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Metallography and resistivity measurements on a 2–17 type alloy

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Metallography and electrical resistivity measurements (ρ_t/ρ_0) were carried out on an isothermally aged bulk alloy with a substitution composition of $Sm(Co_{0.67}Cu_{0.08}Fe_{0.22}Zr_{0.028})_{8.45}$. The as-cast alloy was found to consist of four phases: (A) zirconium-rich phase, (B) samarium- and copper-rich phase, (C) cobalt- and iron-rich phase, and (D) very rich in zirconium phase. After annealing at 1170 °C for 5 h, phase B entered into solid solution, suggesting that the other three phases are the stable phases in this system at this temperature. Large decreases in the electrical resistivity were observed after isothermal ageing at temperatures between 650 and 900 °C inclusive. After an initial decrease in the resistivity values at 650, 700, 750 and 800 °C an increase was observed leading to small peaks. The height of this maximum decreased with increasing ageing temperature and disappeared at 830 °C. This effect can be ascribed to the solubility variations, and an activation energy has been derived from the resistivity peaks.

1. Introduction

Precipitation-hardenable 2–17 type rare-earth permanent magnets with good magnetic properties have been developed during the last 15 years. Mishra *et al.* [1] described the microstructure of these magnets as 2–17 type rhombohedral cells surrounded by 1–5 type boundaries. They also observed a platelet phase normal to the *c* axis and coherent with both the cell and boundary phases in magnets containing 1.5 to 3 wt % Zr. Since it originates with the zirconium addition the platelet phase has been named "z-phase" [2].

The substitutional solid solubility of iron was found to be low in the 1–5 type boundary phase and as a result it enters into the 2–17R phase during ageing. Copper was observed to concentrate in the boundary and platelet phase due to its low solubility in the 2–17R phase and zirconium segregated preferentially into the z-phase [3–5]. Rabenberg *et al.* [2] proposed the $SmCo_3$ type structure for the platelet phase, whereas TEM studies carried out by Fidler *et al.* [6] revealed a hexagonal 2–17 crystal structure. More recently Zhang *et al.* [7] suggested that the z-phase and the matrix phase are stable compositions in the 2–17 type alloy system. The composition of the platelet phase has been found to be inconsistent with a 1–3 phase and the 2–17H phase [7]. Controversy still surrounds the structure of the z-phase.

Since the coercivity mechanism of the $Sm_2(Co, Cu, Fe, Zr)_{17}$ magnets is the pinning of the domain walls by fine coherent 1–5 type precipitates which occurs during ageing [8, 9], these magnets are very sensitive to the heat-treatment procedure. Work in this laboratory [10] has shown that electrical resistivity measurements are an effective means of monitoring the ageing process in this alloy. In the present work the isothermal ageing of a 2–17 type material at different temperatures has been undertaken. The electrical resistivity measurements were carried out on aged samples to monitor and characterize the ageing process. The intention is to employ resistivity measurements as a useful means of monitoring the ageing processes of precipitation-hardened 2–17 type alloys and to provide more information on the nature of the processes which occur during ageing in these complex systems.

2. Experimental procedure

The as-cast alloy of $Sm(Co_{0.67}Cu_{0.08}Fe_{0.22}Zr_{0.028})_{8.45}$ was supplied by Rare-Earth Products PLC and was used to prepare samples for secondary electron microscopy, X-ray microanalyses and resistivity measurements. Metallography specimens were etched in 2 % nital for 8 to 10 sec at room temperature after final polishing with 0.25 μm diamond. Symmetrical blocks were cut from the ingot material for resistivity measurements. The alloy was first solution-treated at 1170 °C for 5 h and then quenched in an argon atmosphere and subsequently isothermally aged at between 650 and 900 °C inclusive. After each ageing step, the samples were quenched and then placed in a specially constructed four-probe resistance rig using a current of 1 A to determine the relative resistivity values (ρ_t/ρ_0 where ρ_t is the resistivity value at the ageing time t and ρ_0 is the initial ρ-value). The errors measured in these measurements amount to ± 0.02 % and are encompassed in the points of the graphs shown in this paper.

3. Results and discussion

3.1. Metallography

X-Ray microanalyses carried out on the as-cast alloy revealed the presence of four phases (Fig. 1):

(A) zirconium-rich phase (dark)
$Sm(Co_{0.64}Cu_{0.04}Fe_{0.15}Zr_{0.16})_{10.93}$

(B) samarium- and copper-rich phase (light)
$Sm(Co_{0.61}Cu_{0.17}Fe_{0.19}Zr_{0.016})_{6.01}$

(C) iron- and cobalt-rich phase (matrix)
$Sm(Co_{0.66}Cu_{0.06}Fe_{0.25}Zr_{0.02})_{8.45}$

(D) phase very rich in zirconium (grey)
$Sm(Co_{0.04}Cu_{0.03}Fe_{0.005}Zr_{0.95})_{73.71}$

The volume percentages of these four phases were determined by image analysis from secondary-electron SEM photographs. The vast majority of the material consisted of B (50 ± 3 %) and C (42 ± 3 %) phases with small amounts of A (8 ± 2 %) and D (0.05 ± 0.005 %).

The as-cast alloy was then homogenized at 1170 °C for 5 h. The SEM micrograph of the solution-treated alloy is shown in Fig. 2. There was no evidence of phase B in this sample and phase A appears to be significantly finer compared with that of the as-cast structure. The compositions of the matrix (C) and phase D were found to be very similar to those of the as-cast material. Determination of the amount of these phases was carried out as for the cast alloy, and the volume percentages are given below:

Phase A (6 ± 1 %)
$Sm(Co_{0.66}Cu_{0.03}Fe_{0.16}Zr_{0.14})_{11.24}$

Phase C(93 ± 2 %)
$Sm(Co_{0.67}Cu_{0.06}Fe_{0.22}Zr_{0.04})_{8.23}$

Phase D (1 ± 0.3 %)
$Sm(Co_{0.04}Cu_{0.05}Fe_{0.015}Zr_{0.93})_{106.47}$

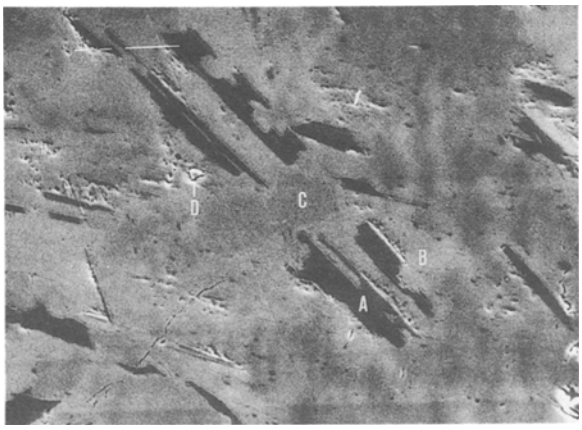

Figure 1 SEM photograph of the as-cast alloy (×1000).

Figure 2 SEM photograph of the solution-treated alloy.

These results are in good agreement with the early studies [10, 11] on 2–17 type alloys. The four phases were observed in a $Sm(Co_{0.65}Cu_{0.10}Fe_{0.23}Zr_{0.02})_{7.1}$ as-cast alloy by SEM studies [12]. Bailey and Harris [10] also reported the existence of zirconium-rich, cobalt- and iron-rich, and samarium- and copper-rich phases in as-cast $Sm(Co_{0.66}Cu_{0.1}Fe_{0.21}Zr_{0.03})_{7.37}$ alloy. Their results and the present work are compared in Table I, and apart from the absence of phase D in the earlier investigation [10], they are in excellent agreement.

Zhang *et al.* [7] observed a zirconium-rich samarium-depleted phase in an isothermally aged $Sm(Co_{0.67}Cu_{0.08}Fe_{0.23}Zr_{0.02})_{8.52}$ alloy and reported this phase as a platelet phase. The results of X-ray analysis on this phase for the different alloys are compared in Table II, which shows that within experimental error the composition of phase A obtained by Zhang *et al.* and that observed in the present work are virtually identical.

Apart from phase B in the as-cast structure, which disappeared after solution treatment, the other three

TABLE I Compositions of as-cast alloys

	Composition (at %)					
Phase	Sm	Co	Cu	Fe	Zr	Substitution composition
A[a]	8.3	58.7	3.8	14.4	14.6	$Sm(Co_{0.64}Cu_{0.04}Fe_{0.15}Zr_{0.16})_{10.93}$
A[b]	8.81	59.26	4.56	14.62	12.75	$Sm(Co_{0.65}Cu_{0.05}Fe_{0.16}Zr_{0.14})_{10.36}$
B[a]	14.25	52.26	15.11	16.97	1.38	$Sm(Co_{0.61}Cu_{0.17}Fe_{0.19}Zr_{0.016})_{6.01}$
B[b]	19.49	37.04	33.00	9.66	0.81	$Sm(Co_{0.46}Cu_{0.41}Fe_{0.12}Zr_{0.01})_{4.13}$
C[a]	10.58	59.23	5.95	22.53	1.68	$Sm(Co_{0.66}Cu_{0.06}Fe_{0.25}Zr_{0.02})_{8.45}$
C[b]	10.69	60.73	5.36	22.33	0.87	$Sm(Co_{0.68}Cu_{0.06}Fe_{0.25}Zr_{0.01})_{8.35}$
D[a]	1.33	3.86	0.31	0.51	93.57	$Sm(Co_{0.04}Cu_{0.03}Fe_{0.005}Zr_{0.95})_{73.71}$

[a] Present work.

[b] Bailey and Harris [10].

TABLE II Comparison of platelet (dark) phase compositions

Source	Composition (at %)					
	Sm	Co	Cu	Fe	Zr	Substitution composition
Bailey and Harris [10]	8.8	59.3	4.6	14.5	12.8	$Sm(Co_{0.65}Cu_{0.05}Fe_{0.16}Zr_{0.14})_{10.36}$
Zhang *et al.* [7]	8.4	59.1	5.1	13.8	13.6	$Sm(Co_{0.64}Cu_{0.05}Fe_{0.15}Zr_{0.14})_{10.90}$
Present work	8.3	58.7	3.8	14.4	14.6	$Sm(Co_{0.64}Cu_{0.04}Fe_{0.15}Zr_{0.16})_{10.93}$

phases were found to exist in the as-cast and homogenized sample, suggesting that they are stable phases in this system at the homogenization temperature.

3.2. Electrical resistivity measurements

The variations of electrical resistivity with ageing time in the temperature range 650 to 900 °C inclusive are shown in Figs 3 to 9. The results are presented in the form ρ_t/ρ_0 against log (time), where ρ_0 is the initial resistivity value and ρ_t is the resistivity measured at time t. The significant features of the graphs can be summarized as follows:

(i) at ageing temperatures between 650 and 800 °C a large decrease in the resistivity is followed by an increase in the ρ_t/ρ_0 values, leading to a small peak;

(ii) the small peak at long ageing times disappears at 830 °C and above;

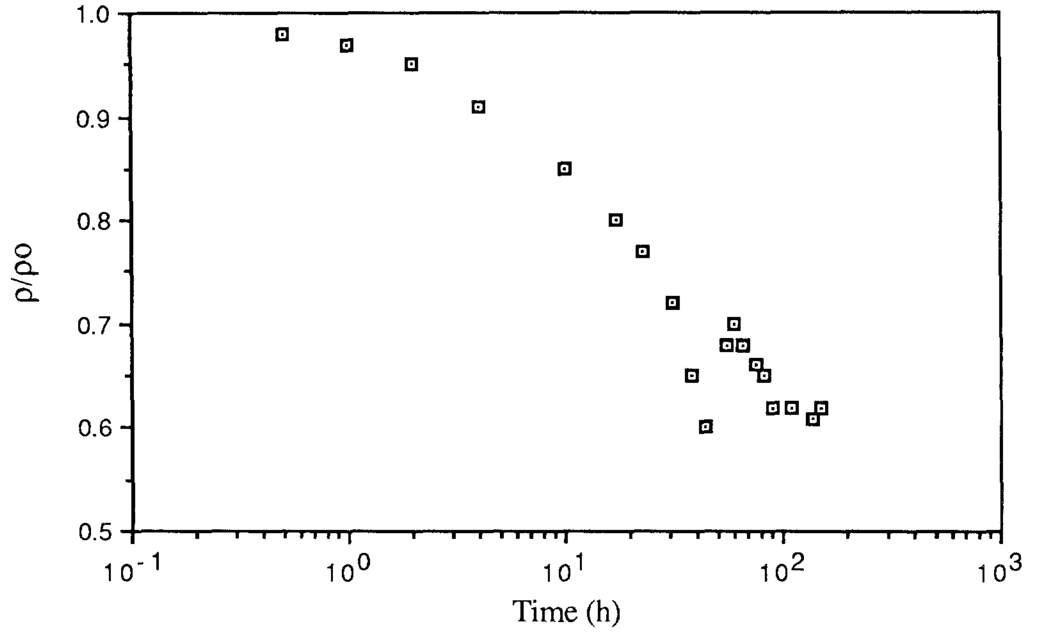

Figure 3 Variation of resistivity with ageing time at 650 °C.

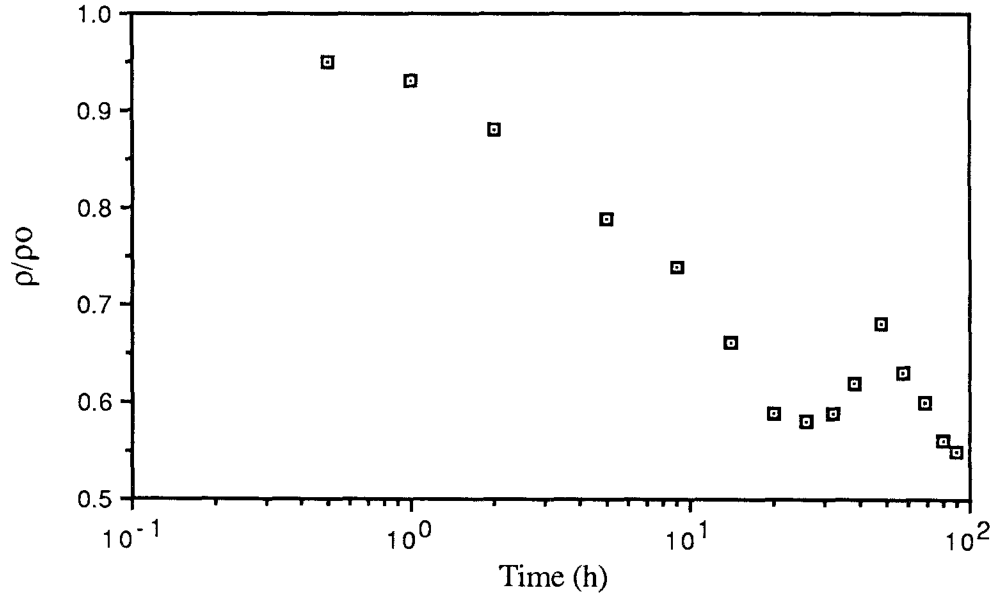

Figure 4 Variation of resistivity with ageing time at 700 °C.

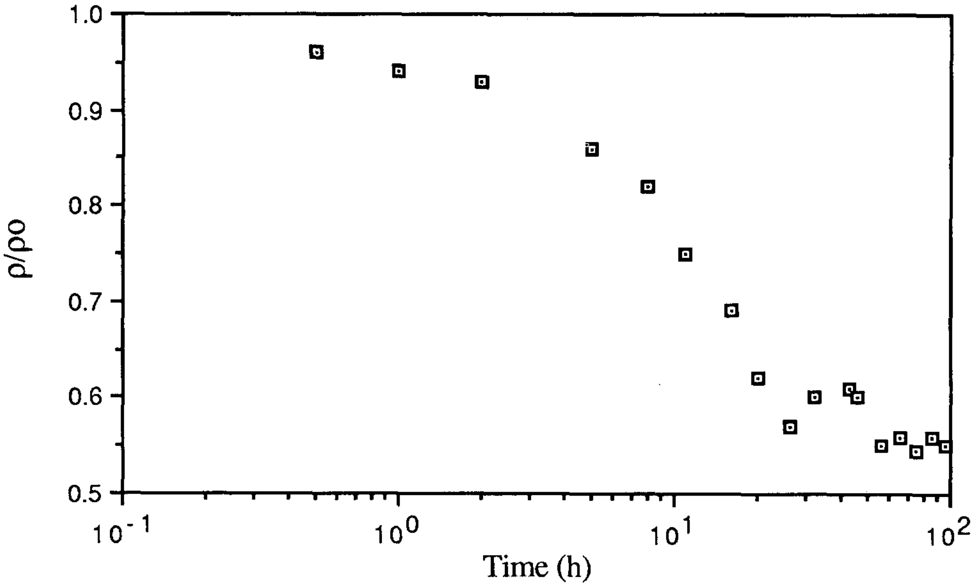

Figure 5 Variation of resistivity with ageing time at 750 °C.

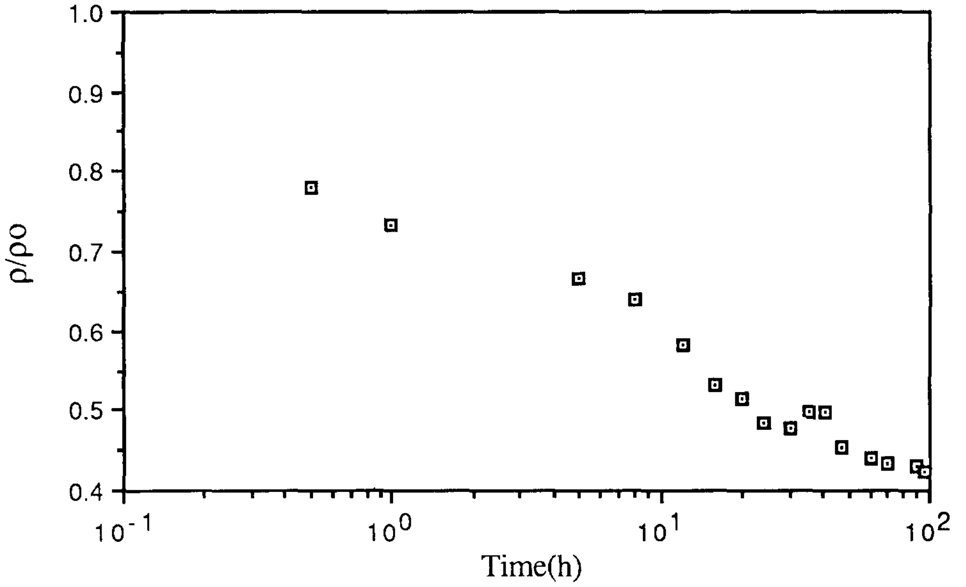

Figure 6 Variation of resistivity with ageing time at 800 °C.

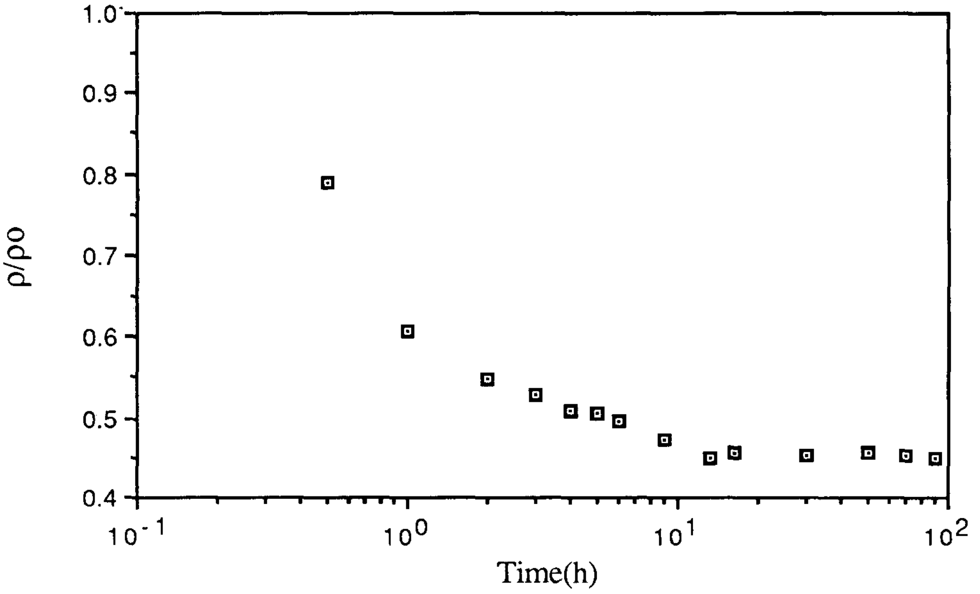

Figure 7 Variation of resistivity with ageing time at 830 °C.

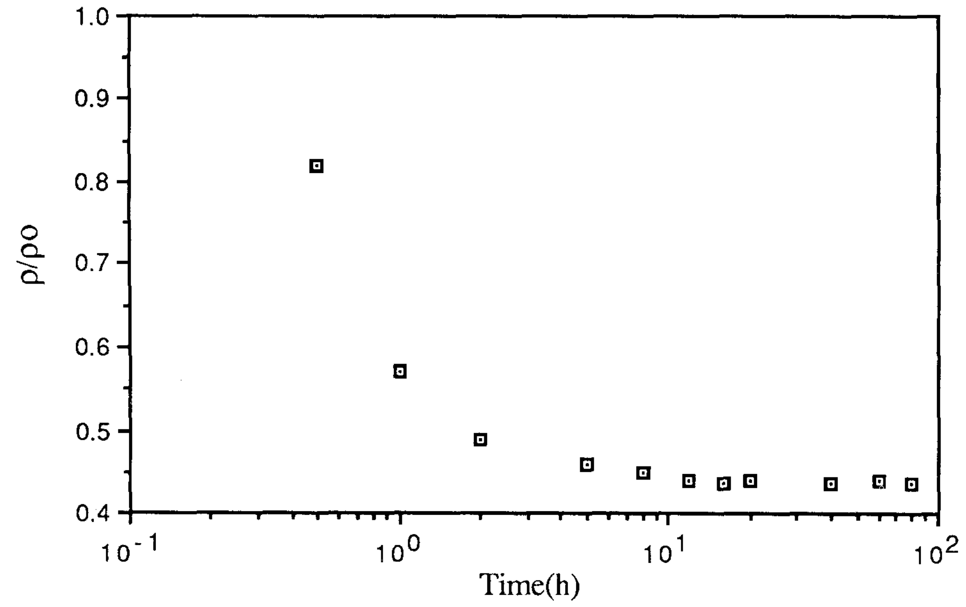

Figure 8 Variation of resistivity with ageing time at 850 °C.

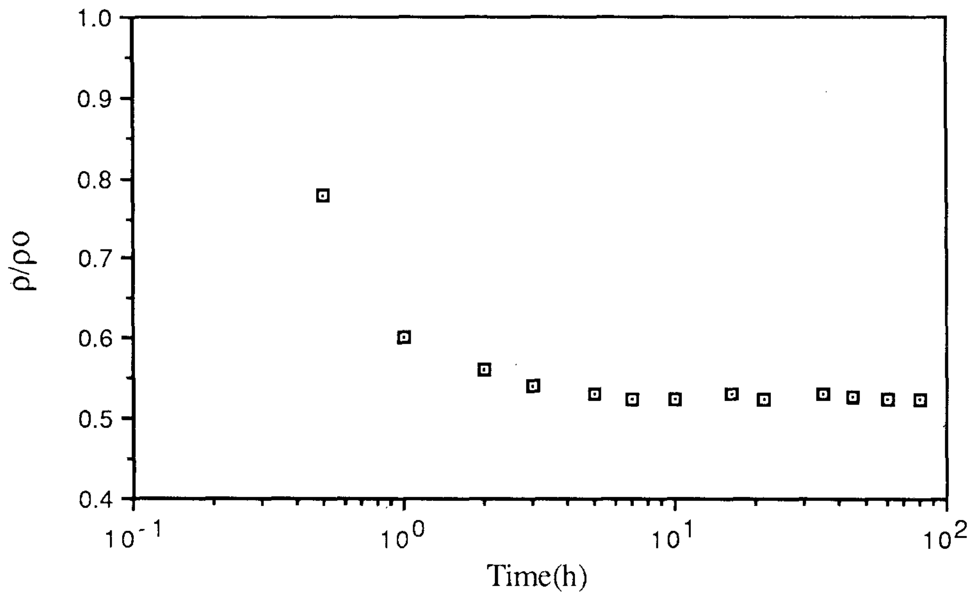

Figure 9 Variation of resistivity with ageing time at 900 °C.

(iii) there is a significant change in the shape of the resistivity curves between 750 and 800 °C;

(iv) there is a practically invariant resistance after long ageing times at 830 to 900 °C; and

(v) there is a large residual resistance at 900 °C.

There are two main contributions to the electrical resistivity value during precipitation, from the matrix phase and from the precipitates. Thus the electrical resistivity of a precipitation-hardened alloy can be given by the equation $\rho = \rho_{\text{matrix}} + \rho_{\text{precipitates}}$. In the present alloy the precipitation process might have been expected to give rise to an initial increase in the electrical resistivity, as observed in classical age-hardening systems [13]. However, there is a small decrease at the beginning of the isothermal ageing treatment between 650 and 750 °C. This could be due to the combined effects of a decrease due to solute redistribution and an increase due to precipitation leading to a small net initial decrease in resistivity. The fact that there is a significant and progressive fall in the resistivity of up to 55 % indicates that the predominant contribution to the resistance change is from the solute redistribution which occurs on ageing and results in a large reduction in the resistance of the matrix phase. Small peaks observed after long ageing times at between 650 and 800 °C may be explained by a longer-term precipitation process giving rise to a resistance maximum which is observable because of the small change in the matrix resistance after long ageing times. TEM studies carried out by Zhang *et al.* [7] on $Sm(Co_{0.67}Cu_{0.08}Fe_{0.23}Zr_{0.02})_{8.52}$ alloy after ageing at 800 °C for 72 h showed the presence of two additional phases, which may also occur in this alloy between 650 and 800 °C and contribute to the precipitation-hardening process indicated by the electrical resistivity peak. The larger residual resistance at 900 °C may be due to the retention of more elements in solution at this temperature.

If the assumption is made that the peak ageing times for the resistivity curves correspond to a common critical precipitate size, then the reciprocals of

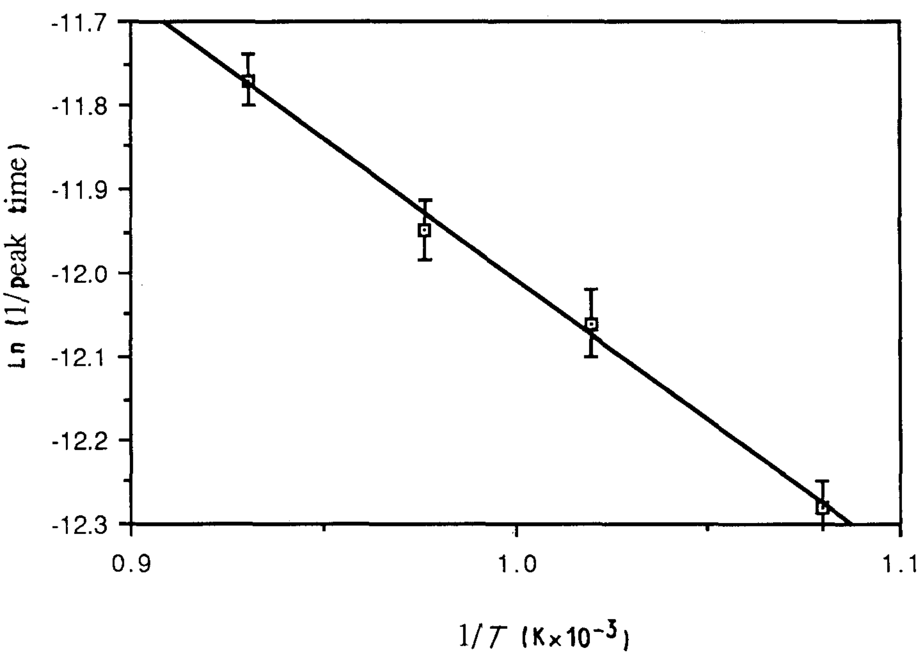

Figure 10 Graph of the logarithm of the time to resistance minimum against the reciprocal of the ageing temperature.

these times would be equivalent to the relative growth rates at the various ageing temperatures. The data have been analysed according to the Arrhenius behaviour, i.e. ln(1/peak times) is plotted against $10^3/T$(K) (Fig. 10).

An activation energy of $279 \pm 23\,\mathrm{kJ\,mol^{-1}}$ is obtained from this linear relationship. This is in excellent agreement with the value of $259 \pm 35\,\mathrm{kJ\,mol^{-1}}$ determined from microhardness measurements [14] on the same alloy, and with the value of $256 \pm 22\,\mathrm{kJ\,mol^{-1}}$ obtained by Bailey and Harris [10] from a similar material.

4. Conclusions

1. The cobalt- and iron-rich phase, zirconium-rich phase, and phase very rich in zirconium were found to be stable phases in this alloy. Apart from the last-named phase, these results were found to be in excellent agreement with previous work [10–12].

2. The alloy showed different resistivity behaviour from the classical age-hardening systems, i.e. there is no increase observed in the ρ_t/ρ_0 values in the early stages of isothermal ageing. This could be due to the predominant influence of solute redistribution giving rise to a reduction in the matrix phase resistance.

3. Following an initial decrease in the resistivity, a small peak is observed on ageing at between 650 and 800 °C.

4. There is a change in the shape of the resistivity curve between 750 and 800 °C.

5. The peak times and the height of the peaks decrease with increasing ageing time and disappear at around 830 °C.

6. The larger residual resistance at 900 °C indicates the retention of more elements in solution at this temperature.

7. A linear relation was found between the inverse of the peak times and an activation energy of $279 \pm 23\,\mathrm{kJ\,mol^{-1}}$ has been obtained from this relationship for the precipitation process in this alloy

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