Available online at www.sciencedirect.com

ScienceDirect

Progress in Natural Science: Materials International 24 (2014) 35–41

Progress in Natural Science Materials International

www.elsevier.com/locate/pnsmi
www.sciencedirect.com

Original Research

# Composition design of superhigh strength maraging stainless steels using a cluster model

Zhen Li[a,*], Ruiqian Zhang[b], Qianfeng Zha[c], Yingmin Wang[c], Jianbing Qiang[c], Chuang Dong[c]

[a]School of Mechanical Engineering, Dalian University of Technology, Dalian 116024, China
[b]Science and Technology on Reactor Fuel and Materials Laboratory, Nuclear Power Institute of China, Chengdu 610041, China
[c]Key Laboratory of Materials Modification, Dalian University of Technology, Ministry of Education, Dalian 116024, China

Received 22 October 2013; accepted 4 December 2013
Available online 14 February 2014

**Abstract**

The composition characteristics of maraging stainless steels were studied in the present work investigation using a cluster-plus-glue-atom model. The least solubility limit of high-temperature austenite to form martensite in basic Fe–Ni–Cr corresponds to the cluster formula $[NiFe_{12}]Cr_3$, where $NiFe_{12}$ is a cuboctahedron centered by Ni and surrounded by 12 Fe atoms in FCC structure and Cr serves as glue atoms. A cluster formula $[NiFe_{12}](Cr_2Ni)$ with surplus Ni was then determined to ensure the second phase ($Ni_3M$) precipitation, based on which new multi-component alloys $[(Ni,Cu)_{16}Fe_{192}](Cr_{32}(Ni,Mo,Ti,Nb,Al,V)_{16})$ were designed. These alloys were prepared by copper mould suction casting method, then solid-solution treated at 1273 K for 1 h followed by water-quenching, and finally aged at 783 K for 3 h. The experimental results showed that the multi-element alloying results in $Ni_3M$ precipitation on the martensite, which enhances the strengths of alloys sharply after ageing treatment. Among them, the aged $[(Cu_4Ni_{12})Fe_{192}](Cr_{32}(Ni_{8.5}Mo_2Ti_2Nb_{0.5}Al_1V_1))$ alloy ($Fe_{74.91}Ni_{8.82}Cr_{11.62}Mo_{1.34}Ti_{0.67}Nb_{0.32}Al_{0.19}V_{0.36}Cu_{1.78}$ wt%) has higher tensile strengths with $YS = 1456$ MPa and $UTS = 1494$ MPa. It also exhibits good corrosion-resistance in 3.5 wt% NaCl solution.


*Keywords:* Maraging stainless steels; Composition design; Cluster structure model; Super-high strength

## 1. Introduction

Maraging stainless steels have been used widely as impeller materials due to their super-high strength, good corrosion-resistance, processing ability and weldability [1]. Typical steel brands are 17-4PH, FV520 and Custom 465, formed by a small amount of different elements, such as C, Mo, Ti, Nb and Cu, alloying of Fe–Cr–Ni ternary basic alloys. High strengths of these alloys were resulted from their microstructure with precipitated phases (carbides, intermetallics and Cu-rich particles) dispersed on the martensitic matrix [2–7]. The materials properties relied greatly on the types of alloying elements as well as their contents so that several composition design methods were proposed to develop new multi-component alloy materials [8–10]. For instance, using Cr-equivalence $Cr_{eq}$ and Ni-equivalence $Ni_{eq}$ the designed alloy could be localized on the Sheffler microstructure graph [8], thus the alloy properties would be forecasted roughly.

In investigating composition rule of multi-component bulk metallic glasses, we proposed a cluster-plus-glue-atom structural model that considered the nearest neighbor configurations between elements [11,12]. This model dissociates an alloy structure into a cluster part and a glue atom part, where the cluster is the nearest neighbor coordination polyhedron in the basic structure. Good metallic glass forming compositions and solid solution alloys have been found to satisfy a universal cluster formula $[cluster](glue)_{1\ or\ 3}$, that is, isolated clusters being matched with one or three glue atoms. Furthermore, the

*Corresponding author. Tel./fax: +86 411 84708615.
*E-mail addresses:* lizhen@dlut.edu.cn (Z. Li), nfmlab@126.com (R. Zhang), qianfeng.zha@gmail.com (Q. Zha), apwangym@dlut.edu.cn (Y. Wang), qiang@dlut.edu.cn (J. Qiang), dong@dlut.edu.cn (C. Dong).

Peer review under responsibility of Chinese Materials Research Society.

Production and hosting by Elsevier

1002-0071/$ - see front matter © 2014 Chinese Materials Research Society. Production and hosting by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.pnsc.2014.01.010

stability of a solid solution can also be determined by the nearest neighbor configuration [13], and thus the content of minor alloying elements could be fixed. For instance, stable solid solutions in Cu–Ni–Fe were described by $[FeNi_{12}]Cu_x$ according to their enthalpies of mixing $\Delta H$ between alloying elements with the base Cu ($\Delta H_{Ni-Fe} = -2$ kJ/mol and $\Delta H_{Cu-Fe} = +13$ kJ/mol) [14], where Fe was solutioned in Cu matrix with the aid of the third element Ni due to the negative $\Delta H_{Ni-Fe}$. That is to say, Fe was assumed to be surrounded by twelve Ni atoms in FCC structure to form a cuboctahedron cluster $FeNi_{12}$, and this cluster is then embedded in Cu matrix. So the solubility limit of Fe was determined as the Fe/Ni ratio of 1/12. Once Fe/Ni ratio excesses 1/12, the second phase would be precipitated and the structure of the solid solution would be destabilized.

Since maraging stainless steels also exhibit a single FCC-austenite structure at high temperature, we will here attempt to explore the composition rule of this kind of steels in light of the cluster-plus-glue-atom model, then design alloys according to the model, and finally characterize the designed alloys by experiments.

## 2. Composition analysis and design based on the cluster model

The austenitic structure at high temperature of maraging stainless steels needs to be transformed to martensite via water quenching in order to enhance the strength of steels. So the amount of Ni and Cr could not be too much, otherwise the austenite–martensite transformation would not be completed. From this point of view, the optimum composition position for this phase transformation should be located at the low limit of austenitic region of the basic Fe–Ni–Cr. According to the cluster structure model, the optimized nearest neighbor configuration in FCC Fe–Ni–Cr solid solution is the cuboctahedron $NiFe_{12}$ centered by the solute Ni while the other Cr serves as glue atom due to that the $\Delta H_{Ni-Fe} = -2$ kJ/mol [14] is more negative than $\Delta H_{Cr-Fe} = -1$ kJ/mol. Thus the cluster formula can be expressed with $[NiFe_{12}]Cr_{1\ or\ 3}$ according to the universal formula $[cluster](glue)_{1\ or\ 3}$.

In a FCC lattice, isolated $NiFe_{12}$ clusters are packed in a FCC-like pattern and the interstices are filled with Cr atoms, as shown in Fig. 1. Different packing of clusters will result in different ratios of clusters to glue atoms. These Cr atoms positioned in octahedral interstices of FCC-like cell packed by $NiFe_{12}$ clusters forms $[NiFe_{12}]Cr_1$ structure model (Fig. 1(a)), while Cr atoms positioned both in octahedral and tetrahedral interstices constitutes $[NiFe_{12}]Cr_3$ model (Fig. 1(b)).

Table 1 lists the compositions of typical maraging stainless steels. Except Ni and Cr, the contents of other alloying elements, such as Nb, Ti and Al, are minor, where Mn, Si, S and P are neglected. They are generally classified into two types: one is strengthened mainly by carbides with Ni content about 4–6 wt% and C content close to 0.1 wt%, and the other is strengthened by $Ni_3M$ (M=Ti, Nb, Al) intermetallic phases with Ni about 10 wt% and super-low C ($<0.03$ wt%). It is noted that the primary role of Ni is to stabilize FCC austenitic structure at high temperature and surplus Ni is used to form

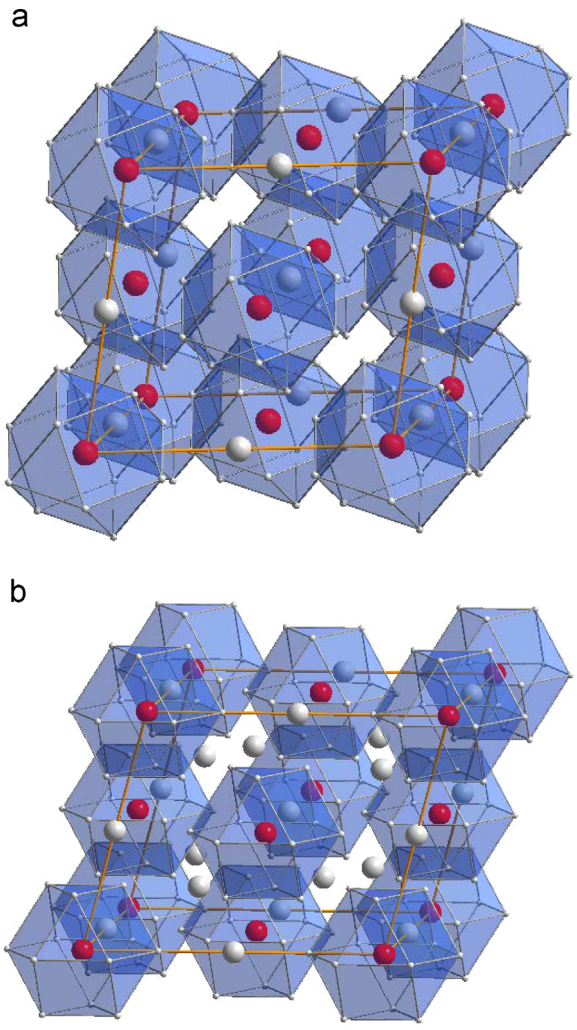


Fig. 1. Isolated $NiFe_{12}$ clusters are packed in FCC-like pattern with Cr atoms in octahedral interstices to form $[NiFe_{12}]Cr_1$ (a) and with Cr atoms both in octahedral and tetrahedral interstices to form $[NiFe_{12}]Cr_3$ (b). Red spheres and white spheres represent cluster center Ni atoms and glue Cr atoms, respectively, and small white spheres are matrix Fe atoms in cluster shell.

$Ni_3M$. Moreover, the strengths of the latter are larger than 1200 MPa, obviously higher than those of the former owing to the strengthening of $Ni_3M$ phases [15]. Fig. 2 gives the Fe–Ni–Cr ternary phase diagram at 1173 K [16], where the least solubility limit of FCC austenite at Fe-rich side is near a straight segment. Fixing Ni content as 6.2 at%, the corresponding Cr content is close to 18.7 at% at this solubility limit. This composition can be exactly expressed with the cluster formula $[NiFe_{12}]Cr_3 = Fe_{75}Ni_{6.25}Cr_{18.75}$ (at%) $= Fe_{75.74}Ni_{6.63}Cr_{17.63}$ (wt%). Moreover, this composition keeps almost constant with increasing temperature [17], which indicates the cluster formula $[NiFe_{12}]Cr_3$ should be an expression of stable FCC solid solution.

In maraging stainless steels, the minor alloying elements could be divided into two kinds: one is to stabilize FCC structure at high temperature, such as Cu and C, same to Ni, the other is to form carbides or $Ni_3M$ phase, and generally has