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Anomalous shift of Curie temperature in iron–nickel Invar alloys by high-energy heavy ion irradiation

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Abstract

$Fe_{0.68}Ni_{0.32}$ Invar alloys are irradiated with 3.54 GeV Xe ions, and with 2.71 GeV U ions at room temperature. Measurements of the magnetic moment of specimens under AC magnetic field before and after irradiation show that the Curie temperature, T_c, for the irradiated region increases with increasing the ion fluence. This phenomenon appears even at low ion fluence, implying that it is attributed to ion-induced high-density electronic excitation. It is well known that T_c of such Fe–Ni Invar alloys strongly depends on the Ni concentration and the external pressure. With increasing the Ni concentration from ~30%, T_c increases, and with decreasing the lattice parameter by the external pressure, T_c decreases. Therefore, the increase in T_c by high-energy ion irradiation can be explained as originating from the lattice expansion and/or the composition change, which are induced by the high-density electronic excitation.

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1. Introduction

Fe–Ni alloys with Ni concentration of around 35% have an extraordinarily low thermal expansion coefficient and their dimension is nearly "*invar*iable" around the room temperature. Therefore, they are called "*Invar* alloys". These alloys show various anomalies in magnetic properties such as the deviation of the magnetization from the Slater–Pauling curve by decreasing the number of outer shell electrons, and the strong dependence of the Curie temperature on the mean distance of the constituent atoms in alloys [1]. These anomalies can be interpreted as due to the instability of the 3d-ferromagnetism in fcc lattice [2,3]. Experimentally, this instability has been observed, for example, as a rapid decrease in Curie temperature under the high pressure [4,5], and a large change in magnetic properties by changing the Ni concentration in alloys [6].

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Mechanical alloying synthesis has been often used to look for new functional materials and to control the magnetic properties of Fe–Ni Invar alloys [7,8]. By this technique, a wide variety of the fluctuation of Ni concentration has been introduced into the alloys [9,10]. Irradiation with swift heavy ions can be another method for the modification of their magnetic properties, because it has been reported that swift heavy ion irradiation can strongly modify lattice structures of materials [11].

In this paper, we report the modification of the magnetic properties in Fe–Ni Invar alloy by using GeV heavy ion irradiation, focusing on the shift of the Curie temperature. The result is discussed in terms of the electronic excitation effects.

2. Experimental procedure

Invar alloy of $Fe_{0.68}Ni_{0.32}$ was prepared for the present experiment. First, iron and nickel metals of purity of 99.9% were melted using an induction furnace and then, cold rolled to the thickness of 1 mm. After annealing at 1000 °C for 3 h, they were quenched into water so as to remain the fcc phase. They were rolled again to reduce the thickness to 55–85 μm, and cut into square platelets of 5 mm × 5 mm. Then, they were annealed again at 1000 °C for 3 h and quenched into water.

The specimens were irradiated with 3.54 GeV ^{136}Xe ions using the RIKEN ring cyclotron, and with 2.71 GeV ^{238}U ions using the GSI-UNILAC accelerator. Before and after the irradiation, the magnetic moment of the specimens, M, was measured by using a specially designed system for rapid measurements. In this system, a pick-up coil and a canceling coil were wound in the opposite direction with each other to pick up the signal proportional to dM/dt. AC-magnetic field, H_{ex}, with the frequency of 80 Hz and the intensity of 1 Oe was applied to the specimen and the output signal was detected using a lock-in amplifier. Inside the pick-up coil was placed a furnace and the temperature was kept at the measuring temperature. As soon as the specimen attached with a thermocouple was placed in the furnace, the measurement started and it ended within a few minutes. This rapid measuring system is especially useful for such specimens as in the present case of irradiated ones that are thermally unstable.

The intensity of magnetization, I, is defined as

$$I = M/V, \tag{1}$$

where V is the specimen volume. The effective field in the specimen, H_{eff}, is, however, not the same as H_{ex}, but depends strongly on the specimen shape;

$$H_{eff} = H_{ex} - 4\pi NI, \tag{2}$$

where N is the demagnetizing factor. In the present case, as H_{ex} is so weak that the specimen cannot be fully magnetized, the total magnetization, M, is given as

$$M = VI = V\chi H_{eff} = V\chi(H_{ex} - 4\pi NI). \tag{3}$$

From Eqs. (1) and (3),

$$M = \left[\frac{V\chi}{1 + 4\pi N\chi}\right] H_{ex} \equiv SH_{ex}, \tag{4}$$

where χ is the magnetic susceptibility, S the slope of experimental M–H_{ex} curve. Here we assume that the Curie temperature is just T_c all over the specimen. Above T_c, as the specimen is paramagnetic, the values of χ and S are nearly 0. On the other hand, below T_c, the value of χ becomes infinite because the specimen is ferromagnetic, and S becomes $V/4\pi N$;

$$S = \begin{cases} 0 & \text{for } T > T_c, \\ \frac{V}{4\pi N} & \text{for } T < T_c. \end{cases} \tag{5}$$

Therefore, we can determine T_c. as the temperature at which the value of S changes from $V/4\pi N$ to 0. When the projected range of irradiating ions is much larger than the specimen thickness, effects of irradiation extend all over the specimen, and the irradiation-induced change in T_c can be detected by the above method.

Next, we consider the case in which the projected range of irradiating ions is smaller than the specimen thickness, and some part of the specimen remains unirradiated. Fig. 1 shows the specimen of h (height) × h (width) × t (thickness) in dimension before irradiation. The direction of H_{ex} is also shown in the figure. The Curie temperature is T_{c0} all over the specimen (Fig. 1(a)), and the temperature dependence of the value of S is shown in Fig. 1(b). After irradiation, the Curie temperature for

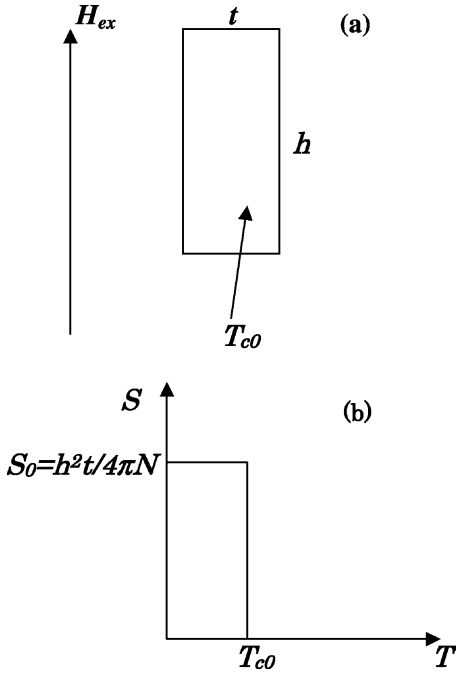

Fig. 1. (a) Distribution of T_c in the specimen before irradiation and (b) temperature dependence of the slope of M–H_{ex} curve, S. Direction of magnetic field is also shown.

the irradiated region is assumed to increase uniformly to T_c' as shown in Fig. 2(a). According to Eq. (5), the value of S, i.e. the slope of M–H_{ex} curve would change from $S_0 = h^2t/4\pi N$ to $S' = h^2R/4\pi N'$ at T_{c0}, and then would change from S' to 0 at T_c', where N and N' are the demagnetizing factors for unirradiated specimen and for the irradiated region of the specimen after irradiation, respectively. Actually, the demagnetizing factor strongly depends on the shape of ferromagnetic region. In the present experiment, as the thickness of the ferromagnetic region is much smaller than its length and width ($t \ll h$), its shape can be approximated as an ellipsoid of revolution, the polar semi-axis length of which corresponds to the thickness of the ferromagnetic region. Under this approximation, the demagnetizing factor is nearly proportional to the thickness of the ferromagnetic region [12]; for unirradiated specimen, $N \sim t$, and for the irradiated region, $N' \sim R$. Then,

$$S_0 = \frac{h^2 t}{4\pi N} = \frac{h^2 R}{4\pi N'} = S' \quad \text{for } T < T_c. \tag{6}$$

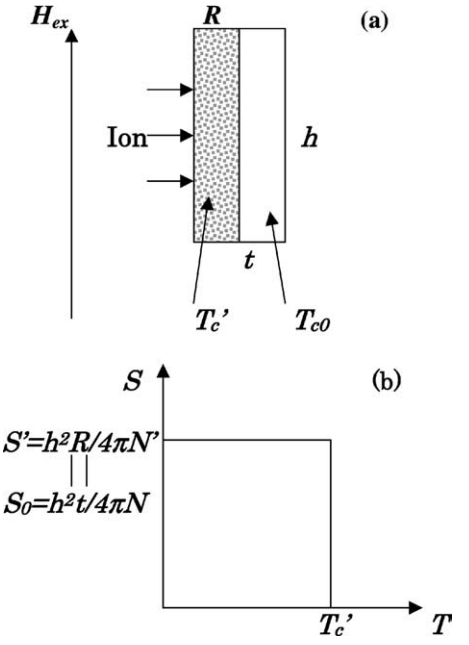

Fig. 2. Same as Fig. 1 except for the partly irradiated specimen.

Therefore, as can be seen in Fig. 2(b), the slope of M–H_{ex} curve is changed only at T_c' from S_0 ($=S'$) to zero. From the above discussion, we have got a very interesting conclusion; even when the projected range of ions is smaller than the specimen thickness, we can detect the Curie temperature only for the irradiated region.

3. Results and discussion

The experimental result for the 3.54 GeV Xe ion irradiation is shown in Fig. 3. As the projected range of the Xe ions (~100 μm) is larger than the specimen thickness (about 60 μm), the ions pass completely through the specimen, and the effect of irradiation extends all over the specimen. In Fig. 3(a), the slope of the experimental M–H_{ex} curve, S, which is normalized to unity at low temperature region, is plotted as a function of specimen temperature. The value of S slightly decreases from unity with increasing the temperature and then, decreases rapidly to zero around T_c. However, the range of the temperature where S rapidly decreases is rather wide comparing usual ferromagnetic metals. This is attributed to the distribution of the

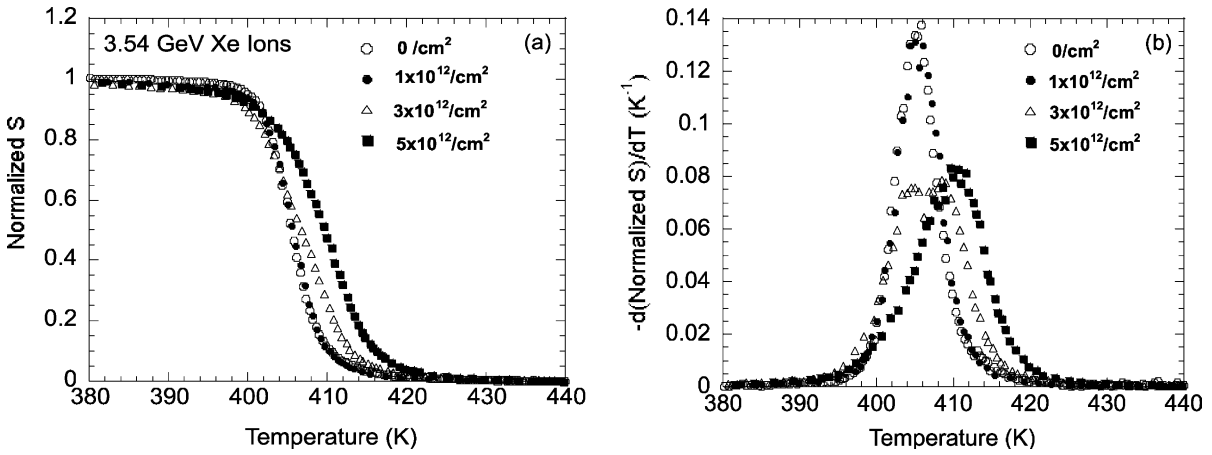

Fig. 3. Temperature dependence of the slope of M–H_{ex} curves, S, for 3.54 GeV Xe ion irradiation (a) and their temperature derivatives (b).

Curie temperature in the specimen. With increasing the ion fluence, the experimental curve is shifted to higher temperature side, implying that the irradiation increases the Curie temperature. To see the change in the Curie temperature by the irradiation more clearly, the temperature derivatives of S–T curves are plotted in Fig. 3(b). Here, we define the temperature at which the value of the derivative has a maximum as the mean Curie temperature, $\langle T_c \rangle$. The figure shows that the irradiation to 1×10^{12} cm^{-2} scarcely affects the Curie temperature, and that the shift of $\langle T_c \rangle$ after the irradiation up to 5×10^{12} cm^{-2} is about 5 K.

By using the TRIM code, the cross section for defect production through the elastic collisions, σ_d, and the energy deposited through electronic excitation per unit length (electronic stopping power), S_e, were calculated for 3.54 GeV Xe ion irradiation as a function of specimen depth. The displacement energy was assumed to be 25 eV. The change in σ_d and S_e was very small through the specimen. This means that the specimen is nearly uniformly affected by the irradiation.

Fig. 4 shows the result for the 2.71 GeV U ion irradiation. The depth dependence of σ_d and S_e was calculated by TRIM code. The projected

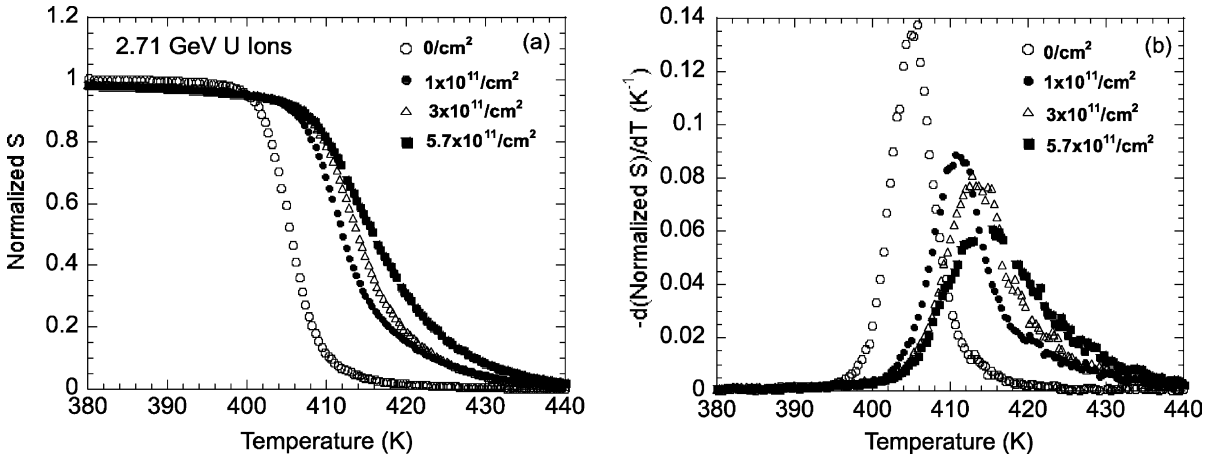

Fig. 4. Same as Fig. 3 except for 2.71 GeV U ion irradiation.

range of the U ions (~45 μm) is smaller than the specimen thickness (about 75 μm), and only 60% of the specimen volume is irradiated with the ions. The experimental curves are, however, shifted as a whole to higher temperature side with increasing the ion fluence. This trend is just the same as shown in Fig. 2(b). As discussed above, even when some part of specimen remains unirradiated, we can estimate the value of T_c only for the irradiated region from the experimental data. From the temperature derivatives of S–T curves (Fig. 4(b)), the mean value of the Curie temperature, $\langle T_c \rangle$, can be deduced for each irradiation.

We consider here whether or not the defects produced by elastic collisions contribute to the change in T_c of the Fe–Ni Invar alloy. By using the ion-fluence and the average value of σ_d through the irradiated region, the concentration of defects produced by elastic collisions can be estimated. If all of the defects survive the thermal agitation of the lattice, the calculated defect concentration is about 60 atomic ppm for the Xe ion fluence of 5×10^{12} cm^{-2}, and about 250 atomic ppm for the U ion fluence of 5.7×10^{11} cm^{-2}. During the irradiation at room temperature, however, most of defects are thermally annihilated, and the concentration of surviving defects is estimated to be only several atomic ppm for Xe irradiation and several tens atomic ppm for U irradiation. Such small amount of defects can hardly contribute to the T_c change in the Fe–Ni alloy. Then, we conclude that the change in the Curie temperature is attributed to the electronic excitation induced by the ions.

Fig. 5 indicates the values of $\langle T_c \rangle$ as a function of ion-fluence for Xe ion and U ion irradiations. From this figure, the rate of increase in $\langle T_c \rangle$, i.e. the increase in $\langle T_c \rangle$ per unit fluence, can be roughly calculated. The rate for U irradiation is an order of magnitude larger than for Xe irradiation. On the other hand, the calculation by TRIM code shows that the average value of S_e over the irradiated region for U ions is only twice as large as for Xe ions. This result suggests that the change in Curie temperature depends superlinearly on the electronic stopping power.

As mentioned before, the Curie temperature of Fe–Ni Invar alloys is quite sensitive to their lattice parameter. An external high pressure can contract the lattice, resulting in the decrease in Curie temperature, while swift heavy ion irradiation induces a large lattice expansion in some materials [13]. If such a lattice expansion is induced by GeV ions in the Fe–Ni Invar alloy, we can explain the increase in the Curie temperature. Swift heavy ions also enhance a selective diffusion of constituent atoms in some alloys and vary their local atomic ratio [14,15]. If such an irradiation enhanced diffusion makes a Ni rich zone in the specimen, the Curie temperature of this zone will increase, because even a small increase in Ni concentration from 32% can induce a large increase in the Curie temperature. To clarify the present result in more details, measurements of lattice parameter and spontaneous magnetization in GeV ion irradiated Fe–Ni alloys are now in progress.

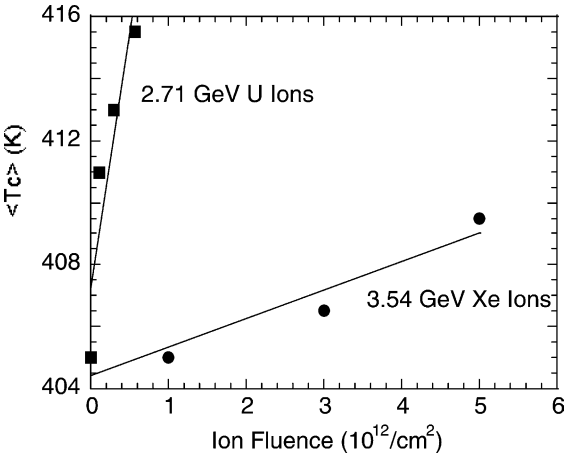

Fig. 5. Mean value of Curie temperature, $\langle T_c \rangle$, as a function of ion-fluence for Xe ion irradiation and U ion irradiation.

4. Summary

The Curie temperature of $Fe_{0.68}Ni_{0.32}$ Invar alloy is increased by GeV heavy ion irradiation. As this phenomenon appears at low fluence of 10^{11}–10^{12} cm^{-2}, it is attributed to the high density electronic excitation induced by GeV ions. The increase in Curie temperature per unit fluence depends superlinearly on the electronic stopping power for the irradiating ions. The experimental

results can be explained as originating from the lattice expansion and/or the composition change induced by GeV ions.

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