JOURNAL OF MATERIALS SCIENCE 31 (1996) 6317–6324

# Influence of heat treatment parameters on the microstructure and properties of some zinc-based alloys

B. K. PRASAD, A. K. PATWARDHAN*, A. H. YEGNESWARAN
*Regional Research Laboratory (CSIR), Habibganj Naka, Hoshangabad Road, Bhopal-462 026, India* and **Metallurgical Engineering Department, University of Roorkee, Roorkee-247 667, India*

The present investigation deals with microstructure and property related changes in a zinc-based alloy induced by varying solutionizing and ageing durations and (solutionizing) temperatures. The influence of partially replacing copper by nickel and silicon in the alloy composition has also been studied on similar lines. The microstructure of the as cast, nickel/silicon-free alloy revealed primary $\alpha$ dendrites surrounded by eutectoid and eutectic $\alpha + \eta$ in the interdendritic regions along with the metastable $\varepsilon$ phase. The addition of nickel and silicon partially altered the basic microstructure of the alloy by forming primary silicon particles and intermetallic compounds. Solutionizing led to the breaking of the dendritic structure and redistribution of the alloying elements whilst ageing formed the T′ phase. The morphology of silicon particles and the (nickel containing) intermetallic compound was noted to be unaltered in the nickel and silicon containing alloy during the heat treatment. The hardness of the alloys increased during solutionizing whilst it reduced after ageing when compared with that of the as cast sample value. The presence of silicon and nickel led to an increase in the hardness of the alloy. It also enabled the alloy to retain a higher hardness during the heat treatment. An increased solutionizing duration led to an initial increase in the hardness with a peak value being obtained which was followed by a reduction in the hardness. The presence of nickel and silicon in the alloy reduced the tendency of a reduction in hardness beyond the peak hardness. The microconstituents also lowered the detrimental influence of the coarsening of the T′ phase. The density of the nickel/silicon-free alloy varied in a narrow range. However within this range, solutionizing caused an increase in the density with duration followed by a reduction and finally a steady state value. The addition of silicon and nickel did not affect the density of the alloy to any great extent. The trend followed by the electrical resistivity was identical to that of hardness. Furthermore, the presence of silicon and nickel increased the resistivity of the alloy. Changes in the properties of the alloys during the heat treatment have been explained on the basis of microstructural alterations caused by the heat treatment.

## 1. Introduction

Zinc–aluminium alloys have emerged as a potential engineering material for a variety of applications [1–5]. However, their major limitations have been dimensional instability due to the presence of copper beyond a specific limit [6, 7] and property deterioration at temperatures higher than 100–120 °C [1, 3, 6].

Dimensional changes of the alloys restrict their use to applications where close dimensional tolerances are not a prerequisite. In addition, the deterioration in properties observed at elevated temperatures limits the use of the alloys as tribocomponents to heavy load and slow to medium speed applications and also to general engineering applications [1–5].

It has been observed that measures taken to minimize the dimensional instability and improve the elevated temperature properties would improve the performance of the alloys in applications involving high temperatures. Moreover, stabilizing the alloy microstructure by the formation of the T′ phase by suitable heat treatments [6–11] and the partial replacement of copper by other alloying elements [11] have been suggested to reduce the problem of dimensional changes. The generation of thermally stable phases is expected to improve the elevated temperature properties of the alloys.

The T6 type heat treatment involving solutionizing and artificial ageing plays a dominant role in controlling the material properties [12–14]. In this context, selection of an appropriate solutionizing temperature is very important. This is due to the fact that temperatures higher than a critical value lead to partial

0022–2461  

melting of the alloy [15, 16]. The detrimental effects of partial melting cannot be reversed and, as a result, the casting has to be rejected. On the other hand, lower solutionizing temperatures, are not desired since they give rise to incomplete homogenization. In addition, the duration of solutionizing is also important since too short a period causes incomplete dissolution of the solute elements yielding inferior properties whilst durations longer than the optimum give rise to poor properties due to the coarsening of the microconstituents [12–14]. Similarly, the ageing temperature and duration also affect the behaviour of the materials and as such an optimum ageing temperature and duration are required to produce good properties.

Available information indicates that although some work has been carried out on the heat treatment of zinc-based alloys [6–11], a systematic study with regard to the influence of temperature and duration on properties is lacking. Furthermore, the influence of partial substitution of copper simultaneously by silicon and nickel on the alloy microstructure and properties and its response to a T6 heat treatment has not been studied.

In view of the above, an attempt has been made to study the influence of solutionizing and ageing on the microstructure and properties of a zinc-based alloy. The effects of adding nickel and silicon as partial substitution of copper have also been studied on similar lines.

## 2. Experimental procedure

### 2.1. Alloy preparation

Zinc-based alloys of desired compositions (Table I) were prepared by a liquid metallurgy route into the form of 20 mm diameter, 150 mm long cylindrical castings using permanent moulds. Special high grade (99.99% pure) zinc was used in the synthesis whilst the other alloying elements such as copper, aluminium, magnesium and nickel had purity levels greater than 99.95%. Silicon in the alloy was added in the form of BS LM6 aluminium–silicon alloy.

### 2.2. Heat treatment

Heat treatments were carried out on 20 mm diameter, 15 mm long samples in an electric furnace in air. The solutionizing temperatures selected were 370 and 400 °C whilst ageing was carried out at 180 °C. The duration of the treatment in both cases ranged from 1–22 h. Prior to ageing, the specimens were solution treated at 370 °C for 10 h. Specimens were quenched in water at ambient temperature after the treatments.

TABLE I Chemical composition of the experimental zinc-based alloys

| Alloy designation | Elements (wt %) | | | | | |
|---|---|---|---|---|---|---|
| | Al | Zn | Cu | Si | Ni | Mg |
| Nickel/ silicon-free alloy | 27.5 | Rest | 2.5 | – | – | 0.03 |
| Nickel and silicon containing alloy | 27.5 | Rest | 1.0 | 1.0 | 0.3 | 0.03 |

### 2.3. Microstructural analysis

Microstructural studies were carried out on metallographically prepared samples (20 mm diameter, 15 mm long) after etching with diluted *aqua regia*. Optical as well as scanning electron microscopy was utilized for the microstructural characterization of the alloys. The wavelength dispersive X-ray spectroscopic (WDXS) facility attached with the scanning electron microscope (SEM) was used to confirm the presence of nickel/silicon containing microconstituents.

### 2.4. Property characterization

The hardness, density and electrical conductivity of the metallorgraphically prepared samples (20 mm diameter, 15 mm long) were measured. An average value obtained from three individual observations is reported in this study.

The hardness was measured at an applied load of 15 kg using a Vicker's hardness tester while the density measurements were carried out by a water displacement technique with the help of a Mettler microbalance. The electrical conductivity of the specimens was determined with a Technofour model 757 conductivity meter. The conductivity values were then converted into electrical resistivity values.

## 3. Results

Fig. 1(a–e) shows the microstructure of the as-cast zinc-based alloys. The influence of adding nickel and silicon on the alloy microstructure can also be seen in the figure. The dendritic structure of a silicon/nickel-free alloy is evident in Fig. 1(a and b). A magnified view clearly reveals a primary $\alpha$ dendrite surrounded by the eutectoid and eutectic $\alpha + \eta$ and the metastable $\varepsilon$ phase (Fig. 1c, regions marked by A, B, C and arrow respectively). The alloy containing nickel and silicon revealed complex nickel-based intermetallic compound(s) and silicon particles (Fig. 1(d and e), regions marked D and E respectively). X-ray dot maps of nickel, silicon and zinc contents in areas corresponding to Fig. 1e, as shown in Fig. 1(f–h) respectively, clearly indicate the presence of nickel/silicon containing phases in the alloy.

Fig. 2(a–e) shows the microstructural features of the alloys solution treated at 370 °C. Breaking of the as-cast dendritic structure (Fig. 1(a and b)) and partial homogenization after solutionizing the nickel/silicon-free alloy at 370 °C for 1 h can be noted in Fig. 2a. The homogeneity approached completion after 10 h of solutionizing (Fig. 2(b and c)) while the microstructural constituents became somewhat coarsened at longer solutionizing durations (Fig. 2d). The nickel and silicon comprising alloy also followed a similar trend (Fig. 2(a–d)) in that complete homogenization was realized after solutionizing the alloy for 10 h at 370 °C

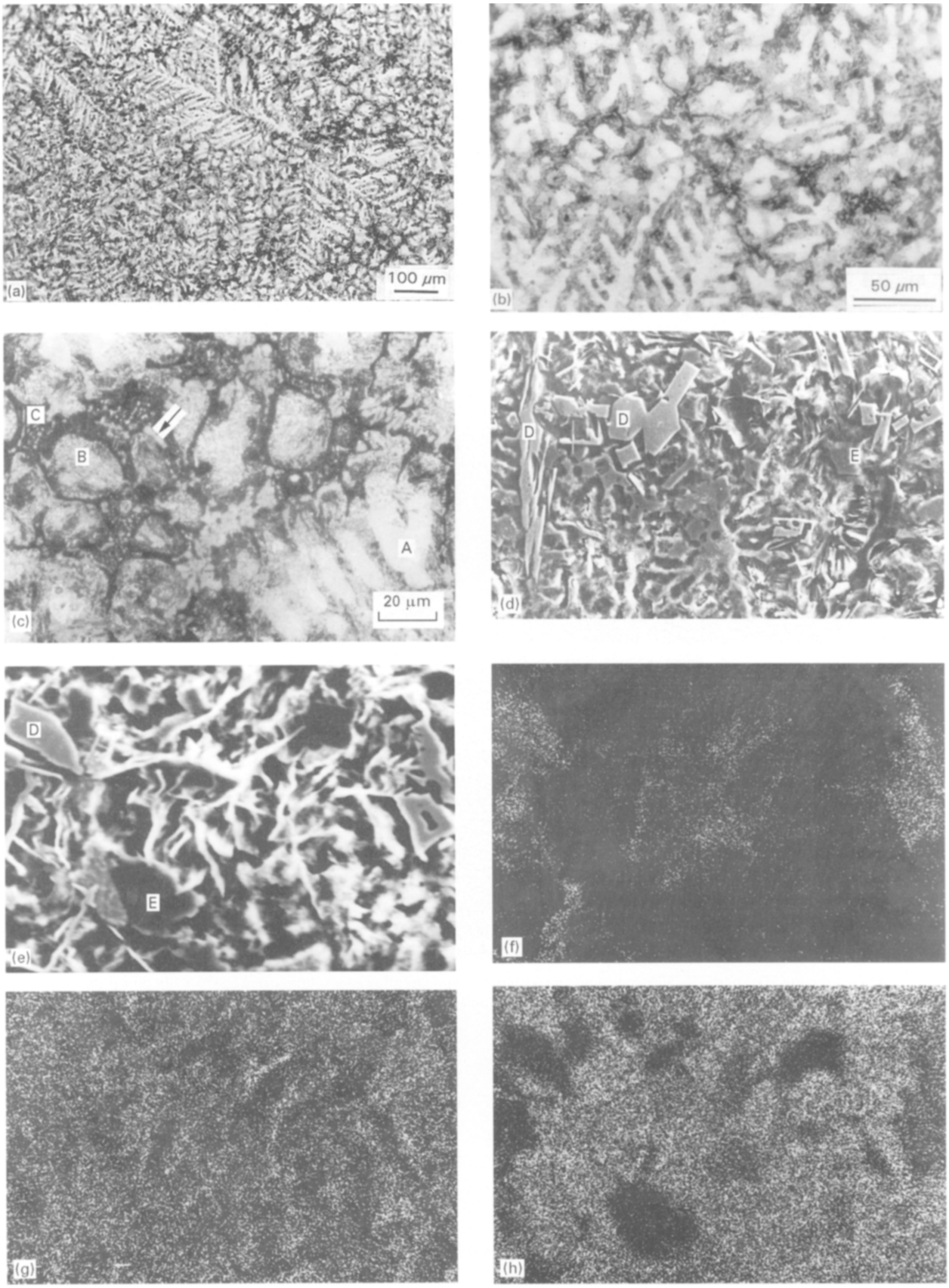


*Figure 1* Micrographs of the as-cast zinc-based alloys: (a–c) not containing nickel and silicon and (d and e) containing nickel and silicon; (f–h) X-ray dot maps of nickel, silicon and zinc corresponding to Fig. 1e. [A: primary $\alpha$, B: eutectoid $\alpha + \eta$, C: eutectic $\alpha + \eta$, Arrow: $\varepsilon$, D: nickel containing compound and E: silicon particle].

(Fig. 2e). Nucleation of a nickel containing phase (region marked A) on a silicon particle (region marked B) can also be observed in Fig. 2e (arrow marked region).

Solutionizing at 400 °C caused partial melting (Fig. 3(a–c)). Interdendritic regions were affected in general (Fig. 3a, region marked B). A significantly refined microstructure in the resolidified regions,

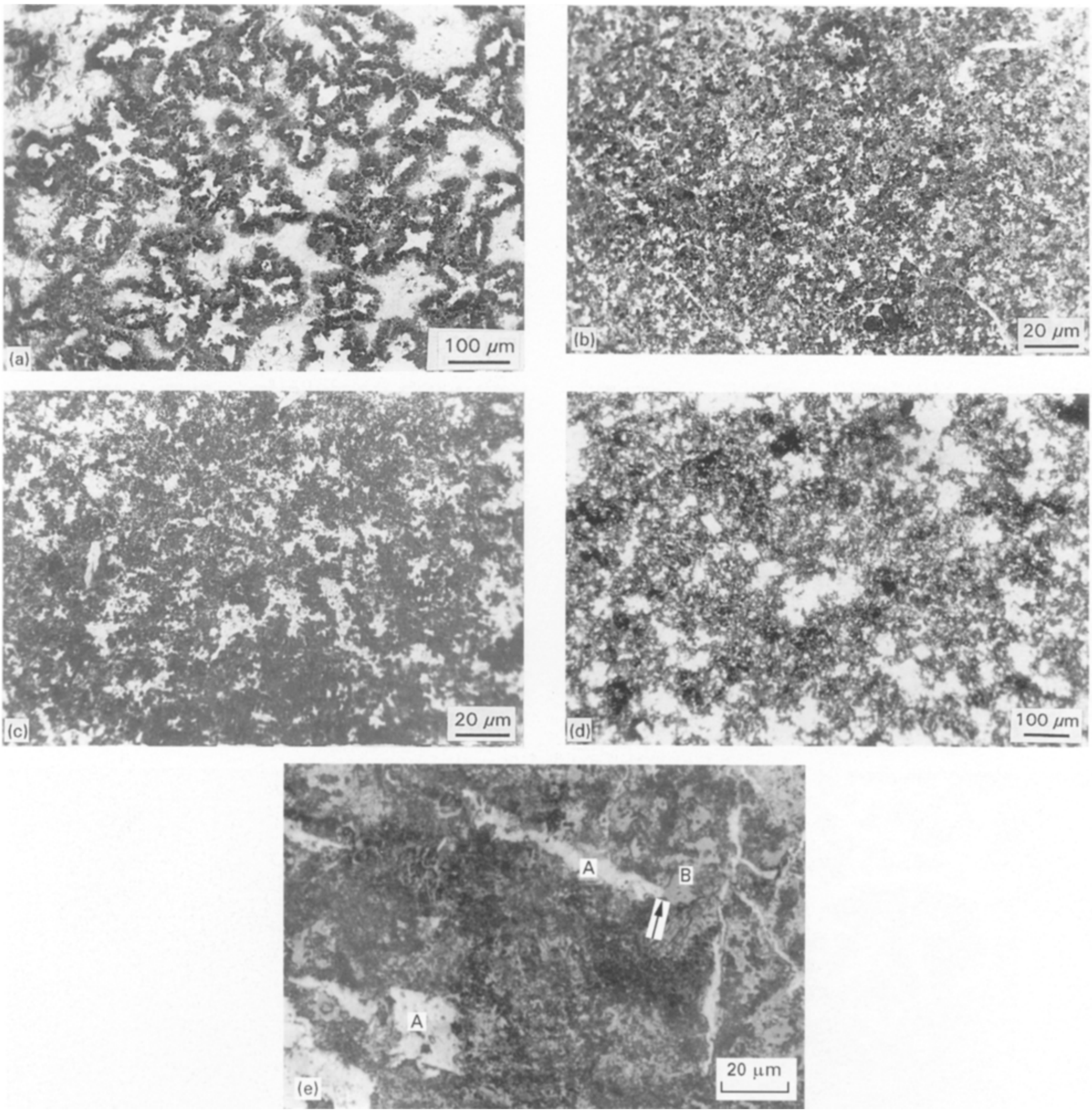


*Figure 2* Microstructure of (a–d) the Ni/Si-free alloy and (e) Ni and Si containing alloy after solutionizing at 370 °C for (a) 1 h, (b and c) 10 h, (d) 22 h and (e) 10 h. [Arrow: nucleation of nickel containing phase on silicon particles, A: nickel containing phase and B: silicon particle].

where partial melting had taken place, can be noticed in Fig. 3b (region marked A). A magnified view clearly shows the extent of the microstructural refinement (Fig. 3c). A similar trend was observed in the alloy containing nickel and silicon except that silicon particles and nickel-based compounds were also present in its microstructure (Fig. 3(d and e)) and also the extent of partial melting was less in this case (Fig. 3(d and e)) than the one not containing the extra elements (Fig. 3(a–c)). Formation of rossettes can also be noted in Fig. 3(d and e) (arrow marked regions).

Ageing the nickel/silicon-free alloy produced the stable T′ phase whose extent of formation and size increased (marginally) with increasing ageing duration (Fig. 4(a–c)). The aged specimens of the silicon and nickel containing alloy contained silicon particles and nickel-based compound(s) along with the T′ phase (Fig. 4(d and e)). The nucleation of a nickel containing intermetallic compound (region marked A) on silicon (region marked B) can also be noted in Fig. 4d (arrow marked region). The presence of the nickel/silicon containing phases was confirmed through X-ray dot mapping of nickel, silicon and zinc (Fig. 4(f–h) respectively) in the areas corresponding to Fig. 4e.

The influence of solutionizing and ageing temperature and duration on the hardness of the alloys is presented in Fig. 5. It may be noted from the figure that both alloys exhibited an overall improved hardness after solutionizing when compared with that in the as-cast condition. Longer treatment durations beyond a critical one (corresponding to the attainment of peak hardness) did not have much influence on the hardness (Fig. 5). Identical observations were also made for the alloy containing nickel and silicon except that it possessed an overall higher hardness than the former alloy. Moreover, increasing the solutionizing

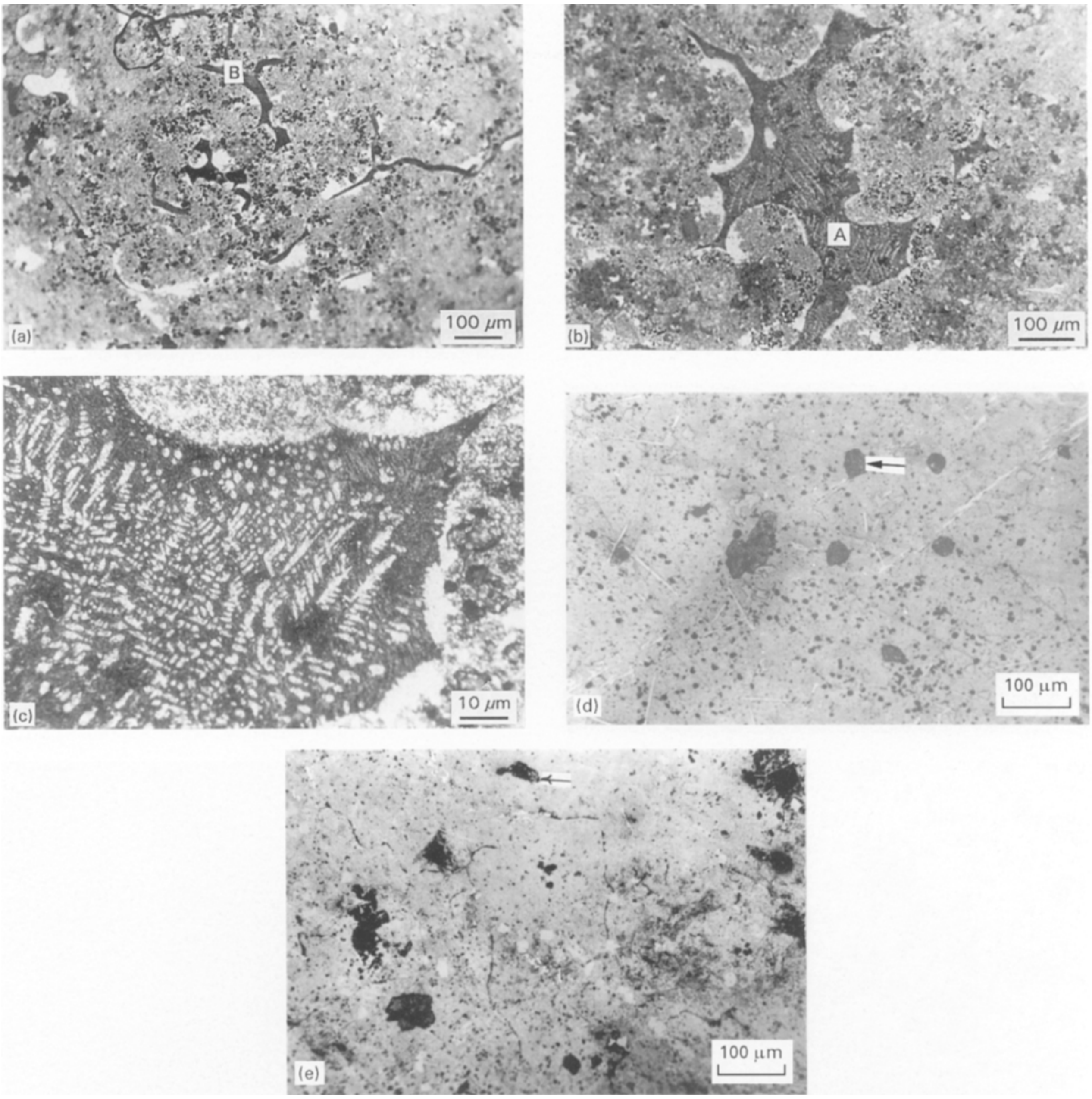


*Figure 3* Microstructural features of (a–c) the Ni/Si-free alloy and (d and e) the alloy containing Ni and Si treated at 400 °C for (a) 1 h, (b and c) 3 h and (d and e) 3 h. [A: refined microstructure, Arrow: rossettes, B: partially melted regions].

temperature deteriorated the hardness of the nickel/silicon-free alloy whereas the hardness of the other alloy remained practically unaffected by increasing the temperature.

Ageing led to a considerable reduction in the hardness values of the alloys as compared to the ones in solutionized and as-cast conditions (Fig. 5). Longer ageing durations further lowered the hardness of the alloys. Once again the nickel and silicon containing alloy attained a higher hardness than that of the one without these elements.

Fig. 6 shows plots of the electrical resistivity versus the duration of solutionizing and ageing. The influence of the solutionizing temperature can also be observed in the figure. A higher resistivity of the nickel and silicon containing alloy than that of the one not containing the elements is evident in the figure. The electrical resistivity of the alloys was influenced by the duration of solutionizing and ageing (Fig. 6) in a manner similar to that of the hardness (Fig. 5). However, increasing the solutionizing temperature caused the resistivity of the nickel/silicon-free alloy to increase while a reverse trend was noticed in the case of the alloy containing the extra elements (Fig. 6).

The influence of heat treatment parameters such as temperature and duration on the density of the alloys is shown in Fig. 7. A narrow range of variation in the property can be noted in the figure. The nickel/silicon-free alloy initially had an increased density which was followed by a decrease and finally it attained a steady state value. A higher solutionizing temperature resulted in an improved density. The property deteriorated somewhat after ageing (Fig. 7). On the other hand, no peak was observed in the density versus duration plot for the nickel and silicon containing alloy.

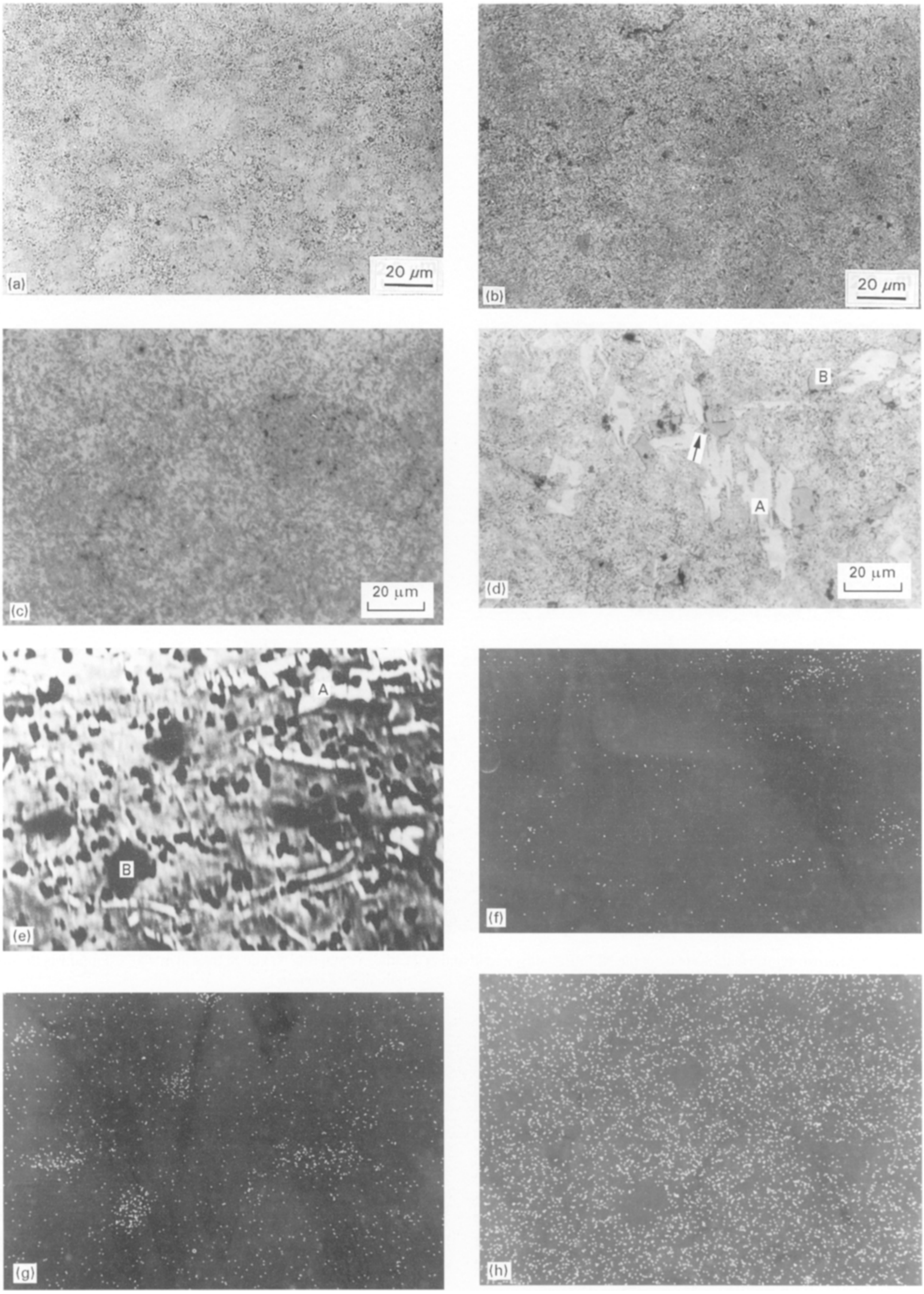


*Figure 4* Microstructure of (a–c) Ni/Si-free alloy and (d and e) Ni and Si containing alloy after ageing at 180 °C for (a) 1 h, (b) 8 h, (c) 22 h and (d and e) 8 h; (f–h) X-ray dot maps of nickel, silicon and zinc corresponding to Fig. 4e. [A: nickel containing phase, B: silicon particles and Arrow: nucleation of nickel containing phase on silicon].

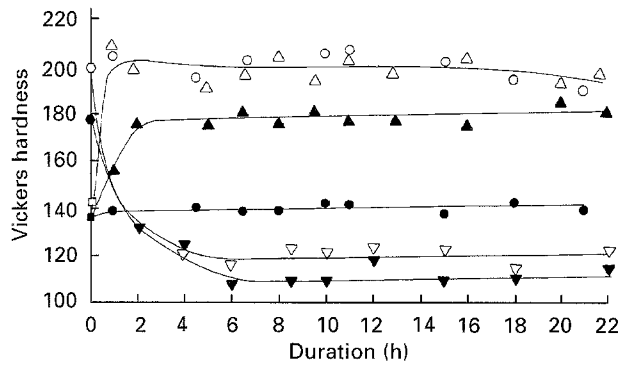


*Figure 5* Hardness versus solutionizing and ageing duration plots. The effect of solutionizing temperature is also shown. The data was taken for the Ni/Si-free alloy at, (▲) 370 °C, (●) 400 °C (▼) 180 °C, (■) as-cast, (⬢) ST 370 °C 10 h and also for the Ni and Si containing alloy at (△) 370 °C, (○) 400 °C, (▽) 180 °C, (□) as-cast and (⬡) ST 370 °C 10 h.

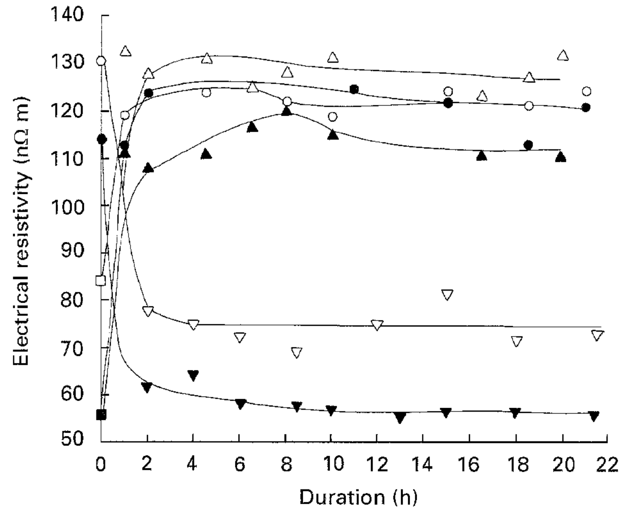


*Figure 6* Electrical resistivity of the alloys plotted as a function of solutionizing and ageing duration. The influence of solutionizing temperature may also be noted in the figure. The data was taken for the Ni/Si-free alloy at (▲) 370 °C, (●) 400 °C, (▼) 180 °C, (■) as-cast, (⬢) ST 370 °C 10 h and also for the Ni and Si containing alloy at (△) 370 °C, (○) 400 °C, (▽) 180 °C, (□) as-cast and (⬡) ST 370 °C 10 h.

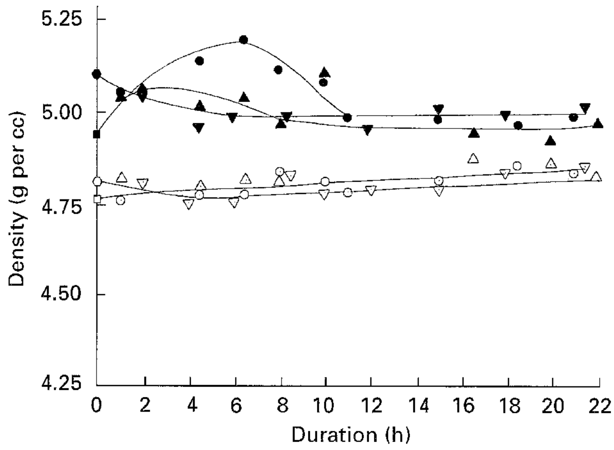


*Figure 7* Density of the alloys plotted as a function of duration of solutionizing and ageing. The influence of solutionizing temperature on the property is also shown. The data was taken for the Ni/Si-free alloy at (▲) 370 °C, (●) 400 °C, (▼) 180 °C, (■) as-cast, (⬢) ST 370 °C, 10 h and also for the Ni and Si containing alloy at (△) 370 °C, (○) 400 °C, (▽) 180 °C, (□) as-cast and (⬡) ST 370 °C 10 h.

## 4. Discussion

The zinc-based alloys used in the present investigation (Table I) conformed to the hypereutectoid composition as far as their aluminium content is concerned [17]. Such a composition leads to the eutectoid transformation forming $\alpha + \eta$ (Fig. 1c, region marked B). Microsegregation resulting from the difference in density and melting point of zinc and aluminium also causes limited eutectic transformation to occur forming (eutectic) $\alpha + \eta$ (Fig. 1c, region marked C). The first phase to solidify is the aluminium rich solid solution ($\alpha$) appearing as primary dendrites (Fig. 1c, region marked A). This is followed by the eutectoid and (a limited amount) of eutectic transformation leading to the occurrence of the $\alpha + \eta$ phases in the interdendritic regions. The existence beyond a critical limit of copper in the alloy allows the formation of the metastable $\varepsilon$ compound (Fig. 1c, arrow marked region) during solidification [10, 18]. Silicon forms discrete particles [10, 11, 19] due to very limited solid solubility with both zinc and aluminium [11] while nickel forms complex intermetallic compounds [20] as is shown in Fig. 1(d–h). The nucleation of nickel containing phase(s) on silicon particles (Figs 2e and 4d) could be attributed to the favourable sites for the nucleation offered by the silicon particles that are formed first during solidification.

Solutionizing the alloy(s) led to the redistribution of the solute elements and to the breaking of the dendritic structure (Fig. 2(a–e)). These factors caused the alloy(s) to homogenize (Fig. 2(b–e)). The refined microstructure of the resolidified regions, where partial melting had taken place, (Fig. 3(b and c)) was due to a significantly higher rate of solidification experienced by the regions during quenching from the solutionizing temperature [15]. It may be noted that the solid regions surrounding the molten ones act as a heat sink during the process of cooling thereby facilitating a higher rate of solidification [15].

The formation of the T′ phase (Fig. 4) takes place during the T6 heat treatment (involving solutionizing followed by ageing) by a four phase reaction with the metastable $\varepsilon$ phase [11, 18]. The observation of no change in the morphology of the nickel-based compound and silicon particles in the microstructure of the alloy containing nickel and silicon during the T6 heat treatment could be due to a lower prescribed solutionizing temperature for zinc-based alloys. In Al–Si alloys, where higher solutionizing temperatures have been used, considerable modifications have been reported during T6 heat treatments [12–14].

An increase in the hardness during the initial period of solutionizing (Fig. 5) could be due to solid solution hardening while a minor reduction in the hardness beyond a specific duration could be due to a coarsening of the microconstituents (Fig. 2(c and d)). The detrimental influence of the coarsening of the phases was checked to some extent in the presence of silicon/nickel containing particles/compounds (Fig. 2e) as is reflected by the higher hardness of the alloy containing the elements (Fig. 5). These particles/compounds were also able to reduce the extent of hardness reduction due to the formation of T′ phase (Fig. 5) during the T6 heat treatment [6, 8, 11].

The change in the electrical resistivity of the alloys (Fig. 6) was primarily due to phase transformations taking place during the heat treatment since only insignificant changes in the density occurred (Fig. 7).

Variations (although minor) in the density of the alloys can be attributed to two factors namely (i) annihilation of lattice defects and (ii) the generation of secondary porosity. The annihilation of lattice defects causes the density to increase while secondary porosity has a reverse effect [13]. Thus an increasing density with solutionizing duration in the case of the nickel/silicon-free alloy could be due to the predominant effect of the annihilating lattice defects. Conversely the reduction in density beyond the peak (Fig. 7) could be a result of the predominance of the detrimental effects of secondary porosity [13, 14]. The attainment of a steady state value may be attributed to a balance between the two factors. The absence of a peak by the nickel and silicon containing alloy (Fig. 7) may be due to the fact that it could have occurred before the first observation was made.

Based on the above observations it can be stated that a T6 heat treatment is not desired as far as zinc-based alloys are concerned since it reduces their hardness (Fig. 5). However, the treatment is essential for alloys that are to be used for applications which need close dimensional tolerances and where higher operating temperatures are expected since a T6 heat treatment offers dimensional stability [6–11]. As far as heat treatment parameters are concerned, solutionizing at 370 ° for 10 h followed by ageing at 180 °C for 6–8 h could be a good proposition since this combination does not lead to much deterioration in hardness, one of the important properties controlling the wear performance of the alloys. Solutionizing at 400 °C is not desired in view of partial melting of the alloy(s). Improved hardness of the nickel and silicon containing alloy suggests that the alloy would be more stable at elevated temperatures even after heat treatment.

## 5. Conclusions

1. Solutionizing the zinc-based alloys caused increased hardness over the as-cast ones due to solid solution strengthening. The presence of nickel/silicon intermetallic compounds/particles further increased the alloy hardness.
2. Hardness of the T6 heat treated alloys reduced when compared with that in the as-cast condition. This was attributed to the formation of the stable T′ phase. In this case also, the nickel/silicon containing compounds/particles were able to control any deterioration in the hardness property.
3. Deterioration in the hardness property at longer soaking durations could be attributed to the coarsening of microconstituents whose effects were controlled to some extent by the hard silicon particles and the nickel containing intermetallic compounds.
4. Minor variations in the density of the as-cast and heat treated alloys suggested the generation of secondary porosity to a negligible extent during the treatment.
5. The optimized T6 heat treatment parameters are a solutionizing at 370 °C for 10 h followed by ageing at 180 °C for 6–8 h in view of lower observed deterioration in hardness of the alloys.

## References


1. K. J. ALTORFER, *Met. Prog.* **34** (1982) 29.
2. T. S. CALAYAG, *Mining Engng* **35** (1983) 727.
3. E. J. KUBEL JR., *Adv. Mater. Proc.* **132** (1987) 51.
4. D. APELIAN, M. PALIWAL and D. C. HERRSCHAFT, *J. Met.* **33** (1981) 12.
5. D. ROLLEZ, M. MEEUS and L. GROOTHAERT, in Proc. Int. Sympo. Zinc–Aluminium (ZA) Casting Alloys, 17–20 Aug., 1986, Toronto, Ontario, G. P. Lewis, R. J. Barnhurst and C. A. Loong (eds.), pp 315–322. Society of Die Casting Engineers (SDCE), USA.
6. E. GERVAIS, R. J. BARNHURST and C. A. LOONG, *J. Met.* **37** (1985) 43.
7. K. LOHBERG, *Z. Metallkde.* **74** (1983) 456.
8. E. GERVAIS, H. LEVERT and M. BESS, *Trans. AFS* **68** (1980) 183.
9. N. MYKURA, Y. H. ZHU and S. MURPHY, In Proc. Sympo. Phase Transformations in Solids, Materials Research Society, Symposia Proceedings Vol 21 (Elsevier New York 1984) pp 841–846.
10. S. MURPHY and T. SAVASKAN, *Wear* **98** (1984) 151.
11. P. P. LEE, T. SAVASKAN and E. LAUFER, *ibid* **117** (1987) 79.
12. B. K. PRASAD, *J. Mater. Sci. Lett.* **10** (1991) 867.
13. *Idem*, *J. Mater. Sci.* **28** (1993) 100.
14. B. K. PRASAD, T. K. DAN and P. K. ROHATGI, *Z. Metallkde.* **83** (1992) 781.
15. B. K. PRASAD and T. K. DAN, *ibid*, **82** (1991) 124.
16. *Idem*, *J. Mater. Sci. Lett.* **10** (1991) 1412.
17. G. R. GODLAK and J. GORDAN, *J. Inst. Met.* **92** (1963–64) 230.
18. S. MURPHY, *Z. Metallkde.* **71** (1980) 96.
19. T. SAVASKAN and S. MURPHY, *Wear* **116** (1987) 211.
20. B. K. PRASAD, Ph. D. thesis, Met. Eng. Dept., University of Roorkee, India. 1994


*Received 10 March 1995*
*and accepted 18 March 1996*