

On the Volume Fraction vs. Temperature Function of Martensitic Transformation in Iron-Base-Alloys

B. Skrotzki, E. Hornbogen, Institut für Werkstoffe, Ruhr-Universität Bochum, D – 4630 Bochum

Introduction

Martensitic transformation in certain Fe–Mn as well as in Fe–Ni alloys produces different morphological crystal structures. In Fe–Mn alloys with more than 14.5 wt.% Mn the hcp ϵ —martensite occurs (1). The crystallography of the lattice transformation from fcc γ to hcp ϵ is very simple since both lattices only differ in the stacking sequence of close packed planes. In the beginning of the transformation thin plates appear in the middle of an austenite grain. The plates grow preferably in longitudinal direction and less in the direction of thickness. ϵ —martensite shows a typical Widmannstätten microstructure. The transformation always stays incomplete. It remains a considerable amount of retained austenite.

In Fe–Ni alloys with an Ni—content between 28 and 32 wt.% the bcc plate martensite with typical lenticular plates is observed. Below 28 wt.% Ni lath martensite occurs (2). The structure may become tetragonal either by interstitials or by ordering of substitutional solute atoms.

In this work the influence of Ge and P additions on transformation temperatures and course was investigated. This is part of a fundamental study of the volume fraction of martensite vs. temperature function for alloys of iron. The determination of the transformation temperatures result from dilatometric and calorimetric measurements. The transformation course was studied using light microscopy equipped with heating and cooling stage. A new approach for quantitative description of the martensitic microstructure is made by fractal analysis. All results are discussed considering the role of mechanical and thermodynamical properties.

Experimental procedures

Different iron–manganese and iron–nickel alloys are melted as 50 g buttons in an argon arc furnace using iron, manganese and nickel of electrolytic purity as starting material. Germanium was present in a purity of 99,999 % and phosphorous was available as a master alloy of 74,6 at.% Fe and 25.4 at.% P. The manganese content amounts to 25.4 and 27.1 at.% (25.1 and 26.5 wt.%) respectively, the nickel content to 26.7 and 29.4 at.% (27.7 and 30.4 wt.%). The Ge—content varies between 0 and 4 at.% the P—content between 0 and 1.6 at.%

The buttons are hot rolled (reduction in thickness of about 50 %) and homogenized for 24 h at 1200 °C. An average austenite grain size of 80 μm was established. For dilatometric measurements specimens of 4 mm diameter and 40 mm length were used. For calorimetric measurements the "DuPont Thermalanalyser 9900" was available. The transformation temperatures are determined by a method of tangent dissection. The transformation course was studied using light microscopy with a heating and cooling equipment. The amount of retained austenite was determined by X—ray analysis using Mo– K_{α} radiation.

Results and discussion

A qualitative hint at effects of solute elements on transformation temperatures is provided by the rule that the crystal structure of the pure solute (bcc or close packed) favours the formation of the α — or γ —phase. The transition metals Ni, Mn, Co stabilize the austenite. Bcc elements, for example V, Cr, Mo, W, stabilize α —Fe. For the elements from the same period their atomic size only differs from iron. The size ratio and consequently the solid solution

1 ⁻	2 ⁻	3 ⁻	4 ⁻	5 ⁻
Cu	Zn	Al Ga	Si Ge Sn	P Al

Table 1: Number of free electrons of some elements

hardening ability increases for the elements from the higher periods Mo, W. Not covered by this rule are Al and the other elements in the environment of Si. They may form metallic or covalent bonds. There is little information on their effects on the martensitic transformation. Their position in the periodic system provides information on possible electronic contribution to the atomic size effects (Table 1). An exploration of the effects of these elements on strength and martensitic transformation was part of this study.

a) Fe-Mn alloys

In alloys with 25.4 at.% (25.1 wt.%) Mn as well as in such with 27.1 at.% (26.8 wt.%) the hardness decreases with increasing Ge-content. This can be attributed to the rising amount of retained austenite at 20 °C (Fig. 1). Increasing Ge-content shifts the transformation to lower temperature, whereby a larger amount of austenite remains.

As M_s lies above and M_f below room temperature, experimental difficulties in determination of these temperatures arise. As Fig. 2 shows, the alloys are predominantly martensitic at room temperature. A_s and A_f respectively could be determined without problem. Fig. 3 shows that A_s increases with increasing Ge-content. Nevertheless the amount of retained austenite increases at room temperature and so a decrease of M_s is assumed.

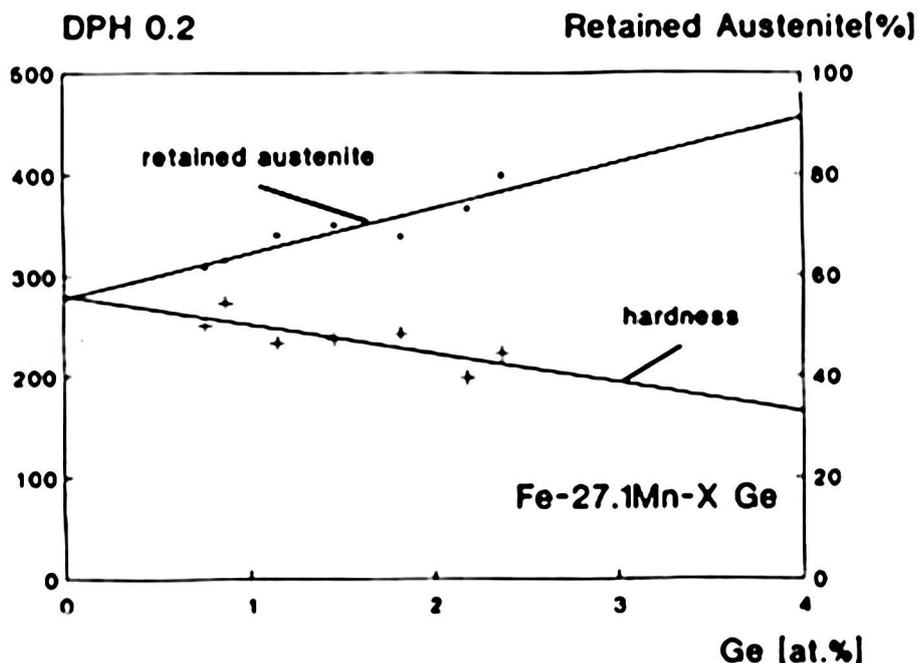


Fig. 1: Microhardness and retained austenite in an Fe-Mn alloy as a function of Ge content

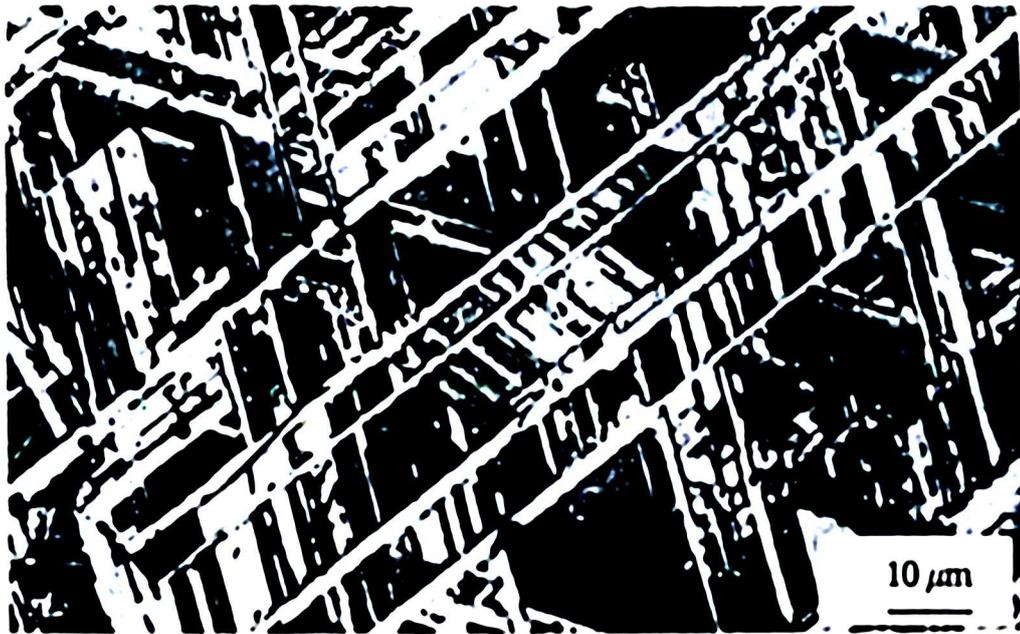


Fig. 2: Microstructure of an alloy consisting of Fe-25.4 at.% Mn-2.2 at.% Ge

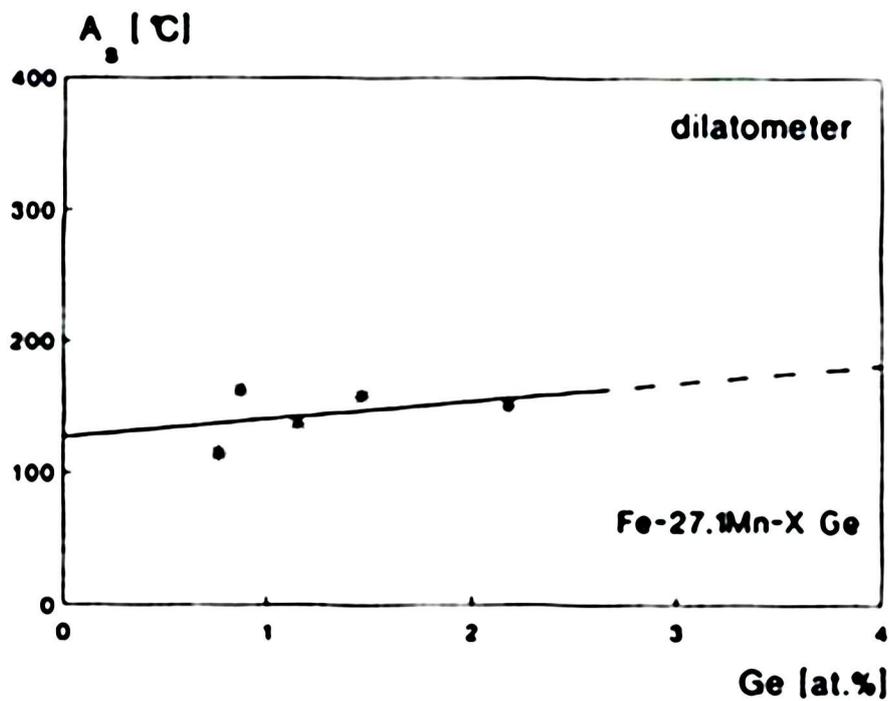


Fig. 3: Austenite start temperature A_s as a function of Ge content in an Fe-Mn alloy

Element	atomic radii [nm]	structure	r_B/r_{Fe}
Fe	0.1242	bcc	1
Al	0.1432	fcc	1.154
Si	0.1176	cubic	0.947
P	0.1090	orthorhombic	0.878
Ge	0.1225	cubic	0.987
Sn	0.1405	cubic	1.132

Table 2: Atomic size and structure of elements in the environment of Si

The Fe–Mn alloys with P additions show a minor increase of the hardness with increasing P–content. Because of the relative small atomic size (Table 2) a stronger solid solution hardening effect should be expected as compared to Ge containing alloys. Altogether, it can be said that both Ge and P give rise to a solid solution hardening of the austenite whereby a stabilisation of the austenite occurs.

b) Fe–Ni alloys

In the alloys with 26.7 at.% (27.7 wt.%) and 29.4 at.% (30.4 wt.%) Ni respectively the hardness in the austenitic state as well as in the martensitic state increases with rising Ge content (Fig. 4). M_s decreases whereas A_s increases (Fig. 5 and 6) which implies an increasing hysteresis of a transformation cycle. In comparison to the Fe–Mn alloys the amount of retained austenite is reduced.

In the following the change in transformation temperatures shall be discussed considering the mechanical and thermodynamical properties (4). The martensite start temperature M_s is de-

DPH 0.1

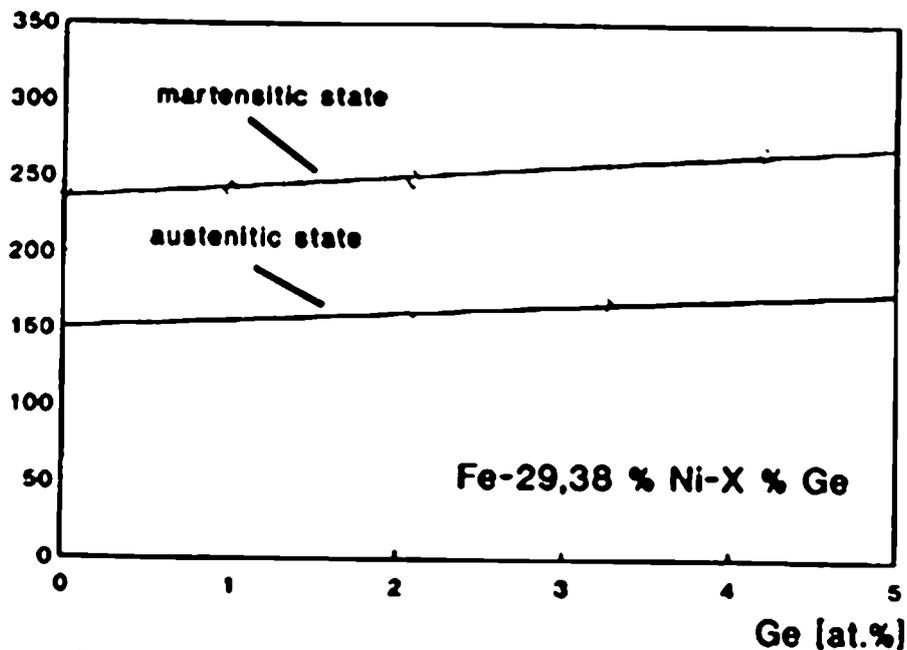
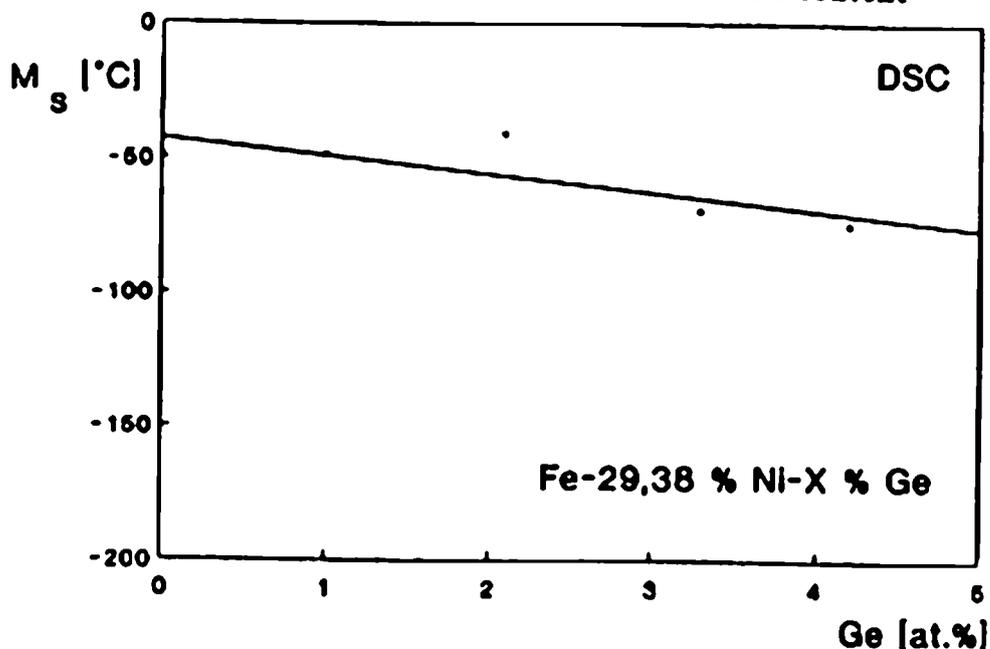


Fig. 4: Microhardness as a function of Ge content



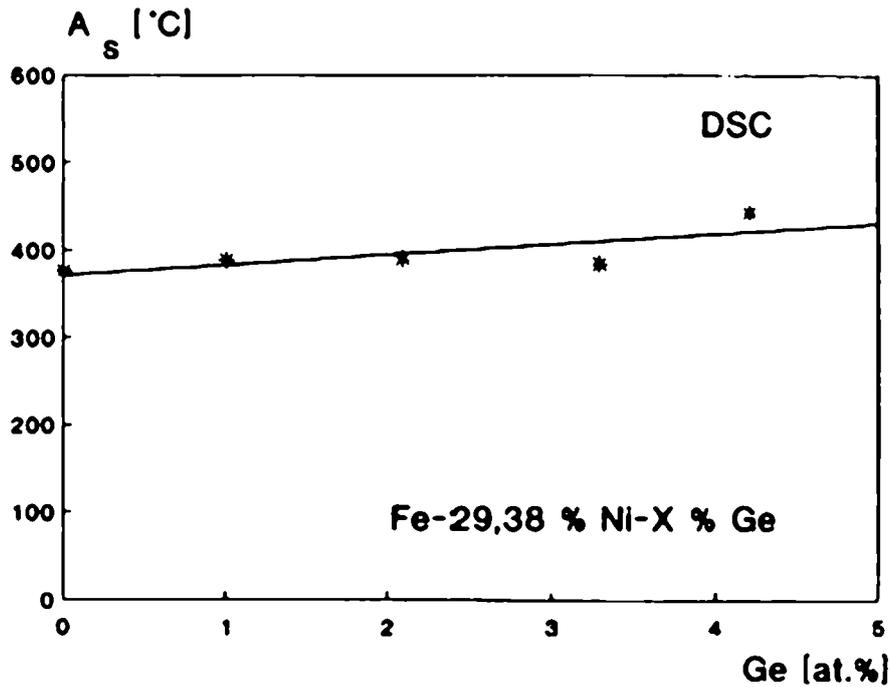


Fig. 6: Austenite start temperature vs. Ge content

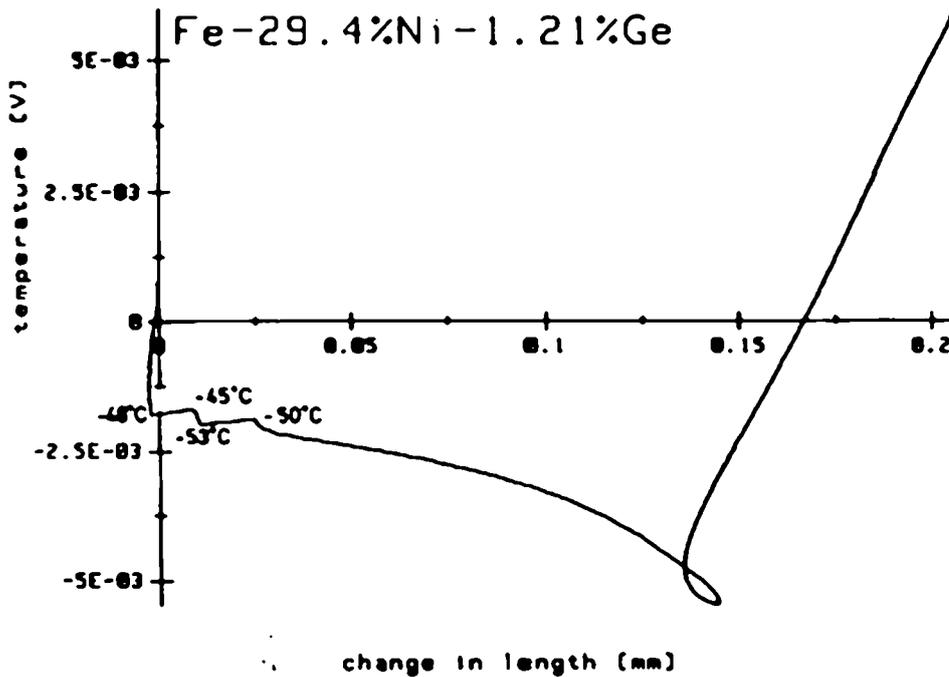


Fig. 7: Change in length with decreasing temperature during a dilatometric measurement. A burst-like transformation in several steps is observed

terminated by the temperature of the metastable thermodynamical equilibrium T_0 and the necessary undercooling ΔT to nucleate the transformation:

$$M_s = T_0 - \Delta T$$

T_0 is defined by the equality of the martensite and austenite free energy of equal chemical composition and degree of order.

The binary phase diagrams Fe-P and Fe-Ge indicate that these solute atoms should increase T_0 in iron. Nevertheless M_s decreases. Transformation interfaces will have to propagate by the motion of partial dislocations which becomes more difficult in a hardened austenite. Thus the increase of T_0 is overcompensated by a considerable increase of ΔT .

As M_s is lowered but A_s increased, the hysteresis becomes greater with increasing Ge content. The rising of A_s can be explained as being due to the solid solution hardening. In the same way as the martensitic transformation the transformation to austenite becomes more difficult because the motion of dislocations is hindered.

The course of the transformation was investigated in a light microscope with heating and cooling equipment. As already shown in the dilatometer and DSC experiments the transformation takes a stepwise course (Fig. 7). At M_s the first generation forms by a burst phenomenon. Local adiabatic heating leads to the measure size in temperature of about 5°C .

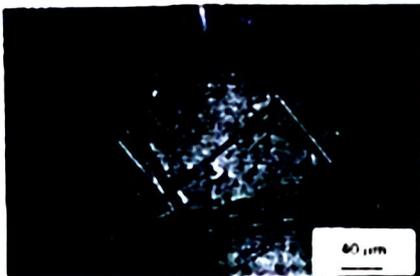
In the light microscope these observations are confirmed. However, the observed start of the transformation was shifted to lower temperatures. Fig. 8 shows a sequence of photographs, which reproduce different states of the transformation. Thus the transformation occurs burst-like in several steps. Each step corresponds to a new generation of martensite. The microstructure which forms by this mechanism can be characterized by fractal geometry.



T = 20°C



T = -113°C



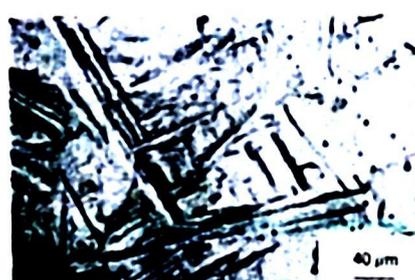
T = -120°C



T = -123°C



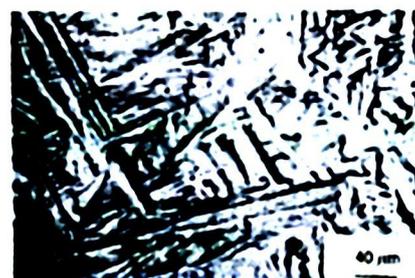
T = -129°C



T = -131°C



T = -150°C



T = -180°C

Fig. 8a,b: Forming of martensite crystals with decreasing temperature in the alloy Fe-26.7 at.% Ni-0.6 at.% Ge

Fractal geometry deals with certain types of disordered, rugged, close to chaotic morphologies (5,6). For such microstructures it is impossible to obtain microstructural parameters such as grain size or particle spacing.

A fractal microstructure is characterized as follows:

- more than 3 self similar fragmentations should be distinguishable (here generations of martensite crystals)
- a constant fractal dimension $D \neq d$ and self similarity should be observable for a range of more than one order of magnitude (d is the integer Euclidian dimension of a microstructural feature).

For a better characterization and understanding of a martensitic transformation fractal analysis could be a helpful method. The microstructure in Fig. 9 shows four different fragmentations of martensite. The self-similarity was tested by considering the ratio of length to thickness of the lenticular particles of martensite, which has to be constant. Then the average size and distribution function of the different martensite crystal generations were measured. The volume fraction of martensite as a function of the number of fragmentations x is shown in Fig. 10.

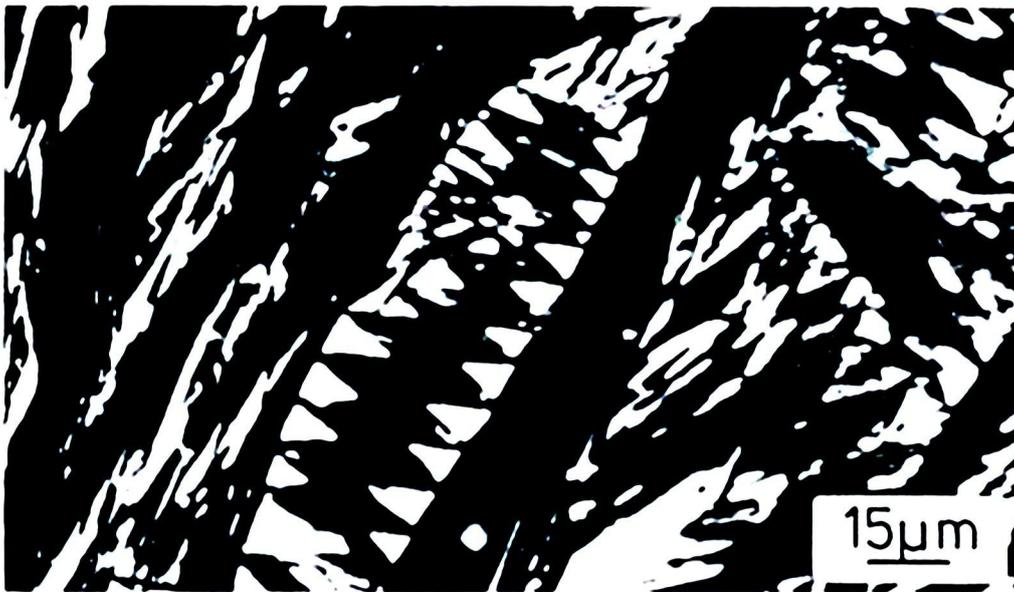


Fig. 9: Fractal martensitic microstructure of an Fe-29.4 at.% Ni-2.5 at.% Ge alloy

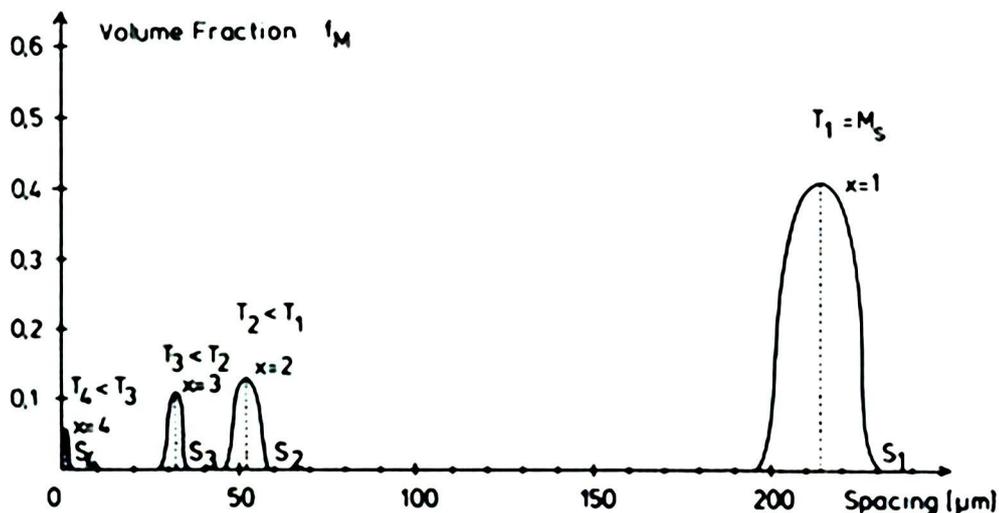


Fig. 10: Volume fraction of martensite as a function of the number of fragmentations x and size distribution of the different generations of martensite crystals

The first generation of martensite crystals $x = 1$ forms at a temperature T_1 with an extension corresponding to the austenite grain diameter S_1 . It transforms a volume fraction $0 < f_{x=1} = 0.41 < 1$. Austenitic/martensitic interfaces are created at which the second generation $x = 2$ can form at a temperature $T_2 < T_1$ with a volume fraction $0 < f_{x=2} = 0.13 < 1$ in the untransformed spaces. The number of fragmentations x depends on the austenite grain diameter and on lateral growth of martensite. With increasing fragmentation further transformation becomes more and more difficult. Therefore, large austenite grain sizes favour an increasing number of fragmentations.

It is also visible that the transformed volume fraction decreases with every fragmentation. These results agree with the observations concerning the stepwise course in the in situ light microscopy, calorimetric and dilatometric measurements.

Acknowledgement

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