Effect of carbon on the mechanical properties of powder-processed Fe–0.45 wt% P alloys

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MS received 9 May 2009; revised 31 December 2009; accepted 5 May 2010

Abstract. The present paper records the results of mechanical tests on iron–phosphorus powder alloys which were made using a hot powder forging technique. In this process mild steel encapsulated powders were hot forged into slabs. Then the slabs were hot rolled and annealed to relieve the residual stresses. These alloys were characterized in terms of microstructure, porosity content/densification, hardness and tensile properties. Densification as high as 98.9% of theoretical density; has been realized. Microstructures of these alloys consist of single-phase ferrite only. Alloys containing 0.45 wt% P; such as Fe–0.45P–2Cu–2Ni–1Si–0.5Mo and Fe–0.45P–2Cu–2Ni–1Si–0.5Mo–0.15C show very high strength. Alloys developed in the present investigation were capable of being hot enough to be worked to very thin sheets and fine wires.

Keywords. Fe–P alloys; mechanical properties; powder metallurgy; forged; ancient iron.

1. Introduction

Archaeological irons often contain levels of phosphorus which are much higher than those found in modern steels. It produces ‘cold short’ behaviour or brittleness during cold working (Rostoker & Bronson 1990; Wiemer 1993; Goodway & Fisher 1988). Phosphorus does not, however, render the iron ‘hot short or brittle’ at high temperature (Goodway & Fisher 1988; Percy 1864) so, in the past the manufacture of an artefact from phosphoric iron by forging should have posed no problems.

Phosphorus has a marked solid solution strengthening effect in ferrite which is of the same order as the interstitial elements, Carbon and Nitrogen. (Tylecote 1986; Allen 1963). It produced marked work hardening in iron when cold worked (Wiemer 1993; Tylecote 1986). The increase in flow stress due to the action of phosphorus promotes cleavage fracture, thus increasing the likelihood of brittle failure in wrought route. (Weng & McMahon 1987) Phosphorus also reduces grain boundary cohesion, thus promoting intergranular failure. It is found

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that the embrittling effect of phosphorus is reduced by the presence of carbon in very small amount (Allen 1963). Phosphorus increases the yield stress and ultimate tensile stress but reduces the elongation and reduction in area at failure, i.e. in both the conventional measures of ductility (Dieter 1988).

In wrought metallurgy Phosphorus is treated as an impurity because in cast steels, phosphorus exhibits strong segregation during solidification, with the formation of inclusions at grain boundaries which lead to embrittlement. Because of this, in the majority of steels its amount does not exceed 0.05%. Cases where certain properties of steels and cast irons are improved by higher phosphorus contents are extremely rare (Lindskog & Carlson 1972).

The main advantages of phosphorus as an alloying element in powder metallurgy are: its ability to form eutectics of relatively low melting points with metals (970, 1150, 1300 and 1048 for the Cu-P, Ni-P, Co-P, and Fe-P systems, respectively); characterized by good fluidity and wettability to metals, alloys and many refractory compounds; high diffusional mobility of its atoms in metals; and its ability to precipitation-harden metals and comparatively low cost (Muchnik 1977). Near-full density pure Fe P/M parts can be very easily manufactured using conventional powder metallurgical process. It was observed that partial replacement of Silicon by a small amount of Phosphorus will activate the sintering process in Fe-Si alloys by the formation of a low melting eutectic, otherwise silicon diffusion is sluggish.

Phosphorus significantly improves ductility and strength of Fe-P based powder alloys (Koczac & Aggarwal 1978). It is therefore, realized that, the Fe-P based alloys, containing alloying elements, such as silicon, molybdenum and nickel could be used for structural applications because of their higher strength than pure iron with reasonably good ductility. Since all these alloying elements (except nickel) are ferrite stabilizers, ferrite phase will be stable even at higher temperatures when substantial alloying is completed.

Copper in Fe-P alloys helps to reduce porosity. The alloying elements molybdenum and Nickel improve the strength of Fe-P alloys. A small amount of carbon is helpful in driving out phosphorus from grain boundaries. Phosphorous also helps carrying alloy constituents into iron matrix. Self-diffusion coefficient of iron (Qu *et al* 1991) and inter-diffusion coefficient of the alloying elements in ferrite is much higher than that in austenite. This diffusion helps in reducing amount of pores in the P/M part. However, during alloying process some additional pores may be created (Qu *et al* 1991) (due to dissolution of elemental particles). If we follow the traditional powder metallurgical process, such as compaction and sintering, for manufacturing high phosphorous Fe-P based alloys, heavy volume shrinkage will be experienced (Moyer 1998). There are several other densification processes available in the literature. Out of all densification processes available, hot iso-static pressing (HIP) is the best as far as density and performance of these P/M parts are concerned. However, the process is extremely costly. Therefore, some pseudo HIP processing could be used for manufacturing these alloys to reduce the cost of processing without sacrificing the benefit of HIP processing. However, HIP process does not have scope of cleaning particle surfaces during processing. Furthermore, existence of prior particle boundaries (PPB) renders them unsuitable because PPB's are source of impurity concentration resulting in inter-particle brittle failure.

In view of this, in the present investigation, the densification of the Fe-P based alloys was carried out by hot powder forging technique (Chandra 2002). Volume shrinkage associated with these alloys is also no more a consideration in hot powder forging. Hot powder forging has another feature which is not available with compacting in a die or HIP. It is essentially the process where shaping and consolidation are deformation based. This causes redistribution of residual impurities if any, situated at the particle surfaces and renders improvement in properties of the final product (Das *et al* 2008).

Figure 1. Cross-section of mild steel capsule used in the present investigation.

2. Experimental

For making Fe–P–Cu–Mo–Ni–Si (with or without carbon) alloys by powder metallurgical technique, Ferro-phosphorus, ferro-silicon, ferro-molybdenum powders were prepared separately by grinding lumps of ferro-phosphorus, ferro-silicon, ferro-molybdenum (containing 22% P, 70% Si, 60% Mo respectively) with the help of mortar and pestle (iron) or filing. Powders with –200 mesh size were employed for preparation of alloys. Pure Copper and Nickel powders having –200 mesh sizes were taken for preparation of these alloys. The powder blends were manually mixed to make desired alloy chemistry. About 500 g of each blended mixture was then poured into a mild steel capsule (as shown in figure 1). The encapsulated powders were heated in a tubular furnace at 1150°C for 45 min in dry hydrogen atmosphere in order to remove the oxide layer from the surfaces of the powder particles. Heated capsules were then forged with a 200 T capacity friction screw press to make slabs using a channel die. Two P/M alloys were made in the present investigation.

These are:

- (i) Fe–0.45 wt% P–2 wt% Cu–2 wt% Ni–1 wt% Si–0.5 wt% Mo alloy
- (ii) Fe–0.45 wt% P–2 wt% Cu–2 wt% Ni–1 wt% Si–0.5 wt% Mo–0.15 wt% C alloy.

The compositions of these alloys are based on the powder mixture. Figure 2 schematically illustrates the process of making slabs through hot powder forging technique. The slabs were then homogenized at 1200°C for 2–3 h depending on the alloy composition to eliminate compositional in-homogeneity. Silicon-containing alloys were heated for 3 h whereas, alloys without Silicon content were heated for 2 h. This is because diffusion of silicon in iron is much slower than the other alloying elements.

All the alloying elements are present in the form of fine particles around pure iron particles. This iron particle is 100% gamma-phase at the homogenizing temperature. Phosphorous (in the form of ferro-phosphorous) combines with this gamma iron powder particle and dissolves in it. As it dissolves, it gets converted into ferrite (figures 3, 4) and as ferrite phase grows out of gamma phase, more and more phosphorous penetrates in it. This helps carry all the other alloying elements in ferrite phase with the exception of carbon. This is because carbon has very low solubility in ferrite. Consequently, carbon is pushed towards gamma-rich region (Erhart & Grabke 1981). As the homogenization proceeds, clear partitioning of alloying elements between ferrite and gamma iron takes place. At the end of homogenization, a major portion of carbon segregates in gamma iron region whereas the other alloying elements are concentrated in the ferrite region. After completion

Figure 2. Schematic diagram illustrating the production of slab by hot forging of encapsulated powder mixture.

of homogenization and lowering of temperatures during furnace cooling there is no gamma phase left as per the equilibrium phase diagram, Carbon diffuses interstitially on cooling, into ferrite, thereby ensuring complete distribution of all the alloying elements including carbon.

Mild steel encapsulation was then removed by machining. The slabs, after removal of mild steel skin, were hot rolled using flat roll and section roll at 900°C to make thin sheets and wires, respectively. Rolling was carried out very slowly at 900°C with 0.1 mm thickness/diameter reduction per pass. The rolling was done using small laboratory scale rolling mill with 10 cm roll diameter. The sheets and wires were then vacuum annealed at 950°C for 40 min to relieve the residual stresses. All the samples prepared this way were characterized in terms of density, microstructure, hardness, and tensile properties as detailed below.

Figure 3. Fe-P binary phase diagram (Kubaschewski 1982).

Homogenized slabs as well as hot rolled and annealed sheets and wires were subjected to metallographic examinations for determining calculated porosity shown in table 2. This includes volume percentage of porosity and grain size. Calculated volume percentage porosities matched with the volume percentage porosities measured by the metallographic method. Hardness of the hot rolled and annealed wires were measured with Vicker's hardness tester using 10 kg load. Samples for tensile testing were either punched out of sheet or prepared from wires. The tensile specimens were tested using Hounsfield tensile tester. The tensile testing was carried out at room temperature with a cross head speed of 1 mm/min. Gauge length of the specimens was 20 mm. Gauge diameter of the tensile sample (wires) was 1 mm.

Figure 4. High temperature gamma loop region of the Fe–P phase diagram (Kubaschewski 1982).

3. Results and discussions

Chemical composition of Fe–P alloys in weight percentage is shown in table 2. Volume percentage porosities were estimated from the measured density of the specimens.

Table 1. Chemical composition of Phosphoric alloys (weight percentage).

Sample	P	Cu	Ni	Si	Mo	C	Fe
(a)	0.45	2	2	1	0.5	-	Balance
(b)	0.45	2	2	1	0.5	0.15	Balance

Table 2. Calculated volume percentage of porosities of the alloys.

Sample no.	As forged density (g/cc)	Rolled and annealed density (g/cc)	Theoretical density (g/cc)	Porosity in rolled and annealed wires, calculated using measured density (vol %)	Porosity in rolled and annealed wires, calculated using quantitative metallographic technique (vol %)
(a)	7.21	7.509	7.623	1.49	3.06
(b)	7.19	7.384	7.596	2.79	3.42

Figure 5. Porosity distribution of the rolled and annealed wires in as polished and unetched condition (magnification 200 X) of the sample (a) and (b) respectively.

Figure 6. Cross-section of hot rolled and annealed alloys (etched with 2% nital) revealing grain structure. Residual alignment of porosity and flattening of pores are observed in all these rolled and annealed alloys.

These estimated volume percentage of porosities are recorded in table 1. In order to verify the correctness of the estimated volume percentage of porosity, the porosities were also measured using quantitative metallographic technique. Rolled and annealed microstructures with the experimentally measured volume percentage of porosity were recorded and shown in figure 5. They are more or less matching with the theoretically calculated volume percentage porosity. The cross-section of the wires showed almost rounded porosity. It is found that copper helps to reduce the volume percentage of porosity in our samples.

Further, the pores are predominantly present in the grain interior as is observed in the microstructures which is beneficial for the mechanical properties. Cross-sections of wires were etched to reveal grain boundaries and are shown in figure 6. The strength of sample (b) was much higher than that of sample (a). The reason for that can be found in the literature.

Carbon displaces phosphorous from the grain boundaries by a site competition effect (Erhart & Grabke 1981; Suzuki *et al* 1985). This causes a reduction in the embrittling

Figure 7. Surface morphology (SEM) and EDAX pattern from different spots of sample (a).

Figure 8. Surface morphology (SEM) and EDAX pattern from different spots of sample (b).

Figure 9. Composition image (secondary image) and line scanning of sample (b).

Table 3. Mechanical Properties of Fe–P alloys.

Sample	Proof stress (MPa)	UTS (MPa)	Total elongation (%)	Hardness (Hv/10 kgf)
(a)	525	852	8.2	331.4
(b)	926.4	1015	8.00	345

effect of phosphorus. Figures 7 and 8 confirm site competition between carbon and phosphorous in our samples. Powder metallurgical phosphoric irons developed in the present investigation are free of any segregation of the alloying elements along the grain boundaries. They get distributed uniformly in the entire structure. This has been confirmed by: Optical microscope (figure 6), Surface morphology (SEM) and EDAX Pattern from different Spots (figures 7, 8), Composition Image (secondary image) and Line scanning (figure 9).

In general, samples containing silicon, molybdenum, and nickel showed large grains. This may be due to the high homogenizing time and temperature used for facilitating effective silicon diffusion. The hardness was found to increase with phosphorus, molybdenum and nickel as well as silicon alloying additions. However, porosity also affected the hardness of these products. The alloy Fe–0.45P–2Ni–2Cu–1Si–0.5Mo having 3.06 vol.% porosity and Fe–0.45P–2Ni–2Cu–1Si–0.5Mo–0.15C with 3.42 vol.% porosity showed considerable improvement in hardness. Their hardness values are 331.4 Hv/10 kgf and 345 Hv/10 kgf respectively.

The Fe–P based alloy (b) containing carbon showed fairly higher strength as compared to alloy (a). Tensile properties, such as proof strength, tensile strength, % elongation and hardness of these alloys are shown in table 3. Figures 10 and 11 showed the engineering stress-strain curves of sample (a) and (b) respectively. These curves showed higher values of total percentage elongation as compare to measured values. Actual values of total percentage

Figure 10. Engineering stress–strain curve of sample (a).

Figure 11. Engineering stress–strain curve of sample (b).

elongation is calculated by formula given below.

$$\text{Total percentage elongation} = \frac{(\text{Gauge length after fracture} - \text{original gauge length})}{\text{original gauge length}}.$$

Here, original gauge length = 20 mm.

The mechanical properties obtained in the present investigation are suitable for structural applications. Few limited tensile tests under cold deformed conditions exhibited UTS well over 900 MPa. However ductility was lowered marginally. This is due to the development of finer grain structures during cold working.

4. Conclusions

The conclusions drawn from the present investigation include:

- (i) Alloys developed in the present investigation have good hot workability.
- (ii) Alloys containing Mo, Ni, Cu and Si (with or without carbon) showed higher strength (> 800 MPa) and higher resilience value with moderate ductility under annealed conditions.
- (iii) As forged and homogenized as well as rolled and annealed Fe–P based alloys developed in the present investigation were characterized using metallographic technique. All the microstructures showed single-phase ferrite grains with porosities well distributed along the grain boundaries as well as inside the grains.
- (iv) Carbon improved the strength without any high reduction in ductility of sample (b) when compared to sample (a).
- (v) Improvement in hardness level due to the combined addition of carbon with phosphorus in alloy (b) was found to be slightly better than that of alloy (a).

References

- Allen N P 1963 *Iron and its dilute solid solutions* (New York: Willey Interscience) 271–308 Archeo-materials Monograph No. 1 Philadelphia PA University of Pennsylvania
- Chandra K 2002 Development of iron-P based soft magnetic materials by P/M route Ph.D. Thesis Department of Metallurgical and Materials Engineering, IIT Roorkee, India
- Das J Chandra K, Misra P S, Sarma B 2008 *Materials Science and Engineering* A479: 164
- Dieter G E 1988 *Mechanical metallurgy* 3rd edn (London: McGraw-Hill)
- Erhart H, Grabke H J 1981 *Met. Sci.* 15: 401
- Goodway M, Fisher R M 1988 *Hist. Metall.* 22: 21
- Koczac M J, Aggarwal P 1978 National powder metallurgy conference proceedings. *Prog. Powder Metall.* 34, 35: 113
- Lindskog P, Carlson A 1972 *Powder Metallurgy International* 4: 39
- Moyer K H 1998 *ASM Hand Book on Powder Metallurgy and Application* 7: 1006
- Muchnik S V 1977 Phosphorus-containing alloys, Encyclopedia of inorganic materials (in Russian) US Kiev 2: 666
- Percy J 1864 *Metallurgy-iron and steel* (London: John Murray)
- Qu X, Gowri S, Lund J A 1991 *Int. J. Powder Metall.* 27(1): 9
- Rostoker W, Bronson B 1990 Pre-industrial iron—its technology and ethnology
- Suzuki S, Abiko K, Kimura H 1985 *Trans. ISIJ* 25: 62
- Tylecote R E 1986 The pre-history of metallurgy in the British Isles London The Institute of Metals
- Weng Y Q, C J McMahon 1987 *Mater. Sci. Technol.* 3: 207
- Wiemer K 1993 Early british iron edged tools—A metallurgical survey Ph D thesis University of Cambridge