A RESISTOMETRIC STUDY OF PRECIPITATION-HARDENING IN Fe-0.5wt%Cu ALLOY

Anwar Manzoor Rana, Rizwan Ahmad, Maqsood Ahmad
Department of Physics, Bahauddin Zakariya University, Multan-60800, Pakistan.
email: anwar_manzoor_rana@yahoo.com

Abstract

Precipitation-hardening study was carried out on Fe - 0.5 wt% Cu alloy by measuring electrical resistivity and Vickers hardness at different ageing temperatures and for long ageing times. On ageing, it was observed that electrical resistivity initially rises with ageing time and then falls after very long ageing at a constant temperature. On the other hand hardness shows only small rise during early stages and rapid rise for further ageing. It may be inferred from XRD patterns, behavior of resistivity and / or hardness that the metastable Cu-rich clusters are formed at the earlier stages of the precipitation process causing only small changes in hardness but large rise in resistivity. These metastable Cu-clusters might have transformed to stable Cu-rich precipitates for long times causing further variations in hardness/ resistivity.

Keywords: Electrical resistivity, GP zones, Vickers hardness, X-ray diffraction.

INTRODUCTION

The great interest in precipitation from solid solution and in the production of internally oxidized materials and cermets is due to the fact that the presence of precipitate and ceramic particles greatly increases the yield stress of a metal crystal. The precipitate particles act as obstacles to dislocation movement and thereby strengthen the heat-treated alloy [Kelly 1975, Smith 1990, Fischer and Jung 1992, Rana and Ansari 1995]. The purpose of this precipitate strengthening is to create in a heat-treated alloy a dense and fine dispersion of precipitated particles in a matrix of deformable metal, in order to produce a material which possesses considerable strength at both room and elevated temperatures [Thomas 1971, Ansari *et al.* 1994, Hwang *et al.* 2002].

Precipitation and particle coarsening have been extensively studied in metallic materials because of their importance in strengthening these materials [Thomas 1971, Scott *et al.* 1992, Ansari *et al.* 1994, Blackstock and Ackland 2001, Marian *et al.* 2001, Hwang *et al.* 2002]. Stability of the precipitate structure is of major concern when precipitation hardened

materials are considered for applications in high temperature and/or irradiation environment [Fischer and Jung 1991, 1992, Fernández van Raap 2002]. Alloys of iron such as Fe-Cu, ferritic and martensitic steels and pressure vessels (PV) steels are used in fissions and fusion reactors. Ferritic and martensitic stainless steels have greater resistance to voids swelling and helium embrittlement than austenitic stainless steels, and so they are considered as structural materials for first walls of future fusion reactors [Fischer and Jung 1991]. In ferritic steels considerable strengthening can be achieved by the precipitation of substitutional elements from iron, i.e. elements that do not form carbides and have a solubility decreasing with temperature, e.g. Cu or Fe_3Al, maximum precipitation hardening occurs in copper steels if bcc copper- rich particles transform and loose coherency [Hornbogn 1983]. In maraging steels and reactor pressure vessels (RPV) steels, Cu-precipitates play an important role in the embrittlement process. Phase separation via precipitation of Cu from the homogeneous solution in pure Fe or in other Fe-base dilute alloys is found to occur at an observable speed in the temperature interval $673K < T_A < 873K$, since for higher temperatures the solution ceases to be supersaturated and below 673K the kinetics of precipitation are extremely slow [Reed-Hill 1973, Solt *et al*. 1991, Wagner and Kampmann 1991, Rana and Ansari 1995].

Because of the complex nature of the precipitation process, it often becomes necessary to invoke techniques which involve changes in physical properties such as hardness and electrical resistivity induced by various phenomena of precipitation. With regard to electrical resistivity the orderly motion of electrons through a crystal, which constitute an electric current, are badly disturbed when an extremely small and uniformly distributed precipitate such as Guinier-Preston (G.P) zone forms. Thus when precipitation starts, there is an initial large rise in resistivity, which then decreases as the average particle size increases during the progress of precipitation phenomena [Rossiter and Wells 1971, Osamura *et al*. 1973, Hilal *et al*. 1975, Rossiter 1980, Ansari 1990]. The rise and fall of resistivity has been observed in a number of Ni and Fe based alloys [Ansari 1990, Ansari *et al*. 1994, Rana and Ansari 1995]. This anomalous initial increase of resistivity has long been considered to result from an abnormal scattering of zones when they reach a critical dimension comparable with the wavelength of the free electrons as suggested by Mott [Langer *et al*. 1975]. Hardness of a material is found to vary with the progress of ageing. It first shows an increase with the precipitation process and then start decreasing as coarsening start.

In the present investigation, precipitation and particle coarsening behavior has been studied in Fe-0.5wt.%Cu alloy by measuring the electrical resistivity and hardness at room temperature after solution treatment, quenching and ageing at different temperatures ranging from 673K to 773K for various times up to 1400 min.

MATERIALS AND METHODS

The Fe-0.5wt%Cu alloy in the form of thin sheets of 0.03cm thickness were provided by the Department of Electrical Engineering, University of Windsor, Ontario, Canada. Samples, enclosed in steel capsules, were solution heat-treated at 1073 K for 90 min. in an electric tube furnace (GERO, SARO, 72-150 GmbH, GERMANY) and then rapidly quenched in ice- water at temperature~ 277 K. These quenched samples (enclosed in Pyrex glass capsules) were then aged at different temperatures i.e. 673 K, 723 K and 773 K for various times upto 1400 min. and then polished by emery papers of different grades to avoid surface contamination and any oxidation. After each heat-treatment, electrical resistivity was measured at room temperature using "Four Probe method", the details are described elsewhere [Ansari *et al.* 1994, Rana and Ansari 1995]. Vickers hardness test was performed at room temperature by using diamond cone indenter (120°) with major load 10kg and minor load 2kg. After each ageing treatment, x-ray diffraction patterns were recorded at room temperature by "D8 Discover Bruker AXS XR Diffractometer", equipped with Cu-Kα radiation. All peaks in the diffraction patterns were indexed for 2θ and d–values. The calculated d-values d_{exp} were then compared with the d-values of different possible phases co-existing in the material as found in the literature of standard x-ray diffraction data [Metals and Alloys Data Book], d_{lit}. The possible phases and corresponding (hkl) values of the planes for which $d_{exp} \cong d_{lit}$ were noted.

RESULTS

ELECTRICAL RESISTIVITY

Electrical resistivity versus ageing time curve for Fe 0.5 wt% Cu alloy aged at 673K shows a steep increase in resistivity during the initial 60 min. of the precipitation hardening process followed by a slight increase in resistivity up to 300 min. ageing time (Fig. 1). The resistivity verses time graph then shows almost constant behavior during the time interval of 300–900 min. At 723 K ageing temperature, only a slight increase in the resistivity of Fe–0.5wt.% Cu alloy was observed up to first 60 min. ageing and then there was a slow and steady decrease in resistivity for further ageing. It was observed that at temperature 773K, during the initial time of ageing, there was a gradual decrease of resistivity up to 600 min. For further ageing, the resistivity shows almost constant behavior.

According to precipitation theories [Wagner and Kampmann 1991, Rana and Ansari 1995], the initial increase in resistivity during earlier stages of precipitation should follow a '$t_A^{1/2}$' law. So resistivity curves as a function of the square root of ageing time '$t_A^{1/2}$' were drawn as shown in Fig. 2. These plots for ageing temperatures of 673K and 723K show a linear behavior for small ageing times up to about 60 min. only and hence follows the above given '$t_A^{1/2}$' law at the initial stages of precipitation process.
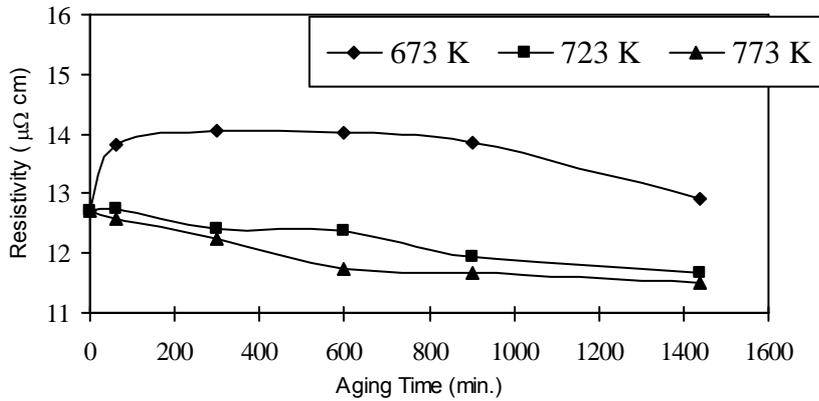
Fig. 1: Plots of electrical resistivity versus ageing time for Fe-0.5wt%Cu alloy aged at 673 K, 723K and 773K.
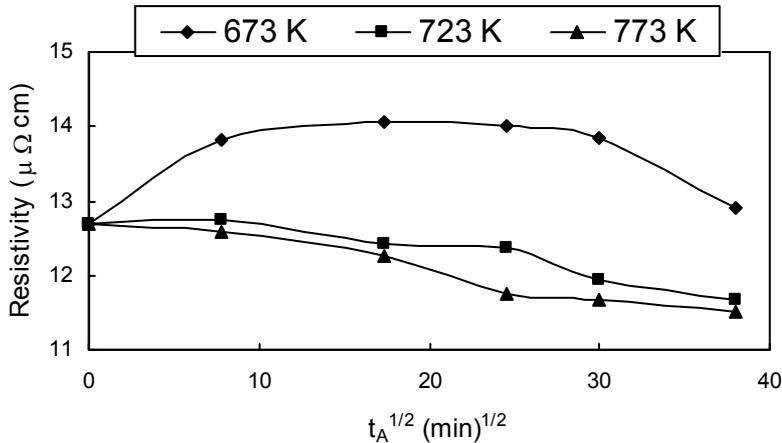

Fig. 2: Plot of electrical resistivity versus square root of ageing time '$t_A^{1/2}$' for Fe-0.5wt% Cu alloy at various ageing temperatures.

Coarsening behavior of precipitates in Fe–0.5wt%Cu alloy was studied during ageing at different temperatures and for long ageing times. The portion of electrical resistivity versus ageing time curves where resistivity decreases can be attributed to this coarsening process. Theoretical models regarding coarsening of precipitated particles [Ansari 1989] suggest that the resistivity data should be plotted as a function of the inverse cube root of ageing time '$t_A^{-1/3}$'. Such plots of resistivity versus '$t_A^{-1/3}$' (ageing time) are shown in Fig. 3. These plots can be used to find

out values of the infinite electrical resistivity 'ρ_∞' by extrapolating the data. Then intercept on the resistivity axis (i.e for $t_A^{-1/3} = 0$) for ρ – '$t_A^{-1/3}$' curves yields the value of infinite electrical resistivity 'ρ_∞'. Using this value of infinite resistivity, coarsening behaviour of precipitates can be expressed by a relation [Ansari 1989, 1990]:

$$\rho = \rho_\infty [1 + (\chi t_A)^{-1/3}]$$

Where χ is a coarsening rate constant. The values of ρ_∞ obtained from Fig. 3 by extrapolating the $\rho - t_A^{-1/3}$ plots are given in Table 1.
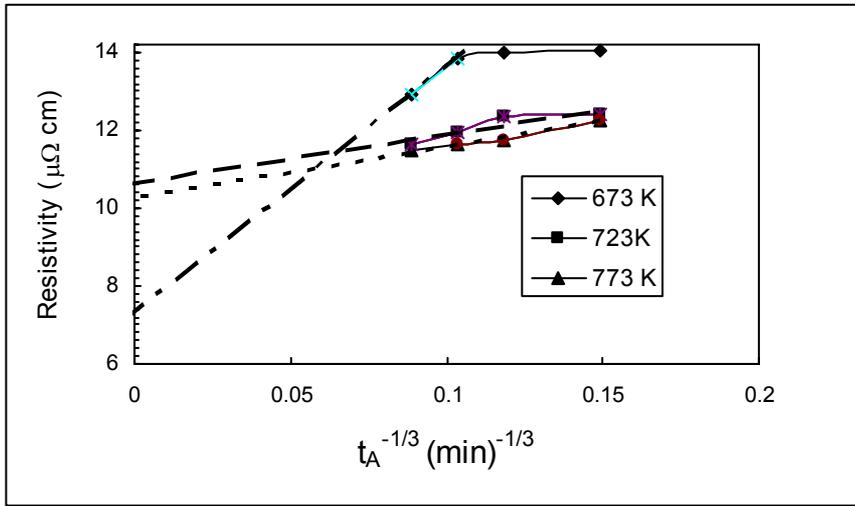

Fig. 3: Plot of electrical resistivity of Fe-0.5wt% Cu alloy as a function of $t_A^{-1/3}$ at various ageing temperatures.

Table1: Values of infinite electrical resistivity extrapolated from Fig. 3.

Sr. No.	Ageing Temperature (K)	ρ_0 ($\mu\Omega$ cm)	ρ_∞ ($\mu\Omega$ cm)
1.	673	12.7	07.30
2.	723	12.7	10.66
3.	773	12.7	10.23

HARDNESS

Vickers hardness of Fe-0.5wt%Cu specimen was measured at room temperature before and after each ageing time at various ageing temperatures. According to phase diagram [Brandes and Brook 1992],

Fe-0.5wt%Cu alloy exists as a mixture of two phases (α-Fe and Cu) at room temperature. Therefore any variations in the microstructure of as received specimen can change its hardness. Specimens aged at 673K for various ageing times up to 1400 min. almost show very small increase in hardness (Fig. 4). Maximum value (68.93 HV) of hardness was observed for 900 min. ageing. At 723K, hardness values show slight increase at the initial stage of ageing followed by almost constant behavior for long ageing times. Specimens aged at 773K for different ageing times show a different behavior as compared to specimens aged at 673K and 723K. The hardness values show a gradual increase during the time interval 60 to 600 min. and then a sharp increase in hardness was observed for long ageing times. Maximum value (99.50 HV) of hardness was observed for 900 min. of ageing.
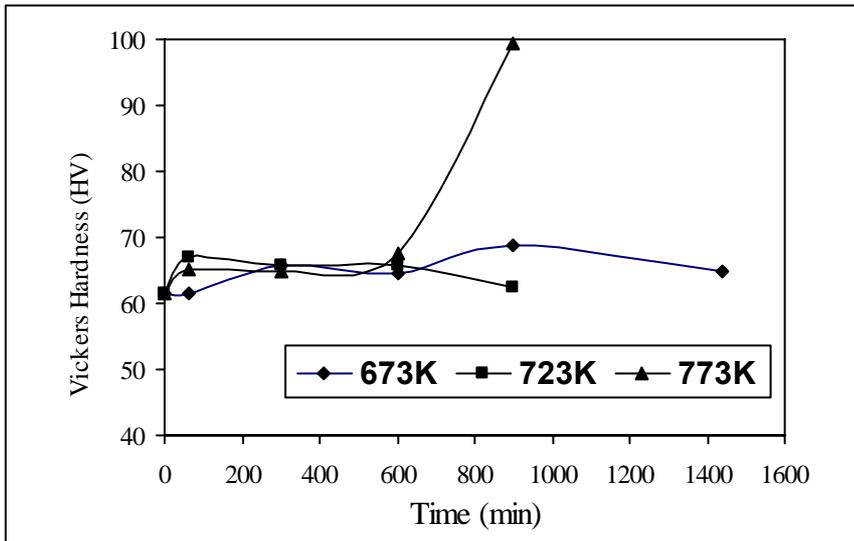

Fig. 4: Vickers Hardness for specimens aged at 673K, 723K and 773K.

X-RAY DIFFRACTION

X-ray diffraction study was performed at room temperature after quenching the specimen and after each ageing at different temperatures for different times. The recorded patterns are shown in Figs.5-8. Quenched specimen was found to consist of Fe_3O_4 (cubic) phase in the α-Fe matrix and no peaks for the precipitated phase (Cu) was observed. The same oxide phase i.e. Fe_3O_4 (cubic) in the α-Fe matrix was observed in samples aged at various temperatures and times along with one or two small peaks of Cu (cubic) as the precipitated phase as shown in Figs. 5-8.
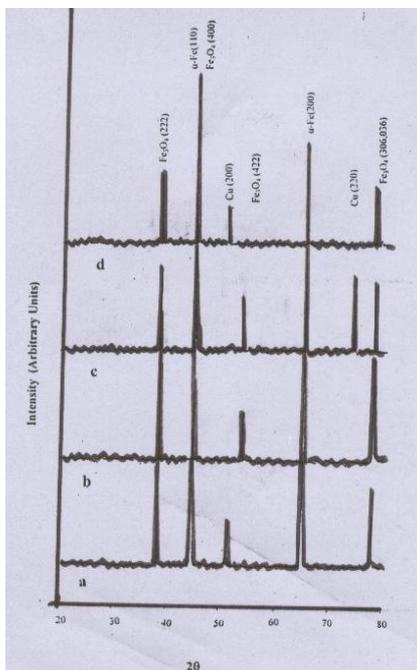
Fig. 5: XRD patterns for a) as received, b) quenched, and aged at 673K for c) 60 min., d) 300 min.
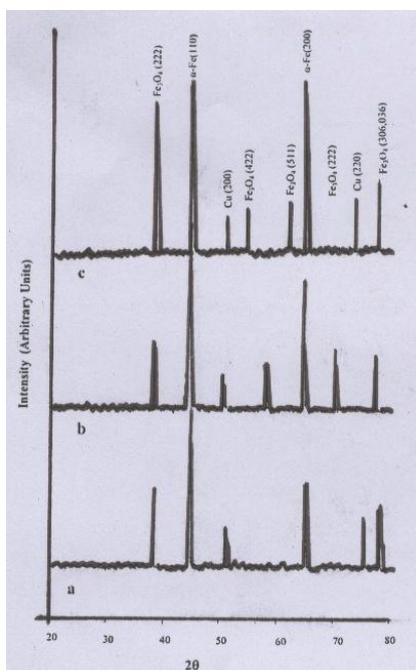

Fig. 6: XRD patterns for specimens aged at 673K for a) 600 min., b) 900 min., and c) 1400 min.
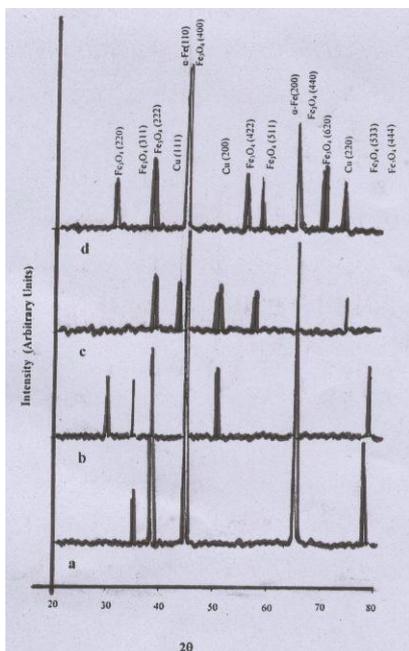

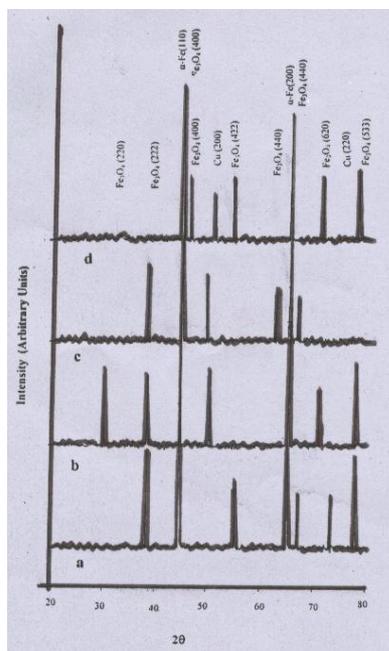Fig. 7. XRD patterns for specimens aged at 723K for a) 60 min., b) 300 min., c) 600 min., d) 900 min.

Fig. 8. XRD patterns for specimens aged at 773K for a) 60 min., b) 300 min., c) 600 min., d) 900 min.

DISCUSSION

The initial rise in resistivity for Fe-0.5wt% Cu alloy during early stages of ageing at 673K and 723K may be referred to as the segregation of solute Cu atoms in small clusters (metastable) coherent with the α-Fe matrix as obvious from Figs. 5-8. The existence of resistivity maximum during the early stages of precipitation process is well known for clusters/GP-zones formation in Fe and Al-base alloys [Osamura *et al.* 1973, Hilal *et al.* 1975, Ansari 1989, Rana and Ansari 1995]. Electrical resistivity maximum can be attributed to a certain size of precipitate cluster giving maximum scattering of conduction electrons per atom in the cluster. Present results seem to be in line with already observed sequence of the precipitation process in Fe-Cu system [Deschamps and Poole 2001]:

α-Fe (Supersaturated solid solution) ⟶ metastable BCC Copper
⟶ 9R Copper (FCC) ⟶ FCC ε –Cu
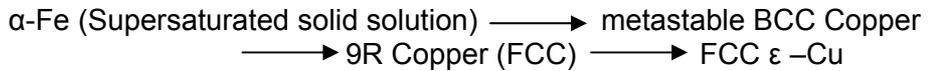
The nucleation of Cu precipitates/clusters could be promoted by the presence of dislocations and/or oxide particles in the α-Fe matrix (Figs. 5-8), which could be a cause for the coarsening of Cu-rich precipitates for long time ageing. This could be represented by the decrease in resistivity/hardness for long ageing times [Ansari *et al.* 1994, Rana and Ansari 1995]. The alloy showed little hardening (in terms of Vickers hardness) in the early stages of ageing process particularly at 673K and 723K and up to 300 minutes ageing at 773K and then a substantial amount of hardness increase (~ 40HV) was observed. This result is in good agreement with that of Deschamps *et al.* [2001] for the Fe-0.8wt.%Cu alloy. The precipitates responsible for the initial hardening process must be very small and hence could be metastable and coherent with the matrix. The peak strength could be related to a critical size of the Cu-precipitates as suggested by Deschamps *et al.* [2001]. They also showed that the BCC Cu-precipitates upto 3 nm size were metastable which transformed to 9R Cu- precipitates on further ageing.

The strengthening is usually described by the modulus of strengthening as suggested by Russel and Brown [1972]. So, strength of the interaction between dislocations/oxide particles and the precipitates increases with the particle size on increasing time of ageing. Whereas Osamura *et al.* [1994] assumed that the hardening during the initial stage is controlled by coherency strains. Thus the decrease in strength could be attributed to the loss of coherency of the precipitates. This could also suggest that when BCC copper precipitates coherent with the α-Fe matrix transform to FCC copper precipitates and loose coherency, their strength and hardness show a decrease.

CONCLUSIONS

The initial rise in resistivity may be attributed to the clustering or G.P zones formation of solute (Copper) atoms. This could also be visualized by a small change in hardness at the initial stages of precipitation hardening process particular at 673 K and 723 K. The decrease of resistivity and large rise in hardness at 773 K could be attributed to the transformation of Cu – clusters (metastable) to more stable Cu – precipitates. This is also obvious from the x–ray diffraction patterns which show clear peaks of Cu at ageing temperature of 773 K for long time ageing. Measured resistivity data during ageing at 723 K and 773 K for long ageing times was found to obey the diffusion controlled coarsening theories.

References

Ansari, M.I. (**1989**) PhD Thesis, Punjab University, Lahore.

Ansari, M.I. (**1990**) *Proceedings of 2nd National Symposium on Frontiers in Physics*, Lahore, Pakistan, p. 60.

Ansari, M.I., Manzoor, A. and Sheikh, Z.A. (1994) *Tr. J. Phys.* **18,** 642-648.

Blackstock, J.J., Ackland, G.J. (**2001**) *Phil. Mag.* A **81**, 2127-2148.

Deschamps, M., Militzter, M. and Poole, W.J. (**2001**) *ISI J. Internat.* **41**, 196-205.

Fernández van Raap, M.B. (**2002**) *J. Phys.: Condens. Matter* **14**, 857-864.

Fischer, J. and Jung, P. (**1991**) *J. Nucl. Matter* **179-181**, 1042.

Fischer, J. and Jung, P. (**1992**) *Phil. Mag.* A **65**(2), 497.

Hilal, A.J., Edwards, J.T. and Wilkes, P. (**1975**) *Phil. Mag.* **32**,189.

Hornbogn, E. (**1983**) In: R.W. Cahn and P. Hassen (Eds.), *Physical Metallurgy*, 3rd edn., Elsevier Sci. Publishers BV, pp. 1073-1137.

Hwang, K.S., Hsieh, C.H. and Shu, G.J. (**2002**) *Powder Metallurgy* **45**, 2.

Kelly, A. (**1971**) In: A. Kelly and R.B. Nicholson (Eds.), *Strengthening Methods in Crystals, Strengthening Methods in Crystals*, Appl. Sci. Publ. Ltd. London, pp. 947-970.

Langer, J.S., Bar- on and Miller, H.D. (**1975**) *Phys. Rev.* A **11**, 1417.

Marian, J., Worth, B.D. and Perlado, J.M., Odette, G.R. and Diaz, T. (**2001**) *Phys. Rev.* B **64**, 94303.

Metal and Alloys Data Book, JCPDS, 1st edn. (Internat. Center for Diff. Data, 1606 Park lane, Swartmore, Pennsylavania 19081, USA).

Osamura, K., Hiraoka, Y. and Murakami, Y. (**1973**) *Phil. Mag.* **28**, 809.

Osamura, K., Okuda, H., Ochiai, S., Takashima, M., Asano, K., Furusaka, M., Kishida, K. and Kurosawa, F. (**1994**) *ISI J. Internat.* **34,** 359.

Rana, A.M. and Ansari, M.I. (**1995**) *Modn. Phys. Lett.* B **9,** 343-350.

Reed-Hill, Robert E. (**1973**) "Physical Metallurgy Principles", 2nd edn., D. Van Nostrand Co., New York.

Rossiter, P.L. (**1980**) *Phil. Mag.* B **42**, 561.

Rossiter, P.L. and Wells, P. (**1971**) *Phil. Mag.* **24** (1971) 425.

Russel and K.C., Brown, L.M. (**1972**) *Acta Metall.* **20**, 969.

Scott, R., Summerfeld, R. and Carter, C.B. (**1992**) *Phil. Mag.* A **65**(6), 1503.

Smithells Metals Reference Book (**1992**) 7th edn., E.A. Brandes and G.B. Brook (Eds.), Butter Worths, Henemall, Ltd.

Smith, W.F. (**1990**) "Principals of Materials Science and Engineering", 2nd edn., McGraw Hill Publishing Co., New York, Ch. 13.

Solt, G., Waeber, W.B., Frisius, F. and Zimmermann, U. (**1991**) *Mater Sci. Forum*, 1.

Thomas, G. (**1971**) In: A. Kelly and R.B. Nicholson (Eds.), *Strengthening Methods in Crystals*, Appl. Sci. Publ. Ltd. London, pp. 793-858.

Wagner, R. and Kampmann, R. (**1991**) In: R.W. Cahn and P. Hassen, E.J. Kramer (Eds.), *Materials Science and Technology*, Vol. 5, VCH Weinheim Germany.