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Effect of additive elements on cold workability in FeCo alloys

KOHJI KAWAHARA
National Research Institute for Metals, 3-12, 2-Chome, Nakameguio, Meguro-ku, Tokyo, Japan

Addition of various elements to equiatomic FeCo alloys and changes in ratio of iron and cobalt have been examined in order to study mechanisms for the improvement of ductility in the alloy. It has been revealed that $Fe_{30}Co_{70}$, one of the alloys having a different Fe/Co ratio, and alloys having additive elements such as carbon, vanadium, chromium, nickel, niobium, molybdenum, tantalum and tungsten ranging from 0.5 to 2 at %, are effective in improving ductility; whereas aluminium, beryllium, boron, copper, gold, manganese, silver, silicon, titanium and zirconium are ineffective. A common feature is found in the effective alloying elements: the elements combine with cobalt to form an Co_3X type compound that can be produced only by diffusion; for instance, Co_3C, Co_3V, Co_3Cr, Co_3Ni, Co_3Nb, Co_3Mo, Co_3Ta and Co_3W. It is suggested, as a way of explaining this common feature, that as a result of the formation of the Co_3X compound, the zones, difficult to cause the order lattice may be produced around the compound particles, and thus resulting in ductility.

1. Introduction

Equiatomic FeCo alloys, which have been used as a soft magnetic material, present an interesting phenomenon: although the alloys are very brittle, an increase in ductility is given by a small addition of vanadium [1–3] and chromium [4, 5]. To investigators who take part in improving workability of brittle materials, like intermetallic compounds, this is an important phenomenon, and many investigations have been reported hitherto. Nevertheless, the mechanism has never been understood.

An approach to inquire into the mechanism may be to find many of the elements that are able to improve the ductility of the alloy. Very little is known on this subject except for the elements of vanadium and chromium. Even the ductility of binary alloys consisting of iron and cobalt has varied largely on evaluation, although the range of ordering is approximately in agreement with that of brittleness: ordering is known to occur from 29 to 70 at % cobalt [6–10] and brittleness, from 25 to 65% cobalt. An Fe–25% Co alloy is found to be ductile [11] and an Fe–27% Co alloy is said to be able to be cold rolled even if the plates are not quenched [12]. For equiatomic alloys, hot forging is usually known to be difficult [4, 13]; whereas, according to Soviet reports [14–17], FeCo alloys cold rolled to 90% have been used as the various specimens, implying that these alloys are ductile.

The present paper is concerned with the influence of the various additive elements on ductility and on microscopic structure, and of the change in the composition of the alloys consisting of iron and cobalt. Additive elements are selected on the basis of the following properties: (a) intensity of reactivity to the impurities expected, (b) magnitude of solubility in iron and cobalt. Phase diagrams and structures of binary Fe–Co alloys and of ternary Fe–Co–V alloys are well known [18–24]: the structure of the binary FeCo alloy is merely ferritic even after quenching and no martensite is observed unless some of the vanadium element is added. The information concerning the other ternary systems, though some are available, can not be utilized because no detail is known in the range of small amounts of added

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elements, i.e. less than about 2 at %. Consequently, the effect of additive elements on structure changes is discussed on the ground of the binary systems between the individual elements and iron or cobalt.

2. Experimental procedures

The materials used were composed of high-purity electrolytic iron and cobalt, additive elements, each of which has a purity of 99.9%, and ferro-alloys for the addition of vanadium, boron and beryllium.

The ingots used, had been made for purposes other than the present investigation, and therefore were not consistent in shape, size and melting process. Ingots over 2 kg were melted in a high-frequency induction furnace *in vacuo*; those under 300 g were arc melted in an argon atmosphere, and cast into rods of 15 mm diameter. Ingot marks, S, M, and G, show the ingots of 120, 120, 270 g; marks, K and F, 3.8 and 2.3 kg, respectively.

The composition of the base alloys used was approximately 50Fe : 50Co, eighteen kinds of elements being added within a range from 0.01 to 4 at %. The chemical composition of these alloys, not being analysed, were assumed to be very close to nominal compositions. The extent of the weight losses in arc melting was considered to be a small amount, since the elements having a high vapour pressure were carefully melted so as not to contact the arc flame directly and hence, to melt by contact with the molten mass consisting of iron and cobalt.

The ingots were heated for two hours at 1050 to 1200° C; hot rolling was carried out in the case of samples over 2 kg to plates of 5 mm in thickness; hot forging was carried out for rods under 300 g to blocks with a section of 5 mm square. The plates are blocks thus obtained, before cold rolling, were reheated at 1100° C for ten minutes, followed by iced-brine quenching.

3. Experimental results

3.1. Effect of varying the ratio of iron and cobalt in FeCo alloys with and without vanadium

Twelve kinds of alloys, ranging from 30 to 70 at % cobalt with and without 2% vanadium, were used to examine workability. The results are shown in Table I.

TABLE I Effect of varying ratio of iron and cobalt in FeCo alloys with and without vanadium on workability

Specimen number	Composition			Workability	
	Fe	Co	V	Hot forging	Cold rolling
F5	70	30	–	good	no
F6	60	40	–	good	no
M3	52	48	–	good	no
M2	50	50	–	good	no
K1	50	50	–	no	–
M1	48	52	–	good	no
F10	40	60	–	good	no
F9	30	70	–	good	good
F7	69	29	2	good	good
F8	59	39	2	good	good
F12	39	59	2	good	good
F11	29	69	2	good	good

All ingots, other than an alloy Kl, $Fe_{50}Co_{50}$, were easy to hot forge. The accomplishment concerning cold rolling, however, depended on the compositions of the alloys; in the case without vanadium, a reduction to 90% was achieved only for an $Fe_{30}Co_{70}$ alloy; in the other alloys cracks generated and propagated in early steps of rolling, namely, in several per cent reduction, so that successive cold rolling became impossible. In the case without vanadium, therefore, the alloys of both sides, i.e. the alloys containing cobalt higher than 70% and less than 30%, can merely be cold rolled; the alloys that are placed in a range from about 30 to about 70% cobalt can not be cold rolled. On the other hand, all of the alloys containing vanadium were able to be cold rolled to 90% reduction. Over a wide variation in ratio of iron and cobalt in the FeCo alloys, it is found that the addition of 2% vanadium is effective in improving hot and cold workability.

3.2. Effect of various additive elements on workability of FeCo alloys

Addition of eighteen elements in the range from 0.01 to 4 at % was made to the alloys consisting of approximately equiatomic composition, workability in hot forging and cold rolling being examined. The results are listed in Table II.

The ingots that hot forging was not accomplished with, are large ingots with 2% molybdenum, 2% tungsten, 2% tantalum, and small ingots with 2% silver and 0.01% carbon. In the case of the small ingots, even the addition of 2% molybdenum, 2% tungsten and 2% tantalum resulted in the accomplishment of hot forging; carbon is also effective under additions of higher than 0.1%. Ineffective elements upon hot forging,

TABLE II Effect of additive elements on ductility of FeCo alloys

Specimen number	Nominal chemical composition (at %)			Workability	
	Fe	Co	X	Hot forging	Cold rolling
M5	49.5	49.5	1V	good	no
S1	50	49	1V	good	no
S2	50	49	2V	good	good
S3	49	48	3V	good	good
S4	48	48	4V	good	good
M16	49.75	49.75	0.5Cr	good	good
M17	49.5	49.5	1Cr	good	good
M14	49	49	2Cr	good	good
S5	50	48	2Cr	good	good
K2	49	49	2Cr	good	good
M18	49.75	49.75	0.5Mo	good	good
M19	49.5	49.5	1Mo	good	good
S6	50	48	2Mo	good	good
K3	49	49	2Mo	no	–
M20	49.75	49.75	0.5W	good	good
M21	49.5	49.5	1W	good	good
S7	50	48	2W	good	good
K4	49	49	2W	no	–
M24	49.75	49.75	0.5Ta	good	good
M25	49.5	49.5	1Ta	good	good
S10	50	48	2Ta	good	good
K7	49	49	2Ta	no	–
M26	49.75	49.75	0.5Nb	good	good
M27	49.5	49.5	1Nb	good	good
S11	50	48	2Nb	good	good
K8	49	49	2Nb	good	no
M22	49.75	49.75	0.5Ti	good	no
M23	49.5	49.5	1Ti	good	no
S8	50	48	2Ti	good	no
K5	49	49	2Ti	good	no
S9	50	48	2Zr	good	no
K6	49	49	2Zr	good	no
M11	49	49	2Ni	good	no
S12	50	48	2Ni	good	good
K9	49	49	2Ni	good	no
S21	49	49	2Ni	good	no
S13	49	49	2Cu	good	no
K10	49	49	2Cu	good	no
S14	49	49	2Al	good	no
K11	49	49	2Al	good	no
S15	49	49	2Au	no	–
S16	49	49	2Ag	no	–
G6	49	49	2Mn	good	no
G7	49	49	2B	good	no
G8	49	49	2Be	good	no
G9	49	49	2Si	good	no
G12	49	49	0.01C	no	–
G13	49	49	0.1C	good	no
G14	49	49	0.5C	good	good
G15	49	49	1C	good	good
G10	49	49	2C	good	good

therefore, are considered to be only two, namely, gold and silver.

The alloys that could not be cold rolled were as follows: for the large ingots, those of 2% niobium; for the small ingots, those of 1% vanadium, 2% aluminium, beryllium, boron, copper, manganese, silicon, titanium and zirconium, respectively, and those of less than 0.1% carbon. The alloys that could be cold rolled were those of 2% nickel and over 2% vanadium, and of over 0.5% chromium, molybdenum, tungsten, tantalum, niobium, and carbon, respectively. Alloys in which nickel was added showed some scatter, but nickel can be regarded as an effective element. Within the limit of the present experiment, it can be concluded that the effective element for improving the ductility of FeCo alloys are as follows: vanadium, chromium, molybdenum, tungsten, tantalum, niobium, carbon, and nickel; the ineffective are gold, silver, aluminium, beryllium, boron, copper, manganese, silicon, titanium and zirconium.

3.3. Structural changes

Microscopic structure of an $Fe_{50}Co_{50}$ alloy is expected to be influenced by an additive element.

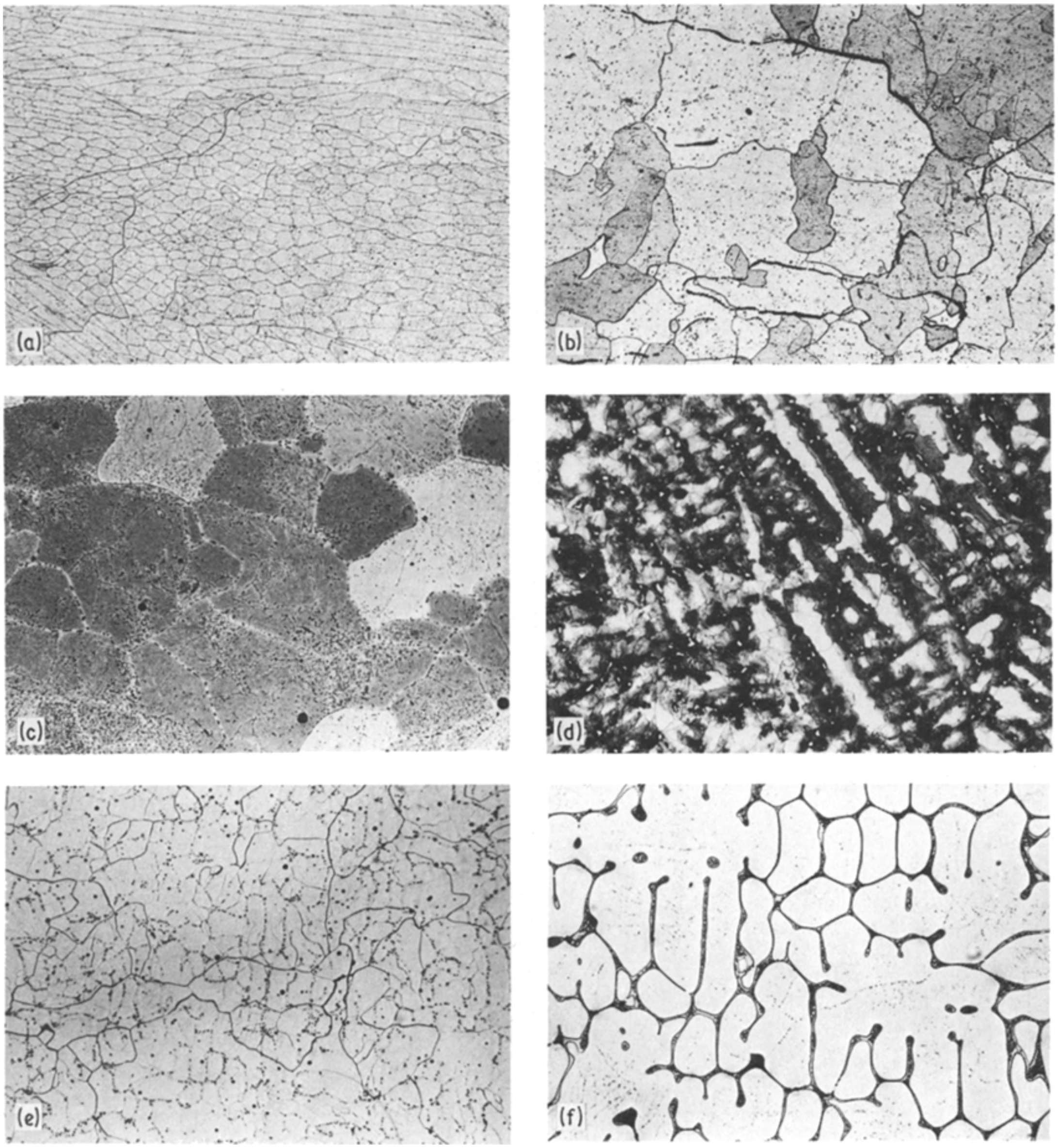

Figure 1 Typical microstructures of FeCo alloys with various elements being added (a) FeCo, as-cast, × 78, (b) FeCo, 1050° C 2 h, × 78, (c) FeCo–2Cu, 1050° C 2 h, × 390, (d) FeCo–2Au, as-cast, × 195, (e) FeCo–2Ag, as-cast, × 195, (f) FeCo–2B, as-cast, × 390, (g) FeCo–2C, 1100° C 10 min, × 390, (h) FeCo–2Cr, as-cast, × 195, (i) FeCo–2Mo, as-cast, × 195, (j) FeCo–2W, as-cast, × 195, (k) FeCo–2Nb, as-cast, × 195, (l) FeCo–2Ta, as-cast, × 195, (m) FeCo–0.5Mo, 1050° C 2 h, × 195, (n) FeCo–0.5W, 1050° C 2 h, × 78.

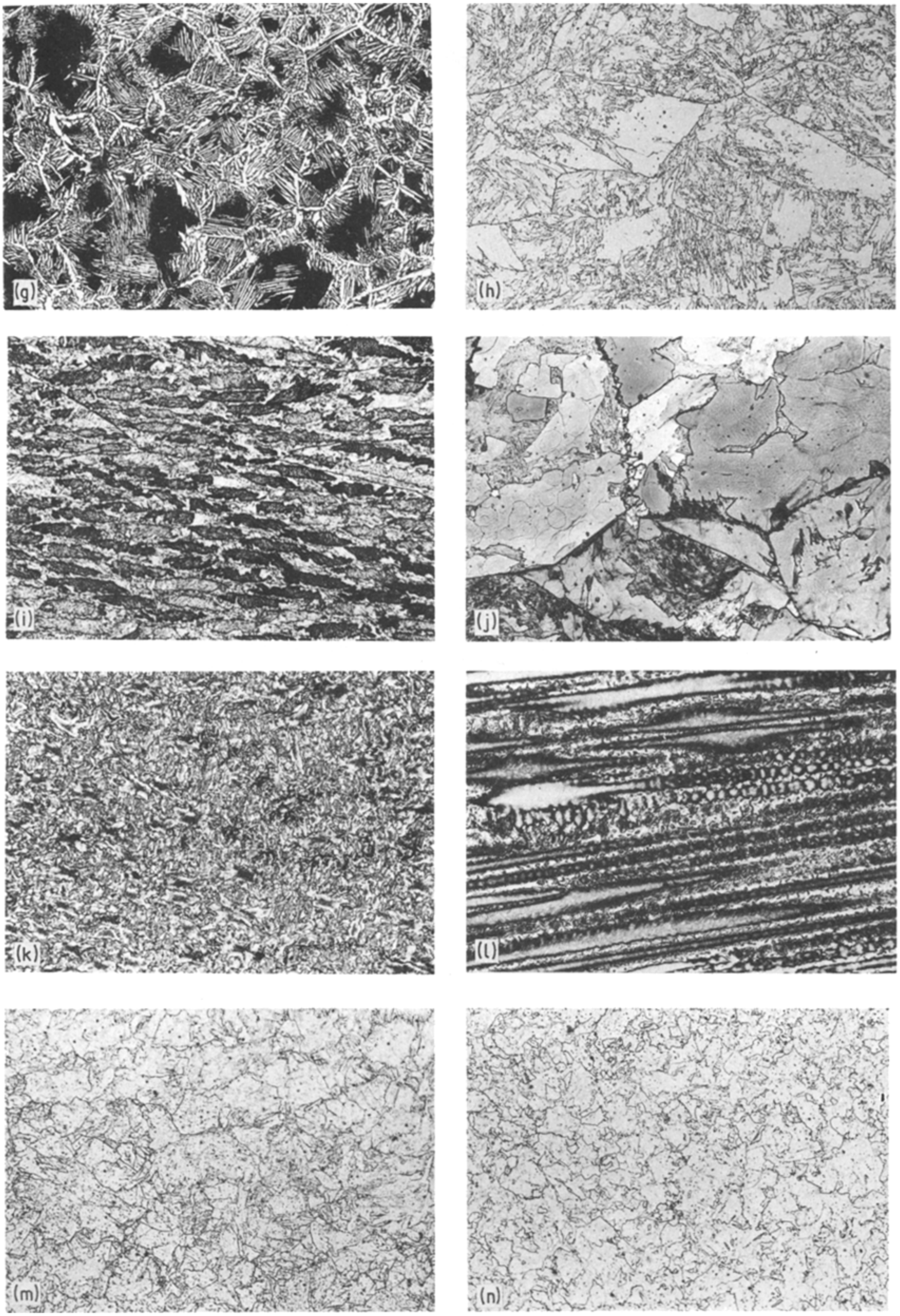

Figure 1 Continued.

Fig. 1 shows some of the structural changes in the alloys with 2% additions.

An binary FeCo alloy, as-cast, shows a cell structure, see Fig. 1a; such a structure disappears when annealed at 1050° C, and ferritic grains are seen with numerous etch pits (Fig. 1b).

In the case of the addition of 2% vanadium, nickel, silicon, aluminium, titanium, and manganese, the structures were similar to those of the binary FeCo alloy and no second phase particles have been observed under the light microscrope in the as-cast and as-quenched states. This result can be expected from binary equilibrium diagrams of Fe–X and Co–X, where X represents each of additive elements: since the solubility limit of such an additive element X in iron or cobalt is sufficiently larger than 2%.

On the other hand, second phases, which were sited at the interstices of the cell structure and in the interdendritic regions, were found in the alloys containing the elements, boron, carbon, zirconium, beryllium, gold, silver, and copper. According to the equilibrium diagrams, the resultant structures are expected because of the low solubility. In the case of copper addition, particles of copper itself are aggregated at the original cell interfaces, and are distributed at boundaries and within grains even after annealing, see Fig. 1c. Distribution of gold and silver is also similar to that of copper, see Figs. 1d and e. For the addition of boron and zirconium there is a network-like product in which evidence of an eutectic reaction can be seen, see Fig. 1f, this remaining even after annealing at 1050° C. Carbon presents a Widmanstatten structure in the as-cast state, which changes into the finer structure by annealing, see Fig. 1g. Second phases were observed also in the alloy containing 2% beryllium, which were scattered in the transgranular and in the intergranular in both the as-cast and as-quenched states from the temperature after annealing at 1100° C.

Some of the elements caused the structure of the FeCo alloy to be changed drastically. Chromium addition offers a massive-martensitic structure, see Fig. 1h, which is well known in the iron-based alloys containing nickel less than about 10%. Molybdenum indicates a feather-like structure, see Fig. 1i. The structures for tungsten, tantalum, and niobium are shown in Figs. 1j, k and l, respectively. Alloys with 0.5% addition of such elements could be cold rolled as shown in Table II, and their structures, except for the fine grains, were similar to that of the binary FeCo alloy; for instance, the structures of the 0.5% molybdenum and tungsten alloys are indicated in Figs. 1m and n, respectively. The structural changes mentioned above were limited to those of the specimens which were as-cast or as-quenched. Cooling rates indeed affected the changes: grain growth and redistribution of second phase particles were occasionally found to occur. In an alloy containing 2% chromium, which showed no particles in a quenched state, the structure showed a tendency to vary from martensitic to ferritic with decreasing cooling rate. In the other alloys except for the chromium alloy, however, the particles that were able or unable to be observed in an as-cast state, were confirmed to be present or to be absent, respectively, irrespective of cooling rates from the temperatures of an austenite region. Consequently whether or not the particles are produced by addition of each element can be sufficiently presumed only either by as-cast or by as-quenched state from 1050 or 1100° C.

From the results the relationship between the structural changes and the additive elements can be divided by four groups: (a) addition of up to 2% vanadium, of 2% nickel, and of below 0.5% chromium, molybdenum, tungsten, tantalum, and nickel, which show the structure similar to that of FeCo alloy and show effect on cold rolling, (b) of 2% silicon, aluminium, titanium, and manganese, which show also the binary alloy-like structure but no effect, (c) of carbon and of a greater amount than 1% chromium, molybdenum, tungsten, tantalum, and niobium, which show the structure containing second phase particles but effect on cold rolling, (d) of copper, gold, silver, boron, zirconium, and beryllium, which also show the structure with second phase particles and no effect. No correlation, as mentioned above, was observed between the structural changes and the elements by which cold rolling is caused: the binary alloy-like structure is not always effective on cold rolling and the structure with second phase particles is not always ineffective. The groups that consist of vanadium, nickel, and of below 0.5% chromium, molybdenum, tungsten, tantalum, and niobium, have indicated the binary alloy-like structure as having improved the ductility of the alloys. On the other hand, the groups consisting of silicon, aluminium, titanium and manganese have shown no such effect, though these elements have also displayed a similar binary alloy-like structure. Other groups, which consist of over 0.5% carbon, 2% molybdenum, tungsten, tantalum and niobium, do show effectiveness, in spite of the fact that these structures were not binary alloy-like, and had second-phase particles. There is no correlation which suggests that the factors thought to make these alloys brittle are connected with any changes which are invisisble under light microscopy.

4. Discussion

Brittleness of FeCo alloys has been considered to be concerned with the existence of the impurities, such as carbon, nitrogen, oxygen, and sulphur [13, 25–27]. The effectiveness of vanadium and chromium has been explained to be due to the effect that these elements, known as carbide–nitride formers, can react with the impurities, and can remove the injurious results attributable to the impurities, i.e. due to a scavenging effect. The strength of the scavenging effect can be estimated, as a first order, by reference to free energy [28]. For carbide, the order of decreasing strength of the scavenging reaction may be as given below: zirconium, titanium, tantalum, niobium, and vanadium; for nitride, zirconium, titanium, aluminium, beryllium, tantalum, niobium, and vanadium; for oxide, beryllium, aluminium, zirconium, titanium, and silicon; for sulphide, zirconium, titanium, beryllium, and manganese.

Carbon, which gives an improvement in ductility, should not be regarded as a harmful but a useful element. The fact that carbon has exerted an effectiveness suggests that oxygen may be responsible for the brittleness, because that carbon addition may remove oxygen.

The strongest deoxidizing group, being composed of beryllium, aluminium, zirconium, titanium, and silicon, can be expected to be the most effective for improving ductility. In contrast to this expection, however, the most effective elements are some of the elements in the medium strong group, i.e. carbon, vanadium, boron, niobium, tantalum, manganese, and chromium, and so are some of the weakest elements, i.e. tungsten, molybdenum, and nickel, rather than the strongest elements. No effect is observed from the addition of zirconium and titanium, although they are some of the strongest elements which can react with the impurities mentioned above. Therefore, the order of strength for oxidizing seems to have no relation to the increase in ductility. This tendency is not only for oxide but also for carbide, nitride, and sulphide.

Scavenging effect will be cancelled, provided the following results occur: (a) the products resulting from a scavenging reaction remain in the alloy, and lead to undesirable properties, (b) in the course of solidification additive elements combine preferentially with either iron or cobalt, and lead to second phase particles. These results, if they occur, will be considered to allow the function of the scavenging effect to disappear or decrease. Such a possibility can be estimated on the basis of binary equilibrium diagrams [29–32]. According to the diagrams, zirconium has compounds of Fe_3Zr and Zr_2Co_{11}; boron, Fe_2B and Co_3B. These compounds, if produced, are expected to be formed during solidification; in fact, second phase particles exist in the spaces of the dendritic arms of the alloys. The cancelling effect is likely to be correct with respect to zirconium and boron additions. However, some questions remain. The elements, such as aluminium, silicon, and manganese, which belong to the strongest group on scavenging action and yet are observed not to yield second phase particles, have shown no improvement in ductility. On the other hand, even the alloys containing second phase particles have enabled some ductility to occur, namely, in the addition of 2% carbon, tantalum, and niobium. It is thus concluded that no correlation has been confirmed between the structural change, under light microscopy, and the improvement in ductility. This presumably implies that, with regard to the brittleness of FeCo alloys, the existence of impurities is a minor factor and other affairs are major.

An attempt has been made to find whether a common point is among the effective elements or not. Attention was paid to the sequence when the compounds involved are generated and a classification into groups was made on the following basis for the purpose of discussion: (a) compounds thought to crystallize from the melts as primary crystals during solidification, termed a solidification-produced compound (in addition to this compound, the compounds may also be included here which are produced by non-equilibrium effects during solidification. But these compounds may be taken off, because they are unstable and can be dissolved by heat treatments), (b) compounds thought to precipitate during annealing of a solid solution, not during solidification, termed a dif-

TABLE III A possible classification of compounds occurring between iron/cobalt and additive elements

Type of compounds	Effective elements								Ineffective elements									
	C	V	Cr	Ni	Nb	Mo	Ta	W	Be	B	Al	Si	Ti	Mn	Cu	Zr	Ag	Au
Diffusion-produced type	Co_3C	Co_3V CoV_3	Co_3Cr $\overset{*}{Co}Cr$	(Co_3Ni) $CoNi_3$	Co_3Nb	Co_3Mo	Co_3Ta Co_5Ta	Co_3W					Co_3Ti	(Co_3Mn)				
	Fe_3C	$\overset{*}{Fe}V$	$\overset{*}{Fe}Cr$	$FeNi_3$	$\overset{*}{Fe}Nb$			Fe_2W	$FeBe_{11}$		Fe_3Al $FeAl$	Fe_3Si Fe_5Si_3		Fe–Mn		$FeZr_4$		
Solidification-produced type		$\overset{*}{Co}V$			$CoNb$ Co_2Nb	$\overset{*}{Co}Mo$ Co_7Mo_5	Co_2Ta $CoTa$ $CoTa_2$	Co_7W_6	$CoBe$	Co_3B Co_2B	$CoAl$ Co_2Al_9 Co_4Al_{13} Co_2Al_5	Co_3Si Co_2Si $CoSi$ $CoSi_2$	Co_3Ti Co_2Ti $CoTi$ $CoTi_2$			$Co_{11}Zr_2$ Co_4Zr Co_2Zr $CoZr$ $CoZr_2$		
	Fe_3C				Fe_2Nb_3 Fe_2Nb	$\overset{*}{Fe}Mo$ Fe–Mo	Fe_2Ta	Fe_3W_2	$FeBe_2$ $FeBe_5$	Fe_2B FeB	$FeAl_2$ Fe_2Al_5 $FeAl_3$	$FeSi$ $FeSi_2$	Fe_2Ti $FeTi$			Fe_3Zr Fe_2Zr		

*Sigma phase.

fusion-produced compound. Possible compounds for the classification have been taken from Hansen and Anderko [29], Elliott [30], Shunk [31], Moffatt [32], and Pearson [33]. The results are shown in Table III.

Nevitt [34] has classified the compounds of transition metals into nine classes. We also referred to this classification for the present compounds, but with his classification no correlation between the effective elements and types of compounds could be found, except that sigma phases belong to the left side column of Table III, i.e. to the group of effective elements.

In the Table III a feature can be found in the column of the effective elements: the diffusion-produced compounds Co_3X, which can be thought to be produced only by a diffusion process, concentrate at the top row in the column of the effective elements. These Co_3X type compounds are found in the alloys with the following addition: carbon, vanadium, chromium, molybdenum, tungsten, tantalum, niobium, and nickel. All the elements correspond to the ductility-producing elements.

On the other hand, it is unclear whether Co_3Ti is either a diffusion type or a solifidication one; Co_3Mn is known to exist only by neutron diffraction [35]; Co_3Ni, even if it exists, would be difficult to confirm, since cobalt and nickel closely resemble each other in the atomic scattering factors. Fe_3C can be taken in both types, depending on their well known double diagram. Only Co_3Mn is isolated from Co_3X type compounds which comprise the ductility-improving elements. The sole exception of Co_3Mn, however, suggests that both processes, melting *in vacuo* and the addition of manganese as a pure metal, have resulted in a low yield of manganese in the alloy. Manganese, thus, may be thought to belong to the effective group. Even with the exception of manganese, titanium and nickel, all the elements carbon, vanadium, chromium, molybdenum, tungsten, tantalum and niobium have a common relationship in that they always have the possibility of the diffusion-produced Co_3X compounds being able to precipitate. This fact should not be overlooked.

Brittleness of FeCo alloys is mostly associated with an order–disorder reaction [4, 13, 25, 27, 36–47]: successive ordering makes it difficult to cross slip, accelerates the generation of stress concentration, and thus leads to brittleness. Suppression and reduction of the ordering, therefore, would increase the ductility of the alloy, provided that problems of impurity were ignored.

For this purpose two events can be considered. Firstly, the chemical composition of binary FeCo alloy should be shifted overall so as not to cause the ordering of the CsCl type to occur. This, however, will result in a decrease of a desired property. Secondly, a certain precipitation should be produced in the matrix of an alloy, and around the precipitates the zones consisting of the composition insufficient to yield the inherent ordering of CsCl type, should be produced, that is, the compositional shift is to be made locally only around the precipitates, not overall. This, in other words, is that disordered zones were produced by local variation of concentration.

Formation of a precipitate, Co_3X, can be predicted to produce the zones mentioned above. In and/or around the zones, the situation that makes the ordering difficult may be presented, because, in the zones, the number of cobalt atoms may be insufficient to permit the ordering to the CsCl type as one X atom may consume three cobalt atoms. Addition of X atom, thus, will result in local concentration-disordered zone, LCD zone.

These results reveal that ductility-improving elements are almost associated with the precipitation of diffusion-produced compounds of Co_3X type, not that of solidification-produced. A decisive difference in both types is in the distribution of the compounds. Solidification generally tends to permit the compounds to be dispersed coarsely and heterogeneously; while the diffusion process, is dispersed finely and homogeneously. It is easily predicted that the distribution thus produced will decisively influence the mechanical properties, particularly brittleness.

It is suggested that formation of the LCD zone around the diffusion-produced compound Co_3X has improved the ductility in this series of FeCo–X alloys.

5. Conclusions

In the binary iron–cobalt alloys, $Fe_{70}Co_{30}$ to $Fe_{40}Co_{60}$ alloys are brittle, but only the $Fe_{30}Co_{70}$ alloy is ductile, being able to cold roll up to 90%.

For the improvement in ductility of $Fe_{50}Co_{50}$ alloys, it has been found that the ductility-improving elements are as follows: carbon, vanadium, chromium, molybdenum, tungsten, tantalum, niobium, and nickel; whereas the ineffective elements are aluminium, beryllium, boron, manganese, silicon, titanium, zirconium, copper, gold, and silver.

It is observed as a common point in the ductility-improving elements, with a little exception, that each of them has a possibility of the precipitation of the diffusion-produced compound formulated by Co_3X.

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