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Effect of carbon on mechanical properties in $Fe_{0.5}Co_{0.5}$ alloys

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Effects of carbon addition on brittleness and ductility in equiatomic iron–cobalt alloys have been investigated. In alloys containing 0.5 to 2 at % C, which are ductile when quenched from 800° C, it is found that brittleness occurs due to decarburization, but ductility is reobtained by the recarburizing of the specimens when preceded by decarburization. This is shown to be independent of factors, such as coarsening of the grains occurring during heat treatments, existence of impurities and the formation of texture produced during cold rolling, and the existence of carbon is an important factor. In addition, it is described that the alloys, having generally been very brittle in the ordered state, have not always shown embrittlement even after ordering, if only cold rolled severely. The effectiveness of carbon in improving the ductility has been discussed under a proposal that host atoms, iron or cobalt, react with carbon atoms to precipitate carbides; around the individual carbides, zones, with the deviation from the equiatomic composition, are formed, thus rendering the ordering difficult; in other words, since production of the resultant unequiatomic zones corresponds to that of disordered ones, it would be expected that the ductility of such specimens depends on the morphology of distribution of the zones, such as volume fraction, uniformity and density.

1. Introduction

Equiatomic FeCo alloys are too brittle to be cold rolled, but small amounts of additive elements such as vanadium or chromium can improve the ductility considerably, as is well known. In a previous paper, besides these elements, the following elements have been shown to affect ductility: carbon, molybdenum, tungsten, tantalum, niobium and nickel [1].

The fact that carbon is effective gives a favourable condition for the investigation of the effects of additive elements. Easy diffusion of carbon in metals can make decarburization or carburization possible. With these treatments, only the effect of an impurity may be separated from any factors, since the changes occurring in the FeCo alloys can be indicated as a function of carbon alone.

We show that the action of impurities is not the main factor for the brittleness of FeCo alloys and that the existence of carbon has an important role: the carbon forms carbides, the formation of which results in, around the individual carbides, the zones that are denuded of cobalt atoms and this makes the ordering of a CsCl type structure difficult. The formation of the carbides corresponds eventually to that of disordered zones and thus the improvement of the ductility would depend on the distribution morphology of the zones.

2. Experimental procedures

The materials used were composed of high-purity electrolytic iron and cobalt, and 99.99 wt % pure carbon. Ingots were prepared in vacuo by high-frequency induction melting. Weights and sizes of the ingots cast were 6.5 kg with a square section of 70 mm and 890 g with a 35 mm diameter for 2 and 0.5% carbon, respectively. The large ingot, after heating at 1200° C for one hour, was forged to a square bar of side 30 mm, and then hot-rolled into two kinds of plates: 5 and 1 mm in thickness with 50 mm width. The 5 mm plates were reheated at 800° C, iced-brine quenched, and then cold-rolled to 90% reduction. The small ingot was heated at 1050° C for ten minutes, forged to a square bar of side 15 mm, and hot-rolled to two kinds of plates of 5 and 1 mm thickness with 20 mm width. The 5 mm plates were cold-rolled to 90% after reheating at 800° C for ten minutes and quenching in iced-brine water.

Decarburization was carried out in a wet hydrogen stream (20° C Dewpoint) at 900° C or 1050° C for ten hours, using specimens of 0.5 mm thickness prepared by cold rolling. On microscopic observation, progress of the decarburization was checked and could be recognized as having been achieved perfectly for the majority of the test pieces used, although a difference in grain size was found in both treatments, namely 900 and 1050° C.

Carburization was carried out in a stream generated from butane gas, at 930° C for three hours (carbon potential of the gas was 1.2%). Carbon contents resulting from the heat treatment were checked by microscope only, no chemical analysis being performed. According to the observation, carbon could be estimated to be over 0.5% in specimens under both conditions.

A method of replicating was employed for the determination of carbide compositions: they were mechanically extracted from deeply etched specimens by cellulose film, fixed with carbon film vaporized on the carbides, scooped onto copper mesh after dissolving the cellulose and washing the carbon film obtained, and then they were submitted to measurement. These carbides were measured by a H-700H analytical electron microscope attached with a Kevex's energy dispersive spectrometer, operating at 200 kV. For the observation of structural changes, a H-500 transmission electron microscope was used operating at 125 kV.

An X-ray diffractometer was used for determining the long-range order parameter, S, with Co$K\alpha$ radiation. Line intensities and profiles were measured and the parameter S was evaluated from the ratio of the superlattice (100) to the fundamental (200) line intensity.

Tensile testing was carried out with a crosshead rate of one millimetre per minute. The specimen dimensions were 20 mm in gauge length, 2 to 3 mm in width and 0.5 to 1 mm in thickness.

For metallographical testing, a solution of 5% nital was used for etching and extraction replicating; a 95% CH_3COOH–$HClO_4$ solution was used for foil observations.

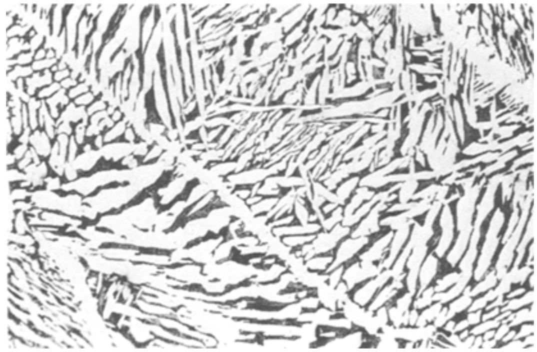

Figure 1 A microscopic structure of an FeCo–2C alloy in as cast, × 165.

Heat treatments were performed in salt baths for ordering, and in a tube furnace, with streaming argon gas, for heating at temperatures over 800° C.

3. Experimental results

3.1. Structures and mechanical properties in annealed states

An as-cast structure of the alloy containing 2% carbon is shown in Fig. 1. Pearlite, the black regions, lies in a ferritic matrix (white). A martensitic structure was not obtained even with quenching from 1100° C where only an austenitic phase exists. The quenching led to a finer structure of pearlite. The plate-like carbides in the pearlitic structure were observed to easily form spherical carbides when heated at temperatures between 750 and 900° C; for example, in the specimens which were severely cold-rolled, such carbides occurred within five minutes of heating at 800° C. This spheroidization strongly affected workability and allowed cold rooling up to 90% to be accomplished, although with the pearlitic structure no cold rooling was undertaken, because of hardening, except up to about 25% reduction. In Fig. 2a spheroidal structure, obtained by heating 2% carbon alloy at 800° C for one hour after hot rolling, is shown, with no pearlitic structure.

Table I shows effects of annealing on mechanical properties. When as-hot rolled, the 2% carbon alloy is very brittle, no ductility being observed. Quenching from 800° C, however, causes a recovery in ductility, irrespective of the differences in carbon content and in rolling conditions. Brittleness of as-hot rolled specimens seems to be due to the formation of a superlattice which occurred during slow cooling from the high temperatures. Therefore, heating to over 800° C and quenching from

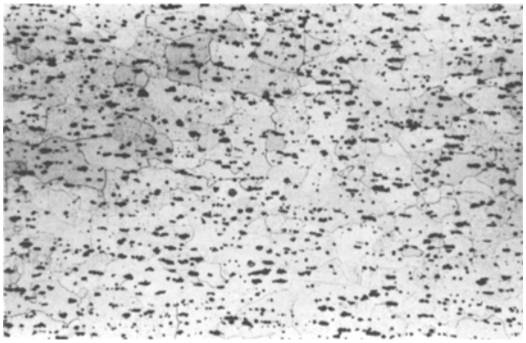

Figure 2 A microscopic structure of an FeCo–2C alloy spheroidized at 800° C for one hour after cold rolling to 90%. Longitudinal section, × 165.

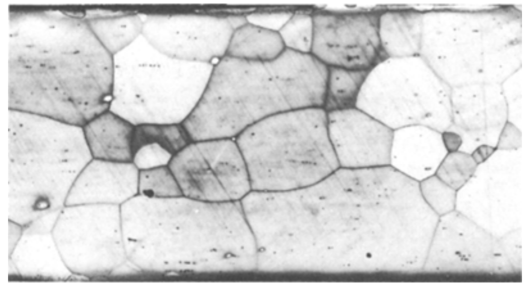

Figure 3 A microscopic structure of an FeCo–0.5C alloy decarburized at 900° C for ten hours after cold rolling. Longitudinal section × 66.

this temperature can be expected to yield the recovery in ductility, since the treatment would be able to suppress the ordering. In Table I the increases in ductility due to such a treatment can be seen for both alloys. For FeCo alloys, eventually, a carbon addition of over than 0.5% can make cold rolling possible, whenever the alloys are quenched from temperatures over 800° C.

3.2. Decarburization and carburization

The alloy containing 2% carbon as well as that of 0.5% was found to have been almost completely decarburized by heat treating during 10 h at temperatures between 900 and 1050° C. Fig. 3 shows an example of the 0.5% alloy decarburized at 900° C for 10 h, and the carbides seen in Fig. 2 are no longer observed. In the treatment at 1050° C for 10 h, grain growth was so rapid that some grains occasionally were observed to have grown to over 3 mm in size.

Carburization was tried for the specimens previously decarburized. Fig. 4 shows a specimen previously decarburized at 900° C and then carburized again at 930° C for 3 h: the vicinity in the centre of the specimen shows an insufficient carburization effect but sufficient grain growth, whereas in the regions approximately one-third from the surface, spheroidized carbides are clearly observed, which indicate the progress of carburization. In order to ascertain the effect of grain growth resulting from decarburization and carburization on the change in mechanical properties, an experiment was undertaken in which a specimen was sealed in an evacuated capsule of a quartz tube to prevent decarburization and then heat-treated to undergo the same process as for decarburization. From this it was found that in the sealed specimen decarburization hardly took place and the structure so obtained was similar to that of the decarburization consisting of very large grains.

In Table II the mechanical properties of the 0.5% carbon alloy are shown. All the specimens could not be quenched from the decarburization and carburization temperatures, and hence they

TABLE I Effect of annealing on mechanical properties of FeCo–C alloys

Content of carbon (at %)	Rolling conditions	Annealing temperature (° C)	Mechanical properties	
			Elongation (%)	Tensile strength (kg mm^{-2})
		as hot rolled	1.3	67.4
2	hot rolled	1100 WQ*	10.5	98.6
		800 WQ	14.5	68.7
		as cold rolled	1.0	126.4
2	cold rolled to 84%	1100 WQ	8.0	119.6
		800 WQ	13.8	81.4
		1050 IBQ	14.5 17.5	76.8 77.5
0.5	cold rolled to 90%	900 IBQ	15.5 16.8	63.2 64.4
		800 IBQ	14.3 14.8	67.3 69.4

*WQ – water quenched.

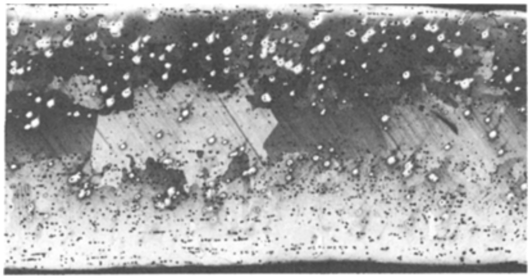

Figure 4 A microscopic structure of an FeCo–0.5C alloy carburized after decarburizing at 900° C for ten hours. Longitudinal section, × 66.

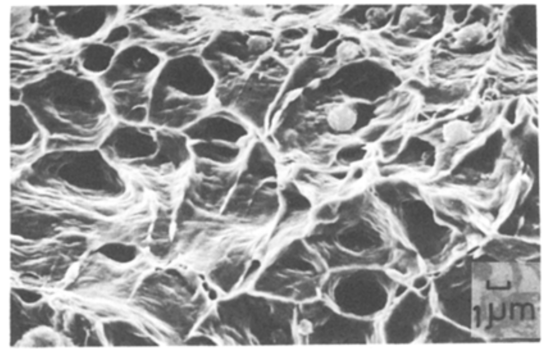

Figure 5 A fractrograph of an FeCo–0.5C alloy carburized after decarburizing at 1050° C for ten hours.

again were finally quenched from 800° C so as to eliminate ordering thought to occur during the cooling. The quenching treatment showed little effect on the further grain coarsening for the specimen preceded by annealing. In the decarburized specimens decreases in elongation and in tensile strength were obviously seen. There are scattered values, which are due to the heterogeneity of decarburization; many carbides were confirmed by microscopy in the specimens showing ductility that represent the scattered values. From the results, decarburization can be concluded to cause the specimens to embrittle.

The carburization can bring about an improvement in ductility. Although an elongation falls, on average, from about 14 to about 5% after the decarburization, unquestionably a recarburization again produces an increase in the elongation to about 14%. On the other hand, the specimens that were sealed in a capsule and then treated under the same condition as the decarburization process have been observed, under metallographical examination, to be the same in grain size and in carbide distribution as those having undergone the treatment, and yet they exhibited a ductility of about 17%, on average. This shows that the embrittlement of FeCo alloys is not due to grain growth, but due to a lack of carbon atoms; the existence of carbon relates directly to the increasing ductility.

Fig. 5 is a fractograph in a carburized specimen, displaying a dimple pattern in which the carbide lie. With the fractography, the specimens having an elongation of more than 13.5% showed dimples without exception, whereas those having an elongation of less than 13.5% showed mixed patterns of dimples, grain boundary cracking and cleavage

TABLE II Effect of decarburization and carburization on mechanical properties of FeCo–C alloys

Content of carbon (at %)	Heat treatments	Annealing temperature (° C)	Mechanical properties	
			Elongation (%)	Tensile strength (kg mm^{2})
0.5	decarburized at 1050° C for 10 h	800 IBQ	0.3 0.5 3.3 9.0 11.5	15.5 32.3 33.3 41.5 46.7
	decarburized at 900° C for 10 h	800 IBQ	4.0 5.5 6.5	42.6 43.3 48.2
	decarburized at 1050° C for 10 h and then carburized	800 IBQ	13.0 13.5	69.4 85.4
	decarburized at 900° C for 10 h and then carburized	800 IBQ	11.0 16.0	62.7 72.7
	heated in capsule at 1050° C for 10 h	800 IBQ	17.0 20.5	62.6 65.7
	heated in capsule at 900° C for 10 h	800 IBQ	13.5 17.0	65.6 65.9

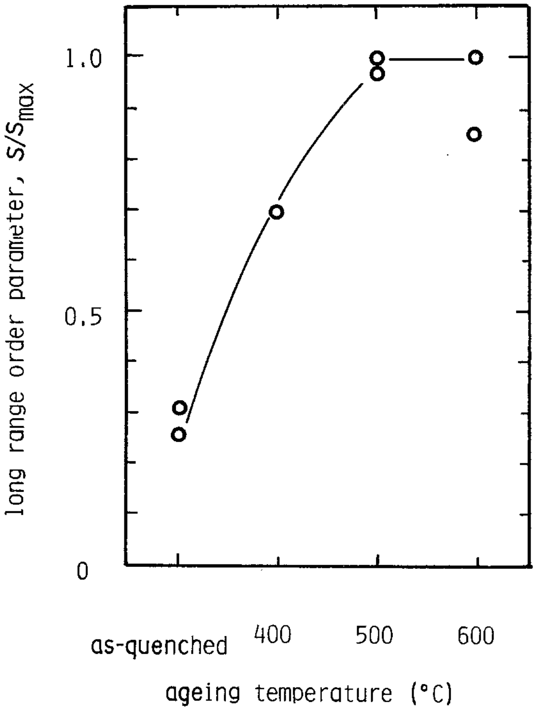

Figure 6 Effect of ageing on ordering in an FeCo–2C alloy cold-rolled to 90% and then aged at temperatures for one hour after heating at 800° C for ten minutes followed by water-quenched.

fracture. The cleavage patterns showed a tendency to increase with decreasing carbon and/or with an increasing degree of ordering.

3.3. Embrittlement resulting from ordering and effect of cold rolling

Progress of ordering, based on the ageing treatment, was examined in specimens containing 2% carbon, which were cold rolled to 90%, heated to 800° C and water-quenched, and then aged at 400 to 600° C for 1 h. The results are indicated in Fig. 6. Even the quenched state shows ordering of about 25%, probably due to the water-quenching. Ageing at 400° C for 1 h presents ordering of about 70%, and a saturated value seem seems to be reached in the ageing processes at 500 or 600° C.

In Table III the effects of different heat treatments prior to ordering on mechanical properties are given for 0.5 and 2% carbon alloys. In the case of 2% carbon, all of the as-hot rolled specimens are brittle, whenever they are aged. Such specimens, though ductile when quenched from 800° C as shown in Table I, have a tendency to embrittle gradually with the increasing degree of ordering.

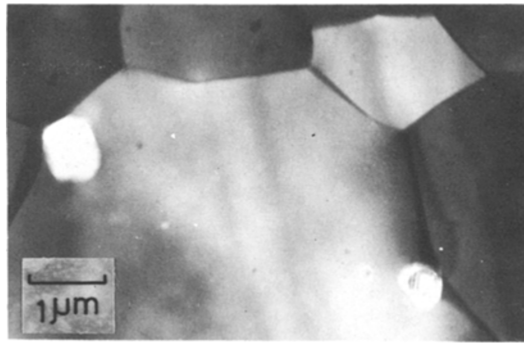

Figure 7 A transmission electron micrograph of an FeCo–2C alloy annealed at 800° C for ten minutes.

In both alloys, of 0.5 and 2% carbon, decarburized specimens are observed to decrease in elongation and in strength with an increasing degree of ordering. The specimens, cold rolled to 90%, however, do not always show embrittlement even after ordering; as for 0.5% carbon the elongation remains constant at about 10%, on average, and for 2% carbon it also retains a value of about 8%. As can be seen in 2% carbon, in the case of the cold-rolled specimens followed by requenching from 800° C, the embrittlement occurring with an increasing degree of ordering, if any, is not so drastic as was expected, compared with the case for the specimens which were aged without cold rolling. These phenomena indicate that cold working is effective for the suppression of the embrittlement, i.e. for improvement of the ductility.

According to the observation of thin foils in the cold-rolled specimens, a complex structure having numerous dislocations was observed, and such a structure could be seen to change into a dislocation-free structure on heating for more than 2 min at 800° C. Fig. 7 represents this example, showing the 2% carbon alloy cold rolled and then quenched after heating for 10 min at 800° C, in which there is a dislocation-free structure and blank holes indicating traces of large carbides. Fig. 8 is a photograph showing the specimen which was aged at 600° C after quenching, in which fine precipitates exist within grains. Whether the precipitates are carbides or not could not be identified, but they are probably carbides. This possibility may be supported by the results shown in Table III: in the 0.5% carbon alloy rolled and then quenched from 800° C, the strength of the specimen which was aged at 400° C during 1 h is somewhat greater than the as-quenched state. In addition, the precipitation may be presumed by com-

TABLE III Effect of ordering on mechanical properties of FeCo–C alloys

Content of carbon (at %)	Rolling conditions and heat treatments	Ordering (° C)	Mechanical properties	
			Elongation (%)	Tensile strength (kg mm^{-2})
2	hot rolled	400 1h	1.3	48.1
		500 1h	2.5	65.5
		600 1h	1.3	51.0
		650 1h	2.5	77.5
	hot rolled and then quenched from 800° C	400 1h	10.0	75.5
		500 1h	6.1	53.6
		600 1h	4.2	44.0
		650 1h	4.0	46.7
	cold rolled to 90%	400 1h	7.2 9.0	62.3 125.0
		500 1h	4.0 10.0	101.6 109.6
		600 1h	4.0 9.0	78.4 138.7
		650 1h	5.3 9.0	95.7 124.2
	cold rolled and then quenched from 800° C	400 1h	10.8 15.5	85.7 90.3
		500 1h	6.3	66.2
		600 1h	4.0	51.9
		650 1h	6.5 9.0	54.9 70.9
	decarburized at 1050° C for 10 h and then quenched from 800° C	400 1h	1.8 8.3	28.9 41.7
		500 1h	3.0 4.5	24.7 29.2
		600 1h	2.5 2.5	21.2 22.2
		650 1h	2.0 3.0	20.8 21.2
0.5	cold rolled to 90%	400 1h	10.0 11.5 12.0	74.3 74.6 131.0
		500 1h	9.5 12.5 13.5	69.6 83.1 107.0
		600 1h	6.0 10.5 12.5	74.9 77.5 126.6
		650 1h	11.0	93.2
	cold rolled and then quenched from 800° C	as quenched	14.3 14.8	67.3 69.4
		400 1h	15.0	89.1
		500 1h	6.3	56.2
		600 1h	3.0	41.7
		650 1h	1.3	40.4
	decarburized at 1050° C for 10 h and then quenched from 800° C	as quenched	0.3 0.5 3.3 9.0 11.5	15.5 32.3 33.3 41.5 46.7
		400 1h	2.3 5.5	31.5 35.3
		500 1h	3.3 4.3	26.1 30.4
		600 1h	2.8 6.0	22.5 26.4
		650 1h	1.3 2.3	18.1 19.4

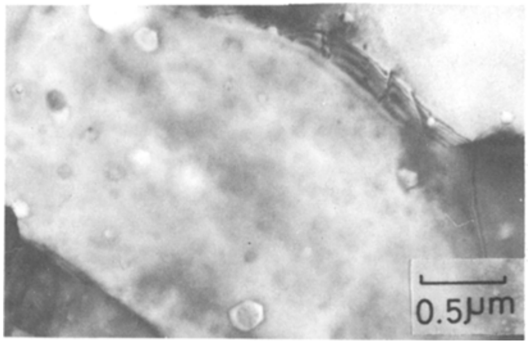

Figure 8 A transmission electron micrograph of an FeCo–2C alloy aged at 600° C for one hour after quenching from 800° C.

paring Fig. 7 with Fig. 8 since particles thought to be carbides can only be observed in Fig. 8 which is the aged specimen. These facts can probably be interpreted by considering that the fine carbides have resulted from precipitation.

3.4. Composition of carbides

The large carbides, which could be observed under the light microscope, were extracted and examined to determine the iron and cobalt components using an analytical electron microscope. Fig. 9 shows the results.

In the as-cast specimen, the iron content is about 54% on average, while the specimens treated at 950 and 1100° C, are slightly cobalt-enriched. The specimen spheroidized at 800° C after rolling to 90%, which exhibits large scattering compared with the three cases now mentioned, has about 58.5% iron on average. Knowing the values of iron and cobalt present, the carbide components of these, though the carbon content could not be measured, is probably a mixture of Fe_3C and Co_3C or to be $(Fe, Co)_3C$.

4. Discussion

The equiatomic FeCo alloys containing 0.5 to 2 at% C, which are sufficiently ductile if only quenched from temperatures over 800° C, have been observed to become gradually brittle with the progress of the decarburization, even though they were quenched from 800° C after the treatment. Although this embrittlement may be thought to be attributed to the grain growth occurring during the decarburization, the doubt may be removed by the results of the experiment in which the specimen sealed in a capsule was heated under the same conditions as for decarburization. The specimen so treated showed similar ductility to that which had not been subjected to such a decarburization process, though the grains occurring during these treatments were large in both specimens. The decarburization-embrittled specimens, moreover, have again showed a ductility, whenever they have again been carburized, in spite of grain coarsening. In view of these facts, it is apparent that the existence of carbon, which is required to be over about 0.5%, controls the brittleness or the ductility of FeCo alloys.

On the other hand, the effectiveness of the carbon addition may be considered to result from the elimination of oxygen thought to be harmful to ductility. This idea, however, is negative, because it cannot explain the reason why a decarburization treatment causes the specimen to embrittle. According to this idea, the ductile specimens hav-

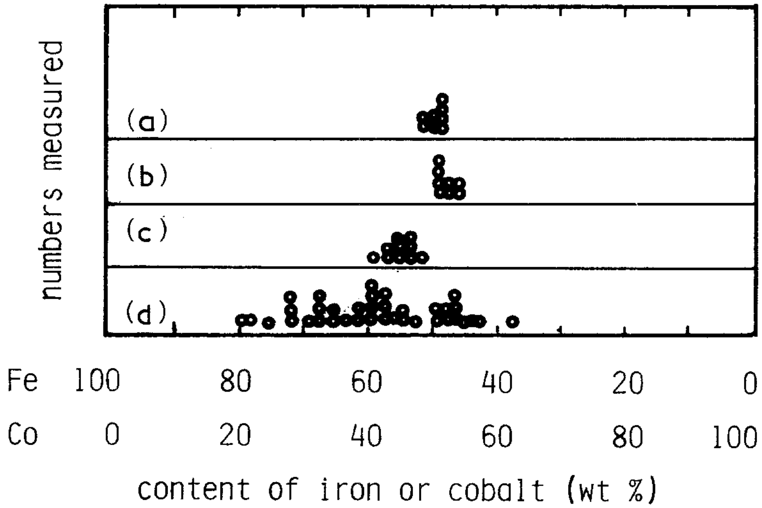

Figure 9 Chemical composition of extracted carbides in different states of an FeCo–2C alloy. (a) Quenched from 950° C, (b) quenched from 1100° C, (c) as cast, (d) quenched from 800° C after cold rolling to 90%.

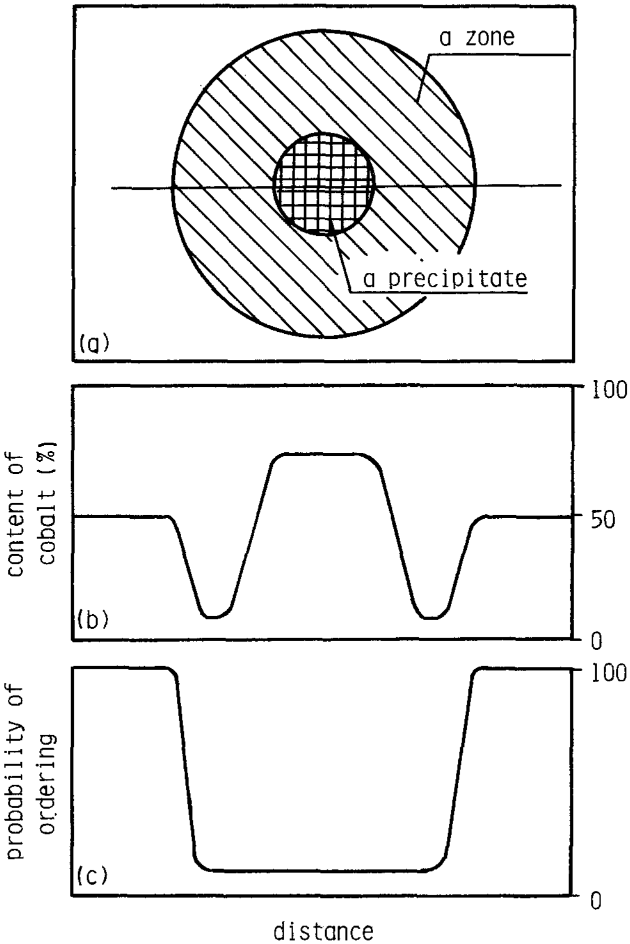

Figure 10 Possible variation in cobalt content and probability of ordering produced by a precipitate around which a local concentration-disordered zones is formed.

ing results from the deoxidization based on the carbon addition, cannot be brittle even though the specimens are subjected to a further decarburization. In this decarburization process oxygen is not considered to increase (from the viewpoint of its diffusion coefficient). Since the decarburization has in fact caused embrittlement, this should be concluded to have been caused by the decrease in carbon.

The recovery of ductility caused by the carburization can never be interpreted in terms of impurity-induced embrittlement [2–5], because it is not considered that during carburization oxygen escapes from the specimen, even though it enters. Other impurities such as nitrogen and sulphur also are not considered to escape during the carburization or to enter during the decarburization, from or into the specimens, respectively. Thus, as suggested in the previous report [1], the brittleness of FeCo alloys can be concluded not to be associated directly with existence of the impurities.

Observed from the fractography of the ductile specimens, the existence of carbon as carbide appears to be an important factor since they have been observed to exist at each centre of the dimples. The existence of carbide may result in many problems, e.g. those of the properties of the carbide itself, of the relationship on the coherency between the carbide and the matrix, etc. From an entirely different point of view, a concept has previously been proposed to account for improving the ductility of FeCo alloys. The local concentration-disordered zones, termed LCD zones, are formed around individual precipitates, and the formation of the zones, which corresponds to the formation and dispersion of disordered zones, must eventually cause ductility in the FeCo alloys. In Fig. 10 this zone is illustrated, including some possible effects. There is a precipitate (Fig. 10a). As a result a zone is formed around the particle and the cobalt content in the zone decreases, depending on reaction with carbon (Fig. 10b). Hence the probability of ordering also decreases in the zone, and thus a disordered zone is produced eventually (Fig. 10c).

Many phenomena can be explained by this concept. The embrittlement due to decarburization and the recovery of ductility due to carburization are considered to be caused by the escaping and entering of carbon required to form the zones. In addition, the most probable evidence is the effect of severely cold rolling: in specimens so rolled, the ductility, even after ordering, has not always disappeared but has remained to some extent, though with no rolling the ductility has largely decreased. In the rolled specimens of FeCo–V alloys, Pinnel *et al.* [6] have pointed out similar phemomena, showing that the rolled specimens, even after an ordering treatment, exhibited increases in ductility and in strength simultaneously. The rolling effect can be explained to be due to a variation in the precipitation site of the carbides, since the number, uniformity and the density of the carbides can be easily predicted to depend on these sites which are thought to increase proportionately with the rolling reduction.

Considering the rolling effect, the formation of texture that accompanies rolling must be commented on. A negative view can be derived from the fact that the specimen heat-treated in a capsule is sufficiently ductile, whereas the specimen decarburized is very brittle irrespective of the same heat treatment condition. The grains in both cases are, similarly, so very large that no texture is observed, and the texture is not considered to control the mechanical properties. This difference in the ductility, therefore, suggests the intervention of the existing carbon.

Shaskov *et al.* [7] also have found a similar effect of cold working on the ductility in compounds, concluding that the effect is because the density of the impurities dispersed may be diluted by increasing the degree of working and consequently the damage arising from this may also be diluted. In the present alloys, however, the mechanical properties are not associated with the effects stemming from the impurities: it is revealed that the properties depend only on either the escaping or entering of carbon. Besides his interpretation, the LCD zones concept might be worth while adopting.

The LCD zones, if produced in a sample, may result in some possible effects. The improvement of the ductility in FeCo alloys depends strongly on the morphology of the distribution of the zones, the volume fraction, the uniformity and the density of the carbides in the case of FeCo–C alloys. Although it is known in FeCo alloys that finer grain samples are more favourable for the ductility than larger ones [5, 8, 9], the problems in obtaining the size or the shape of the grains may be ignored, with further modification in the morphology. The severe cold rolling is considered to be one of the modifications.

5. Conclusions

In FeCo (0.5 to 2 at% carbon) alloys, decarburization results in embrittlement, and recarburization for the specimen previously decarburized brings about ductility again. The variation in ductility and in brittleness depended only on the existence of carbon, i.e. the entering and escaping of carbon, respectively, and depended neither on the existence of impurities, nor on grain coarsening and nor on the texture formed during rolling. Besides these phenomena, in the light of the facts that the specimens severely cold rolled do not always exhibit embrittlement even after an ordering treatment, a model has been proposed that the variation in mechanical properties could possibly be controlled by local concentration-disordered zones formed around the individual precipitates.

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