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Grain Boundary Wetting Phase Transition in the Mo-Ni System

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Abstract—The dihedral angle θ at the intersection of a grain boundary in Mo bicrystals with the (solid Mo)/(Ni-based liquid) interface was measured for symmetric tilt <011>{011} grain boundaries (**GBs**) with a tilt angle ϕ of 20°and 70° at various temperatures. The temperature dependencies θ*(T)* give an evidence of the GB wetting phase transition at T_w. The GB wetting tie line for the high-energy GB (ϕ = 70°) coincides with the peritectic temperature T_e or lies just above it. T_w for the GB with a low energy (ϕ = 20°) is about 20°C higher than T_e. Liquid film migration was also observed at the 70° <011>{011} GB above T_e.

1. Introduction

Liquid phase sintering is widely used for manufacturing of parts made from refractory alloys because the addition of metals with a lower melting temperature like Ni or Cu enhances drastically the consolidation process of Mo or W [1, 2]. In fact, the behaviour of liquid phase sintering depends critically on the competition between the diffusional and non-diffusional processes, like grain boundary (**GB**) migration, liquid film migration (**LFM**), and GB penetration of a liquid phase [3–5]. The last process can proceed only if the dihedral contact angle in a triple point "GB – two solid/liquid interphase boundaries" θ = 0. The temperature T_w can exist such that for $T>T_w$ θ=0 and for $T<T_w$ θ>0. Above this temperature the GB is completely wetted by the liquid phase and penetration can occur [6–8], while at lower temperatures the wetting is incomplete and the liquid films along the GBs are not formed. This change at T_w has a name of GB wetting phase transition [7, 8]. The value of T_w is governed by the ratio of energies of GB and solid/liquid interphase boundaries. Above T_w GB cannot exist in the equilibrium with a liquid phase which must separate the individual solid grains [9]. This phenomenon has been encountered in many systems [10–12]. The behaviour of the liquid phase sintering has not been treated so far from the viewpoint of GB wetting phase transitions. This is due to the lack of information about the temperature dependence of the GB dihedral contact angle. T_w depends essentially on the GB energy. Therefore, the dependencies θ*(T)* should be measured with the aid of individual GBs in bicrystals. In present work the temperature dependencies θ*(T)* have been studied for two GBs with different energies in Mo bicrystals in contact with a Ni-rich melt.

2. Experimental

Symmetrical tilt <011>{011} GBs with misorientation angles of 20° and 70° were chosen for the measurements. The bicrystals were produced from Mo of 99.95 wt.% purity. Mo single crystals were grown in a vacuum electron-beam floating zone melting apparatus [13]. To stabilize the

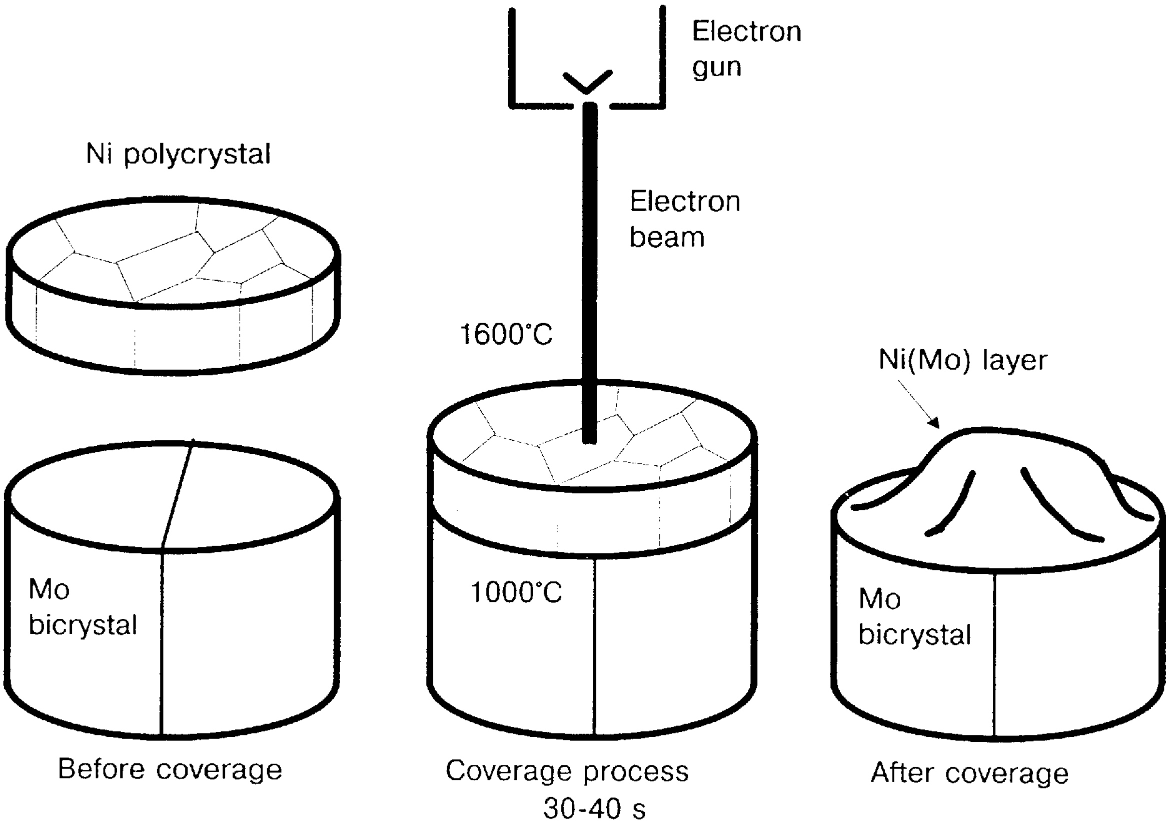

Fig. 1. Coverage of a Mo bicrystalline sample with a Ni layer.

temperature distribution in the liquid zone, a circular water-cooled copper electron gun was used. To prepare single crystalline seeds of different orientations, a single crystal was grown and cut to obtain cylindrical pieces of 15–20 mm length and 10–25 mm diameter. Two parallel surfaces of a seed were checked carefully by X-ray diffraction with an accuracy of about 1° and carefully polished in order to make very clean and mirror-like surfaces. The upper surface, normal to the growth axis of the seed holder, was prepared by cutting, grinding and polishing. Both ends of the initially cylindrical Mo ingots were cut normally to the growth axis and polished. Before growing, the lower holder with a seed on top of it, a cylindrical ingot and an upper holder were joined together by in-situ local electron-beam welding of the contacting surfaces. The seeding procedure consists of melting of a narrow liquid zone in the seed just under the seed/ingot interface. After an initial liquid zone is created, the electron gun is being moved up vertically together with the liquid zone until the whole specimen would become single crystalline. Thus, after such a procedure the single crystalline seed and zone-remelted specimen represent one elongated grain which has the same crystallographic orientation in all areas. A seed is then cut off from a grown single crystal by a spark erosion machine[12].

In principle, the growing procedure for Mo bicrystals is similiar to that for single crystals. The bicrystalline seeds need a similiar careful preparation as monocrystalline ones but because they are made up of two half-cylinders, the quality of the interface between them is of great importance. They were carefully ground, etched and polished to obtain clean and flat surfaces to be joined together. The bicrystalline seeds are composed using two single-crystalline halves. The misorientation angle θ of a tilt GB was formed by oriented cutting of single crystals. All individual samples were cut from the same bicrystal.

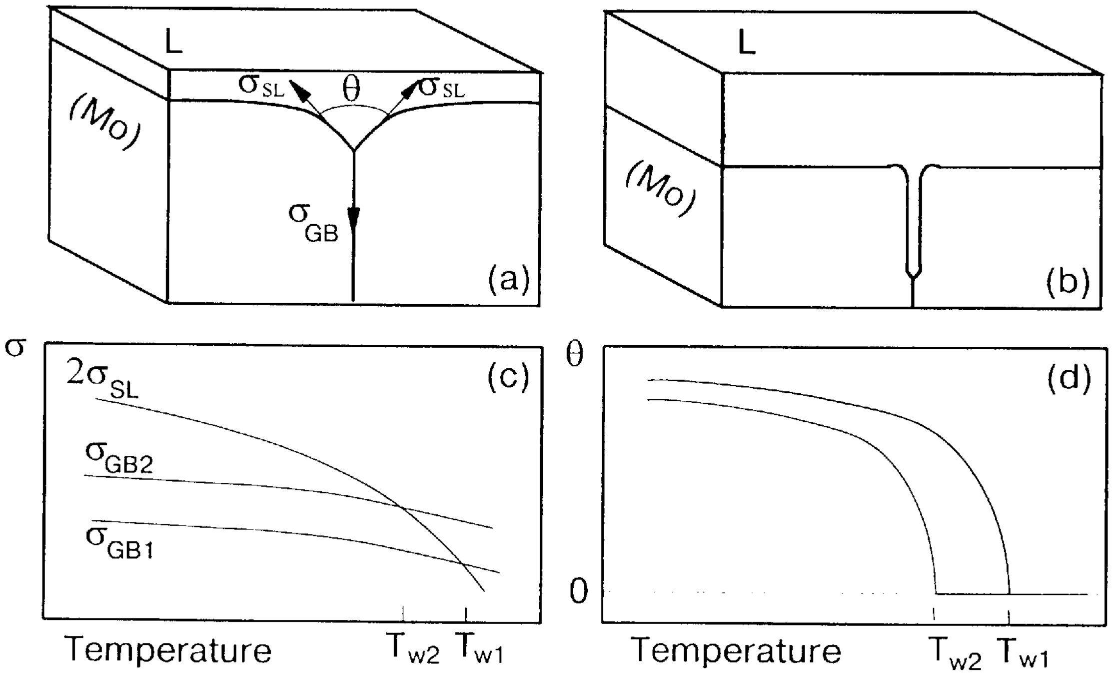

Fig. 2. (**a**) A bicrystal in contact with a liquid phase at $T<T_w$. The GB is incompletely wetted. The contact angle $\theta > 0$. (**b**) The GB is completely wetted, $T > T_w$, $\theta=0$. (**c**) Schematic dependencies of $2\sigma_{SL}(T)$ together with $\sigma_{GB1}(T)$ and $\sigma_{GB2}(T)$ for two different GBs. They intersect at the temperatures T_{w1} and T_{w2} of the GB wetting phase transition. (**d**) Schematic temperature dependencies of the contact angle θ corresponding to the curves drawn in Fig. 1(c).

For the wetting experiments a layer of Ni was applied on the surface of the Mo bicrystals. For this purpose the axial electron beam gun was used. The scheme of making the coverage is shown in Fig.1. The Mo tablets were heated up to about 1000°C by an electron beam, and then a drop of Ni was used to provide a good surface wetting. Usually this procedure took about 30-40 s. Then the solidified droplet of the Ni-rich alloy was thinned in order to have a flat layer of thickness about 0.3 mm thick. The covered samples were annealed in a vacuum of 3×10^{-4} Pa at different temperatures (1320, 1340, 1360, 1380, 1580, 1780°C) above the eutectic temperature of the Mo–Ni system (T_e = 1309°C [14]). The annealing temperature was maintained constant within ±2°C for 1 h. The cooling time was about 5 min. After cooling the samples were embedded in a holder and then mechanically ground and polished to make a polished surface perpendicular to the GB and solid/liquid interface. The polished surface was etched for a few seconds in the solution 1g NaOH + 3g $K_3Fe(CN)_6$ + 20 ml H_2O at room temperature.The contact area between the GB and the interphase boundary has been photographed in an optical microscope, and the contact angle θ was measured with an accuracy of about 0.5° (Fig. 2). In some cases LFM was observed on the GBs. The distance *l* of liquid film migration was measured at 10 to 20 points in an optical microscope, and the mean value <*l*> was determined.

3. Results and Discussion

The contact angle θ and the mean distance <*l*> of the **LFM** for GBs studied were measured at different temperatures (Table 1). The GB with ϕ = 70° is wetted at all temperatures studied. Therefore, the temperature of the GB wetting phase transition $T_w(\phi = 70°)$ coincides with T_e or lies just above it (below 1320°C). The GB with $\phi = 20°$ was wetted at all temperatures studied

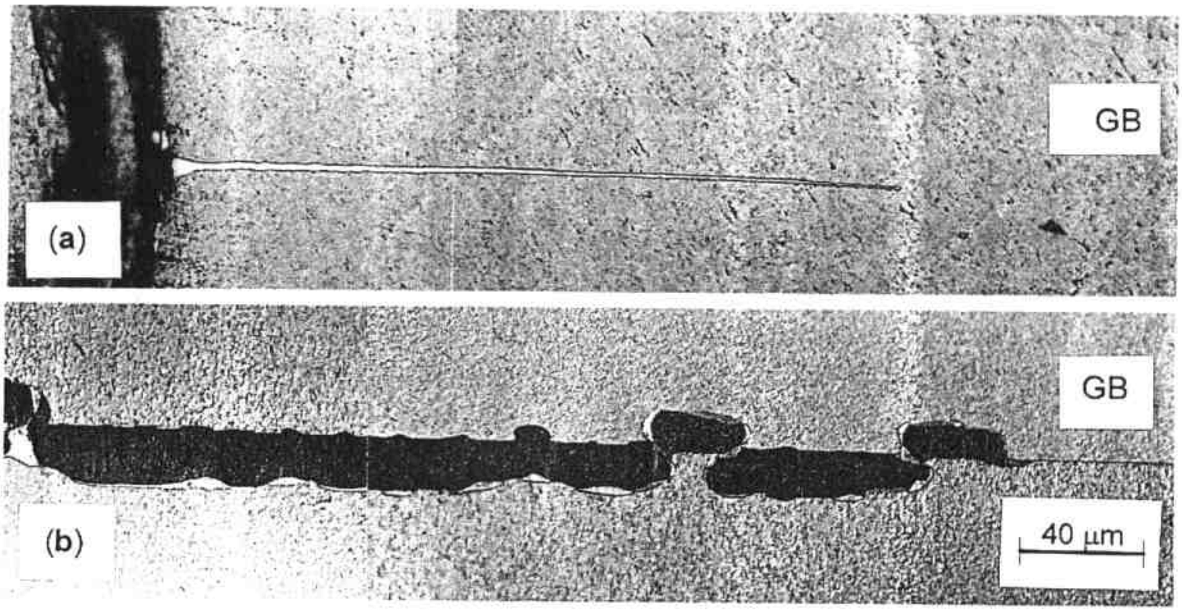

Fig. 3. GBs in Mo wetted by Ni-rich melt. (**a**) 20°<011>{011} GB, 1360°C, no LFM present. (**b**) LFM on the 70°<011>{011} GB at 1340°C.

Table 1. Contact angle θ and mean distance $\langle l \rangle$ of the liquid film migration for 20°<011>{011} and 70°<011>{011} tilt GBs in Mo at different temperatures.

GB		Annealing temperature, °C					
		1320	1340	1360	1380	1520	1720
20° <011>{011}	θ, deg	19	0	0	0	0	0
	$\langle l \rangle$, μm	0	0	0	0	0	0
70° <011>{011}	θ, deg	0	0	0	0	0	0
	$\langle l \rangle$, μm	4±0.8	16±0.6	9±1	9±1.5	0	0

except 1320°C. Therefore, θ decreases drastically with increasing temperature and reached zero between 1320 and 1340°C. The Mo–Ni bulk phase diagram is shown in Fig. 4. The tie lines of the GB wetting phase transitions are shown in the (Mo)+L field. A pronounced LFM was found at 70°<011>{011} tilt GB at the lower temperatures (1320–1380°C). At the higher temperatures (1580 and 1780°C) no LFM was observed for this GB. At the 20°<011>{011} tilt GB no LFM was found.

Since their prediction by Cahn [15] the study of wetting phase transitions has been of great experimental and theoretical interest, primarily for planar solid substrates and fluid mixtures [16–18]. Particularly, it was experimentally shown that the wetting transition is of first order. The discontinuity of the surface energy was measured, and the hysteresis of the wetting behaviour was observed [19, 20]. The wetting phenomena on solid/solid interfaces, for example on GBs, were experimentally less studied [7]. The important difference is that in the case of GB wetting only two phases coexist, namely a liquid phase and a solid one containing the boundary between the misoriented grains (Fig.2). Therefore, the contact angle θ depends only on two different surface energies (the GB energy σ_{GB} and the energy of the solid/liquid interphase boundary σ_{SL}) instead of three ones in the usual experiments (Fig. 2a):

$$\sigma_{GB} = 2\,\sigma_{SL} \cos(\theta/2). \qquad (1)$$

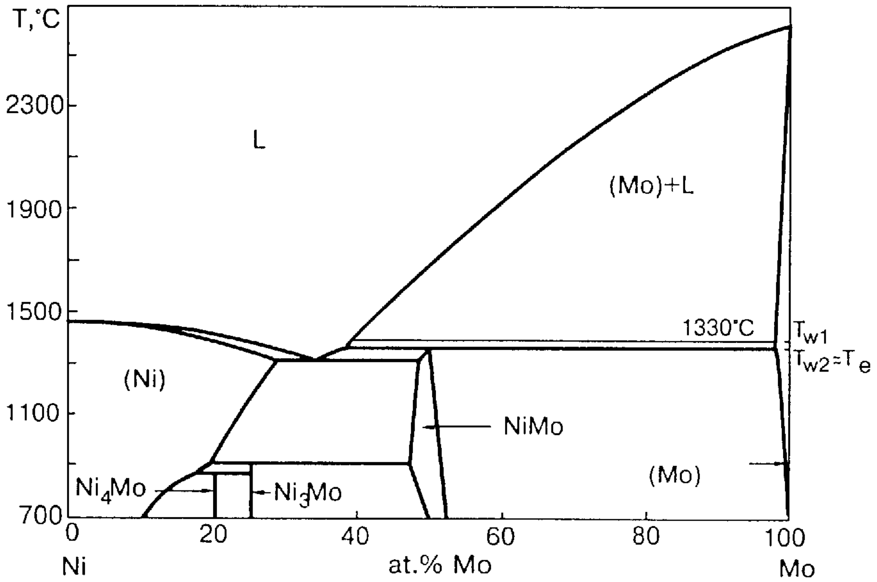

Fig. 4. The Mo–Ni bulk phase diagram (thick solid lines) [14] along with the tie lines of the GB wetting transition (thin solid lines) at T_{w1} for the 20°<011>{011} GB and at T_{w2} for the 70°<011>{011} GB.

If $\sigma_{GB} < 2\sigma_{SL}$, the GB is incompletely wetted and the contact angle $\theta > 0$ (Fig.2a). At the temperature T_w of the GB wetting phase transition $\sigma_{GB} = 2\sigma_{SL}$. At $T \geq T_w$ the GB is completely wetted by the liquid phase and $\theta = 0$ (Fig. 2b). If two GBs have different energies the temperatures of their GB wetting transitions will also differ: the lower σ_{GB}, the higher T_w (Figs 2c and d).

The misorientation angles of the <011> tilt GBs were chosen so that the GBs have different energies like in previous works for the systems Cu–In [10] and Al–Sn [11]. Unfortunately, the data of direct measurements for GB energies in Mo are absent. Therefore, we used the data of computer modelling [21, 22]. They fit very well to the known experimental values of σ_{GB} for metals with a face-centred cubic (**fcc**) lattice [23]. According to [21, 22], a deep minimum at $\phi = 70°$ exists for fcc metals (symmetric twin GB), but is absent for the bcc metals like Mo. In our case, σ_{GB} ($\phi = 20°$) = 3400 mJ/m^2 is lower than σ_{GB} ($\phi = 70°$) = 3900 mJ/m^2. Consequently, the temperature T_w of the GB wetting transition for $\phi = 70°$ should be lower than T_w for $\phi = 20°$. The data obtained (Table 1 and Fig. 3) support this conclusion. Actually, in a fcc metal (Cu) T_w for the GB with $\phi = 77°$ (close to the twin misorientation) is higher than for the GB with $\phi = 141°$ [10]. According to [21, 22], σ_{GB} ($\phi = 141°$) in a fcc lattice is equal to σ_{GB} ($\phi = 20°$). Therefore, our data provide experimental evidence to the results of computer calculations for σ_{GB} [21, 22].

If the energies σ_{GB} and σ_{SL} depend linearly on the temperature, the phenomenological theory [15, 20] predicts for a wetting phase transition of first order—analogously to fluids on a solid substrate—that the temperature derivative of the macroscopic GB energy has a discontinuity Δ at T_w given by

$$\Delta = \partial(2\sigma_{SL})/\partial T - \partial\sigma_{GB}/\partial T = -2\sigma_{SL}\,\partial(\cos\theta)/\partial T. \qquad (2)$$

This equation is obtained by differentiating the law of cosines for the triangle built by σ_{SL}, σ_{GB} and σ_{SL} (Fig. 2 a) at T_w where $\cos\theta = 1$. If the GB wetting phase transition is of second order $\partial\sigma_{GB}/\partial T = \partial(2\sigma_{SL})/\partial T$ at T_w. In principle, the $\theta(T)$ dependencies measured close to T_w permit to estimate the values of $\partial(\cos\theta)/\partial T$ and, therefore, to find the order of GB wetting phase transition as it was made, for example, for Al–Sn system [11]. We can estimate the right-hand part of Eq.(2) knowing that $2\sigma_{SL} = \sigma_{GB}$ at T_w and using the value σ_{GB} = 3400 mJ/m^2 for the 20° <011>{011} tilt GB in Mo [21, 22]. For the 20°<011>{001} tilt GB in Mo $\partial(\cos\theta)/\partial T \approx 3$ /mK and the discontinuity $\Delta \approx 10$ mJ/m^{2}K. These values are higher than in the Al–Sn system due to the higher energy of GBs in Mo though $\partial(\cos\theta)/\partial T$ is of the same order of magnitude [11]. Unfortunately, in our case the GB wetting phase transition in the Mo–Ni system proceeds at (or slightly above) the peritectic temperature T_e and only qualitative informations were obtained about the difference of T_w for both GBs studied. Further careful experiments with small temperature steps (about 1°C) just above T_e should be made in order to obtain the detailed temperature dependence of the contact angle.

LFM on the 70°<011>{001} tilt GB in Mo at 1380°C was discussed from the point of view of coherency strain energy [24]. Now we see that LFM is very pronounced at the 20°<011>{001} GB between 1320 and 1380°C but disappears at higher temperatures and is not present at the 20°<011>{001} GB at all temperatures studied (Table 1 and Fig. 3). This behaviour is difficult to explain by differences between σ_{GB1} and σ_{GB2}. It might rather be due to the loss of coherency for the 20°<011>{001} GB and for the 70°<011>{001} GB at the higher temperatures.

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References

[1] G. Petzow, W. J. Huppmann, Z. Metallk. **67**, 333 (1976).
[2] W. J. Huppmann, H. Rieder, Acta metall. **23**, 965 (1975).
[3] Y. J. Baik, D. Y. Yoon, Acta metall. **38**, 1525 (1990).
[4] W. H. Rhee, Y. J. Baik, D. Y. Yoon, Acta metall. mater. **41**, 1263 (1993).
[5] H. Fredriksson, A. Eliasson, L. Ekbom, Int. J. Refractory Metals & Hard Mater. **13**, 173 (1995).
[6] A. Passerone, N. Eustathopoulos, P. Desrè, J.Less-Common Metals, **52**, 37 (1977).
[7] E. I. Rabkin, L. S. Shvindlerman, B. B. Straumal, Int. J. Mod. Phys. B **5**, 2989 (1991).
[8] B. B. Straumal, W. Gust, Mater. Sci. Forum, **207–209**, 437 (1996).
[9] V. Glebovsky, B. Straumal, V. Semenov, V. Sursaeva, W. Gust, High Temp. Mater. & Processes **14**, 67 (1994).
[10] B. Straumal, T. Muschik, W. Gust, B. Predel, Acta metall. mater. **40**, 939 (1992).
[11] B. B. Straumal, D. Molodov, W.Gust, J. Phase Equilibria, **15**, 386 (1994).
[12] V. N. Semenov, B. B. Straumal, V. G. Glebovsky, W. Gust, J. Cryst. Growth, **151**, 180 (1995).
[13] V. G. Glebovsky, V. V. Lomeyko, V. N. Semenov, J. Less-Common Metals **117**, 385 (1986).
[14] T. B. Massalski et al. (editors), "*Binary Alloy Phase Diagrams*", ASM International, Materials Park, Ohio (1990), updated (1993).
[15] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).
[16] S. Dietrich, in "*Phase Transitions and Critical Phenomena*", edited by C. Domb and J. H. Lebowitz, Academic, London (1988), Vol. 12.
[17] D. Jasnov, Rep. Prog. Phys. **47**, 1059 (1984).
[18] G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).
[19] H. Kellay, D. Bonn, J. Meunier, Phys. Rev. Lett. **71**, 2607 (1993).
[20] J. W. Schnidt, M. R. Moldover, J. Chem. Phys. **79**, 379 (1983).
[21] D. Wolf, J. Appl. Phys. **69**, 185 (1990).
[22] D. Wolf, J. Mat. Res. **5**, 1708 (1990).
[23] A. Otsuki, M. Mizuno, Trans. Jap. Inst. Met. **27**, 789 (1986).
[24] E. Rabkin, D. Weigand, B. Straumal, V. Semenov, W. Gust, Y. Brechet, Phil. Mag. Lett. **73**, 187 (1996).