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学位論文題目	Numerical simulation of thermal desorption spectrum of hydrogen in high strength martensitic and austenitic stainless steels （高強度マルテンサイト鋼とオーステナイトステンレス鋼における水素昇温脱離分析のシミュレーション）
審査会	主査　榎本正人　　委員　高橋東之 委員　篠嶋妥　　委員　伊藤吾朗 委員　太田弘道

論文内容の要旨

Thermal desorption analysis (TDA) is widely used to analyze the diffusion and trapping of hydrogen in materials. While thermal desorption spectrum is thought to represent the energy and density of trap sites, the temperature and shape of the peak depend on the size of specimen and the conditions of hydrogen-charge and thermal analysis. Moreover, TDA spectrum is very different between bcc and fcc iron in which the lattice diffusivity of hydrogen differs several orders of magnitude. Accordingly, the influences of charging and testing conditions on the spectrum are studied by numerical simulation based upon McNabb-Foster model. Simulations were conducted in medium carbon martensitic steels and austenitic stainless steels for comparison with experimentally obtained spectra in these steels.

In the McNabb-Foster theory a number of parameters are required to conduct simulation, not only the energy and site density of trap sites, but also the kinetic coefficients (pre-exponential factor) of trapping and detrapping, the values of which are usually not well-established. Hence, before conducting simulations the applicability of the so-called Kissinger equation to TDA spectrum is studied using the McNabb-Foster model. It is shown that a Kissinger-type equation can describe diffusion-controlled desorption after a certain amount of pre-exposure prior to the analysis, albeit the pre-exponential coefficient depends on the specimen size. Moreover, the Choo-Lee plot which is used to determine the detrapping energy from TDA spectra with varying ramp rate can also be applied to diffusion-controlled desorption.

In martensitic steels the peak temperature of TDA spectrum are often considerably lower than those of deformed pure iron. In the literature it is well-known that carbon and hydrogen have a repulsive interaction at close proximity and carbon segregates to dislocations in lath martensite during quenching in low and medium martensitic steels. Hence, a computer program was developed to incorporate carbon segregation to dislocations into the M-F model; it is treated in the same way as hydrogen trapping, albeit detrapping is assumed not to occur. Introducing a parameter which represents the

carbon-hydrogen interaction, experimental TDA spectra could reproduced well in some low and medium carbon martensitic steels.

It is reported that TDA spectra of austenitic stainless steels depend largely on the charging and testing conditions. The dependences of spectrum on the specimen thickness and ramp rates, experimentally reported in Ni alloys and stainless steels, were reproduced fairly well solely from the lattice diffusivity, which implies that the influence of trap sites on the spectrum was often not significant. The initial hydrogen distribution appears to have a large influence on the spectrum; the difference of peak temperature as large as 200°C in SUS304 steel between cathodic charge and hydrogen charge under high-pressure environment could be accounted for from the difference in the penetration of hydrogen in the specimen. Moreover, two peaks can occur when hydrogen is initially confined to the rim of the specimen, because one part of hydrogen diffuses and escapes from the surface in a short time, and the other part diffuses inward and comes back to the surface later.

In this study, McNabb-Foster theory proved to be very useful in analyzing and simulating the hydrogen desorption spectrum in both high strength martensitic and austenitic stainless steels in which the lattice diffusivity of hydrogen differs several orders of magnitude, albeit we need to choose carefully the values of many parameters involved in the simulation. In particular, Kissinger equation and its derivative form Choo-Lee plot proved to be useful in the evaluation of hydrogen detrapping energy if the thermal desorption experiment is performed under proper conditions.

論文審査の結果の要旨

水素昇温脱離分析は、鋼中水素の存在状態の分析に幅広く使われているが、昇温スペクトルは水素チャージや分析条件に大きく依存することが知られている。申請者は、シミュレーションによって、試験片サイズ、昇温速度、水素の初期分布、炭素濃度を系統的に変化させて、これらの因子がスペクトルに及ぼす影響をそのメカニズムとともに明らかにした。また、これまで特定の条件（脱離律速）でしか解析に適用できないと考えられていた式(Kissingerの式)が、それ以外の条件（拡散律速）でも適用できることを示した。これらの知見は、この分野の進展に大きく貢献するものであり、博士（工学）の学位に相応しい。