98	Johnson Matthey (sheet)	1	60	5	1	6	$\leqslant 0.1$	$\leqslant 10$	1	$\leqslant 0.1$	$\leqslant 0.2$	10
5	99.98	INCO Nickel 270 (sheet)	$\leqslant 5$	70	0.5	1	1	20	$\leqslant 10$	1	0.3	$\leqslant 0.2$	30

which did not enable determination if a single mechanism gave rise to the phenomena observed.

3.2.1. Tempering and annealing treatments to obtain equilibrium segregation behaviour

The trials were carried out on nickel Grade 1 (99.3%) and Grade 2 (99.4%) whose analysis (Table I) shows that the two grades are practically equivalent.

(1) In order to achieve homogenization, Grade 1 nickel was annealed in a quartz capsule (at 10^{-3} Pa) at 1150° C for 4 h followed by quenching in water. Several samples of this nickel were isothermally-annealed at 625° C for periods ranging from 1 h to 13 days. This temperature was chosen on the basis of the date provided by Henry *et al.* [20] and by [12].

(2) Grade 2 nickel, the grade richest in sulphur, was submitted to a homogenization annealing under dynamic vacuum (at 10^{-1} Pa) at 1200° C for 24 h followed by quenching in water. A series of Grade 2 nickel samples were submitted to isochromous annealing for 4 days at temperatures varying from 400 to 1000° C. Previous studies [12] showed that the greatest amount of embrittling segregation was produced on tempering for 4 days at temperatures in the range 600 to 700° C.

3.2.2. Recrystallization thermal treatments producing non-equilibrium segregation

These tests were carried out on nickel of Grades 3, 4 and 5 in the form of 1 mm thick sheets cold-worked by a mechanical shaping treatment (cold-rolling). The different alloys were maintained at various temperatures for 4 h and thus the minimum temperature required for primary recrystallization of the metal was determined for each of the three nickel grades by a number of thermal treatments followed by an optical metallographic examination and a measure of the hardness.

The annealing of Grades 3, 4 and 5 for primary recrystallization were carried out at 800° C, 600° C and 400° C, respectively, for 4 h under a dynamic vacuum (of 10^{-1} Pa).

3.3. Operating conditions

3.3.1. Electrochemical test

The electrochemical etchings were carried out in 2N sulphuric acid at 20° C at a potential corresponding to the position energy value of the transpassive peak. The current intensity used at this potential is equal to three-quarters of the peak maximal intensity. For example, for Grade 1 nickel, the etching potential was 1500 mV and the etching time was chosen such that 15 coulombs crossed every square-centimetre of the metal. The conditions were chosen such that a constant potential was maintained, thus promoting reproducible etching. After etching the appearance of the intergranular grooves obtained was examined with a scanning electron microscope.

3.3.2. High-resolution sulphur microprint of Baumann microprint

The surfaces on which the Baumann microprints were made were first lightly electrochemically-etched in order to facilitate subsequent characterization with a scanning electron microscope. This etching was devised to create intergranular grooves whose width did not exceed 0.1 μm. The experimental conditions of the test, as conceived in our laboratory, have already been described in a detailed manner [19].

4. Results

After electrochemical etching the grain boundaries have different aspects depending on the thermal treatments to which they were submitted.

4.1. Nickel homogenized at high temperature : Treatment 1 (see Section 3.2.1.)

4.1.1. Influence of annealing time in isothermal conditions at 625° C

In the series of pictures of nickels tempered at 625° C (see Fig. 1a to c), different aspects of the grain boundaries created by electrochemical etching were observed. The samples, having been submitted to 4 days of annealing, have deep intergranular grooves, while those exposed to longer (8 days) or shorter periods (6 h) have very open "V"-profiles.

Baumann micro-imprints were formed on samples tempered for 6 h, 4 days and 8 days. Characterization by scanning electron microscopy revealed an alignment of silver sulphide, Ag_2S, precipitates on the grain boundaries of the nickel tempered for 4 days (Fig. 1d). No alignment of Ag_2S grains is observed on the samples annealed for 6 h and 8 days.

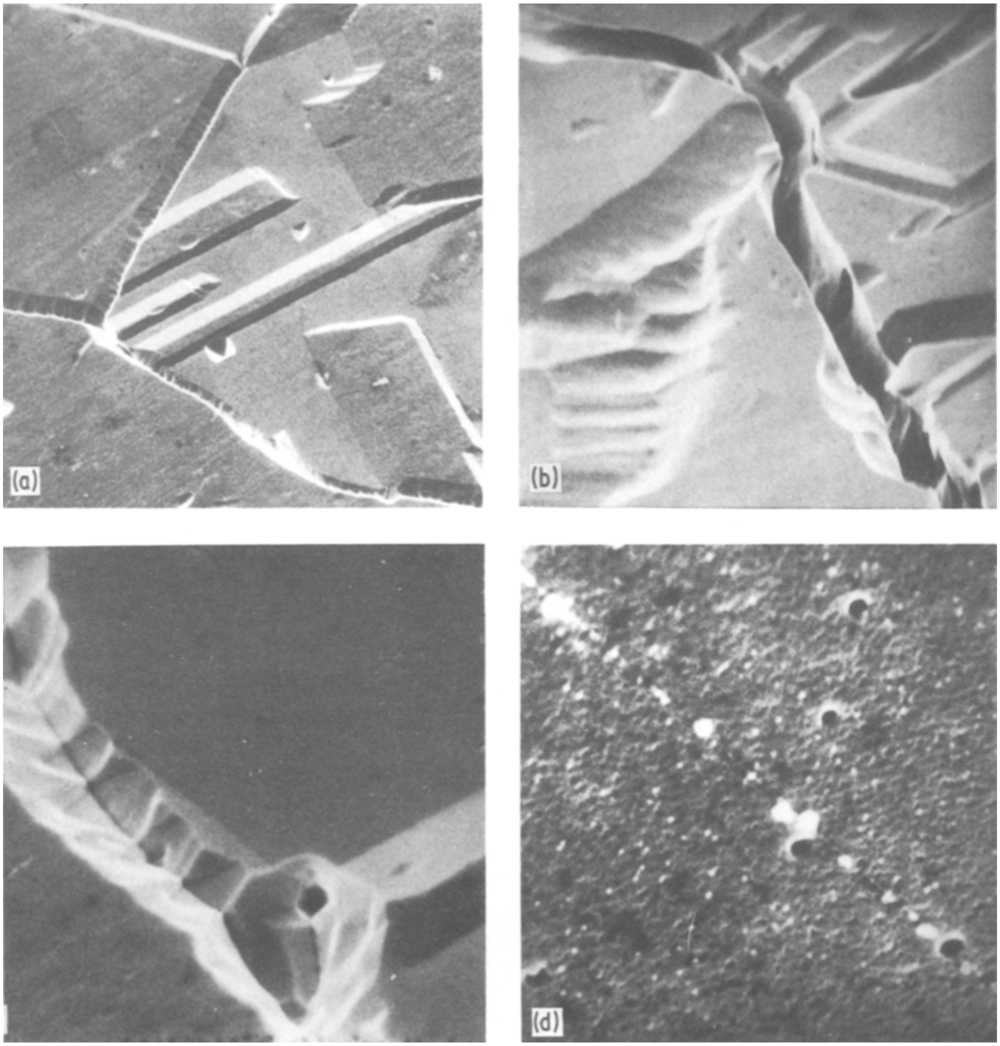

Figure 1 SEM images of electrochemical test and Baumann microprints observed on Grade 1 nickel (99.3% pure) following tempering times at 625° C (equilibrium segregation). (a) 6 hours, X 500; (b) 4 days, X 740; (c) 8 days, X 2420; (d) 4 days, X 6800.

4.1.2. Influence of the anneal temperature: Treatment 2 (see Section 3.2.1.)

The series of pictures taken of Grade 2 nickel after 4 h of annealing are represented in Fig. 2. The photographs illustrate the variety of grain-boundary morphologies observed, depending on the annealing temperature. Thus, deep grooves are observed for temperatures of 600 and 700° C. The Baumann micro-imprints made on these Grade 2 samples reveal the presence of sulphur in the grain boundaries. This test is negative for the samples annealed at 500 and 800° C.

4.2. Annealing of cold-worked nickel (treatment as described in Section 3.2.2.)

The recrystallization anneals already described were carried out on nickels of Grades 3, 4 and 5. Under these conditions, after electrochemical etching, deep grain boundaries are observed and the Baumann microprint reveals the presence of intergranular sulphur.

When the annealing treatments were carried out at 800° C, for the same period of 4 h, these results were not obtained for Grades 4 and 5. On the other hand, nickel of Grade 3 continued to demonstrate

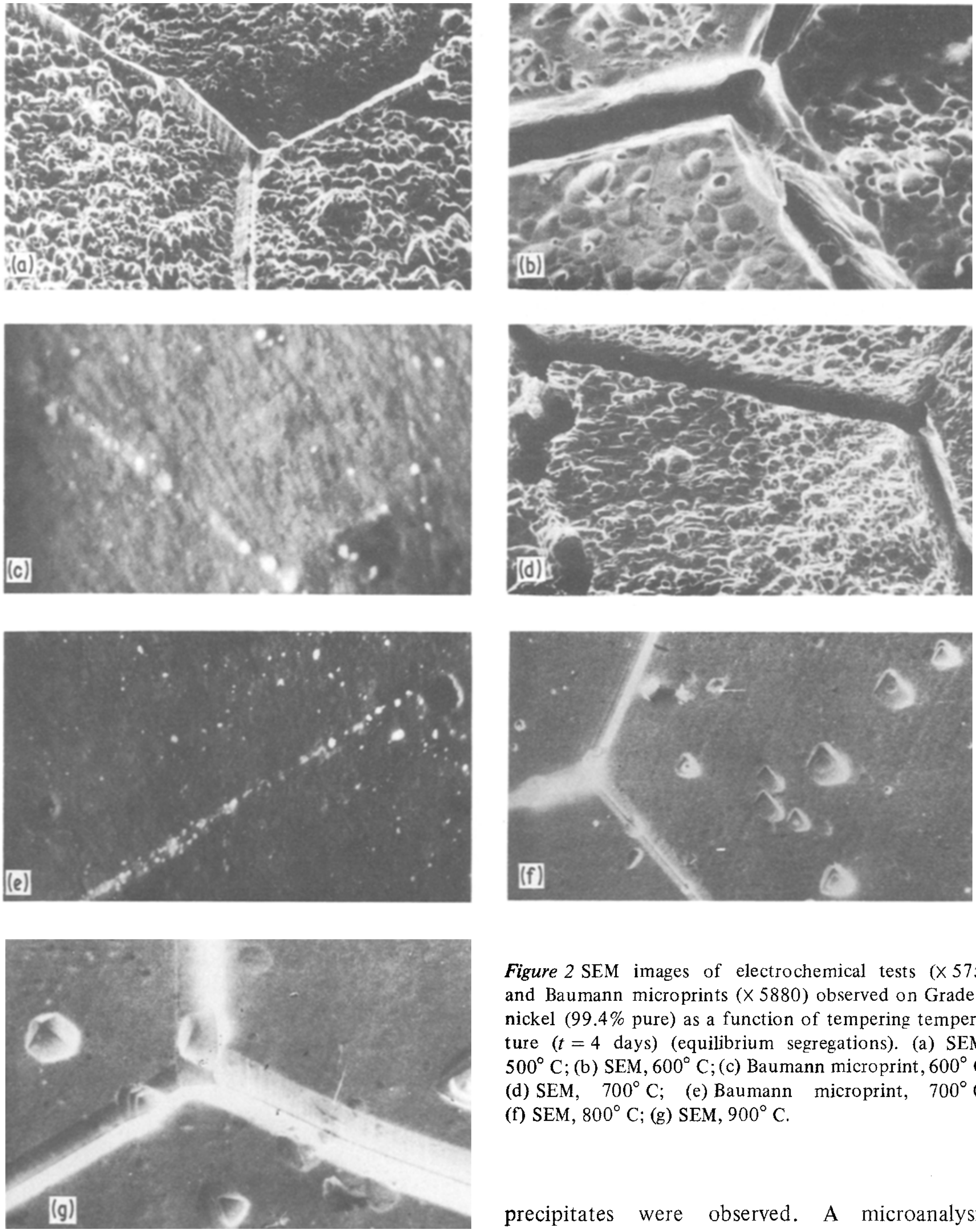

Figure 2 SEM images of electrochemical tests (X 575) and Baumann microprints (X 5880) observed on Grade 2 nickel (99.4% pure) as a function of tempering temperature ($t = 4$ days) (equilibrium segregations). (a) SEM, 500° C; (b) SEM, 600° C; (c) Baumann microprint, 600° C; (d) SEM, 700° C; (e) Baumann microprint, 700° C; (f) SEM, 800° C; (g) SEM, 900° C.

a very high intergranular activity. This activity manifested itself in the appearance of deep grooves, when the potential was maintained in sulphuric acid and in a positive reaction to the Baumann test.

When the sample was submitted to weaker etching in the range of the first activity of nickel in sulphuric acid, a great number of intergranular precipitates were observed. A microanalysis revealed that they contained sulphur, calcium, silicon and aluminium (see Fig. 3).

5. Interpretation

The preceding results cannot be accounted for by any single mechanism based only on diffusion. For example, such an explanation cannot explain why the intergranular segregation is most rapid at the lowest temperature in the purest nickel grade.

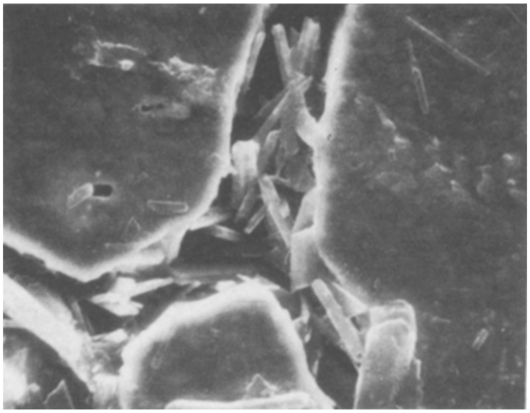

Figure 3 Intergranular precipitations (S, Ca, Si, Al) in Grade 3 nickel (99.6% pure) obtained after a prolonged annealing at 800° C (SEM image × 1110).

Thus, a commercial-grade nickel sample (Grade 1) reaches its maximum intergranular segregation state after having been maintained at 625° C for 40 h and a nickel sample of higher purity (Grade 4) reaches this maximum after being maintained at 600° C for only 4 h.

It is proposed, therefore, that two mechanisms play a role: one leading to an equilibrium segregation, as described by McLean [20] and the other leading to a non-equilibrium segregation mechanism [which we shall study using the results obtained for the reference nickel (Grade 1)].

5.1. Equilibrium segregation

5.1.1. *Experimental results obtained for the reference grade: Grade 1 nickel and correlation with AES results [5, 12]*

For the annealing times of 2 to 5 days, this maximum segregation manifested itself by (see Section 4.1. and Fig. 1):

(a) a maximum sensitivity to electrochemical etching leading to the formation of very deep intergranular grooves;

(b) a positive Baumann microprint; and

(c) appearance of a maximum in the intergranular embrittlement (fracture stress 0.2% proof stress) [12].

The results are close to those obtained by Wache [6–9] who reported a maximum loss in ductility for a similar tempering carried out for nickel. Complementary analysis by AES was carried out on intergranular fracture surfaces in collaboration with Larere *et al.* [5, 12]. The average value of the S to Ni Auger peak-height ratio, h_{S152}/h_{Ni848}, reaches a value of 0.55 which corresponds to the half of the maximum segregation at a free surface.

The maximum intergranular concentration of segregated sulphur was determined to be 45% for identical annealings at 625° C (2 days $<$ time of annealing $<$ 5 days).

It was deduced that, for the tempering times studied (2 to 5 days), the measured content of sulphur at saturation is equal to values deduced from the work of Perdereau [22] on chemisorbed sulphur layers. Complementary works [23, 24] showed that an adsorbed two-dimensional compound (Ni–S) was formed on the surface for this same sulphur concentration. We also postulate that the sulphur was present in the form of a two-dimensional compound, Ni–S, and was located in the boundary plane. This supposition is consistent with the suggestion proposed by Guttmann [25]. The compound was probably similar to the one obtained on the free surface either by segregation or by adsorption [5]. The presence of such a two-dimensional sulphide is supposed to be the condition required for preferential etching of the boundary during the electrochemical test and the Baumann microprint.

For tempering times less than 2 days, on fracture surfaces embrittled by hydrogen, the intergranular concentration of segregated sulphur, C_S^{GB}, increases proportionately with the square-root of time [12], thus justifying the kinetic model of McLean [26].

The value of the bulk diffusion coefficient, D, of sulphur in nickel at 625° C was determined as $4.8 \times 10^{-13}\ \mathrm{cm^2\ sec^{-1}}$. This value is between that obtained at 625° C by Vladmirov [27] ($D = 1.6 \times 10^{-13}\ \mathrm{cm^2\ sec^{-1}}$) and by Wang and Grabke [28] ($D = 1.3 \times 10^{-12}\ \mathrm{cm^2\ sec^{-1}}$).

The annealing of Grade 1 nickel, carried out under isothermal conditions at 625° C, revealed two successive stages:

(1) first, a stage during which the intergranular sulphur concentration increased with time to a maximum corresponding to the maximum embrittlement [12];

(2) then, for tempering periods greater than 5 days, the sulphur segregation disappears, being replaced by an intergranular precipitation of nickel sulphide enriched in aluminium [12], characterized by the lack of boundary sensitivity to the electrochemical test (see Section 4.1. and Fig. 1) and the

disappearance of Ag_2S grain alignment to the formation of clusters localized on the grain boundaries [19].

These results are in agreement with other observations of the disappearance of the intergranular embrittlement [12].

5.1.2. Thermodynamic aspect and estimate of the total energy of the sulphur segregation in the grain boundaries (Grade 2 nickel)

The kinetic results obtained for the reference grade (Grade 1 nickel) show that the thermodynamic model of McLean applies [20]. This model enables calculation of the intergranular concentration of the solute, Y_X^{GB}, at thermodynamic equilibrium. The entropy term is negligible and the McLean equation can then be written

$$Y_X^{\mathrm{GB}} = \frac{C_X^{\mathrm{b}} \exp\left[(-\Delta G_X^{\mathrm{GB}})/(RT)\right]}{1 + C_X^{\mathrm{b}} \exp\left[(-\Delta G_X^{\mathrm{GB}})/(RT)\right]}, \quad (1)$$

where R is the gas constant and T is the absolute temperature. Y_X^{GB} is actually the ratio of the number of solute atoms in the boundary to the number of sites "favorably" distorted such that

$$Y_X^{\mathrm{GB}} = \frac{C_X^{\mathrm{GB}}}{C_{X(\max)}^{\mathrm{GB}}}, \quad (2)$$

where $C_{X(\max)}^{\mathrm{GB}}$ was determined by Auger analysis on the fracture surfaces obtained *in situ* [5] so that $C_{X(\max)}^{\mathrm{GB}} = 0.44$, and C_X^{b} is the bulk concentration of solute X and ΔG_X^{GB} is the segregation energy of solute X. At the boundary, $\Delta G_X^{\mathrm{GB}} < 0$ and can then be expressed as

$$\Delta G_X^{\mathrm{GB}} = RT \ln C_X^{\mathrm{b}} \left(\frac{1 - Y_X^{\mathrm{GB}}}{Y_X^{\mathrm{GB}}}\right). \quad (3)$$

To determine ΔG_X^{GB}, it suffices to know the evolution of the segregation decrease with temperature (compare with Equation 3). The experimental results obtained by electrochemical test, in keeping with those of the Baumann microprint (see Fig. 2) for Grade 2 nickel (99.4%), only show that the intergranular sulphur segregation was greatest at temperatures between 600 and 700° C.

In the absence of accurate data on sulphur segregation at 700° C, it was assumed that it was equal to 95% of the absolute saturation value. This allowed us to determine the lower bound of $\Delta G_{\mathrm{S}}^{\mathrm{GB}}$, in a similar manner to Dumoulin and Guttmann for Fe–Sb and Fe–Mo alloys [29].

For the following conditions: $T = 973$ K, $C_{\mathrm{S}}^{\mathrm{b}} = 104.10^{-4}$ (At) and $Y_X^{\mathrm{GB}} = 0.95$ we obtain $\Delta G_{\mathrm{S}}^{\mathrm{GB}} = -98 \text{ kJ mol}^{-1}$.

We suppose that the segregation energy is nearly equal to the heat of segregation: $\Delta G_{\mathrm{S}}^{\mathrm{GB}} \simeq \Delta H_{\mathrm{S}}^{\mathrm{GB}}$. Then, the absolute value of $\Delta H_{\mathrm{S}}^{\mathrm{GB}}$ is equal to twice the absolute value of the dissolution enthalpy, $\Delta H_{\mathrm{S}}^{\mathrm{diss}}$, of sulphur in nickel at 700° C ($\Delta H_{\mathrm{S}}^{\mathrm{diss}} = -49 \text{ kJ mol}^{-1}$) [30]. This value should be compared with that obtained for copper $\Delta G_{\mathrm{S(Cu)}}^{\mathrm{GB}} = -65 \text{ kJ mol}^{-1}$ [31] and $\Delta H_{\mathrm{S(Cu)}}^{\mathrm{diss}} = -31 \text{ kJ mol}^{-1}$ [32]. Thus, for these two metals $\Delta H_{\mathrm{S}}^{\mathrm{GB}} \simeq 2\Delta H_{\mathrm{S}}^{\mathrm{diss}}$. Furthermore, $\Delta G_{\mathrm{S(Ni)}}^{\mathrm{GB}} < \Delta G_{\mathrm{S(Ni)}}^{\mathrm{surf}} = -180 \text{ kJ mol}^{-1}$ [33] ($\Delta G_{\mathrm{S}}^{\mathrm{surf}} \simeq \Delta H_{\mathrm{S}}^{\mathrm{surf}} = \Delta H_{\mathrm{S}}^{\mathrm{ads}} - \Delta H_{\mathrm{S}}^{\mathrm{diss}} = -230 + 50 = -180 \text{ kJ mol}^{-1}$).

Using Equation 3 and the estimated values of $\Delta G_{\mathrm{S}}^{\mathrm{GB}}$, we were able to extrapolate the ratio $Y_{\mathrm{S}}^{\mathrm{GB}}$ as a function of temperature from Fig. 4; the curves differ for each grade because the sulphur concentration is different. For Grade 2 nickel, it was established that for a temperature greater than 800° C, the amount of sulphur segregation strongly diminishes.

The results obtained for this same grade (Grade 2) (see Fig. 2) show that at 800 and 900° C no deep grooves are present after the electrochemical test; furthermore, at these temperatures the Baumann microprint test is negative. The only explanation to account for the present of deep grooves and a positive Baumann test at 600 to 700° C is that a maximum intergranular sulphur segregation has occurred.

In addition, Fig. 2 shows that, for Grade 2 nickel, there are no deep grooves after 4 days tempering at 500° C. However, the thermodynamic model indicates that the segregation should have been at its maximum at this temperature (see Fig. 4). It is evident that the kinetics of intergranular segregation must play a role. According to the model of McLean:

$$C_{\mathrm{S}}^{\mathrm{GB}} = \frac{4 C_{\mathrm{S}}^{\mathrm{b}} (Dt)^{1/2}}{(\pi)^{1/2} d}. \quad (4)$$

$C_{\mathrm{S}}^{\mathrm{GB}} = 0.23$ at 500° C if D is 1.27×10^{-15} cm^2 sec^{-1} [27], t is 3.5×10^5 sec, $C_{\mathrm{S}}^{\mathrm{b}}$ is 104×10^{-6} At and d, the "boundary thickness", is 5×10^{-8} cm.

Using Equation 4, the intergranular sulphur concentration obtained after 4 days tempering was extrapolated from Fig. 4. This concentration was calculated using a bulk diffusion coefficient determined from values obtained by Vladimirov [27]; the values for Grade 1 (analogous to Grade

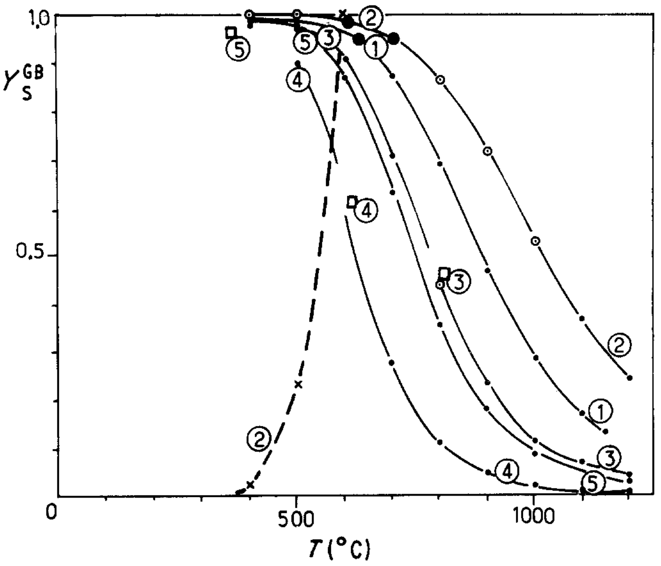

Figure 1 Calculated evolution of the ratio $Y_S^{GB} = C_S^{GB}/C_{S(max)}^{GB}$ as a function of tempering temperature for different nickel grades (equilibrium segregation, $\Delta G_S^{GB} = -98$ kJ mol^{-1}). The dotted line represents the value of the ratio Y_S^{GB} for Grade 2 nickel after a tempering time of 4 days. C_S^{GB} = sulpur concentration in grain boundary. $C_{S(max)}^{GB} = 0.43$ [5]. ● positive Baumann microprint and very deep intergranular groove (equilibrium segregation). □, ⊙ Positive, Baumann microprint and very deep intergranular groove (non-equilibrium segregation).

2) nickel are very close to those of Vladimirov (see Section 5.1.1.). We note that for a period of 14 days, the maximum segregation can be induced only at temperatures above 595° C; this is in accordance with the results obtained at 600° C.

5.2. Non-equilibrium segregation

There is a large disparity in the recrystallization temperatures observed for three nickel grades, Grades 3, 4 and 5. In each case, the presence of maximum intergranular concentrations was observed following the recrystallization annealing (both tests are positive). It can be assumed that the grain boundary of the recrystallized phase traps certain impurities, most particularly sulphur, by sweeping the cold-worked matrix. Thus, the intergranular sulphur concentration must be high, at the end of the primary recrystallization. Using Grade 5 nickel as an example, the value of the equilibrium intergranular concentration of sulphur at the recrystallization temperature (400° C) calculated using the model of McLean gives a result close to saturation (99%). However, at this temperature, this concentration can be reached only after a very long period of time. This fact confirms that the equilibrium mechanism postulated cannot account for the intergranular segregation observed experimentally.

We again suggest the possibility of a non-equilibrium mechanism. This hypothesis was checked by carrying out the annealing at a higher temperature which insured a negligible amount of segregation. Thus, for this nickel, when the recrystallization annealing was carried out at 800° C for 4 h, neither sensitivity to intergranular etching nor sulphur enrichment is detected by the Baumann microprint. In Fig. 4, the equilibrium concentration at this temperature is 35% of the maximum concentration. A kinetic calculation shows that this concentration can be easily reached at this temperature after 4 h. Thus, recrystallization of a cold-worked metal takes place at 400° C under isothermal conditions and provokes an intergranular segregation of sulphur.

All results obtained for Grade 4 nickel can be explained in the same manner. The state of intergranular segregation obtained is a stable state, identical to the equilibrium state, but it is achieved through a non-equilibrium process which is much more rapid kinetically than the process proposed by McLean [26].

Finally, after a thermal recrystallization treatment of 4 h at 800° C of Grade 3 nickel, an intergranular sulphur enrichment was detected by the two tests and the presence of an intergranular precipitate was observed (see Fig. 3) in increasing quantities with increasing time.

Thus, sulphur which segregated as a result of the recrystallization of nickel precipitated out other impurities (Ca, Si, Al) in the grain boundary. This microprecipitation became increasingly apparent as the time and temperature of annealing were increased. In this case the intergranular sulphur build-up is a stable state established by the precipitation of an insoluble sulphide phase in the grain boundaries. Identical results are obtained for the reference commercial-grade nickel in the second stage described in Section 5.1.1. (Grade 1).

The notion of non-equilibrium was conceived to explain certain metallurgical phenomena such as the intergranular hardening observed in various alloys [34–37]. This segregation is linked to solute enrichment in the region of the sinks and sources of vacancies which are present in the surfaces and grain boundaries. When a strong vacancy–impurity interaction exists, the vacancy diffuses impurity atoms which provokes a segregation of impurities in the region of the vacancy sinks. In the case of a moving interface (i.e., recrystallization of cold-worked metals) the interface can behave like a semi-permeable surface, removing strongly interacting atoms as it moves.

These phenomena, essentially of a transient nature, can lead to a permanent segregation only if the impurity atoms are trapped, if the process takes place in temperature intervals in which the segregated state constitutes the stable state of the system or if the return to equilibrium occurs infinitely slowly. If these conditions are not present, the segregation disappears with time if the diffusion is sufficiently active.

6. Conclusions

(a) Results obtained by AES for commercial-grade nickel (99.3%) led us to believe that the reactivity of the nickel grain boundaries to the electrochemical tests and Baumann microprints [19] correspond to the existence of intergranular segregation of sulphur which could be characteristic of two-dimensional sulphide. It is not yet possible to verify the existence of such a compound; the LEED experiments which could allow us to observe its presence cannot be carried out on fracture surfaces. However, grain boundaries which could be studied can be created by "putting" two surfaces together; one of these would have a bidimensional sulphur compound adsorbed on it. For Grade 1, we verified with AES that the maximum intergranular sulphur concentration corresponds to the maximum response of the electrochemical test and reactivity of the Baumann microprint. By extrapolating the results obtained for Grade 1, it can be assumed that there exists a maximum intergranular sulphur segregation in other grades. Furthermore, we propose to correlate the amplitude of the electrochemical etching with the intergranular sulphur concentration [38].

(b) After quenching and tempering, an equilibrium mechanism consistent with the results was obtained. The intergranular segregation energy of sulphur in nickel, i.e., $-98\ \mathrm{kJ\ mol^{-1}}$, was deduced from the results obtained with the electrochemical test, using the model of McLean [20]. The evolution of the maximum intergranular concentration of sulphur in terms of the temperature for the different grades of nickel was calculated. The equilibrium mechanism of McLean [20] accounts only for the high intergranular concentrations detected in nickel samples with high sulphur content, at least for our short annealing times.

(c) A non-equilibrium mechanism permitted explanation of the results obtained after recrystallization treatments. The kinetics of the intergranular segregation linked to the recrystallization are much more rapid than those of McLean. The purer is the nickel, the lower is the temperature at which this sulphur segregation is a maximum. To solve these problems, the anneal must be carried out at a higher temperature, thus promoting either the redissolution of sulphur (for the purest grades) or precipitation of sulphides (for the least-pure grades).

(d) These different results must be taken into account when choosing the thermal treatments required to prepare a particular nickel grade for use in an industrial study. However, the presence of third elements (in the most impure grades) should be considered in the analysis of these phenomena.

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