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The kinetics of atomic and magnetic ordering of Co-based amorphous ribbons as affected by iron substitution

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Abstract

Amorphous Co-based ribbons with general compositions $Co_{80-x}Fe_xB_{10}Si_{10}$ have been prepared by the melt-spinning technique where iron has been substituted for cobalt by varying x from zero to eight At% in steps of 2At%. The kinetics of glass formation and crystallization as affected by a slight change in composition is studied by differential thermal analysis (DTA). It is observed that the thermodynamics of the metallic glass in respect of the formation of glassy state and its stability is affected by the complexity of the composition. The magnetic ordering of Co-based amorphous ribbons is measured both, by A.C. and D.C. magnetization as functions of temperature. D.C. measurements are made by using a vibrating sample magnetometer and A.C. initial permeability is measured by using a furnace in which the heating wire is wound in accordance with the bifiller technique. It is observed that, with increasing amount of iron, the glass-transition temperature (T_g) increases monotonically. The Curie temperature (T_C) and saturation magnetization (M_s) also increase with increasing iron content. The results are explained as due to higher magnetic moments of iron atoms and increased exchange interaction between iron and cobalt atoms.

Keywords: Amorphous; Atomic and magnetic ordering; Kinetics

1. Introduction

The kinetics of the rearrangement of existing defects responsible for magnetic relaxation phenomena must generally be considered separately from the kinetics of the changes in the glassy state of amorphous ribbons and their structural relaxations [1]. In amorphous ribbons, a number of physical properties change due to structural relaxations. Such changes can be followed up by measuring one of the suitable properties during the temperature variation. The change of composition affects atomic ordering through nucleation and growth of crystallites. The glass-transition temperature (T_g) and crystallization temperature (T_x) which occur when there is a long-range ordering of atoms, is associated with changes in the free energy of the system. This has been investigated by differential thermal analysis as a standard technique [2,3]. The long-range ordering of atoms depends on the free-energy difference between the crystalline state and the amorphous state. Co–Fe-based amorphous ribbons are of special interest because these magnetic system, with a high percentage of Co having negative magnetostriction and with small amounts of Fe having positive magnetostriction,

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are expected to behave as low magnetostrictive materials with high permeability. This expectation is based on the corresponding behaviour of crystalline Fe–Co alloys with strong correlation between positive and negative magnetostriction of iron and cobalt giving rise to soft magnetic materials.

The change of composition affects the growth kinetics in a complicated way which can only be determined experimentally. The composition of the alloy affects both, T_g and T_x, because the time needed for the constituent atoms to attain long-range ordering depends on their bond energies [4,5]. Since T_g and T_x are affected by the heating rate as well as by composition, the formation of nucleation centres and their growth need to be inhibited to avoid crystallization.

The Curie temperature (T_C) is a basic parameter in the study of magnetic phase transitions in ferromagnetic amorphous ribbons. It is well known that T_C of an alloy in the crystalline and amorphous states differs. In spite of chemical and structural disorder, an amorphous ferromagnet most often demonstrates a well-defined ferromagnetic ordering temperature (T_C) which has been confirmed by the magnetization vs. temperature curve, Mossbauer effect and specific heat measurements [6]. As an additional verification to the transformation in respect of glass transition and crystallization, the magnetic-phase transition, such as ferromagnetic ordering and magnetization process, has been studied. The results are compared in respect of their temperature dependence and very consistent results have been obtained.

2. Experimental

2.1. Preparation of amorphous ribbons

The amorphous $Co_{80-x}Fe_xB_{10}Si_{10}$ ribbons are prepared by the melt-spinning technique [7–9]. The amorphous ribbons were ca. 25 μm thick and 6 mm wide. Although amorphous materials can be produced for all compositions in principle, the eutectic composition is the most convenient one which corresponds to the maximum value of the reduced glass-transition temperature and minimum cooling rate of the melt for producing amorphous ribbon. The amorphousness of the ribbons has been confirmed by X-ray diffraction using CuK_α radiation which shows that the samples used for this experiment were in a good amorphous state.

2.2. Differential thermal analysis (DTA)

The thermal characteristics of amorphous ribbons with composition $Co_{80-x}Fe_xB_{10}Si_{10}$ [$x = 0, 2, 4, 6$ and 8] were measured by DTA method at a heating rate of 10°C/min. For DTA measurements a Shimadzu micro DTA system model DT30, manufactured by Shimadzu Corporation, Kyoto, Japan, was used.

2.3. T_C measurement

The Curie temperature, which is a measure of exchange interaction between the magnetic atoms, is quite complicated in the case of amorphous alloys to be calculated from the first principle and as such is very much an experimental parameter. Theory is helpful only as a guideline in rationalizing the results obtained experimentally. T_Cs of the amorphous samples of toroidal shapes have been measured from the temperature dependence of permeability by a laboratory-built technique using a furnace in which a heating wire is wound bifillerly and two identical induction coils are wound around the specimen in opposite directions, such that the current-induced flux in the two coils cancel each other and only the magnetic induction in the specimen contributes to the measured deflection. The whole setup is introduced in a furnace, and by measuring the temperature dependence of the differential flux through the two coils and from the sharp fall of AC. permeability with temperature, the ferromagnetic transition Curie temperature is determined.

For temperature control, we used the same facilities for the vibrating sample magnetometer and for A.C. permeability measurement. Since the thermocouple was not in contact with the sample, we estimate the temperature error to be $\pm 1^\circ$C. The error in the estimation of temperature of the oven is possibly a bit larger, since samples were lying along the temperature profile of the high-temperature oven [10]. However, in the measurement of the temperature dependence of magnetization, the error in the estimation of temperature is <1.5°C.

3. Results and discussions

The compositional dependence of T_g and T_x of amorphous $Co_{80-x}Fe_xB_{10}Si_{10}$ alloys are studied for different values of x. It has been observed that the crystallization temperature of these alloys, measured by DTA method at a heating rate of 10°C/min., depends on Fe content when the contents of silicon and boron as metalloids are kept unchanged. The results are presented in a summarized form in Fig. 1 for comparison between samples of different compositions. No secondary crystallization phase was observed in this DTA curve. This indicates that the eutectic point remains nearly unchanged for this system and all the compositions are equally favourable for producing amorphous ribbons. Fig. 2 shows the dependence of T_g and T_x on Fe content of the amorphous alloys. T_g of these alloys increases slowly but monotonically with the increase of Fe content. The values of T_x which are higher than those of T_g, remain practically constant for all the compositions. The numerical values of T_g and T_x for all the samples are shown in Table 1.

T_C has been estimated from the permeability, μ vs. T, curves for different amorphous ribbons. Temperature dependence of A.C. permeability of the samples subjected to a heating rate of 12°C/min. are shown in Fig. 3. Fig. 3 shows that the A.C. initial permeability of Co–Fe amorphous system increases with increasing iron content and has the maximum value at 6 At.% of iron. Beyond this point, there is a decrease in the permeability with increasing Fe content. The results are explained as due to minimum magnetostriction of the alloy of composition $Co_{74}Fe_6B_{10}Si_{10}$, where the positive contribution to magnetostriction due to Fe atoms compensates the negative magnetostriction of the Co atoms most effectively. The numerical values of T_C for all the samples are shown in Table 1. Fig. 4 shows the dependence of T_C on the iron content. T_C of co-based amorphous ribbons increases with the increase of Fe content. Temperature dependence of magnetization of the samples measured by using vibrating sample magnetometer from room temperature to 800°C is shown in Fig. 5. With increasing values of iron in the amorphous alloy the magnetization increases, which is quite consistent with the results of crystalline Co–Fe alloys and is explained as due to higher magnetic moment of iron atoms. The Curie temperature for the amorphous system, however, increases with increasing amounts of iron substitution as observed by A.C. initial permeability measurements and also from the temperature dependence of magnetization obtained by vibrating sample magnetometer. Both the measurements gave the same value for the Curie temperatures of each composition. For accurate determination of the Curie temperature, dM/dt curves have been plotted as shown in Fig. 6 and derived from Fig. 5. Sharp peaks of dM/dt for the different compositions indicate that the T_c values are well defined and the measurements are quite accurate.

Although the Curie temperature of Co (1057°C) is higher than that of Fe (770°C) in the amorphous state, the exchange interaction between the magnetic ions is increased by the replacement of Co by Fe, quite contrary to the crystalline state. This is in keeping with the results presented in Refs. [11,12], where Cargill and Ishikawa have found an enhancement of Curie temperature with iron substitution up to 10 At.%. Since the exchange interactions in the amorphous magnetic system is of the RKKY type, which occurs via the conduction electrons, the distance between the magnetic atoms is very important. It is thus likely that the addition of iron helps the conduction electrons to enhance the exchange interaction and, hence, the Curie temperature up to a certain range. There is good correlation between T_g as obtained from Fig. 5 and T_C as obtained from Fig. 6 for all the compositions. It is thus observed from the results shown in Table 1 that amorphous ribbons with increase of iron content are more convenient as a soft magnetic material for their elevated T_g, T_C and M_s.

Table 1

$Co_{80-x}Fe_xB_{10}Si_{10}$	T_g	T_x	T_C	M_s
$x = 0$	418°C	564°C	408°C	893.23 mT
$x = 2$	430°C	570°C	420°C	915.17 mT
$x = 4$	433°C	558°C	429°C	947.77 mT
$x = 6$	442°C	560°C	438°C	960.10 mT
$x = 8$	455°C	565°C	443°C	964.58 mT

4. Conclusions

The Co–Fe alloy system is very convenient for producing stable amorphous ribbons over a range of

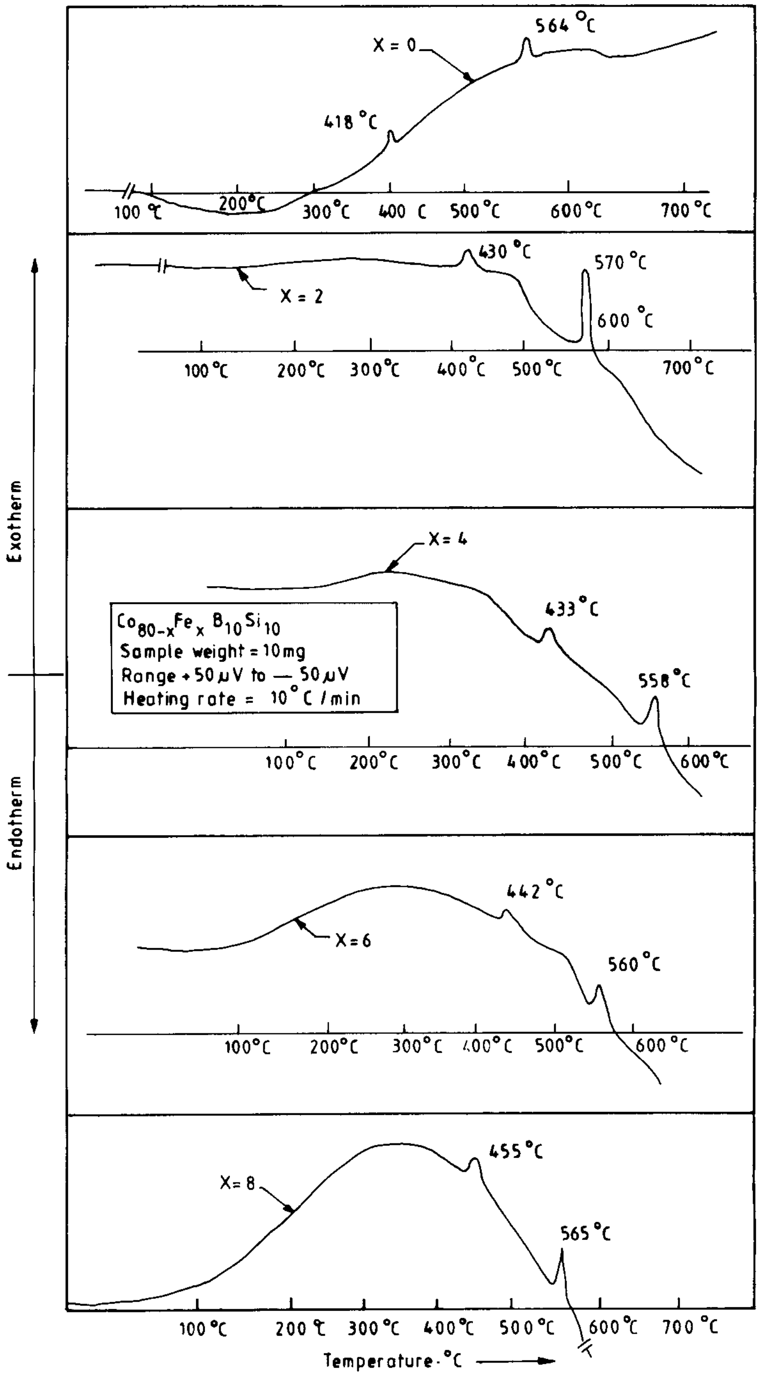

Fig. 1. Determination of T_g and T_x from DTA graph of amorphous ribbons with compositions $Co_{80-x}Fe_xB_{10}Si_{10}$ [$x = 0$, 2, 4, 6 and 8].

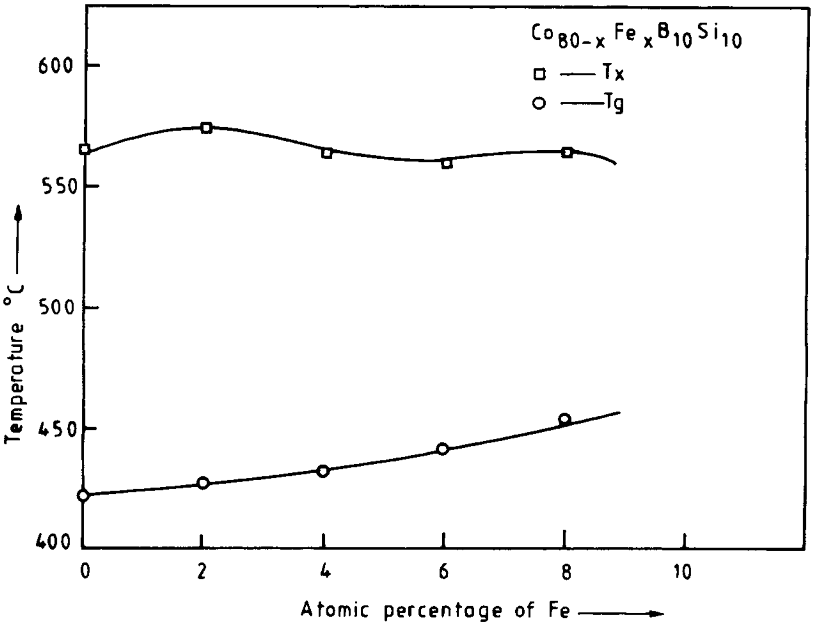

Fig. 2. Variation of T_g and T_x due to change in the iron content in $Co_{80-x}Fe_xB_{10}Si_{10}$ amorphous ribbons.

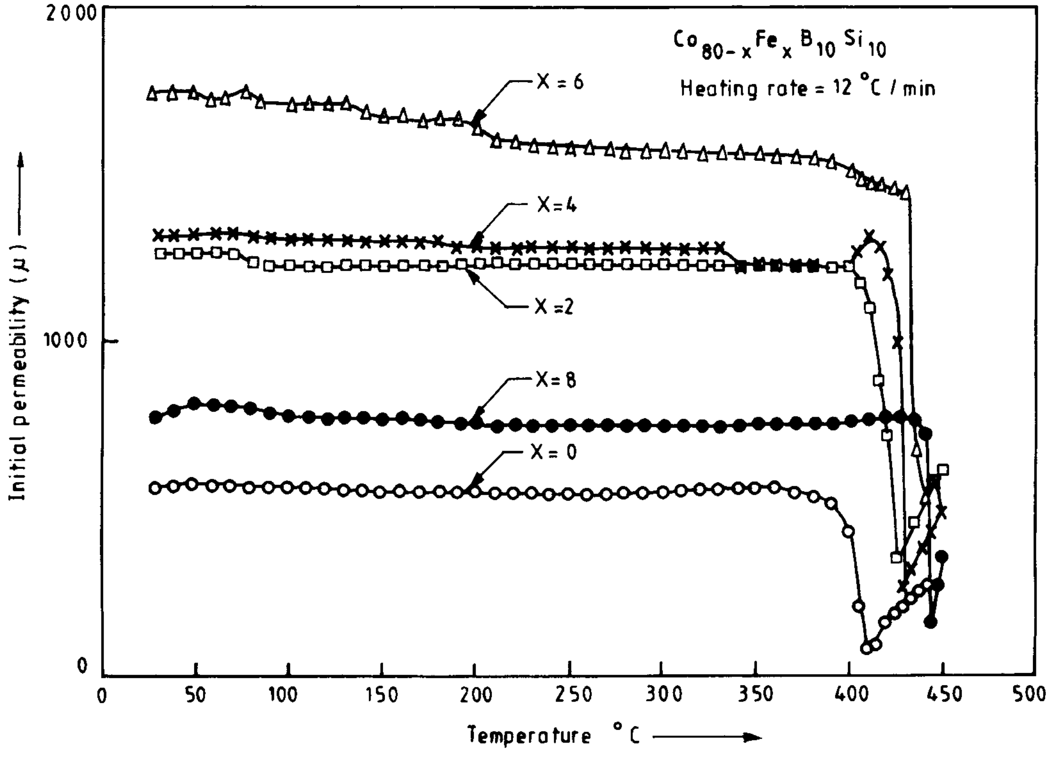

Fig. 3. T_C determination from temperature dependence of permeability of amorphous ribbon with compositions $Co_{80-x}Fe_xB_{10}Si_{10}$.

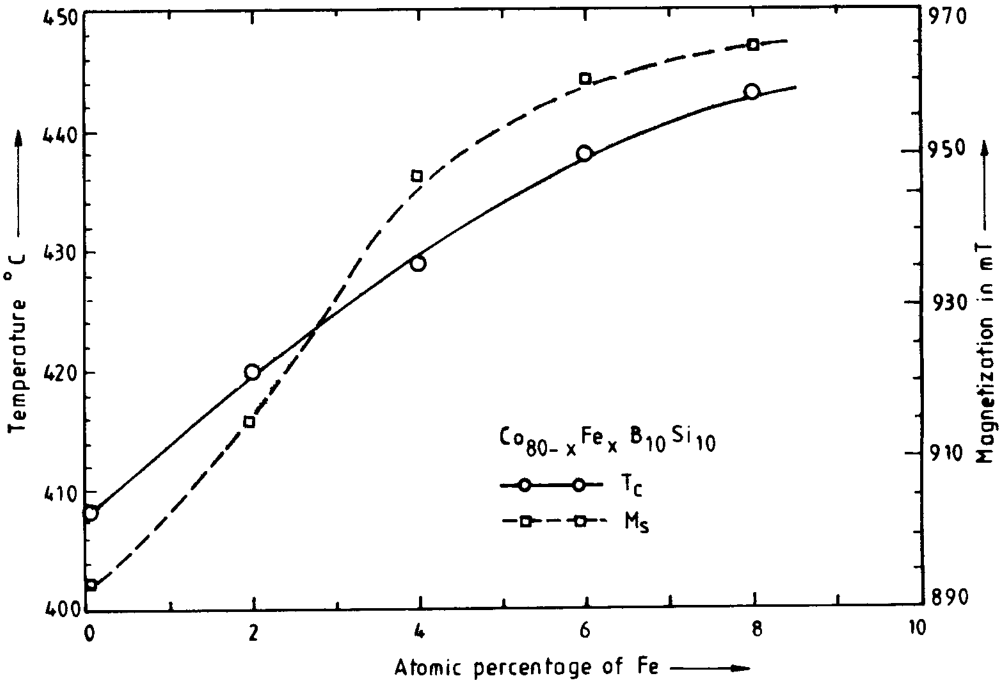

Fig. 4. Variation of T_C and M_s due to change in the Fe content in $Co_{80-x}Fe_xB_{10}Si_{10}$ amorphous ribbons.

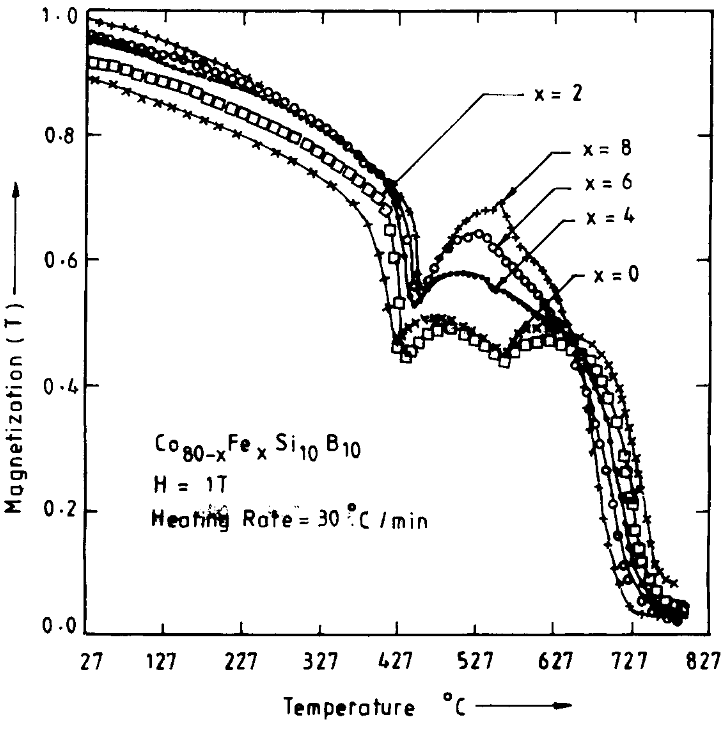

Fig. 5. Temperature dependence of magnetization of amorphous ribbons with composition $Co_{80-x}Fe_xB_{10}Si_{10}$.

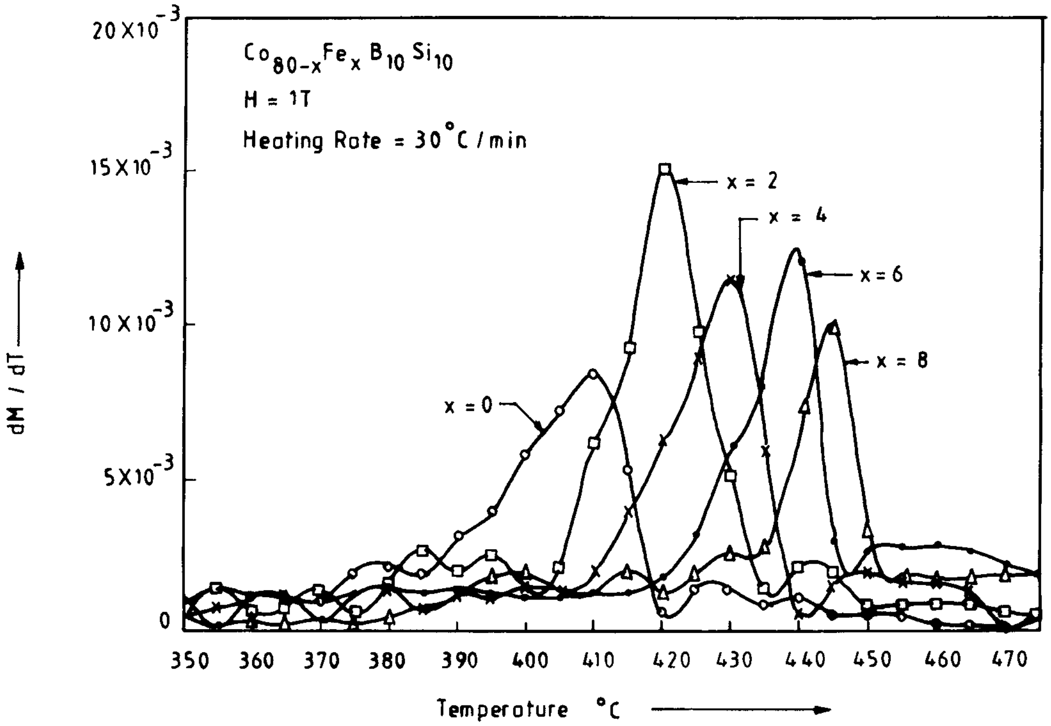

Fig. 6. dM/dt vs. temperature curve of amorphous ribbons with composition $Co_{80-x}Fe_xB_{10}Si_{10}$.

compositions. The Co–Fe alloys in the amorphous state behaves quite differently from the corresponding crystalline state in respect of Curie temperature. This shows that the exchange mechanism in the amorphous state is quite different from that in the crystalline state. Magnetic moment, however, shows similarity in both, the crystalline and amorphous states. From the technological point of view, the Co–Fe system is better, both in respect of enhancement of saturation magnetization and Curie temperature. Addition of Fe increases T_g which is favourable in respect of stability of the amorphous state. Substitution of Fe changes the A.C. initial permeability with a maximum value of $x = 6$. This is explained as due to minimum magnetostriction that results at this composition.

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