A study of the alloying elements in the model alloy studied by Thermoelectric Power and Electrical Resistivity

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1. Introduction

It has been shown that the thermoelectric power (TEP) and electrical resistivity (ER) measurements have the potential to provide information and assessment of microstructural changes such as precipitations and effects of alloying elements. The changes of TEP and ER caused by thermal aging of Fe - Cu model alloys have been measured. The amounts of precipitation volume fraction were calculated on the basis of the combined resistivity and Seeback coefficient model, and the variations of TEP and ER were explained in terms of the behavior of precipitations during the aging process. The TEP increased and ER decreased during the thermal aging, and these changes are explained in terms of copper precipitations.

2. Experiment

A set of simple model alloys called VM series called as VD, VG and VH were used in this study, the chemical composition is shown in Table 1. The variations in alloying elements were used to determine the individual and combined effects of impurity elements upon resistivity and thermoelectric power. The measurements of Seeback coefficient S were performed using a thermo electrical power (TEP) instrument made by Techlabs of St. Julien-Les-Metz, France. The ER was measured at room temperature using four probe methods to nevertheless mimize the phonon contribution and to have well defined measurement.

| Tab | le | 1. | Che | emic | al | compos | itions | of | al | loy | VM | l seri | es |
|-----|----|----|-----|------|----|--------|--------|----|----|-----|----|--------|----|
|-----|----|----|-----|------|----|--------|--------|----|----|-----|----|--------|----|

| Code | Cu | Mn | С | Ν | Ti | |
|------|------|------|------|--------|-------|--|
| | | | | (Appm) | | |
| VD | 0.88 | 1.03 | 0.00 | 10 | 0.000 | |
| VG | 0.51 | 0.06 | 0.01 | 20 | 0.000 | |
| VH | 0.91 | 0.01 | 0.01 | 20 | 0.000 | |

2.1 Method of analysis

The approach used to estimate the amount of precipitation is based on the combined resistivity and Seeback coefficient (RSC) analysis model. In this model, dilute concentration S and ρ (Mathiessen's rule in the case of ρ) vary linearly with the atomic fraction of the key solutes: Cu, Ni, Mn, P and Si.

$$\Delta S = \kappa_{Cu} \Delta X_{Cu} + \kappa_{Mn} \Delta X_{Mn}$$
$$\Delta \rho = k_{Cu} \Delta X_{Cu} + k_{Mn} \Delta X_{Mn}$$

coefficient κ_i and k_i (units of $\mu\Omega$ -cm/at.% and $\mu V/^{\circ}C/at.\%$) were found by least square fitting variable subsets of alloys with a range of normal compositions including systematic variables in Cu, Ni, Mn, Si and P. The volume fraction of the precipitates (f_p) is given by the sum of compositional changes of Cu and Mn.

$$f_p = \Delta X_{Cu} + \Delta X_{Mn}$$

3. Results and discussion

Fig. 1 shows the evolution of the TEP value of model alloy VD, VH and VG for different ageing time at corresponding aging temperature of 275, 300, 325 and 350 °C. The TEP values were slightly increased with initiation of aging. This attributed to the annihilation of excess vacancies created by the sample preparation. The initial TEP value of sample VD is slightly higher than that of sample VH, but with initiation of aging the trends were reversed. The TEP value of VG which has 0.5% Cu contents shows extraordinary higher TEP value compare to the alloy VD and VH and shows less sensitivity on the aging time and temperature. For the ageing temperature less than 300°C, the measured TEP



Fig. 1. The variation of the TEP values of model alloy VD, VH and VG for different ageing time at corresponding aging temperature of 275, 300, 325 and 350 $^{\circ}$ C.

is nearly constant after small initial increase in all model alloys. The rise in TEP values is marginally higher at 350°C than at 325°C even though more copper is expected to precipitate at 325°C because of its comparatively lower solubility at 325°C in iron than at 350°C. This is most likely because of the higher



Fig. 2. The variation of the room temperature resistivity values of model alloy VD, VH and VG for different ageing time at corresponding aging temperature of 275, 300, 325 and 350 $^{\circ}$ C.

diffusivity of copper atoms at 350 °C leading to comparatively faster precipitation kinetics. The changes of ER show inverse trend with TEP results as shown in Fig. 2. The alloy VG which have high TEP values shows low resistivity values. Precipitation of copper due to aging decreases resistivity and increases TEP. This relation can be attributed to the fact that TEP and resistivity variation during precipitation are mainly due to the same phenomena, i.e. the decrease of the quantity of elements (Cu, Mn) in solid solution. Slightly decrease and relative large decrease of ER were observed for the samples annealed less than the temperature of 325 °C and 350 °C, respectively. Such behavior is explained by the creation of CRPs activated by a diffusion process associated with aging temperature increase. It is known that the depletion of copper from solid solution causes a fall in resistivity of the material [1]. Fig. 3 shows the change of precipitation volume fraction as a function of aging time in the samples corresponding aging temperature. The volume fractions obtained by RSC model are relatively well accord with small angle neutron scattering (SANS) results [2]. The precipitates volume fraction of sample VH is larger than that of sample VD even though these samples have the same copper contents. This attributed that Mn suppresses the creation of copper precipitate. Mn decreases the precipitates size and increase precipitate number density by lowering the interfacial energy at the iron matrix copper precipitates interface, which in turn reduces the driving force for copper coarsening [3].According to the SANS experiments, the number of Cu precipitates is an order of magnitude greater in an Fe-Cu-Mn alloy than in a binary alloy of similar Cu contents [4]. For the aging temperature less than 300° C, the alloy VD and VG show almost same precipitation volume fraction even though they have different copper contents, but the alloy VD and VH show the different volume fraction even though they have same copper contents. For the aging temperature 325° °C, the alloy

VH has slightly larger volume fraction than VD. But the trend was reversed at



Fig. 3. The change of precipitates volume fraction of model alloy VD, VH and VG for different ageing time at corresponding aging temperature of 275, 300, 325 and 350 $^{\circ}$ C

the aging temperature of 350° C, i.e. The volume fraction of VD is larger than that of VH. The precipitation volume fraction of VD increase with increasing aging temperature; at the aging time of 2000 hr the precipitation volume fraction change from 0.01 to 0.22, 0.01 at% at 275 °C, 0.04 at% at 300 °C, 0.08 at% at 325 °C, and 0.22 at% at 350 °C. Therefore, it seems to be that the suppressing effect of copper precipitation by manganese relatively important in the low aging temperature.

3. Conclusions

TEP measurements are very sensitive to the precipitation of small quantity of copper due to the aging after isothermal annealing. The change of TEP shows inverse trend that of resistivity, precipitation of copper due to aging increases TEP and decreases resistivity. This relation can be attributed to the fact that TEP and resistivity variations during precipitation are mainly due to the same phenomenon, i.e. the decrease of the quantity of the element copper in solid solution. From the behavior of the TEP and precipitation volume fraction, the manganese suppresses the creation of copper precipitation, and the suppressing effect is relatively important in the low aging temperature.

REFERENCES

[2] S. Arajs, F.C. Schwerer, and R.M. Fisher, Phys. Stat. Sol. 88 (1969) 731.

[1] Y. Meyzaud, P. Parniere, Mem. Sci. Rev. Met. 71 (1974) 415.

[3] S.G. Glade, B.D. Wirth, P. Asoka-Kumar, G.R. Odette, UCRL-JC-152567, Feb. 2003, Positron Annihilation Spectroscopy and Small Angle Neutron Scattering Characterization of the effect of Mn on the nanostructural features formed in irradiated Fe-Cu-Mn alloys.

[4] M.K. Miller, B.D. Wirth, G.R. Odette, Mater. Sci. Eng.A353 (2003)133.