

Light Metal Alloys for Hydrogen Storage

Collaborative research project at the University of Iceland

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Use of Hydrogen As Fuel

It is widely believed that hydrogen will within a few tens of years become the fuel that powers most vehicles and portable devices, i.e. hydrogen will become the means of storing and transporting energy. The reason is the depletion of oil and the relatively facile production of hydrogen from the various renewable sources of energy - hydroelectric, wind, solar, geothermal - with water being the only raw material needed. To release the energy, hydrogen can be burned in an efficient and clean way in a fuel cell to form water again, or made to drive an electrochemical cell as in the commonly used nickelhydride battery. As concerns over air pollution and global warming increase, the incentive to switch to clean and efficient hydrogen economy becomes greater and the transition may occur well before oil reserves are depleted (after all, Stone Age did not end because mankind ran out of stones!). This development is of particular interest to people living in Iceland, a country rich in renewable energy resources but poor in raw materials [1,2]. It seems imperative that Icelanders follow closely the advances in hydrogen technology and, preferably, move to a front-line position and contribute to the development.

While hydrogen has many obvious advantages, there remains a problem with storage and transportation. Pressurised hydrogen gas takes a great deal of volume compared with, for example, gasoline with equal energy content - about 30 times bigger volume at 100 atm gas pressure. Condensed hydrogen is about ten times denser, but is much too expensive to produce and maintain [3]. There are also obvious safety concerns with the use of pressurised or liquified hydrogen in vehicles. Nevertheless, hydrogen powered cars are being produced today installed with high pressure hydrogen gas fuel tanks (see for example <http://www.toyota.co.jp/motorshow2001/english/eco/fchv/fchv4.html> and <http://www.toyota.co.jp/motorshow2001/english/eco/move/index.html>). In a pilot study soon to begin here in Reykjavík, three buses will be run on hydrogen gas as first step in a large implementation study (see <http://www.nyorka.is/>).

Metal Hydrides as Hydrogen Storage Devices

Metals can absorb hydrogen in atomic form and thereby act as hydrogen "sponges" [4]. Around 50 metallic elements of the periodic table can absorb hydrogen in great quantity and the possible choices of hydrogen storage materials are, therefore, enormous. Many scientific and engineering studies have been carried out of the absorption/desorption of hydrogen in metals and development of such storage devices. Daimler-Benz, for example, produced in the early 1980s a car fueled by hydrogen where the storage tank was a chunk of FeTi metal alloy [5]. The volume of this storage device is less than a factor of two greater than the equivalent gasoline tank, but the problem is that the hydride is 20 times heavier [3]. The only successful

commercial large-scale application of metal hydrides as hydrogen storage so far is the metal hydride battery, which has supplied battery power to many small electrical appliances such as mobile phones and portable computers. Metal hydrides have so far not become useful as storage devices for hydrogen gas even though they have some distinct advantages over pressurised hydrogen gas, both improved safety and reduced volume.

Magnesium Hydride

If metal hydrides are to become important energy carriers in mobile vehicles, the mass of the system needs to be reduced from today's devices, such as FeTi. This puts strong constraints on the chemical elements which can be used. A very promising approach is to use magnesium. The hydride, MgH_2 , can store up to 7.6 % weight percent of hydrogen [3,4,6]. The automobile industry has set 5% weight percent as a target for efficient hydrogen storage. But there are three problems with pure Mg: (1) The rate at which hydrogen absorbs and desorbs is too low because diffusion of hydrogen atoms through the hydride is slow. This has been illustrated conclusively by a multilayer Ni-Mg film study carried out by Ólafsson, Hjörvarsson and coworkers who could observe directly the limited growth of the magnesium hydride into the Mg metal from the Mg/Ni interface [7]. Problem (2) is that the hydrogen molecules do not readily dissociate at the surface of Mg to generate the hydrogen atoms that diffuse into the metal. Transition metals can catalyse this bond breaking/formation event at the surface, but not main group elements [4,8-10]. Problem (3) is that hydrogen atoms bind too strongly with the Mg atoms, i.e. the enthalpy of formation of the hydride is too large, so that the hydride needs to be heated to very high temperature, around 350 C, in order to release hydrogen gas at high enough pressure (over 1 atm) [3,4,6]. A useful metal hydride should release the hydrogen in the temperature range between 50 and 100 C. It is important to distinguish between problems (1) and (2) although they both have to do with the kinetics of loading and unloading. These problems could be solved efficiently by different means, as explained below. Problem (3) remains unsolved.

The first problem can be reduced by forming a composite of small Mg crystals loosely agglomerated together as opposed to having a large chunk of Mg crystal. Recently, a US patent has been awarded for such a material formed by ball milling (pieces of Mg metal are placed in a rotating drum containing steel balls) [10]. The clusters are micrometer sized as seen in the scanning electron microscopy (SEM) images in figure 1. The size of the magnesium grains in this composite is 30-200 nm. Hydrogen loading and unloading of this material was found to be reasonably fast.

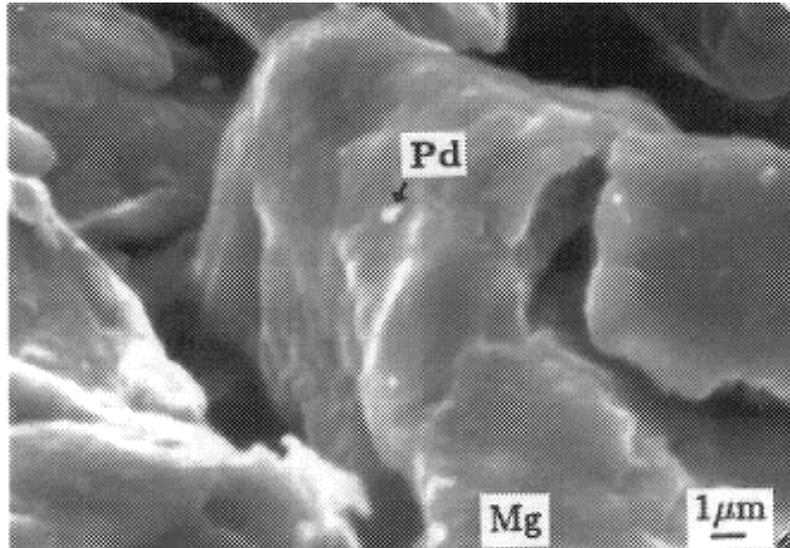


FIG. 1: A scanning electron microscopy (SEM) micrograph of a powder of Mg particles which have small Pd clusters attached on the surface in order to catalyse the break up of hydrogen molecules during adsorption [10].

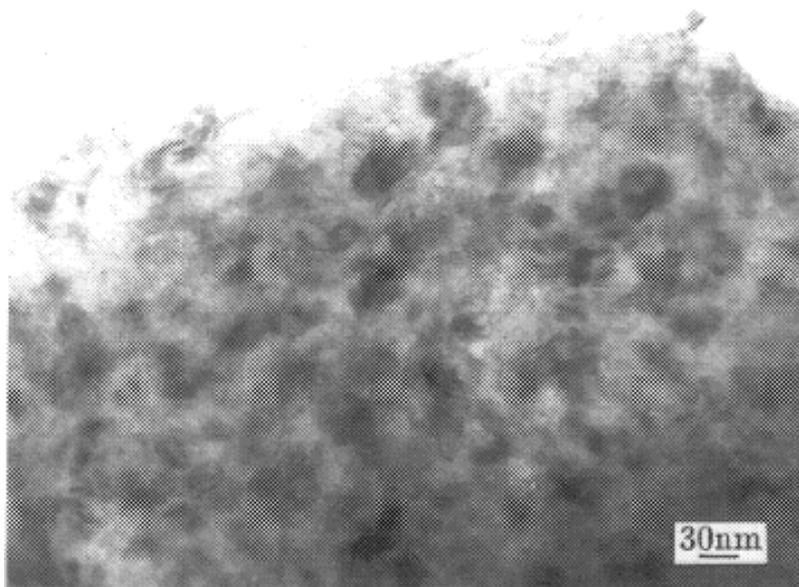


FIG. 2: A transmission electron microscopy (TEM) micrograph of the powder showing the nanocrystalline structure of the particles [10]. The dark regions represent crystalline domains, while the lighter regions are less dense and likely amorphous.

The transmission electron micrograph (TEM) shown in figure 2 reveals the crystalline structure of the particles. It is possible to create even smaller clusters (using, for example, colloidal chemistry techniques) and these are likely to give even faster rate of adsorption and desorption. This has apparently not been tried with Mg, but nanoscale hydrides of other metals have been studied, such as Pd [4]. There, it was found that the thermodynamic properties are also modified because of the large fraction of subsurface sites (i.e. sites in between surface layer and second layer in the

crystal). Those sites have different binding energy and entropy for hydrogen atoms. The dynamics and equilibrium between hydrogen in surface, subsurface and bulk sites has been studied theoretically by Doll and co-workers [12,13].

Another approach to improving the kinetics is to blend in another chemical component. For example, by mixing in Ni [8] or Sc [14]. Channels with lower binding energy and smaller migration barriers for the hydrogen are apparently formed and maintained throughout the hydride, thus enabling fast loading and unloading. This may occur because holes where the hydrogen atom sit are now surrounded by two types of atoms forming bonds of different strength with the hydrogen atom. Griessen and co-workers have been leaders in the analysis of the absorption of hydrogen in metal alloys [4,15]. The alloy hydride can also have different diffusivity because the alloy has a different lattice structure than pure magnesium. The problem is that these metals, Ni and Sc, are heavy and greatly reduce the weight percent of hydrogen in the hydride.

The second problem, the dissociation of hydrogen molecules on the surface, can be solved by adding a small amount of a catalytically active metal on the *surface* of the Mg clusters, as shown in figure 1. This has been shown to work quite well [10]. Another approach, is to form an alloy of Mg with some catalytically active component such as Ni, Fe, V or Pd in small amounts - on the order of a few percent. Mechanical alloying can be used to mix these metals together into nano-composite structure [3,8,9]. However, these heavy transition metal atoms are only needed on the surface of the clusters, where the hydrogen gas dissociates and it is preferable not to have them mix into the interior of the grains. One could, in principle, find a catalytic transition metal that naturally migrates to the surface of the clusters and coats the surface.

The third problem with pure Mg as a hydrogen storage device is the most serious one, namely the high enthalpy of formation of the hydride. Some improvement has been shown to occur by adding Ni or Cu to Mg [3]. The desorption temperature of the Mg₂Ni alloy is about 50 degrees lower than for pure Mg, but this is still far from low enough. The addition of the heavy transition metal greatly reduces the storage capacity, down to 3.6% from 7.6% in pure Mg. A better solution would be to add a light metal that has low affinity to H, for example Al or another light main group element that competes with H for the valence electrons of Mg. This strategy has apparently not been tried and will be pursued in the proposed project.

To summarise: During the last tens of years, metallurgist have studied several alloying mixtures of Mg with heavy transition metals and this has solved problems with the kinetics (problems 1 and 2) at the expense of significantly reduced weight percent of hydrogen. The most efficient approach appears to be the formation of composites with small grains, preferably on nm length scale, which solves problem (1) and then add small amount of a heavy, catalytically active transition metal on the surface of the small grains to solve problem (2). This has been accomplished in the system shown in figures 1 and 2 [10]. The remaining problem, which apparently has not been addressed much and still remains in the system shown, is the large enthalpy of formation of the hydride. One could approach this problem by alloying Mg with other *light, main group* elements, selecting the other component(s) mainly to reduce the hydrogen-Mg bond strength. There is no need to choose a heavy transition metal

and thereby significantly reduce the weight percent of hydrogen in the hydride. This possibility has apparently not received much attention and will be the major focus of the proposed project. In the present project, we will be pursuing this kind of research at the University of Iceland by making, measuring and simulating various Mg alloys. Initially, the focus is on well defined systems such as thin films, where the chemical composition and atomic ordering can be characterised and the measured hydrogen uptake can be cleanly related to the structural and chemical properties of the material. This is analogous to the work of Kasemo and co-workers on the hydrogen uptake in thin magnesium films [16]. We will, then, study ways of making and characterising nano-scale clusters of these same systems.

Theoretical Studies

We have so far focused in this review of the state-of-the-art almost exclusively on experimental studies of metal hydrides. In principle, theoretical calculations especially computer simulations could help identify promising metal alloys for hydrogen storage. However, this has not happened so far because of two problems. First of all, the theoretical calculations have until now been hampered by the lack of knowledge of the interaction between hydrogen atoms and metal atoms. Secondly, the long time-scale evolution that would need to be simulated in order to reproduce (a) the atomic scale structure of the material formed in the lab and (b) the formation of the hydride when placed in contact with the gas. This kind of simulation study would need to cover on the order of seconds in real time, while direct classical dynamics simulations of atoms typically only cover on the order of a nanosecond using a weeks worth of CPU time on a fast computer, even when a simple, and approximate description of the atomic forces is used (such as EMT and EAM). We now discuss how both of these problems have recently been solved for the purposes of this study, thereby opening up the possibility of using theoretical simulation studies to guide the search for better metal hydrides.

Approximate approaches for describing the interaction of hydrogen with metal atoms such as the effective medium theory (EMT) [17] and embedded atom method (EAM) [18] have contributed greatly to the qualitative understanding of metal/hydrogen systems, but they are not accurate enough to be used for predicting reliably materials properties, such as binding energy and diffusion activation energy of hydrogen atoms in metals. An example of the limitation of these approximate approaches is given by a recent study of hydrogen at the Cu(110) surface where EAM is found (by Doll and co-workers, our collaborator - private communication) to give qualitatively different results than the much more accurate first principles Density Functional Theory (DFT) calculations [19]. It has only become possible quite recently to approach these types of problems with DFT and carry out calculations with predictive capability. This is illustrated by a recent calculation by Henkelman and Jónsson of the dissociation of methane at an Ir(111) surface where the activation barrier found by detailed and expensive experimental measurements could be reproduced by the DFT calculations (but, only when a large enough system was used to represent the surface) [20]. Such theoretical calculations in close connection with the experimental studies will be the basic approach in the proposed research program.

The reason it is possible now to carry out theoretical, parameter free calculations with predictive power is first of all due to improvements in the basic methodology (functionals with higher accuracy) [21], improved implementation with fast computational algorithms to solve the DFT equations [22], improved algorithms for finding migration paths and activation energy barriers [23], and finally much faster computers. Time is now ripe for using theoretical calculations not only to help interpret experimental results, but to predict which systems are most likely to have the desired properties.

An example of the computational approach is shown in figures 3 and 4 [24].

NEB: H_2 Dissociation on Ni(111)

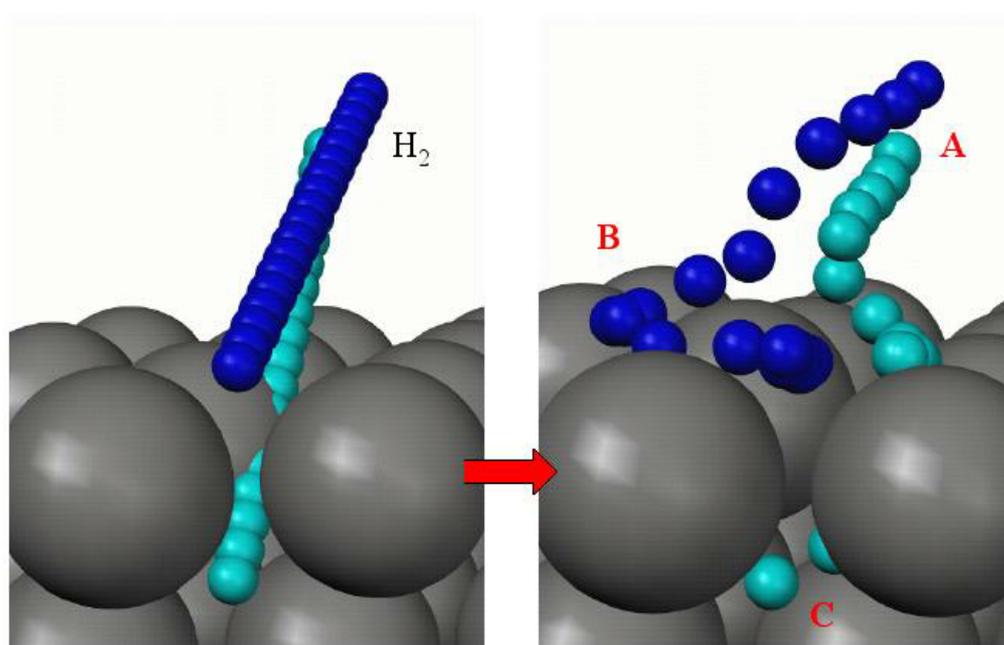


Fig. 3: Theoretical DFT calculation of the dissociation of a hydrogen molecule at a Ni(111) surface and migration of one of the hydrogen atoms to a subsurface site.

The initial state of the calculation is shown to the left (figure 3). A sequence of images or snapshots of the system are generated to map out a path between the initial state - a hydrogen molecule high above the surface - and a final state where the molecule has dissociated and one of the hydrogen atoms has gone subsurface. To the right in figure 3 is shown the optimised, minimum energy path, which is the path of largest statistical weight. It shows that the molecule first dissociates above one of the surface Ni atoms and the two adsorbed hydrogen atoms first bind in threefold surface binding sites. In reverse, this path also shows how hydrogen gas is desorbed from a Ni metal. The bond formation/breaking cannot occur on the side of a surface Ni atom, in between adjacent surface and subsurface sites, as had been suggested [25].

NEB: H₂ Dissociation on Ni(111)

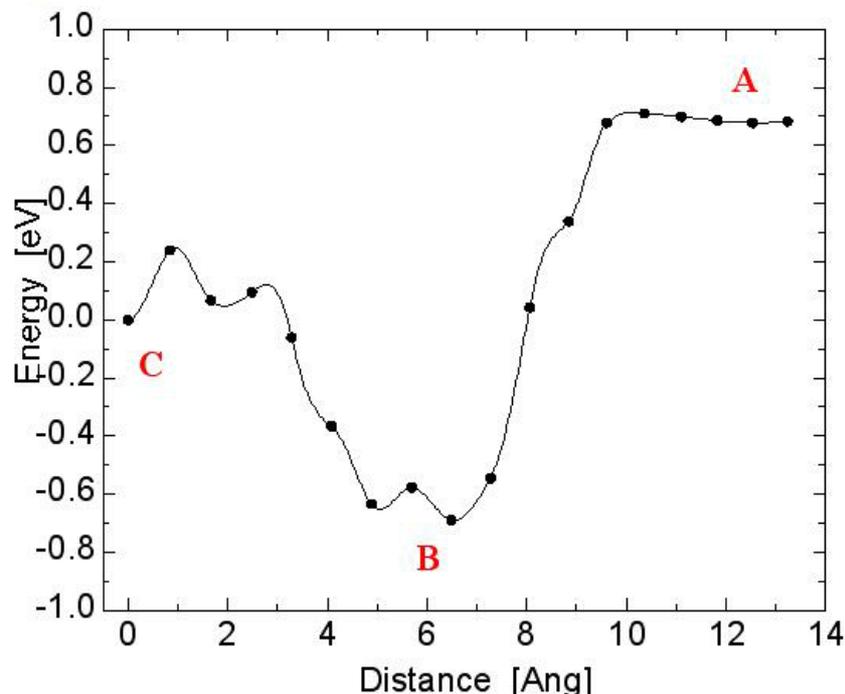


Figure 4: The energy of the H₂-Ni(111) system as the hydrogen molecule (A) dissociates and one of the hydrogen atoms moves into a subsurface site while the other remains on the surface (C), as shown in figure 3. These are results of DFT calculations with no adjustable parameters [24].

Here, the mechanism and energetics of hydrogen molecule dissociation and migration of a hydrogen atom into a subsurface site were studied by first principles DFT calculations (without any fitting parameters or other input from experimental measurements on H/Ni). The optimal path was obtained by using the Nudged Elastic Band method [26-28]. The calculation revealed that the catalytic action of the Ni atoms is only found at the under-coordinated side of the surface metal atoms, not in the hole between surface and subsurface sites. The direct recombination of hydrogen atoms from an atom in a subsurface site to form a desorbing hydrogen molecule does not occur because of the lack of catalytic activity at that site, not because of "site blocking" as had been suggested. The activation energy barrier for going from the surface site (path from B to C) to the subsurface site turns out to be 0.5 eV, quite high, in good agreement with experimental measurements [25]. This activation energy can be used to estimate rate of diffusion of hydrogen atoms into the subsurface sites. This is one example of how these first principles theoretical calculations can be used to learn about the atomistic mechanism and predict the rate of basic microscopic processes that determine the functionality of materials, such as the metal hydrides.

The second problem, the time-scale problem, has also hampered computer simulation studies of solids. In the present context, one would like to be able to

simulate both the formation of the material (either thin film formed by sequential deposition of atoms, or agglomeration and annealing of nanocrystalline composites). But, there is a *billionfold* separation in time scale between what can be simulated directly by numerically solving the classical dynamical equations of motion and the required time scale to reproduce processes relevant in the laboratory (such as surface diffusion of metal atoms and hydrogen atoms, grain boundary diffusion, bulk diffusion, phase transitions, etc.) [29]. Very recently, there has been considerable progress in the development of new simulation algorithms that can bridge this time-scale gap [30-33]. These have, in particular, been applied to the study of crystal growth by deposition [32-33], the type of growth process that will be used to make materials in the proposed study. By simulating the formation of the multilayer films and other materials formed by deposition, one can gain insight into the effect of controllable parameters, such as deposition energy and surface temperature, on the atomic scale ordering in the materials, including chemical component separation and formation of voids and defects. The Jónsson group has implemented their simulation method in a distributed fashion so as to make use of a number of computers loosely connected by the internet (analogous to the SETI screen-saver). A description of this software development effort and the results of simulations, including an animation of the simulated growth of an Al(100) surface can be found at <http://www.eon.hi.is>. This state-of-the-art computer simulation methodology, both in terms of the simulation algorithm and the implementation on distributed computers, will be used in the proposed study to learn about the materials grown in the laboratory as well as the diffusion of hydrogen atoms on the surface and inside the solids.

The simulations described above are necessarily limited to very small representations of the system, typically consisting of a hundred to a thousand atoms (subject to periodic boundary conditions to eliminate edge effects). In order to learn about the larger scale morphology of the materials, it is necessary to do away with the coordinates of all the atoms in the system and formulate the problem in terms of a continuum description of the material. The information about atom binding energy and diffusion obtained from the atomistic calculations can, in principle, be fed into a continuum description in order to simulate the surface morphology, for example, or the concentration of hydrogen atoms, as a function of location and time. This kind of consistent coupling between microscopic, short length scale description and a continuum, large scale description is one of the highly active research areas in computational condensed matter physics/chemistry and materials science today [29]. Little work has been done so far on the continuum modeling of a growing material. Freund and Jónsdóttir developed a finite element approach and applied it to the time evolution of surface morphology during epitaxial growth [34]. The important step for future development is to use the accurate microscopic simulations to learn what functional forms and parameters to use in the continuum description of the system in order to ensure an accurate description of the system.

Experimental Methodology

Thin Films:

As mentioned above, the state-of-the-art experimental methodology for preparing well defined systems where clear connection can be made between material composition/structure and material properties involves growing thin films by deposition of atoms of selected type. Only a few studies of hydrogen absorption into

metal alloys have been carried out using this approach, one example being ref. [16]. Other examples are detailed measurements of hydrogen uptake and hydrogen-hydrogen interaction in thin vanadium layers carried out by Ólafsson, Hjörvarsson and co-workers [35,36]. There, the hydrogen uptake was monitored by conductance measurements and, more rigorously (for comparison), with X-ray diffraction studies carried out in Zabel's lab in Germany (our collaborator). This work represents the first studies of hydrogen uptake in multilayers by conductance measurements and establishes the method as a valid in-situ approach to these kinds of studies. Conductance measurements will be an important tool in the proposed studies where hydrogen uptake will be monitored as a function of temperature and pressure to establish the thermodynamic properties of the hydrides, such as enthalpy and entropy of formation. The thin film samples will be grown by sputter-deposition [37], as described in more detail in section (14). This method provides great deal of control over the composition and, to some extent, the atomic scale structure of the thin film. Materials that are far from thermodynamic equilibrium can be formed, such as multilayer films and amorphous films, greatly extending the possibilities outside the domain of thermodynamically stable crystals.

Nanocluster Composites:

While thin films are the ideal avenue for careful and well characterised experimental studies, the most promising material identified that way would most likely, as explained above, be useful in a hydrogen storage device only in the form of a composite of small crystalline particles, possible as small as a few nm. The technology for forming such nanoscale composites in significant quantities is rapidly evolving. The need for such materials arises in many different contexts. Small clusters of transition metal alloys have, for example, been made to optimise magnetic properties [38]. Precipitates are used to inhibit grain growth and an understanding of the precipitation process is important in order to form the most effective dispersion of small particles. Such composites of small transition metal clusters are found to have superior magnetic properties. Another example where small cluster size can lead to improvements is nano-structured steel. By a combination of several methods such as the one mentioned above, a nano-structured steel is produced as a coating with superior hardness (16 Gpa) and chemical resistance [39].

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