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Résumé.- L'influence d'hydrogène absorbé sur la structure magnétique d'alliages invar c.f.c. $Fe_{65}Ni_{35}$, $Fe_{66}Mn_3Ni_{31}$ et $Fe_{69}Ni_{28}C_3$ a été étudiée par spectrométrie Mössbauer. Au fur et à mesure de l'hydrogénation électrolytique, la contribution à bas champ interne du spectre d'absorption, qui est supposée être à l'origine de l'effet invar, se modifie profondément et il apparaît une forte proportion de phases hydrures. L'analyse des spectres montre que les hydrures, qui ont la même structure c.f.c. que la matrice, conservent uniquement une composante fortement ferromagnétique. Cet effet de l'hydrogénation est interprété par un remplissage de la bande 3d par les électrons de l'hydrogène dans un modèle de bande de Stoner. Un effet inverse, précédemment observé sur un alliage $Fe_{55}Ni_{45}$, avec un champ interne de l'hydrure 15% plus petit que celui de la machine, peut être expliqué par le même modèle.

Abstract.- The effect of absorbed hydrogen on the magnetic structure of f.c.c. invar alloys, $Fe_{65}Ni_{35}$, $Fe_{66}Ni_{31}Mn_3$ and $Fe_{69}Ni_{28}C_3$, was studied by means of ^{57}Fe Mössbauer effect. As the electrolytic hydrogenation preceeded, the characteristic absorption spectrum with low internal field components, which is believed to be an origin of the invar effect of these alloys, was drastically changed and hydride phases appeared in large fractions. The spectral analysis showed that the hydrides with the same f.c.c. structure as the matrix phase lost the weak field components and only strong ferromagnetic components remained. This effect of hydrogen on the magnetic structure of invar alloys was interpreted in terms of 3d hole filling with electrons from solute hydrogen in the Stoner's band model. A reverse effect found by a previous study on a non-invar $Fe_{55}Ni_{45}$ alloy that the internal field of the hydride became about 15% smaller than that of the matrix phase was explained by the same model.

1. Introduction.- The f.c.c. Fe-Ni based alloys with relatively limited concentrations around $Fe_{65}Ni_{35}$ known as "Invar alloys", show anomalous properties in addition to a very small thermal expansion coefficient such as a steep decrease of the saturation moment from the top of the Slater-Pauling curve in the iron rich side. Several models which attributed these anomalies to magnetic interaction have been proposed /1-3/. The Mössbauer effect is a powerful tool to clarify the complicated magnetic structures, and Shiga et al. /4/ and Gonser et al. /5/ were the first to find a characteristic wide spread internal field distribution including weak ferro- and/or antiferromagnetic components depending on the alloy concentration. On the other hand, f.c.c. Fe-Ni alloys are known to form a f.c.c. β-hydride phase by electrolitical hydrogenation, and our recent Mössbauer study /6/ has shown that hydrogen infused in a non-invar ferromagnetic $Fe_{55}Ni_{45}$ alloy reduces the magnetic moment of iron in the β-hydride. Accordingly, in the present study, the effect of hydrogen on the magnetic structure of invar alloys, especially on the characteristic weak internal field component, was studied and the results were discussed in terms of the change of the electronic structure of 3d band by hydrogen including those in the case of non-invar $Fe_{55}Ni_{45}$ alloys.

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2. Experimental procedures.- The alloys of f.c.c. invar $Fe_{65}Ni_{35}$ and $Fe_{66}Ni_{31}Mn_3$ were prepared by melting in an induction furnace and homogenized at 1100°C. An $Fe_{69}Ni_{28}C_3$ alloy was obtained by carburizing a homogenized $Fe_{71}Ni_{29}$ alloy. The third element, manganese or carbon, was added in order to stabilize the f.c.c. phase. Specimens were rolled and polished and the final thickness of 30 μm was obtained. Hydrogen was introduced electrolytically in $1N-H_2SO_4$ solution at 20°C with a current density of $0.5 A/cm^2$. Immediately after hydrogenation, X-ray diffraction analysis was carried out and then the measurement of Mössbauer effect by using ^{57}Co source in copper was done at liquid nitrogen temperature. The amount of absorbed hydrogen was measured by collecting the released gas from a specimen upon heating.

3. Result and discussion.- In figure 1 a), the Mössbauer spectrum of hydrogen free $Fe_{66}Ni_{31}Mn_3$ invar alloy at 77 K is shown. A wide spread spectrum especially with a large fraction of absorption around zero velocity is observed. The distribution of internal magnetic field was calculated by Fourier analysis and the low field component was quantitatively detected as is shown in figure 2 c) with solid line.

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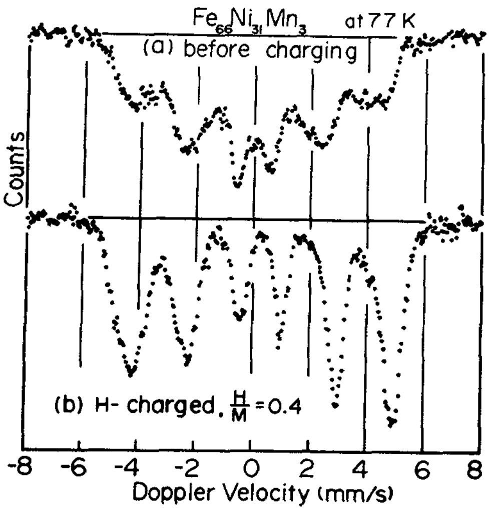

Fig. 1 : The Mössbauer spectra of $Fe_{66}Ni_{31}Mn_3$ invar alloy at 77 K. (a) before hydrogenation; (b) hydrogen charged. The amount of hydrogen is 0.4 in hydrogen-metal atom ratio.

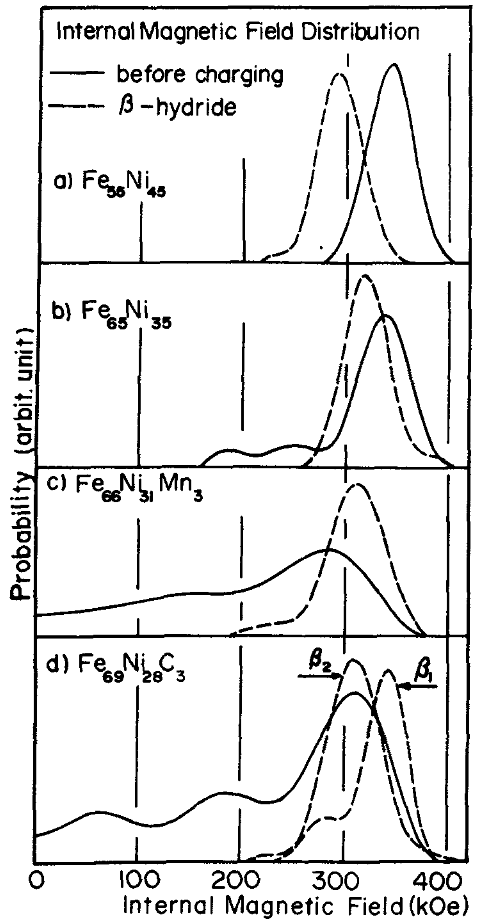

Fig. 2 : The internal magnetic field distribution, where solid lines show those of alloys before charging and broken lines show those of hybrides (a) $Fe_{55}Ni_{45}$; (b) $Fe_{65}Ni_{35}$; (c) $Fe_{66}Ni_{31}Mn_3$; (d) $Fe_{69}Ni_{28}C_3$.

Those of non-invar $Fe_{55}Ni_{45}$, invar $Fe_{65}Ni_{35}$ and $Fe_{69}Ni_{28}C_3$ are also shown in a), b) and d) in figure 2 respectively. Non-invar $Fe_{55}Ni_{45}$ alloy exhibits a typical ferromagnetic distribution without the low field components, while the invar alloys show additional distribution of weaker field component, extends down to 160 kOe in the case of $Fe_{65}Ni_{35}$ and even down to 0 kOe in the case of $Fe_{66}Ni_{31}Mn_3$ and $Fe_{69}Ni_{28}C_3$ alloys as before mentioned. By an intense hydrogenation, the characteristic weak field absorption was diminished and, instead, the fraction of strong ferromagnetic part increased with increasing hydrogen content, finally exhibiting a typical ferromagnetic patterns as in figure 1 b) shows in the case of $Fe_{66}Ni_{31}Mn_3$. Similar remarkable changes were also observed in $Fe_{65}Ni_{35}$ and $Fe_{69}Ni_{28}C_3$ invar alloys. X-ray diffraction analysis in these four alloys showed the formation of β-hydride phase which also have f.c.c. structure. In the alloys of $Fe_{55}Ni_{45}$ and $Fe_{65}Ni_{35}$, single β-phase which showed a lattice expansion of about 4% relative to the matrix f.c.c. γ-phase appeared. In $Fe_{66}Ni_{31}Mn_3$ and $Fe_{69}Ni_{28}C_3$ alloys two f.c.c. hydride phases, $β_1$ and $β_2$ appeared. The lattice expansion of these phases are about 2.5% and 5% respectively, which suggests that $β_2$ has a higher concentration of hydrogen than that of $β_1$. All of the above changes thoroughly disappeared by desorption of hydrogen, and the original spectra were recovered. It is therefore doubtless that hydrogen is responsible for all of these changes. The internal field distributions of the β-phases are shown in figure 2 with broken lines. In the case of non-invar $Fe_{55}Ni_{45}$ alloy, average internal field is reduced by 15% as mentioned before and shown in figure 2 a). In the invar $Fe_{65}Ni_{35}$ alloy, however, the peak of the internal field distribution in β-phase was reduced by about 6%, while the characteristic lower field components disappeared, as are seen in figure 2 b). It was obvious that the hydrogen atoms changed the weak ferromagnetic coupling between iron atoms into strong ferromagnetic one. This effect was confirmed by the clearer changes observed in $Fe_{66}Ni_{31}Mn_3$ and $Fe_{69}Ni_{28}C_3$ alloy, which are shown in figure 2 c) and d); the lower field components widely spread down to 0 kOe were converted into strong ferromagnetic ones as the broken lines show. In this distribution two hydride components, $β_1$ and $β_2$ coexist although the analysis to separate them was not always successful in the case of $Fe_{66}Ni_{31}Mn_3$.

By changing the time of hydrogenation and that of aging and taking X-ray and Mössbauer patterns repeatedly, identification of the components of the two phases was performed. As shown by the right hand side broken line in figure 2 d), the β_1-phase is completely ferromagnetic with the average field of 340 kOe, while the β_2-phase of the left which contains more hydrogen is strong ferromagnetic as well but the average field is reduced down to 310 kOe. It is worthy of note that, in accordance with the above changes in the magnetic structures, the characteristic behavior of low thermal expansion of these alloys was lost by hydrogenation and was regained by aging.

The origin of the above mentioned interesting effect of hydrogen on the magnetic structure of Fe-Ni based alloys, either invar or non-invar, was attributed to the change in the 3d electronic configurations and tentatively understood by means of Stoner's band model /7/. As shown in figure 3 a), a non-invar ferromagnetic alloy may have a large amount of 3d holes only in the down spin state in the characteristic density state curve.

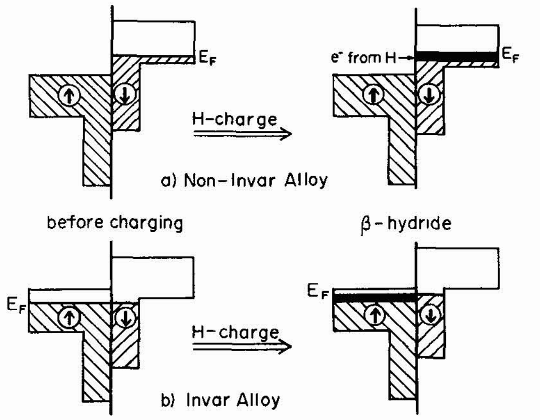

Fig. 3 : The change of band structure by hydrogen (a) non-invar alloy (b) invar alloy.

By a hydrogenation, the holes will be occupied by the electrons donated from hydrogen and, accordingly, the internal field will decrease, as was actually observed in $Fe_{55}Ni_{45}$ alloy. On the other hand, however, in the invar alloys, up spin band may also have holes as shown in figure 3 b) by which the before mentioned low field components and steep decrease of magnetic moment in the iron rich side can be accounted for. By the hydrogenation, the up spin holes will be filled by the electrons from hydrogen and, in addition, transfer of electrons from the down spin band will occur to increase the moments of weekly coupled iron atoms. By further hydrogenation, the up spin holes will be filled completely and electrons from hydrogen will fill the down spin holes, which can explain the magnetic behavior of β_1 and β_2 phase.

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